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Modeling the Effect of Acid Rain of HNO_3 on Corrosion Susceptibility of Roofing Sheet

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Abstract— **The effect of Nitric acid on weight loss and fractal dimension for five types of roofing sheets namely, Stone Coated Roofing Sheet (SCRS), Zinc Corrugated Roofing Sheet (ZCRS), Emboss Aluminium Roofing Sheet (EARS), Small Curve Corrugated Roofing Sheet (SCCRS) and Aluminium Zinc Corrugated Roofing Sheet (AZCRS) were investigated. The samples were immersed in acid rain solution simulated from various concentrations of Nitric (HNO_3) acid. The experiments were designed using Central Composite Design (CDD) of Response Surface Methodology (RSM) based on three factors. These are concentration c, (0.00 ppm – 350.00 ppm), time of exposure t, (1week – 2week) and pH, (4-7) of acid solution. Weight loss of each sample was determined by the difference in weight before and after immersion in acid solutions. The influences of these parameters on weight loss were obtained from analysis of variance. Microstructural analyses of the corroded samples were carried out using an optical metallurgical XJL-17 microscope while fractal analysis was carried out on the microstructures obtained. At c = 350.00 ppm, t = 1.5 weeks and pH = 4, the highest weight loss of 0.0086 was obtained when ZCRS was immersed in HNO_3 solution. The lowest weight loss of 0.0031 was obtained when EARS was immersed in HNO_3. Based on ANOVA, the weight loss is significantly influenced by all input variables as well as their combinations. EARS has finer grains which reduce intergranular corrosion. ZCRS with fractal dimension (D) of 1.9618 has the worst level of corrosion HNO_3 solution. EARS with D of 1.9177 have the least level of corrosion HNO_3 solution.The results showed that time, concentration and pH significantly influence corrosion. It also showed that, EARS has the least weight loss and corrosion level in acidic medium.**

Index Terms— **Concentration, Fractal dimension, Roofing sheet, weight loss.**

I. INTRODUCTION

Olatunji (2009), reported that the major problem facing most of production and manufacturing industries which has a direct impact both on these industries and our national economy as a whole is corrosion and its grave effects on materials failures cannot be overemphasized. Huge economic losses resulting from plant shutdowns, material losses and contamination are some evident facts. The combined effect of atmospheric climatic and pollutant factors on metallic materials has been identified by Obia and Obiot (2010),as a major factor of its deterioration, generally called corrosion reaction. This reaction which resulted to rust of materials was reported by Scully (1990), as electrochemical oxidation process. According to (Awajiogak and Emmanuel, 2013), corrosion seeks to reduce the binding energy in the metals and is accelerated by acid rain most especially in oil producing environments.

The industrial atmosphere usually accelerates the corrosion of metal roofing sheets when heavy mists and dews occur in these areas. Metal roofing sheets as one of the construction materials, when exposed to industrial environment also tend to revert to lower-energy oxide state. It has been observed in recent times that the grade of roofing sheet used in construction is more susceptible to corrosion than those that were used in the 1940s – 1950s. Besides, the recent advances in industrial activities especially in the oil and gas industries where the environment has been heavily polluted with contaminants have exacerbated the corrosion rate of roofing sheet. The principal pollutants in oil producing area are sulfur dioxide (SO_2) and nitrogen oxides (NOx). Its chemical reaction with rain leads to formation of acid rain. Acid rain will damage the metal roofing sheet in acidic environment at a very fast rate which will invariably reduce the life span of the metal roofing sheet (Obia and Obiot, 2010). However, different metal roofing sheets demonstrate different levels of resistance to corrosion caused by acid rain/ acid precipitation in this environment (Obia and Obiot, 2010). Hence, the need for adequate knowledge about durability of specific roofing sheet in relation to its environment which will go a long way in cost effectiveness of desired metal roofing sheet.

