Effect of Climate Change Pollutants on the Corrosion Rate of Steel in Rural, Urban and Industrial Environments

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Abstract
Ever since industrial revolution, the world climatic conditions have been deteriorating due to the ever increasing amount of air pollutants injected into the atmosphere. This has adversely affected the health of living organism, plants and the environment that host them. Building structures are not left out in the devastating effects of air pollution as metallic components are easily oxidized leading to corrosion. Corrosion of steel materials due to environmental pollutants has become an issue of great concern to researchers all over the world. This paper looked at the effect of climate pollutants in the air as they affect weathering steel in rural, urban and industrial environment. The corrosion process in steel over time and how it varies in rural, urban and industrial environments were considered. The overall objective of this work is to underscore the factors that have impact on the progressive deterioration of materials exposed to atmospheric weathering. The climate and air pollution parameters that affect material losses are identified and their numeric values obtained vie dose response functions. The results obtained show that SO_2 corrosion rate of industrial environment is about five times that of rural environment while that of industrial to urban and urban to rural corrosion rates are slightly above two times for each.
Keywords: Climate Change, Building Materials, Air Pollution, Corrosion Rate and Global Warming

1.   INTRODUCTION

According to Duke (2011), the cliffs and beaches of Britain are shrinking, disappearing into the surrounding sea because of coastal flooding, erosion and land slide arising from climate change. Other nations of the world are experiencing it in diverse manners. For instance, Nigeria is no exception to these observations as all the factors have been verified both in the coastal areas and the hinterland. Researches by Ede and Oshiga (2014) and Ede et al. (2015) have all proved reduced number of rainy days and increased intensity of rainfalls in Lagos, Nigeria and that the negative impacts on buildings collapse and infrastructure decay are evident. The main form of damage by air pollution to building and building materials include discoloration, failure of paintings, loss of essential details in artworks and structural failures according to Feenstra (1984). Determining the effect of such loss from building materials and predicting the likely corrosion loss of ferrous materials due to the influence of atmospheric corrosion are still in infant stage, Ngene (2012) and ExternE (1998).

The overall objective of this work is to underscore the factors that have impact on the service life and deterioration of materials exposed to atmospheric weathering in various environments. Understanding how air quality affects the corrosion of materials of construction is of essence, however, valuation of material damage is usually difficult. It is therefore important that the climate and air pollution parameters that affect material losses are identified and their numeric values used for a known location to determine how they affect various environments.

2.   LITERATURE REVIEW
2.1 Climate Change Predictions and Air Pollutants

Climate change data from IPCC's Synthesis Report (2007) refers to observable change through statistical analysis of means and other variable properties over a period of time usually above a decade. This change in climate with time may be due to natural causes or it may be due to human activity. Warming of the climate system is observed to have been responsible for the increase in global average temperature, melting of ice and rise in global average sea level. As observed by Houghton (2004), various human activities in the industry, in the field, in form of deforestation, in transportation or at home are resulting in emissions of gaseous pollutants of increasing amounts. Carbon dioxide is observed as a good absorber of radiated heat coming from the earth's surface and the increases quantity of carbon dioxide acts like a shield covering over the earth surface, thereby causing the earth to warm more than it would normally be.

According to Hulme et al (2002) in Brimblecombe et al (2008), "London climate will change over the current century. From the model analysis using the HadCM3, temperature is expected to rise by $4°C$ by 2080 under the A2 Emission Scenario and precipitation will increase in winter and decrease in the summer". London air pollution was observed to have increased from the industrial revolution period (1700 -1970). Temperature projection is one of the widely used parameter in the determination of global climate change. Houghton (2004)

describes a global average rise due to increase in greenhouse gases of $0.6°C$ by 2000 and projected to increase in the range of $2°C$ to $6°C$ by 2100. During the 20th century, the annual mean of Central England temperature warmed by about $1.1°C$. The 1990s were exceptionally warm, by historical standards, about $0.6°C$ warmer than the 1961-1990 average as observed in the Hadley Centre (Met office) records. Temperature of South England is project to increase the highest in summer under the high emission scenario according to Land Use Consultants (2003) and by 2080s the increase is expected to reach $5°C$. For low emission scenario, the summer temperature is expected to rise between $2-3°C$ for the same period. The impact of this will be a rise in the number of extreme warm days with a corresponding decrease in the number of heating degree days especially in winter.

There will be change in rainfall patterns, making summer drier and winter wetter, with the resultant decrease in relative humidity. It is projected that rainfall and evaporation will decrease in summer and autumn under the high and low emission scenarios.

The dominate form of emission in United Kingdom is burning of fuels containing sulphur, typical of coal and heavy oils, used by power plants and refineries. Domestic use of coals for heating and other purposes is reducing in significance, though still in use in some regions in the country. Pollution caused by SO_2 emission cause acidification of soils and water, often further down the source of production in form of acid rain.

