International Journal of Applied Engineering and Technology ISSN: 2277-212X (Online)
An Online International Journal Available at http://www.cibtech.org/jet.htm
2013 Vol. 3 (4) October-December, pp.9-17/Awajiogak and Emmanuel

Research Article

ESTABLISHING KINETIC PROCESSES OF CORROSION ON ZINC/IRON ROOFING SHEET IN COASTAL/INDUSTRIAL ENVIRONMENT

***Awajiogak A. Ujile and Emmanuel O. Ehirim**
Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology
P.M.B. 5080, Port Harcourt, Nigeria
**Author for Correspondence*

ABSTRACT

Mathematical correlations were developed to predict the behavior of iron roofing sheets on exposure to different environmental conditions. The analytical results from Atomic Absorption Spectroscopy (AAS) of chromium, iron oxide and zinc contents for the locations considered were fed into the developed equation. Corrosion rates were determined by weight loss method and model equation, and the results from the two methods are in agreement. The rate constants for location A is 0.36/hr; and location B = 0.174/hr; location C = 0. Corrosion rates by weight loss method were 0.514mpy and 0.221mpy for locations A and B respectively within the first five years; while corrosion effects on roofing sheet were noticed to be 0.0068mpy at location C from 5 – 10 years. The developed model provides solutions which have direct application to the prediction of corrosion rates on iron roofing sheets.

Key Words: *Salt Loadings, Kinetics, Rust, Chemical Changes, Active Ingredient*

INTRODUCTION

Most metals slowly oxidize when exposed to atmospheric conditions, changing to another form such as the mineral ore from which they were produced. Rusting iron and steel produce reddish iron oxide. Some metals such as gold and certain stainless steels are more resistant than others to this process (or more noble) and remain largely unaffected. The process of chemical reversion, or corrosion, is accelerated by air pollutants, acid rain, salts and the presence of dissimilar metals. In coastal environments metals corrode rapidly under the influence of airborne salts and high humidity (NSW, 1998)

Corrosion is the degradation of material through environmental interactions. Thermodynamics and kinetics form the basic fundamentals of corrosion. Thermodynamics indicates whether a specific corrosion process is possible while kinetics determine the actual rates of corrosion.

A significant amount of energy is always put into a metal when it is extracted from its ores placing it in a high energy state. One principle of thermodynamics is that a material always seeks the lowest energy state. In other word, most metals are thermodynamically unstable and will tend to react with something in their environment (eg. Oxygen, water) in order to reach a more stable energy state such as oxide. The process by which metals convert to the lower energy oxides is called corrosion.

Iron, tends to be highly reactive with most environment because of its natural tendency to form iron oxide. When it does resist corrosion it is due to the formation of a thin film of protective iron oxide on its surface by reaction with oxygen of the air. This film can prevent rusting in air at 99% RH, but a contaminant such as acid rain may destroy the effectiveness of the film and permit continued corrosion (Kearny, 2013). Construction materials like corrugated iron roofing sheets 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 of building located in such areas. Environmental factors which affect corrosion rate include: type, chemistry, concentration, phase, conductivity, velocity, and thin layer wetting etc (Ujile and Ehirim, 2009).

Coastal areas are known to have very high salt loadings in the air because of complex interactions between ions, wind effect and perhaps certain elements that emanate from the sea. The investigation therefore is to consider processes of these interactions and develop model equations that could describe the deterioration of active ingredients and formation of corrosion products on zinc/iron roofing sheets at the three locations, as shown in figure 1.

Investigations have shown a strong relationship between the corrosion rate of zinc and the SO2-concentration (Zheng *et al.,* 1991). During the last decades (Deans and Lee, 1987) numerous field and laboratory research programs have been conducted to investigate the corrosion behavior of zinc under different types of atmospheres. Few studies are related to zinc roofing sheet (Ovri and Iroh, 2013). Their work did not consider the effect(s) of industrial pollutants exuded from flare on zinc sheet. There was synergism amongst the factors in their contribution to corrosion impact (Obia and Obot, 2010). Atmospheric corrosion of roofing materials has also been done in most temperate regions of the world (Gradel and McMGill, 2011; Cole *et al.,* 1999). However, less scientific research has been carried out in recent past on atmospheric corrosion of roofing materials in the humid, highly industrial tropical regions of south-southeast where this work was carried out. Besides, there is no kinetics process established on this subject matter from any literature.