II. MATERIALS AND METHODS

Five different type of roofing sheets samples :Stone coated roofing sheet (SCRS) (YX37-208-825), Zinc corrugated roofing sheet (ZCRS) (YX28-210-840/1050), Emboss aluminium roofing sheet (EARS) (YX25-100-900), Small curved corrugated roofing sheet (SCCRS) (YX18-78/836/988), Aluminium zinc corrugated roofing sheet (AZCRS) (YX25-200-1000), were sought for in roofing sheets selling distributors in Osogho Osun State, Nigeria and cut into 20mm x 30mm.The samples were first washed in ethanol solution, degreased, scrubbed and cleansed with 120 number abrasive papers in accordance with ASTM GI standards (Chotimongkol *et al*, 1999 & Cole *et al*, 1999). Each specimen was then weighed on the Analytical weighing balance with 0.1mg readability and its initial weight recorded. The samples were immersed in a prepared solution of HNO_3 of different concentration ranging from 0.000ppm to 350.00 ppm with different pH ranging from 4 to 7. The experiment was design using design expert 8.03 software. Weight loss as response was taken by difference between the

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weight of the sample before and after immersion. The obtained data of weight loss was statistically analyzed and the model equations were generated.

The pattern microstructure of the samples were taken and fractal dimension of the corroded surfaces of the samples was numerically characterized using equation 1 (Lu and Hellawell, 1999).

$$P = P_E \delta^{D-1} \ . (1 < D < 2 \ . and \ . \delta_m < \delta < \delta_M) \quad \ldots(1)$$

Where P_E is the measured perimeter, P is the true perimeter, δ is the yardstick, δ_m and δ_M are the upper and lower limits respectively, for any shape.

The fractal dimension, D, (1<D<2) therefore describes, the complexity of the contour of an object. It can be more practically called the roughness (Huang and Lu, 2002).

When δ < δ_m the measurement is not sensitive to the yardstick chosen, therefore giving a smaller value of the slope, while $\delta < \delta_M$, the size of the yardstick exceeds that of the individual feature being measured so that the measurement loses meaning because the object falls below the resolution limit of the yardstick used for measurement (Lu and Hellawell, 1999).

To calculate the perimeter P of the corroded parts, the Slit Island Method (SIM) (Bigeralle and Lost, 2006) introduced by (Mandelbort, 1983) is used. It is expressed as

$$Log_e P = 0.5 D log_e A_T \quad \ldots\ldots (2)$$

$$P = e^{0.5} loge A_T \quad \ldots\ldots (3)$$

Total corroded area A_T = Area of yardstick x Number of yardsticks

Using the Eq. (1), (2), and (3) above, interactive software in Matlab programming language was developed to obtain the numerical values of the fractal dimension D.

III. RESULTS AND DISSCUSSION

Table 1 shows the result of weight loss of each of the specimens (five different roofing sheets) immersed in acidic test solutions of HNO_3. Equation (4),(5),(6),(7) and (8) represent model equations generated from the obtained datas for SCRS, ZCRS, EARS, SCCRS and AZCRS respectively. A stands for Concentration, B for Time (week) and C stands for pH.

Weight Loss = +0.065-1.575E-003* A +6.250E-004* B-7.625E-003* C-2.125E-003 * A * B-7.375E-003 * A * C+0.012 * B * C (4)

Weight Loss =+1.592E-003+5.325E-004* A+5.000E-005* B+3.250E-004 * C-3.000E-004 * A * B+3.750E-004 * A * C-1.500E-004 * B * (5)

Weight Loss =+3.900E-003+1.900E-003* A-1.538E-003* B-1.125E-004* C-3.625E-004 * A * B+1.250E-005* A * C-2.250E-004* B * C (6)

Weight Loss =+1.240E-003+3.600E-004* A-1.375E-004* B+3.375E-00* C +3.875E-004* A * B-8.750E-005* A * C-4.750E-004* B * C (7)

Weight Loss = +1.460E-003+1.400E-004* A+7.875E-004* B+1.250E-005*C+6.625E-004* A * B-6.250E-005*A* C-7.250E-004 * B * (8)

Figure 1 to 5 shows the effect of two combinatory factors on weight loss response while keeping one factor at constant and generally the result established the increase in weight loss with synergy of two factors for all the roofing sheets.

The model equations developed from the analysis of results gave the predicted life span of the roofing sheets to be 5 years for SCRS when exposed to HNO_3. It was 3 years for ZCRS when in HNO_3, while for EARS, the life span was 16 years in HNO_3, medium. Twelve years was predicted for SCCRS in HNO_3 and finally, 4 years was the predicted life span of AZRS in HNO_3 exposure (Table 2). The current market price of each of the samples in Osogbo, Osun State Nigeria were also listed in table 2

Figure 6 and 7 shows the pattern microstructure of the samples before and after immersion in acidic medium of HNO_3 with concentration of 175 at pH of 4 for the duration of two weeks. The evaluation of fractal features of the corroded surfaces was conducted to know the fractal dimension (D) ranging from 1 to 2 (1 < D < 2) for each of the roofing sheet in acidic medium of HNO_3 as shown in table 3.

