

Corrosion Effect of Gas Flaring On Galvanized Roofing Sheet in Imo State, Nigeria

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Abstract

The effect of air pollutants due to gas flaring on the corrosion of corrugated galvanized steel roofing sheets in Imo state is the subject of this work. Seven months monthly analysis of the ambient atmospheric gases was taken which showed that methane gas has an overall mean value of 6.21ppm with a coefficient of variation of $\pm 27.2\%$ and ($r=-0.64$) and sulphur-dioxide of mean value of 0.58ppm with coefficient of variation of $\pm 17.4\%$ and ($r=-0.54$), contribute more to corrosion. The corrosion rate of the galvanized samples exposed on racks was monitored using the electrochemical method using a Cu/CuSO₄ with saturated calomel electrode of which a lowest corrosion potential of -1021mV was obtained at 500meters and -1018mV at 1000meters away from flare source in Izombe and -1011mV at a none gas flare site, Federal University of Technology, Owerri (FUTO). The weight loss were taken monthly regressed with atmospheric pollutants. A maximum weight loss of 7.62mg was obtained at 500meters away from flare source in Izombe followed by 4.23mg at 1000meters from flare source while 1.17mg weight loss was obtained in FUTO which shows that Gas flaring has serious deteriorating effect on galvanized roofing sheet.

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I Introduction

Gas flaring is the combustion of unutilized excess gas during oil exploration and exploitation ⁽¹⁾. This forms one of the most environmental problems associated with crude oil exploration. Gas flaring is a common practice in the oil production process that is not restricted to Nigeria only. Libya for instance flares about 21% of its natural gas, while Saudi Arabia, Canada and Algeria flare 20%, 8% and 5% respectively. In 2002, Nigeria flared about 76% of its natural gas and about 60% in 2006 ⁽²⁾. This implies that Nigeria has one of the worst rates of gas flaring in the world, hence described as a gas province with a bit of oil in it.

1.1 Survey

The deterioration of metal exposed to the natural atmosphere constitutes atmospheric corrosion. This corrosion process is controlled by the climatic conditions at the exposure site. The main factors are the availability of moisture and the extent to which the air is polluted, but other less important ones as temperature contribute.

Moisture can reach a metal surface directly in liquid form as a result of precipitation processes i.e. rain and dew but the water vapour that is always present in air can also, under certain conditions, cause metal to corrode at relative humidities well below saturation. This important fact was demonstrated by Vernon in a series of classical experiments of which some showed that corrosion is minimal in pure air of less than 100% relative humidity but that, in the presence of minute concentrations of impurities, such as sulphur dioxide, serious corrosion can occur without visible precipitation of moisture once the relative humidity of the air rises above a critical and comparatively low value. ⁽³⁾ Although humidity plays a vital part, the impurities in the air are decisive in determining the rate of corrosion in atmosphere of the requisite humidity of which in their absence corrosion is not serious even in highly humid air. Hence there is need to determine the role atmospheric pollutants play in the corrosion of galvanized steel in Imo state a case study of Izombe a gas flaring site and FUTO a non-gas flaring site.

1.2 Corrosion of Galvanised Mild Steel

The largest single use of zinc is in the form of zinc coating. This is due to the fact that both zinc and its alloys have excellent resistance to corrosion in the atmosphere and in most natural waters. The property which gives zinc this valuable corrosion resistance is its ability to form a protective layer consisting of zinc oxide and

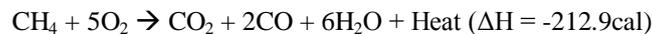
hydroxide or of various basic salts depending on the nature of the environment when the protective layers have formed and completely cover the surface of the metal, the corrosion proceeds at a greatly reduced rate.

The presence of water does of course increase the rate of corrosion, when water is present the initial corrosion product is zinc hydroxide which is then converted by the action of some air pollutants in very damp conditions unprotected zinc sometimes forms a loose and more conspicuous form of corrosion product known as wet storage stain or white rust.

Furthermore industrial atmospheres usually accelerate the corrosion of galvanized steel when heavy mists and dews occur in these areas. They are contaminated with considerable amounts of acid substances and the film of moisture covering the metal can be quite acidic and can have a pH as low as 3. Under these conditions the zinc is dissolved but as the corrosion proceeds the pH rises and when it has reached a sufficiently high level basic salts are once more formed and provides further protection for the metal. As soon as the pH of the moisture film falls again, owing to the solution of acid gases, the protective film dissolves and renewed attack on the metal occurs⁽³⁾. Anderson considered the principal features which control the rate of corrosion of zinc as (a) The frequency of rainfall and dew fall (b) The acidity of the atmosphere and (c) The rate of drying⁽⁴⁾.

1.3 Flare Gas Reactions

The composition of flare gas which undergo combustion include CH₄, C₂H₄, C₃H₈, C₄H₁₀, C₅H₁₂ and others with respective composition by volume of 47, 18, 20, 5, 9 and 1 respectively. Since gas flaring is the controlled burning of natural gases associated with oil production. It is a combustion reaction represented by the equation of reaction.



The above named compounds in table1 present in the flared gas undergo combustion during flaring to release oxides of Nitrogen, carbon, and sulfur (NO_x, CO₂, CO, SO_x), particulate matter, hydrocarbons and ash, photochemical oxidants and hydrogen sulphide⁽⁵⁾.