The aim of this study is not only to establish kinetics model of corrosion processes on iron/zinc roofing materials, but also to determine the rate of corrosion of the roofing sheet on buildings located in industrial/coastal environment. Three locations in Akwa Ibom State of Nigeria were considered in the study.

Location A - Industrial/coastal environment (where flares from oil/gas activities and salt laden air predominates)
Location B - Only coastal environment
Location C - Hinterland (where there is no effect of the industrial/coastal impact)

This work therefore is to incorporate the industrial activities of oil/gas on zinc roofing sheet which is predominantly the major material being used for buildings in the area.

Kinetics of the Corrosion Processes on Iron Roofing Sheets - Mathematical Formulation

Air moving across the earth's surface picks up additional loads of substances. In the troposphere, potential air pollutants mix vertically and horizontally and often react with each other or with the components (pollutants) of the atmosphere.

Let us assume ideal mixing of the reaction components and the active protective ingredients in the composition of the zinc roofing sheet. If the reaction components from the atmosphere come into contact with iron roofing sheets (by bulk flow, wind effect or rain effect) whose thickness, T can be changed at a mass rate of flow m_1, and is removed from the iron roofing sheet at a mass rate of flow m_2, then the number of moles of any substance (active protective ingredient) in the roofing sheet will change with time. This change in concentration of the active protective ingredient will result in change in volume (thickness), corrosion and hence deterioration of the roofing sheet. The cross-sections of zinc roofing sheet at time t and time t +dt are shown (a) and (b) respectively. Let the initial concentration of the substance A in the iron roofing sheet be C_{A0}. If ideal mixing of all components is assumed and achieved on the roofing sheet (taking an elemental cross- section); the concentration of the substance as it is disposed by rain or wind effect will decrease. Let it be denoted by C_A. The true rate of the chemical reaction relative to the substance A could be denoted by J mathematically as follows:

From kinetics $J = KC_A^n$ (1)

where J = the rate of the chemical reaction gmol/cm^3. sec
C_A = the concentration of reactants gmol/cm^3
K = reaction rate constant sec^{-1} (for 1st order reaction)
n = order of reaction =1

The material balance equation for the process can be represented as follows:

Accumulation = Input – Output – Depletion (2) change in number of moles of substance A in the roofing sheet per unit time

=

Number of moles substance A (active ingredient) introduced into the roofing sheet per unit time

—

Number of moles substance leaving the roofing sheet by rain or wind effect per unit time

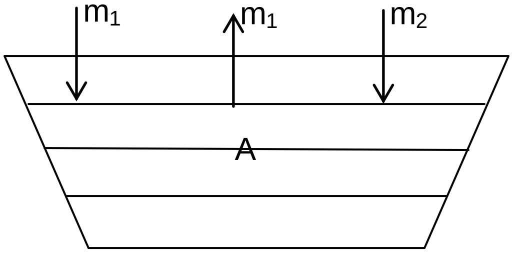
—

Number of moles substance *A* that have reacted on the roofing sheet surface with other complexes in atosmphere per unit time

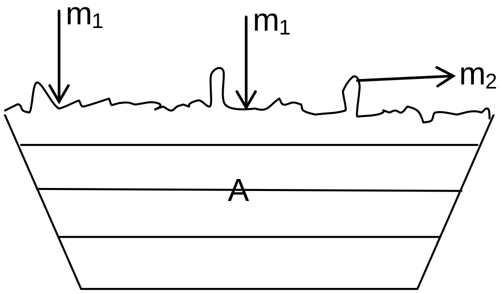
Equation 3 can be represented in a mathematical form by inserting the values of the corresponding quantities as follows:

$$\frac{d(C_A ST)}{dt} = C_{A0}\frac{M_1}{\rho} - C_A\frac{M_2}{\rho} - J\frac{M}{\rho} \qquad (4)$$

where ρ = density of the reaction mass, kg/m^3
S = surface area, (m^2)
T = thickness of the roofing sheet (m)
ST = volume (m^3)