According to Durowoju, *et.,al, (2013)*,the closer the value of D to 1 the better the corroded surface and the farther away from 1 the worst the corroded surfaces of the roofing sheets. It was observed that, ZCRS with fractal dimension (D) values of 1.9618 exhibited the worst corroded surfaces in HNO_3 acidic medium, while EARS with fractal dimension (D) values of 1.9177 exhibited the least corroded surfaces in HNO_3 acidic medium.

Table 1: Box Behnken experimental design and the weight loss response of SCRS, ZCRS, EARS, SCCRS and AZCRS in acidic medium of HNO_3

Run	*Factor1A: Conc. ppm*	*Factor 2B: Time Wk*	*Factor 3C. pH*	Response Weight Loss % SCRS	ZCRS	EARS	SCCRS	AZCRS
1	350.00	2.00	5.00	0.0496	0.0059	0.0015	0.0025	0.0035
2	175.00	1.50	5.00	0.0351	0.0054	0.0019	0.0024	0.0031
3	0.00	2.00	7.00	0.000	0.000	0.000	0.000	0.000
4	350.00	1.50	4.00	0.0744	0.0086	0.0031	0.0034	0.0038
5	175.00	1.00	6.00	0.0296	0.0039	0.0018	0.0017	0.0021
6	0.00	1.00	7.00	0.000	0.000	0.000	0.000	0.000
7	350.00	1.00	5.00	0.0324	0.0045	0.0029	0.0013	0.0024
8	175.00	2.00	6.00	0.0309	0.0022	0.0005	0.0014	0.0017
9	175.00	1.50	5.00	0.0355	0.0054	0.0020	0.0027	0.0031
10	0.00	1.50	7.00	0.000	0.000	0.000	0.000	0.000
11	175.00	1.50	5.00	0.0349	0.0055	0.0017	0.0028	0.0032
12	175.00	1.00	4.00	0.0592	0.0043	0.0022	0.0015	0.0019
13	175.00	1.50	5.00	0.0344	0.0056	0.0019	0.0026	0.0033
14	0.00	1.50	7.00	0.000	0.000	0.000	0.000	0.000
15	175.00	1.50	5.00	0.0348	0.0055	0.0018	0.0027	0.0033
16	350.00	1.50	6.00	0.0482	0.0040	0.0019	0.0015	0.0019
17	175.00	2.00	4.00	0.0574	0.0044	0.0016	0.0028	0.0034

Table 2 Number of years of Selected Roofing Sheets in Acidic Medium at 175 Concentration and pH of 4 with their current market price per bundle

S/N	Types of roofing sheet	Predictive No of years of Roofing Sheets in Acidic Medium of HNO_3	Current Market Price ₦
1	Stone Coated	5	2850 per m^2
2	Zinc Corrugated	3	17600 per bundle
3	Emboss Aluminium	16	18200 per bundle
4	Small Curve Corrugated	12	14400 per bundle
5	Aluminium Zinc Corrugated	4	1400 per m^2

Table 3 Fractal Results for all the types of materials at concentration of 175 and pH4

Variables	HNO_3
Type 1	1.9382
Type 2	1.9618
Type 3	1.9177
Type 4	1.9239
Type 5	1.9275

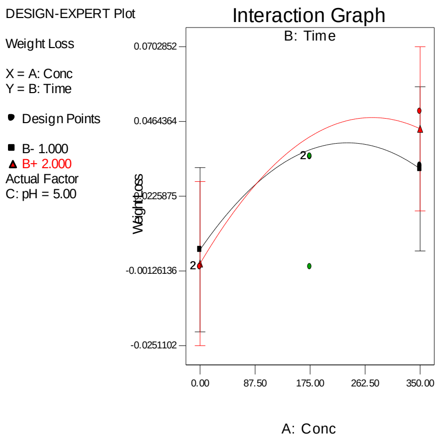

Fig. 1:Response surface plot for weight loss response of stone coated roofing sheets in HNO_3 medium (with constant pH)

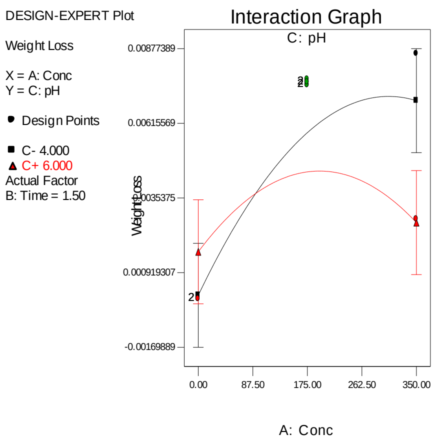

Fig. 2: Response surface plot for weight loss response of zinc corrugated roofing sheets in HNO3 medium (with constant time).