Though Complexity of atmospheric chemistry as well as the diverse nature of pollutants make prediction of atmospheric corrosion difficult. Thus it is difficult to pinpoint a particular pollutant responsible for such effect. More so, some of the variable could be acting in synergy to promote corrosion hence scientific literature often base predictions on direct measurement of observed corrosion rates and correlating them to the various atmospheric parameters⁽⁶⁾. There is also problem of analyzing specifically the gas evolution as a result of agricultural and construction activities in order to determine the percentage being ejected in the atmosphere by the gas flaring industry and the problem of atmospheric condition as rain or wind or dust particles reducing the concentration of the gases at a particular.

1.4 Study Area

The Izombe village is located in Oguta local government Area of Imo State, South eastern Nigeria where Addax Petroleum Production company has its flow station at Izombe. Izombe is located in Imo State and is part of the Niger Delta region of Nigeria having a mobile phone/cellular frequencies of 900, 1800HZ. Its decimal coordinate is 5627 and 6.871. Latitude/ longitude coordinates is between N5⁰³⁷ 35¹¹ and E6⁰⁵² 16¹¹ and 243 miles (391km) away from Abuja South. Local time is UTC/GMT off set 1 hour and time zone is Africa/Lagos. Sunrise and sunset is between 6.44am and 6.42pm with the closest airports as Sam Mbakwe International Airport, Port Harcourt Airport and Enugu Airport while Closest Seaport is Onne Port Harcourt Seaport. Izombe is found within the humid tropical equatorial zone.

FUTO is located at between longitude 6⁰⁵⁹0E and 6⁰⁵⁸0E and latitude 5⁰²³0N and 5⁰²⁴0N. It is found in the rainfall forest zone of Owerri West. The altitude is 55m above sea level low land areas of South eastern rainfall agro-ecology of the humid tropics characterized by heavy rainfall and mean monthly temperature ranging from 23.8 to 29⁰c. Agriculture is a major socio-economic activity in the site with the Back swamp physiographic unit being influenced by seasonal flooding of the Otamiri River⁽⁷⁾.

1.5 Objectives of the work

The research is aimed at finding out:

- i. If gas ejection into the atmosphere contribute to the deterioration of galvanized Iron roofing sheets.
- ii. The role each individual gas plays in the corrosion process.

- iii. The effect of flare gases or pollutants on the acidity of rainfall.

II Experimentals

2.1 Samples preparation

The sample is a galvanized mild steel of elemental content carbon 0.18%, Manganese 0.7%, Silicon 0.1%, Phosphorus 0.03% and Sulphur 0.3% with the rest as iron (Fe) produced by hot-dipping and corrugated.

The long corrugated sample of galvanized roofing sheet were cut to a uniform size of 100mm x 80mm each using metal scissors. The specimen pieces were first washed in ethanol solution, cleaned and then degreased by scrubbing with bleach-free scouring powder. The cleaning action was to present a uniform surface by removing any extraneous particles especially metallic debris that could promote corrosion. A sample was selected and the surface was analyzed quantitatively using Automatic ARC 3460 Optical Emission Spectrometer of multichannel type with flexible and powerful OXSAS analytical software spectrometers prior and after exposure and the results are shown in the table below:

Table1: Surface elemental composition of exposed and unexposed samples

Element	%composition of unexposed sample	%composition of sample exposed in FUTO	%composition of sample exposed at 1000m in Izombe	%composition of sample exposed at 1000m in Izombe
Al	19.68090	18.51165	13.92120	11.27510
Fe	0.00010	0.00012	0.00210	0.00347
Cu	1.52999	2.43127	1.43900	1.41920
Ti	0.13938	0.12191	0.03038	0.03001
Cr	0.98793	0.51930	0.37164	0.12115
Ni	1.07155	1.11916	0.25562	0.27512
Si	0.83789	1.03485	0.36131	0.31212
V	0.21363	0.24060	0.05501	0.06507
Mg	0.50142	0.67623	0.09054	0.12590
Pb	29.96894	18.51165	3.95430	1.89512
Mn	10.06818	7.42674	10.05364	10.12718
Zn	35.00009	30.56238	29.46722	25.47829

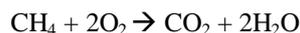
2.2 Gas Analysis

Monthly Atmospheric ambient gas analysis was carried out using the crown con gasman E.E 89/336/EEC Gas Analyzer with specific sensitivity to the various monitored gases.

2.2.1 Monitored Gases

The gases monitored were carbon monoxide (CO), carbon IV oxide (CO₂), sulphur dioxide (SO₂), Nitrogen IV oxide (NO₂), Ammonia (NH₃), methane (CH₄) and hydrogen Sulphide H₂S. These gases were monitored due to the role they play in promoting corrosion of materials exposed to the atmosphere, increasing or decreasing the acidity and basicity of the atmosphere as the case may be. In the industrialized economies, Sulphur- dioxides has been found to be the major industrial exhaust that degrades building materials ⁽⁶⁾. Ammonia though the only basic gas has a consequential effect of increasing the alkalinity of the atmosphere and hence will help predict which atmosphere is non corrosive. Methane on its own has the risk of enhancing

corrosion in the presence of moisture, it also reacts with oxygen in the air to form carbon dioxide and water vapour.