(a) Cross section of roofing sheet at t = 0



(b) Cross section of roofing sheet at time t + dt

Let us denote $\frac{m_1}{\rho} = \omega_1$ *and* $\frac{m_2}{\rho} = \omega_2$

where ω_1 *and* ω_2 are volumetric flow rates at different times t = 0 and t = t + dt respectively.
Hence equation 4 becomes

$$\frac{d(C_A v)}{dt} = C_{Ao}\omega_1 - C_A\omega_2 - Jv \tag{5}$$

equation 5 is the general process model of the dynamic behavior of components in the iron roofing sheet when in contact with atmospheric pollutants.

Solution to the Model Equation

Combining equations 4 and 5 for a first order reaction the result becomes:

$$\frac{d(C_A v)}{dt} + C_A\omega_2 + KC_A v = C_{Ao}\omega_1 \tag{6}$$

But C_AV = number of moles of component A

$$v\frac{dC_A}{dt} + C_A\frac{dv}{dt} = C_{AO}\omega_1 - C_A\omega_2 - KC_A v \tag{7}$$

Assuming, $\omega_1 = \omega_2$, because of the wind effect on contaminants that affect corrosion complexes.
Then equation 7 becomes;

$$v\frac{dC_A}{dt} + C_A\frac{dv}{dt} = \omega_1(C_{AO} - C_A) - KC_A v \tag{8}$$

Assuming negligible change in volume, dv/dt = 0
equation 8 becomes

$$v\frac{dC_A}{dt} + KC_A v + \omega_1 C_A = \omega_1 C_{AO} \tag{9}$$

$$\frac{dC_A}{dt} = \left(K + \frac{\omega_1}{v}\right)C_A = \frac{\omega_1 C_{AO}}{v} \tag{10}$$

Equation (10) is the general model of the kinetic process of corrosion on iron roofing sheet.
Using Euler method, the solution of Eq (10) becomes;

$$C_A = \frac{\omega_1 C_{AO}}{v}\left[1 - e^{-(K + \frac{\omega_1}{v})t}\right] \tag{11}$$

MATERIALS AND METHODS

Methodology

Figure 1 shows the map of Akwa Ibom State, Nigeria with the location of Esit Urua, A, Ibaka B and Ikono, C.

The environmental conditions of these areas, relative humidity, ambient temperature, dew point were determined with whirling hygrometer and the results obtained as 88%-98%, 28°C – 35°C, 26°C – 30°C respectively for locations A and B; for location C, the relative Humidity, ambient temperature and dew point were in the following ranges: 60%-90%; 28°C – 37°C and 25°C-28°C.

Iron roofing sheets were removed from different roofs depending on the age limit under consideration. Usually, one to three pieces of roofing sheet (SWAN BRAND) of 0.15mm thickness were removed from buildings that were covered in less than one year; <1; 1-5 years; 5-10 years; 10-15 years; and 15-30 years. This exercise was carried out at the three locations and a new one replaced for the owners.

10cm x 15cm specimen sample from each of the roofing sheets was cut and sent for analysis. The results from Atomic Absorption Spectroscopy (AAS) analysis are shown in tables 1 and 2.

The zinc, chromium, iron oxide film (rust), sulphate and chloride content were determined for the various periods and the results obtained shown in table 1.0 in columns 3, 4, 5, 6 and 7 respectively

Figure 1: Map of Akwa Ibom State, Nigeria showing study locations

RESULTS AND DISCUSSION

The results of the analysis are shown in table 1.