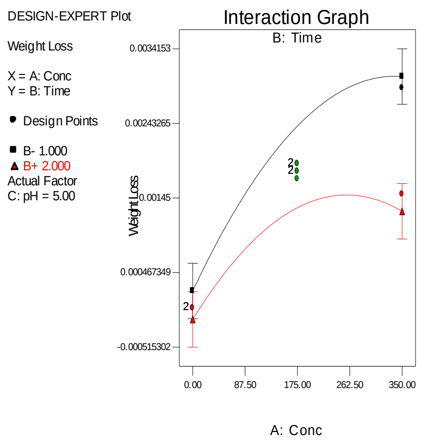

Fig. 3: Response surface plot for weight loss response of emboss aluminium roofing sheets in HNO_3 Medium (with Constant pH)

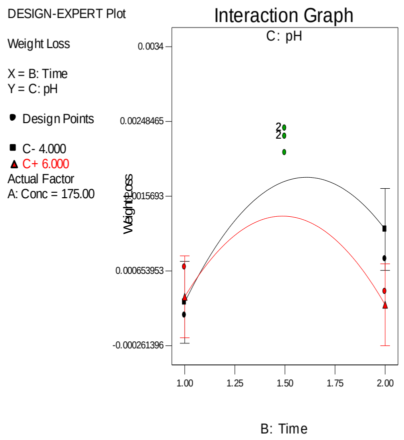

Fig. 4: Response surface plot for weight loss response of small curve corrugated roofing sheets in HNO_3 medium (with constant concentration).

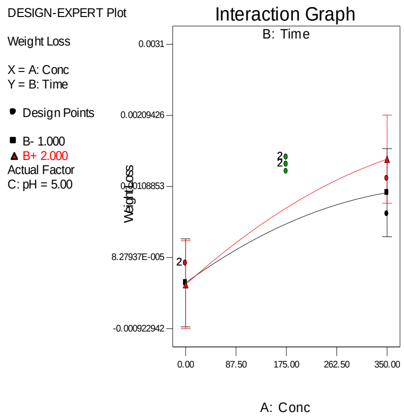

Fig., 5: Response surface plot for weight loss response of Aluminium zinc corrugated roofing sheets in HNO3 Medium (with Constant pH).

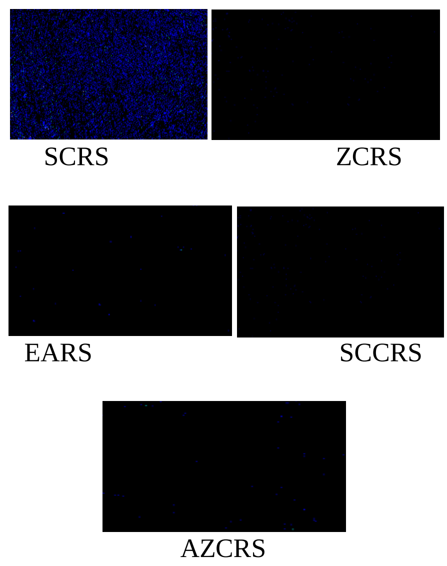

Fig. 6: The pattern of microstructure of the samples before immersion in acidic medium.