The reaction is very exothermic, releasing a large amount of heat. If the combustion is complete, the only apparent pollutant produced is carbon dioxide and for every kilogram of methane that is burnt, 2.74kg of carbon-dioxide is produced. Nearly 2^{24} times as much carbon-dioxide is the most prevalent green house gas responsible for climate change. Nitrogen-dioxide (NO_2) along with Sulphur -dioxide can also cause acid rain. They also form acids in the presence of moisture and these can be corrosive to building material at high concentration. These gases were monitored at 2 points at the respective sites and averaged.

2.3 pH and Rain Data

The monthly rain data of Owerri obtained from Nigeria Meteorological Agency Owerri Station shown and the monthly pH of rainfall samples collected with plastic buckets at the sites taken using the Tocado mp220 pH meter standardized between 4.0 and 10.0 with buffer solutions calibrated according to the national institute of standard to determine the extent of rain acidity are shown in Table 2 and 3 below respectively:

Table 2: Summary of Rainfall data

Month	Total Rainfall(mm)
January 2011	0.0
February 2011	133.7
March 2011	84.4
April 2011	114.8
May 2011	528.3
June 2011	189.3
July 2011	305.2
August 2011	506.7
September 2011	366.0
October 2011	241.2
November 2011	49.7
December 2011	24.8
January 2012	TR
February 2012	74

Table 3: Monthly Rainfall pH Values

Month	FUTO pH values	Izombe(1000m) pH values	Izombe(500m) pH values
July	6.8	5.9	5.6
August	6.9	6.1	5.7
September	6.9	6.2	5.6
October	6.8	6.5	6.1
November	—	—	—
December	6.7	5.7	5.2
January	—	—	—

2.4 Sample Exposure

The methods of corrosion monitoring adopted in this work include

1. **Surface Examination:** Involving quantitative analysis of surface element of the samples prior and after exposure to determine the extent to which the base metal has been exposed and macroscopic examination to find out the extent of oxidation of the exposed surface

2. Weight Loss Measurement: Where the monthly weight loss was taken with a sensitive mechanical weighing balance ADVENTURER AR 2140 Ohms with readability of 0.001g and maximum weighing ability of 210g by subtracting the final weight from the initial weight after cleaning the surface of the samples with brush and washing with ethanol.

3. Electrochemical Corrosion Testing: Using the CU/CUSO₄ half cell with saturated calomel electrode, contact was made on the structure itself and an electrolyte (water). The voltage values were taken using digital high impedance multimeter in (-mV).

2.5 Sample Exposure

After the cleaning process the sample specimens each properly labeled were suspended on a wooden rack with plastic strings tied to woods fixed into the rack frame and the assembly inclined at an angle of 30° to the horizontal surface. Each rack was stationed in an open field away from trees and building at an elevation of 1.5m above the earth surface to avoid contact with corrosive dirt in rain splashes from the surrounding around. The chosen slope was the average gradient of roofs in the study sites. The samples on each rack were in triplicates to ensure greater reliability of result. There were a total of 3 stations across the two research sites; one at 500m and the other of 1000m from the flare point in Izombe and one positioned centrally at Workshop-2 in FUTO. The period of exposure was seven months, from July, August, September and October representing the rainy season and November, December and January representing the dry season.

III Experimental Results

3.1 Gas Analysis

Monthly ambient gas analysis results are given in Table 4 and plotted in figures 1 to 7.

Table 4: Gas analysis results

		CO (ppm)	H ₂ S (ppm)	NH ₃ (ppm)	SO ₂ (ppm)	NO ₂ (ppm)	CH ₄ (ppm)
FUTO	Mean rainy values	2.125	0.0013	0.045	0.03	0.0213	0.03
	Mean dry values	2.58	0.037	0.07	0.06	0.043	0.7
	overall mean value	2.32	0.023	0.056	0.043	0.03	0.32
	SD	0.334	0.014	0.0159	0.017	0.012	0.400
	CV (%)	14.39	60.9	28.4	38.8	40	125
IZOMBE (1000M)	Mean rainy values	3.54	0.13	0.005	0.35	0.043	1.58
	Mean dry values	4.00	0.17	0.01	0.46	0.06	4.29
	overall mean value	3.74	0.147	0.0071	0.400	0.05	2.74
	SD	0.34	0.024	0.007	0.063	0.012	1.48
	CV (%)	9.09	16.33	98.6	15.78	24	54
IZOMBE (500m)	Mean rainy values	3.78	0.15	0.033	0.50	0.05	4.98
	Mean dry values	4.49	0.19	0.017	0.7	0.11	7.84
	Overall mean value	4.08	0.167	0.013	0.58	0.08	6.21
	SD	0.43	0.022	0.0088	0.101	0.037	1.69
	CV(%)	10.51	13.17	67.65	17.37	46.25	27.24

3.2 Gas Monitoring

The macrographs showing the extent of oxidation of the exposed surfaces are shown in Plates 1 to 3.