Table 1: Concentration levels of active ingredient considered in roofing sheets in the study locations

Sample Location	**Sample identification**	**g/100g**		**(mg/kg)**		
	A_{11}	6.45	0.022	32.95	<1.0	25
	A_{21}	1.67	0.019	26.07	<1.0	30
Esit Urua	A_{31}	1.48	0.009	31.93	<1.0	20
	A_{41}	0.98	0.015	22.14	<1.0	35
	A_{51}	1.80	0.024	30.90	<1.0	28
	B_{11}	2.56	0.019	26.66	<1.0	36
	B_{21}	1.56	0.013	13.97	<1.0	52
Ibaka	B_{31}	1.14	0.011	14.81	<1.0	56
	B_{41}	0.92	0.008	15.90	<1.0	49
	B_{51}	1.25	0.014	18.61	<1.0	46
	C_{11}	1.39	0.013	26.89	<1.0	51
	C_{21}	1.43	0.014	17.37	<1.0	49
Ikono	C_{31}	2.08	0.021	15.59	<1.0	45
	C_{41}	1.18	0.015	17.60	<1.0	40
	A_{51}	1.29	0.024	19.47	<1.0	38
(Conc) new zinc roofing sheet		10.2	0.035	41.56	<1.0	<1.0
		zinc	chromium	Iron oxide	sulphate	chloride

Table 2: Estimated corrosion on samples of zinc coated steel from the study areas

Sample Location	**Sample identification**	**Surface area (cm^2)**	**Surface area ($inch^2$)**	**Initial weight (g)**	**Final weight (g)**	**Weight loss (g)**	**Duration* (Years)**	**Corrosion rate (mpy) (wt loss x 22300) / a.d.t.**
	A_{11}	407	65.12	48	35	13	1-5	0.514
	A_{21}	38	60.8	50	48	2	5-10	0.034
Esit Urua	A_{31}	220.73	35.32	55	48	7	10-15	0.1225
	A_{41}	364.64	58.34	50	37	13	15-30	0.091
	A_{51}	385.2	61.63	50	48	2	<1	0.501
	B_{11}	363.5	58.16	40	35	5	1-5	0.2214
	B_{21}	208.52	33.36	30	25	5	5-10	0.1544
Ibaka	B_{31}	208.52	33.36	30	25	5	10-15	0.093
	B_{41}	284.2	45.47	37.5	25	12.5	15-30	0.0965
	B_{51}	418	66.88	50	48	2	<1	0.462
	C_{11}	440	70.4	50	50	0	1-5	0
Ikono (control)	C_{21}	473	75.68	50	49.5	0.5	5-10	0.0068
	C_{31}	404	64.64	75	74	1.0	10-15	0.00543
	C_{41}	409	65.5	62.5	62	0.5	15-30	0.00268
	A_{51}	517.5	82.8	55	55	0	<1	0

**Final weight was taken after mechanical cleaning of the corrosion product by mild abrasive cleaning, Density = 7.909g/cm^3, thickness, t = 0.015cm (for most areas); Surface area considered are those exposed to the atmosphere. $\rho = 7.14g/cm^3$*