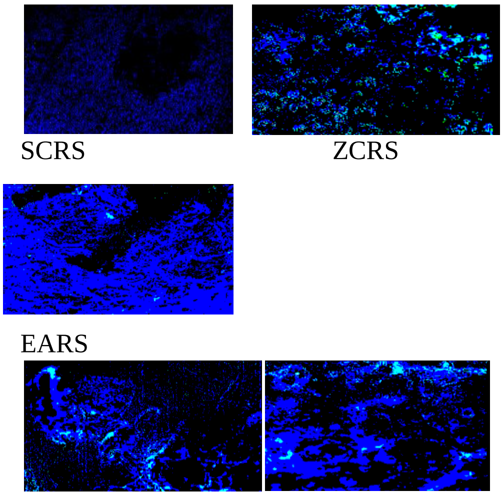

Fig. 7: The pattern of microstructure of the samples after immersion in acidic medium of HNO_3 with concentration of 175 and pH of 4

IV. CONCLUSION

With indication of least corroded surfaces exhibited by EARS, and low percentage of weight loss in acidic medium of HNO_3 EARS is therefore recommended for use in acidic environment where the liberation of NO_2 gas into the atmosphere is predominant (most especially oil producing environment).

APPENDIX

Table 4 ANOVA Test for Weight Loss Response of Stone Coated Roofing Sheets in HNO_3 Medium

Variables	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Significant Level
Model	0.001107	6	0.000185	527.2857	0.0019	Significant
A	2.21E-05	1	2.21E-05	63	0.0155	Significant
B	2.08E-06	1	2.08E-06	5.952381	0.0248	Significant
C	0.00031	1	0.00031	885.9524	0.0011	Significant
AB	2.41E-05	1	2.41E-05	68.80952	0.0142	Significant
AC	0.00029	1	0.00029	828.8095	0.0012	Significant
BC	0.0006	1	0.0006	1715	0.0006	Significant

Table 5 ANOVA Test for Weight Loss Response of Zinc Corrugated Roofing Sheets in HNO_3 Medium

Variables	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Significant Level
Model	4.22E-06	6	7.03E-07	312.2593	0.0032	Significant
A	2.52E-06	1	2.52E-06	1120.222	0.0009	Significant
B	1.33E-08	1	1.33E-08	5.925926	0.0053	Significant
C	5.63E-07	1	5.63E-07	250.3704	0.0040	Significant
AB	4.8E-07	1	4.8E-07	213.3333	0.0047	Significant
AC	7.5E-07	1	7.5E-07	333.3333	0.0030	Significant
BC	9E-08	1	9E-08	40	0.0241	Significant

Table 6 ANOVA Test for weight loss response of Emboss Aluminium Corrugated Roofing Sheets in HNO_3 Medium

Variables	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Significant Level
Model	4.51E-05	6	7.52E-06	1203.104	0.0008	Significant
A	3.21E-05	1	3.21E-05	5134.222	0.0002	Significant
B	1.26E-05	1	1.26E-05	2017.2	0.0005	Significant
C	6.75E-08	1	6.75E-08	10.8	0.0014	Ssignificant
AB	7.01E-07	1	7.01E-07	112.1333	0.0088	Significant
AC	8.33E-10	1	8.33E-10	0.133333	0.7500	Insignificant
BC	2.02E-07	1	2.02E-07	32.4	0.0295	Significant

Table 7 ANOVA Test for Weight Loss Response of Small Curve Corrugated Roofing Sheets in HNO_3 Medium

Variables	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Significant Level
Model	4.13E-06	6	6.88E-07	131.0952	0.0076	Significant
A	1.15E-06	1	1.15E-06	219.4286	0.0045	Significant
B	1.01E-07	1	1.01E-07	19.20635	0.00483	Significant
C	6.08E-07	1	6.08E-07	115.7143	0.0085	Significant
AB	8.01E-07	1	8.01E-07	152.5397	0.0065	Significant
AC	4.08E-08	1	4.08E-08	7.777778	0.1081	Insignificant
BC	9.03E-07	1	9.03E-07	171.9048	0.0058	Significant

Table 8 ANOVA Test for Weight Loss Response of Aluminium Zinc Corrugated Roofing Sheets in HNO_3 Medium

Variables	Sum of Square	Degree of Freedom	Mean Square	F Value	Prob > F	Significant Level
Model	6.57E-06	6	1.1E-06	208.6261	0.0048	Significant
A	1.74E-07	1	1.74E-07	33.18519	0.0288	Significant
B	3.31E-06	1	3.31E-06	630	0.0016	Significant
C	8.33E-10	1	8.33E-10	0.15873	0.7288	Ssignificant
AB	2.34E-06	1	2.34E-06	455.873	0.0022	Significant
AC	2.08E-08	1	2.08E-08	3.968254	0.1846	Insignificant
BC	2.1E-06	1	2.1E-06	400.4762	0.0025	Significant

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