The results of the rates of corrosion of the samples monitored by potential and weight loss methods are shown in Tables 5 and 6 and plotted in Figures 6 and 7 below:

Table 5: Weight loss results

Time (days)	FUTO Weight loss(mg)	Izombe(1000m) Weight loss(mg)	Izombe (500m) Weight loss(mg)
0	0	0.00	0.00
28	0.34	1.07	2.53
56	0.51	2.82	4.17
84	0.78	3.14	5.68
112	0.87	3.78	6.72
140	0.93	3.94	6.98
168	1.05	4.16	7.14
182	1.17	4.23	7.62

Surface area of sample= 8cm x10cm = 80cm² =0.008cm²

Table 6: Result of Potential Measurement

Days	Month	FUTO (potential (mV))	Izombe1000m (potential (mV))	Izombe (500m) (potentialmV)
0	July	-1047	-1047	-1047.33
14	August	-996	-975	-950.33
28		-982.33	-974.67	-825.33
42	September	-975.33	-820.33	-840.33
56		-961.67	-913.67	-921.33
70		-979.67	-929.67	-1004.67
84	October	-994.67	-972.33	-1008.3
98		-1007.67	-1002.33	-1015.33
112	November	-1008.67	-1009.67	-1018.67
126		-1017.33	-1017.27	-1023.33
140	December	-1009.25	-1018.33	-1025.33
154		-1004.0	-1014.67	-1019.33
168	January	-1001.30	-1011.67	-1017.33
182		-926.33	-1007.33	-1009.69