**as given by home owners; Loss/unit area was calculated for the zinc.*

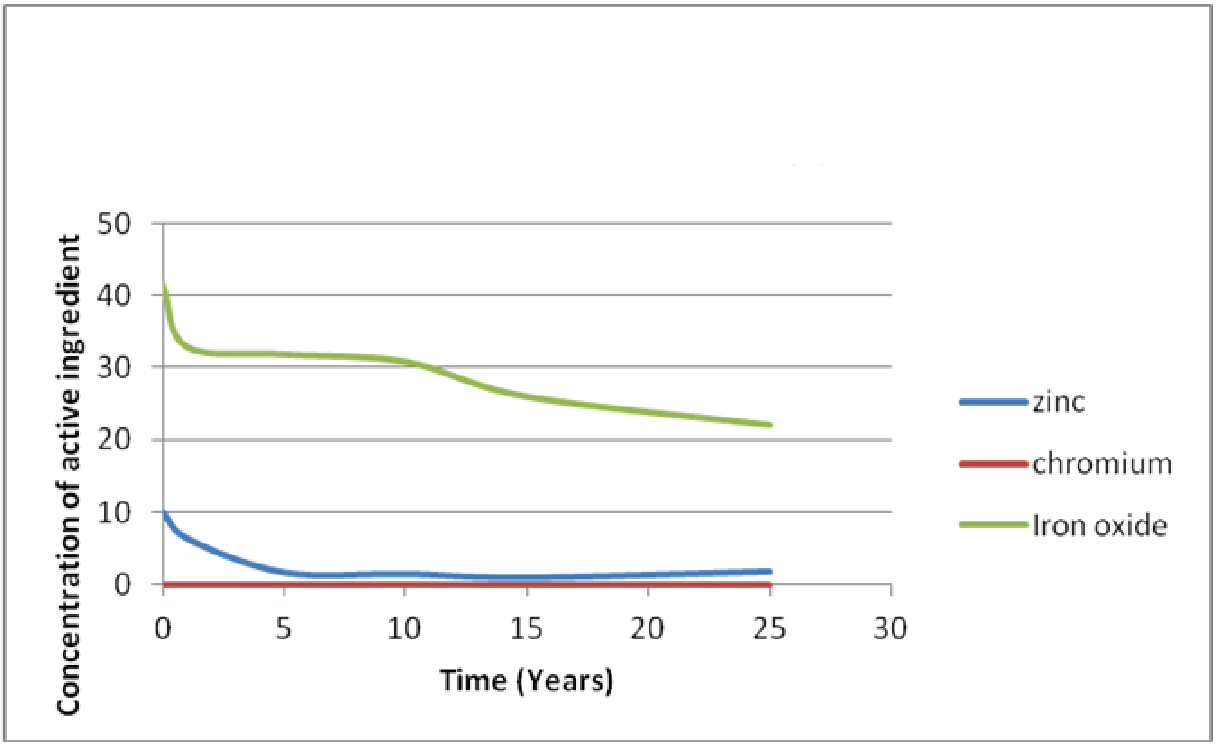


Figure 2: Esit Urua-Concentration profile of active ingredient

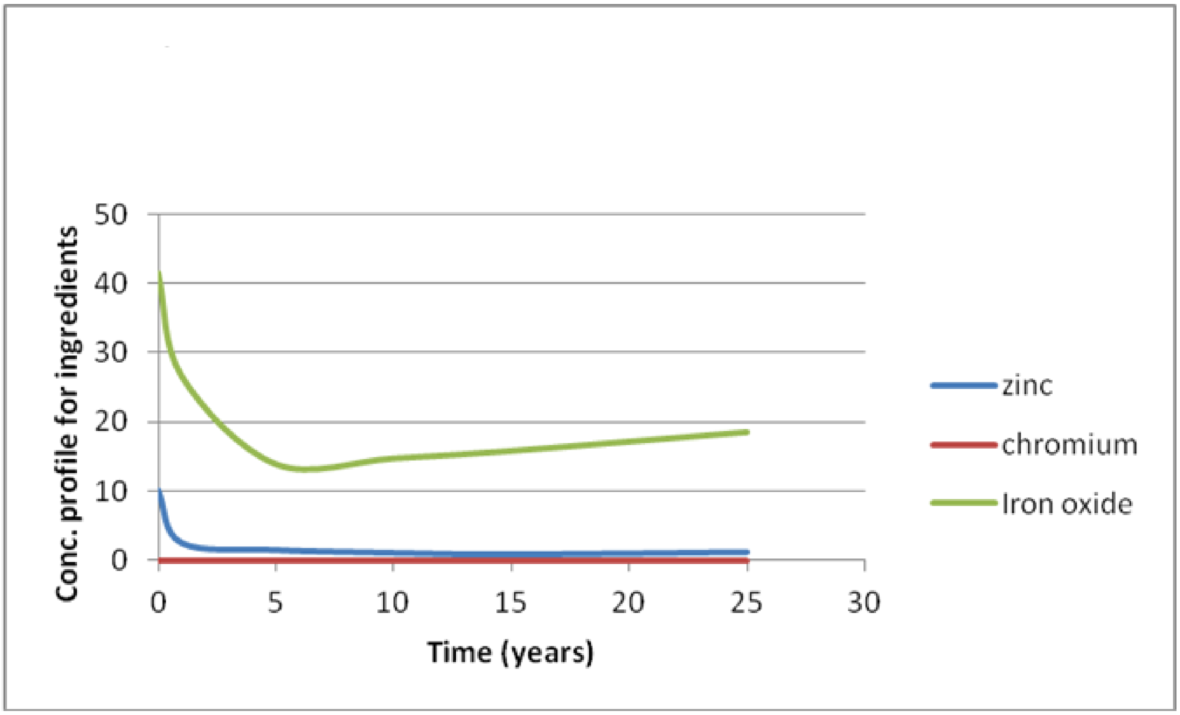


Figure 3: Lbaka-concentration profile for active ingredient

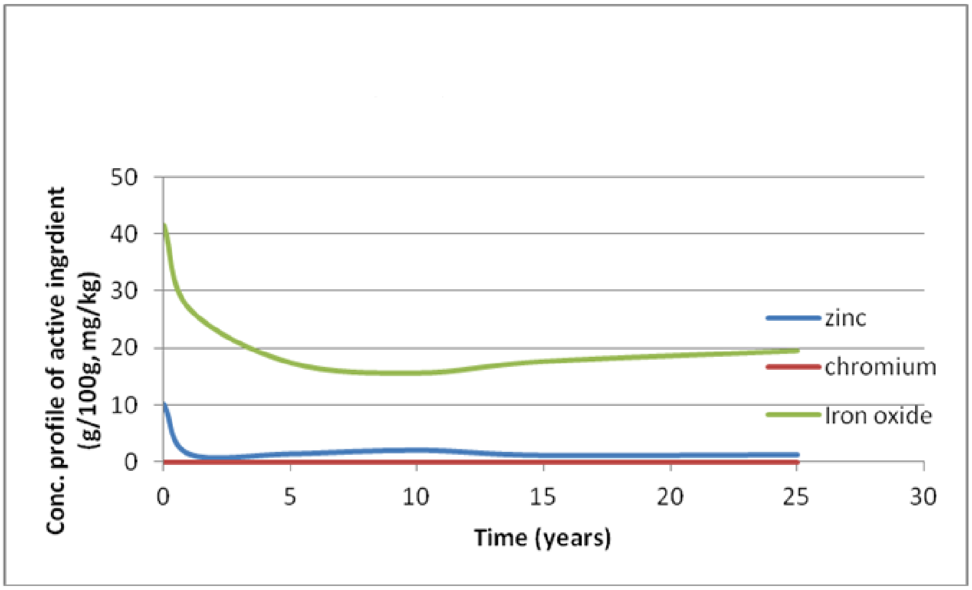


Figure 4: Lkono-concentration profile of active ingredients

Model Equations

Taking log on both side of equation (11)

$$\text{Log } C_A = \log\left(\frac{\omega_1 C_{AO}}{v}\right) + \left(K + \frac{\omega_1}{v}\right)t \quad (12)$$

K can be determined from equation 12

$$\log(C_A) = \log\left(\frac{\omega C_{AO}}{v}\right) + \left(K + \frac{\omega}{v}\right)\text{t}$$

Plot of log C_A against t gives slope as (K + ω / v) and the intercept as $\log\left(\frac{\omega C_{AO}}{v}\right)$

Fig.2 shows the depreciation of the active ingredients in the iron roofing sheet in the city of Esit Urua, where the effects of coastal/industrial activities are predominant. From this figure it can clearly be observed that there was appreciable depreciation of the active ingredients occasioned by the industrial activities in the area. It can also be observed that iron oxide and zinc depreciated more than chromium. This may be attributed to the formation of passive chromium oxide films that materially retards the oxidation process. Another important observation is that Esit Urua, a city situated closest to the oil/gas operations activities experienced the most depreciation in the active elements than Ikono located farthest from the industrial areas (see fig. 1). This clearly shows that areas closest to the plants suffer a lot of material damage by corrosion.