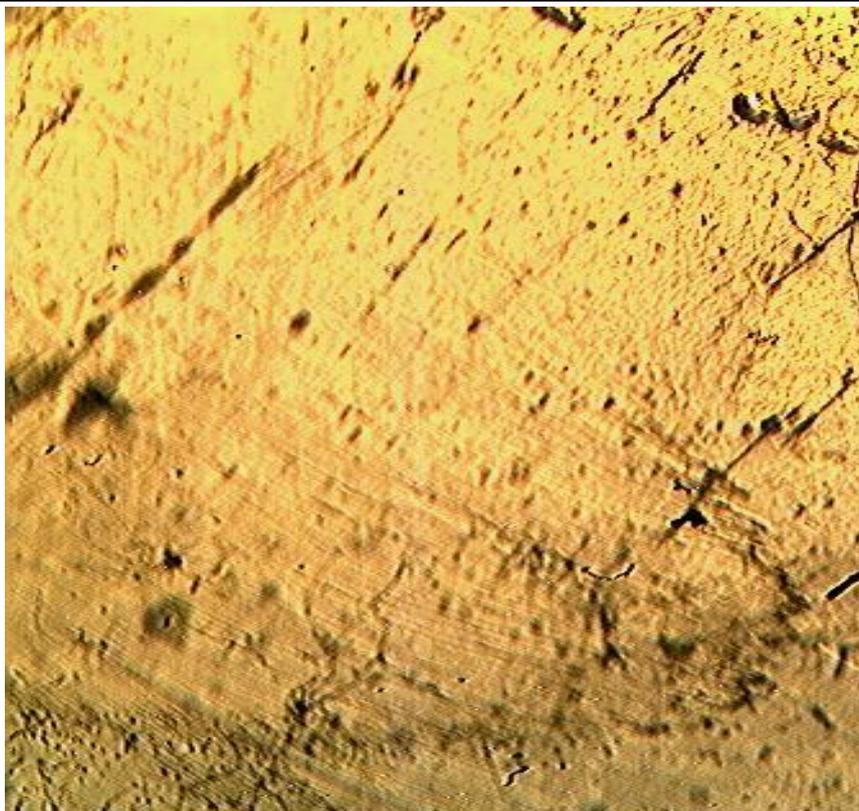


Plate 1: Macrograph of exposed sample in FUT0

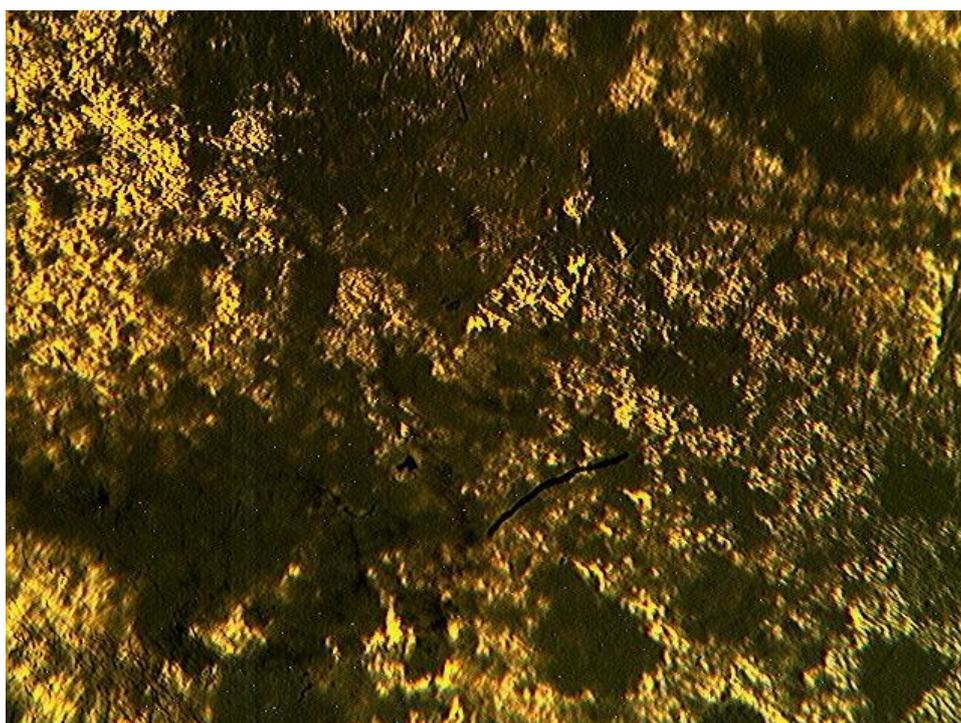


Plate 2: Macrograph of exposed sample at 1000 m at Izombe

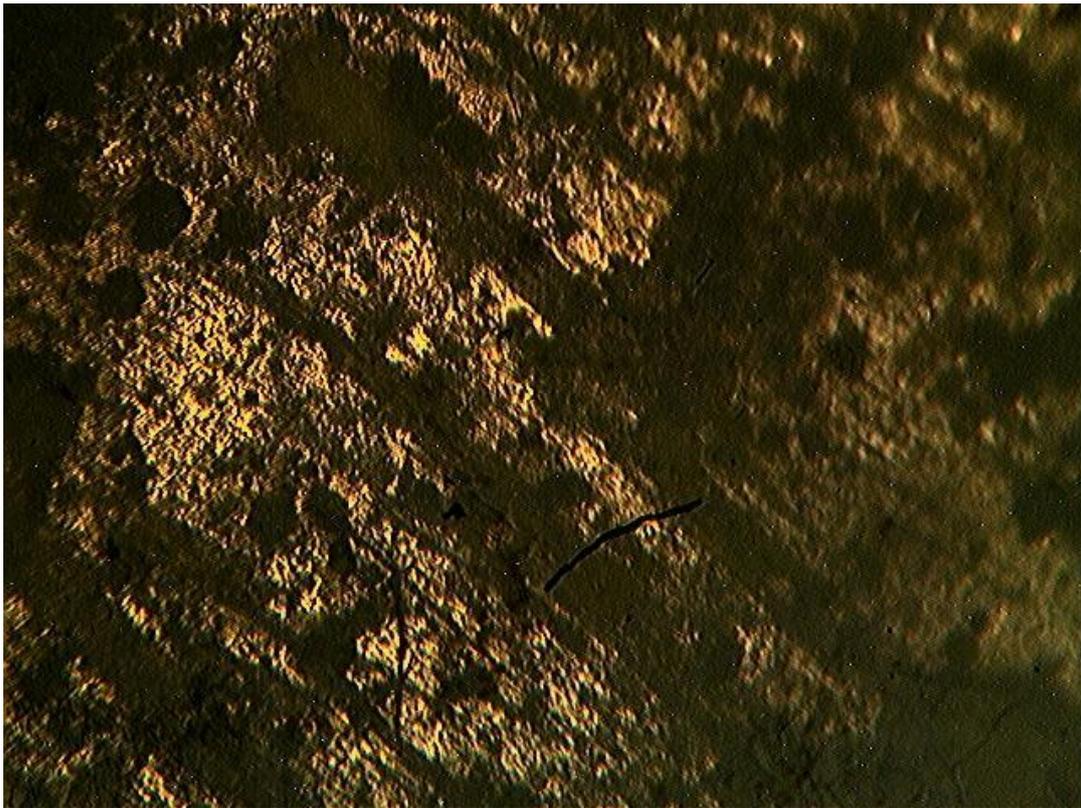


Plate 3: Macrograph of exposed sample 500 m at Izombe

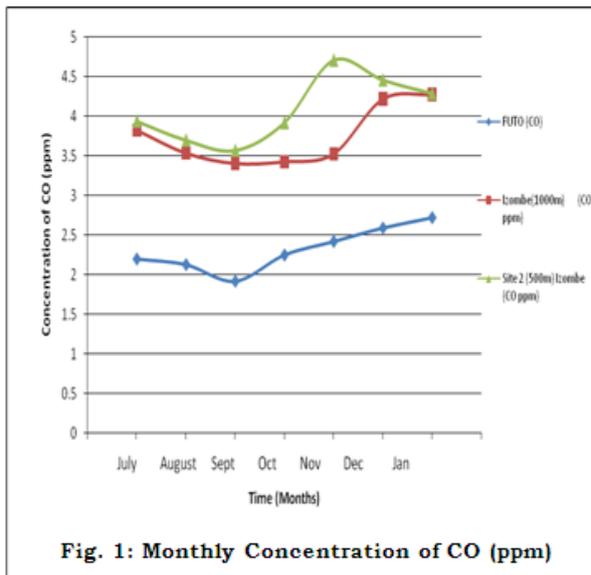


Fig. 1: Monthly Concentration of CO (ppm)

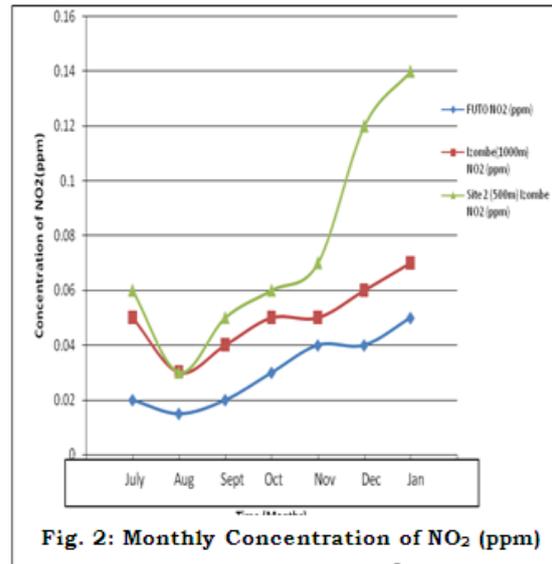
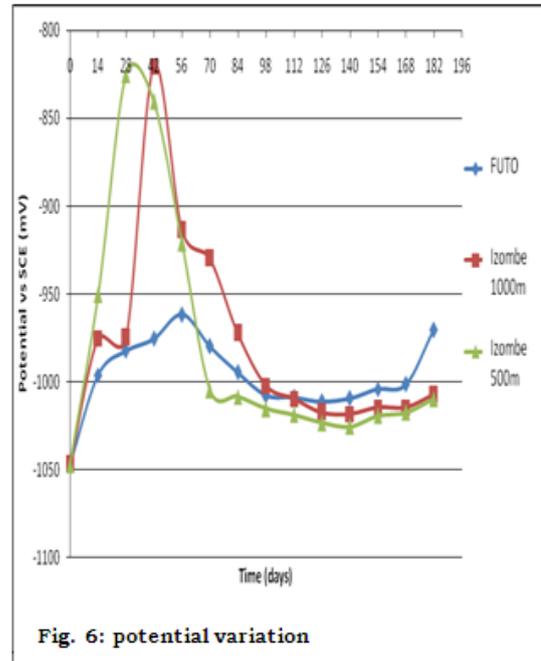
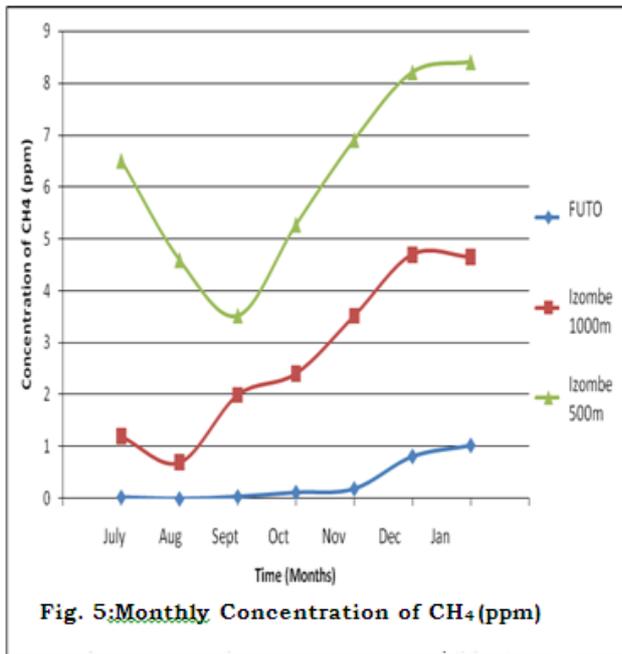
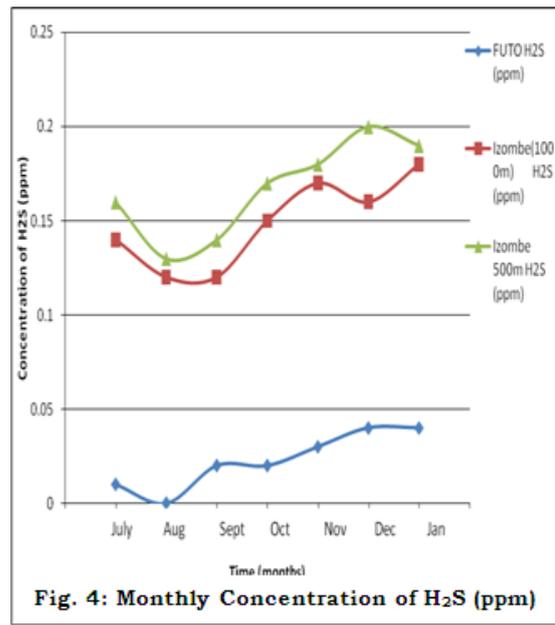
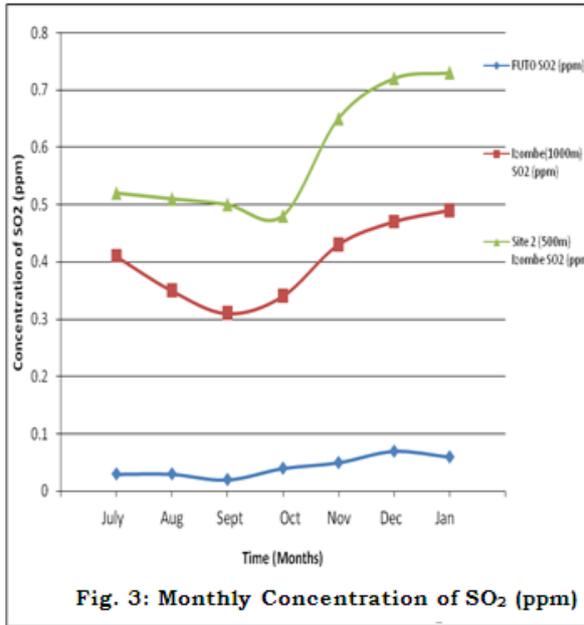