Fig. 3 shows the depreciation of zinc, chromium and iron oxide in the city of Ibaka. Ibaka is a coastal city with heavy rainfall throughout the year. It can be seen that the depreciation of active ingredients follow the same trend as seen in figure 2. It can be affirmed that most of the factors causing corrosion in this region may be purely due to the salt laden atmosphere from Atlantic Ocean and rainfall. This is partly due to the oxidizing agent such as air which naturally accelerates corrosion of materials. Also the formation of acidic rain helps to accelerate corrosion in coastal areas. Table 2 illustrates the estimated corrosion rates on samples of zinc coated steel from the study areas. Observation shows that corrosion rates are greatest at Esit Urua, closest to Ibeno (there exists oil terminal) as compared to Ibaka and Ikono farther away from plant operations. Indeed, the city of Ikono has the lowest corrosion rate as indicated in figure 5.

The above observations are corroborated by the values of the calculated rate constants K, in Equation 12 within the first 5 year-period, for the three locations: Esit Urua, K =0.36/hr; Ibaka, K = 0.174/hr; and Ikono K = 0. It is important to note that corrosion effects on the roofing sheet were noticed to be 0.0068 m.p.y at Ikono from 5-10 years. Therefore the effect of corrosion is least in the hinterland than in the industrial/coastal areas.

Conclusion

The kinetic processes of corrosion rates established in this work are applicable in any environment similar to the one considered (coastal/industrial). The correlations of rate constants to corrosion rates are innovations that should be studied further for baselines to determine corrosion rates. This should override the weight loss method that most times gives low precision and unreliable data.

The research has shown clearly that corrosion of the iron/zinc roofing sheet is more pronounced in the industrial/coastal environment when compared to the city of Ikono in the hinterland of Akwa-Ibom state. That is to say in the minimum, that the industrial activities in these regions have brought about an accelerated corrosion rates.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support from Faith Link Nigeria Ltd for the opportunity to carry out the studies.

REFERENCES

Cole IS, Neufeld AK, Kao P, Ganther W, Chitomongkol L Barmornsut C, Hue NV, Bernado S and Purwadaria A (1999). Development of performance verification methods for the durability of metallic components in Tropical Countries. *Proceedings of the 11th Asian- Pacific Corrosion Control Conference* **92** 55-57.

Deans SW and Lee TS (1987). Degradation of metals in the Atmosphere. Philadelphia P. A. American Society for Testing and Materials.

Graedel TE and McGill W (2011). Degradation of materials in the Atmosphere. *Environmental Science Technology* 1093 – 1100.

Kearny NJ (No Date). Corrosion Resistance to Atmospheric Corrosion. http://www.corrosion-doctors.org/Corrosion-Atmospheric/Corrosion-resistance.htm, accessed 14 December 2013.

Obia and Obot (2010). Atmospheric corrosion of metallic roofing sheet in building construction in the Niger Delta region of Nigeria; *Journal of Environmental Issues and Agriculture in Developing Countries* **2**(& 3).

Ovri JEO and Iroh M (2013). Corrosion Effect of Gas Flaring On Galvanized Roofing Sheet in Imo State, Nigeria, *The International Journal of Engineering and Science (IJES)* **2**(1) 339-345.

Ujile AA and Ehirim E (2009). Evaluating a technique for solving corrosion process models on oil and gas facilities. *Conference Proceedings 4th Annual Corrosion Management Summit. 11- 14 October, 2009,* Hilton Abu Dhabi Hotel, Abu Dhabi, United Arab Emirates.

Zheng Y, Wang Z and Zhang F (1991). Influence of acid deposition on atmospheric corrosion of zinc. *Journal of Environmental Science*, China **3**(2) 53-60.