Fig. 2: Monthly Concentration of NO₂ (ppm)



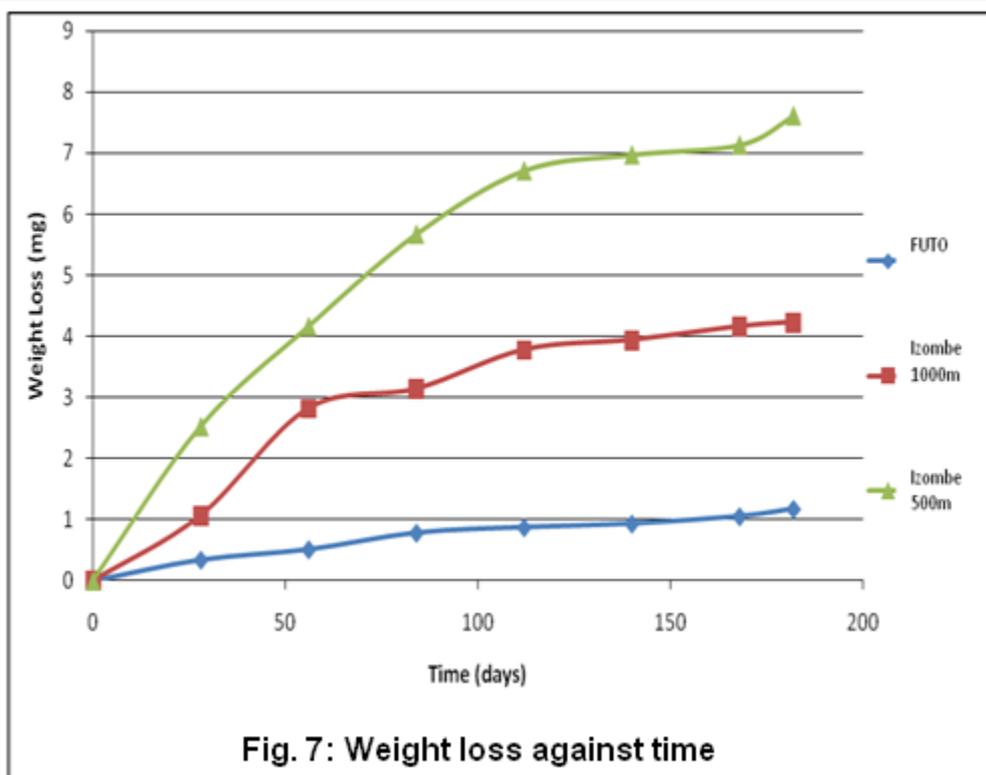


Fig. 7: Weight loss against time

IV Discussion Of Results

4.1 Corrosion Monitoring

4.1.1 Analysis of Surface Elemental Composition

The surface elemental content of the sample prior to exposure and after exposure shown in table 1 reveal a higher percentage composition of the galvanizing element Zinc (Zn) and Lead (Pb) of 35% and 29% respectively with a very low percentage composition of the base element Iron Fe (0.00010%). This implies that the coatings (galvanizing elements) are exposed while the base metal (mild steel) with a higher percentage of Iron Fe is completely protected. After seven months exposure the sample at FUTO showed a reduction in the percentage of the surface composition of zinc and Lead (Pb) to a value of 30.56% and 18.51% respectively with an increase in the surface percentage elemental content of Iron to 0.00012%. This is an indication that deterioration of the surface coating has slightly taken place with an exposure of the base metal. The samples exposed at site 1 and 2 1000meters and 500meters from flare stack at Izombe show a reduction in percentage of surface Zinc and Lead(Pb) to 29.47% Zn and 3.95% Pb and 25.48% Zn and 1.89512% Pb respectively and a higher percentage of Iron to 0.00210% Fe and 0.00347%Fe. This signifies that the surfaces of the samples at 500m has eroded more than those at 1000m followed by the samples exposed in FUTO indicating that further exposure leads to a more deterioration of the surface coating and concurrent exposure of the base metal which is less corrosion resistant.

Furthermore the macrographs shown in Figures 1to 3 revealed darker phases for sample exposed at 500meters away from flare source than that exposed at 1000meters from the flare source indicating that the sample surface experienced more oxidation as we move close to the flare source. The sample exposed at FUTO showed lighter phases which indicated less surface oxidation compared to that experienced in the sites above.

4.1.2 Potential Monitoring

It can be seen that an initial increase in potential occurred in the first two months. This is due to the fact that hot-dip galvanizing is primarily a method of applying coating of zinc on mild steel to prevent it from corroding. The base metal here is a mild steel with standard electrode potential of (-0.44v) being coated with zinc of standard electrode potential of (-0.76v). Hence the deterioration of the coating (zinc) leads to the exposure of the base metal which is more electropositive than zinc metal.

The evolution of the open circuit potential for the three stations revealed an initial decay probably due to dissolution of the native zinc oxides existing on the surface, then the potential slightly decreased in the anodic

direction followed by stabilization. This potential shift is probably due to the development of oxide film on the surface. Hence for FUTO site, the potential rose initially and maintained an average but undulating curves showing that the corrosion was taking place at a slower pace and at some interval after two months passivation ensues indicating that the rate of corrosion was minimal.

The site1 at 1000m Izombe showed a gradually increasing potential with rate twice faster than the initial rate after first one and half month to peak at (-820mv) while the lowest potential attained was (-1021mv) indicating more corrosion rate than that of FUTO. Concurrent passivation and mild corrosion rate took place within the end of September and early part of November. Generally rapid and erratic potential values were obtained between August and ending of October being periods with higher rainfall values as shown in table 2. On the other hand the potential of the samples at the site 2 of Izombe 500meters away from the stack showed a rapid increase within the first one month, indicating an initial attack of the surface coating. The potential then peaks at (-825mv) lower than that of the site 1 and a series of undulating values were obtained within the next two months indicating passivation and subsequent corrosion. The lowest value of potential was obtained after three months with the value of (-1025mv). This shows that corrosion occurred more in this site more than the previous sites.

4.1.3 Weight Loss

The weight loss values showed that the maximum mean weight loss of the samples in FUTO was 1.17mg. The loss of weight was much more pronounced within the first four months whose period fall within rainy season. The site at Izombe 1000m from flare stack showed a maximum weight loss of 4.23mg which is higher than that experienced in FUTO. The first two months showed a gradual increment in weight loss but was more significant in the third month and the fourth one. There was also decline in the last three month which are mainly dry season period.

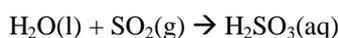
Furthermore, the sample exposed at 500 meters away from the flare stack showed a maximum weight loss of 7.62mg. This value was higher compared to the two sites above indicating more corrosion. This is in line with the findings of Obia that weight loss decreases with distance away from the flare site i.e. there is a negative correlation of weight loss with distance, thus the further a station is from the source of pollution the less the effect ⁽⁶⁾. Generally, the weight loss values increased at a higher rate within the early first four months which were rainy and declined gradually in the last three dry months as shown in Figure 7.

4.2 Atmospheric Gas Effect

The Figures 4 to 8 generally indicate that there was more concentration of atmospheric gas pollutants in the dry season than in the rainy season. Further regression of acidic gases SO₂, NO₂, H₂S and CH₄ separately with the monthly weight loss gave the following results

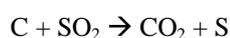
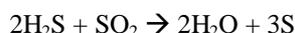
$$R_{CH_4}=-0.6 \quad R_{SO_2}=-0.54 \quad R_{NO_2}=-0.68 \quad R_{H_2S}=-0.79$$

Of which methane and sulphur-dioxide gave more positive regression values indicating that they participate more in promoting corrosion of galvanized roofing sheet close to the flare site. The result is supported by the fact that sulphur IV oxide is very soluble in water, one volume of water dissolving about 70 volumes of the gas. The resultant solution is trioxosulphate IV acid according to the equation



of which further oxidation may lead to tetra-oxosulphate VI acid which in the presence of substantial amount in the atmosphere leads to the formation of acid rain.

Other reactions of sulphurdioxide include oxidizing hydrogen sulphide and also carbon from the oil gas according to



The reaction leads to the formation of more atmospheric sulphur and CO₂ which participates strongly in enhancing atmospheric corrosion.

4.3 Rainfall pH

The result of pH of collected rainfall samples recorded in Table 3 compared with the result of gas analysis indicated that the acidic gases NO_2 , SO_2 , H_2S and CH_4 , concentration increases with decrease in pH, indicating higher acidity and increases with increase in NH_3 concentration, in the case of FUTO.

V Conclusion

This seven (7) months research work cutting across rainy and dry seasons whereby samples of corrugated galvanized steel roofing sheets were exposed at 500m and 1000m away from flare source in Izombe and FUTO a non gas flaring environment showed that the potential versus saturated calomel electrode results were more erratic within the flare region than FUTO, decreasing to minimum potential of -1018mV and -1025mV for the flare site against -1011mV. The weight loss gave a maximum value of 7.62mg and 4.23mg for samples exposed at 500meters and 1000meters away from the flare source in Izombe as against the control site samples in FUTO which gave maximum weight loss of 1.17mg. Furthermore, the concentration of the gases were higher in the dry season than in the rainy season and when regressed separately with the weight loss near the flare source gave the following results: $R_{\text{CH}_4}=-0.6$ $R_{\text{SO}_2}=-0.54$ $R_{\text{NO}_2}=-0.68$ $R_{\text{H}_2\text{S}}=-0.79$ with respective coefficient of variation of +. 27.2%, +.17.4%, +.46.25% and +.13.7% which clearly indicated that corrosion was more in Izombe than in FUTO. Also the nearer an environment is to a flare source, the more corrosion effect and that methane gas and sulphur-dioxide with more positive regression values contributes more to the corrosion process.

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