It is projected, according to UKCIP98, that by the 2020s, carbon dioxide concentrations for the Medium-low and Medium-high scenarios would be, respectively, 19% and 34% higher than the 1961-90 average of 334ppm, and by 2080s, 49% and 109% higher.

Air pollution is harmful to the environment and particularly detrimental to human health. Researches have shown air pollution as the cause of higher incidence of bronchitis-emphysema in larger cities (McDermoll, 1961), of influenza, lung cancer, asthma and pulmonary heart disease. Air pollution leads to deterioration of plants. Buildings are not left out in the devastating effects of air pollution as metals are oxidized leading to corrosion. Properties and crop damages due to air pollution in the US alone amount to billions of dollars annually (Maunder, 1970). The modification of the natural vegetation has affected several important climate parameters such as surface roughness as well as the hydrological properties of the surface (Lockwood, 1979). According to Barry and Chorley (1976), were it not for the removal of CO_2 from the air by the land biosphere and the oceans, the increase of the pollutant in the atmosphere would have been about 20%. Studies such as those carried out at the Hadley Centre (SCOPAC, 2001) predict that in Southern England, it will continue to get warmer, rainfall will continue to increase in winter and decrease in the summer, but with an overall increase in both total and effective rainfall, that sea level will continue to rise, that there is also the possibility of higher number of extreme weather, rainfall and storm events. Essentially, these predictions would appear to be continuation of current trends but with expected increased rate of change.

Faced with these challenges, human's engineering skills and ability to deploy his technological capability is required now and in the future as it grapples with the challenges of ensuring that it does not live at the mercy of the climate. In any case, a proper land use planning, site selection, use of green areas and buffer zones can assist in cushioning the effects (Bach, 1972).

2.2 Effects of Air Pollutants on Building Materials
As the earth's climate changes, man-made protective barriers against harsh environmental conditions are affected in many ways. Materials used to build protective structures against environmental impacts deteriorate in various manner over time.

Wood
In many Engineering structures, such as building, railway and bridge structures, wood form part of the materials exposed to the environment. Direct atmospheric pollution does not however affect wood as much as the problem caused by water and humidity. Uncontrolled variations of relative humility in the environment and precipitation are the principal hazard to the preservation of wood in and outdoors (Kozlowski, 2007).

Woods are complex materials and they differ greatly in their porosity and water resistance. Example is the hard wood, though few of them can withstand outdoor exposure without protection. A greater bulk of exposed wood, such as softwood, if left unprotected would become water logged and develop excessive porosity through bacterial action or rot (Banks and Evans., 1984).

With respect to concrete material, Ede et al. (2014) posited that timber has a positive impact towards reducing carbon emissions, and actively helps in storing atmospheric CO_2 thereby reducing global warming. Also, the adoption of timber as a construction material saves a lot of energy thereby reducing global warming. (Ede et al, 2015).

Natural Stone
Serious attack on natural stone by atmospheric pollutants is confined to limestone and calcareous sandstones

(UKBERG, 1990). It has been observed that stone, particularly granite, are not seriously affected by pollution. Stone damage problems are also known to occur through frost damage or by crystallization of soluble salts. The occurrence of weathering of stone is mainly due to carbon dioxide present in the atmosphere.

Masonry
Research by (UKBERG, 1990) has shown that there is low evidence of damage to brickwork by industrial pollutants. Bricks are noted to be stable without protection except when damaged by frost acts. Renderings are also not adversely affected by acid pollutants but a substrate can be affected by sulphate action.

Concrete
The main binding material for concrete is Portland cement, an alkaline material subject to acid attack. The damage to concrete as a result of climate impart may be in the form of spalling, surface erosion and corrosion of embedded steel. Apart from surface erosion, damage to concrete may likely be in form of natural carbonation and ingress of chloride ions as against interaction with pollutants such as SO_2 (ExternE, 1998a).

Corrosion of embedded steel reinforcement in concrete affects its durability. The alkaline nature of the cementitious concrete protects the reinforcement from corrosion. Expose of concrete to air and rain over a period of years neutralizes the alkalinity, causing the pH of the cement paste to fall and leaving the steel open to corrosion (UKBERG, 1990). The interactions of CO_2 and SO_2 in the atmosphere with calcium hydroxide of the cement paste bring about the neutralization of the pH (Lahdensivu et al., 2009).

2.3 Weathering Carbon Steel Affected by Pollutants
Carbon steel is high strength, low alloy weldable structural material which possesses good weather resistance in many atmospheric conditions with minimal need for protective coatings (SCI, 2003). Weathering steel contains alloying elements such as Nickel, Copper, Phosphorus and Chromium (SCI, 2006, Kihira et al., 2005).
Metals atmospheric corrosion is achieved by electrochemical process, which takes place in corrosion cells with anodes and cathodes.

$$Fe \rightarrow Fe^{2+} + 2e \qquad (1)$$

A wet electrolyte is needed for atmospheric corrosion. This is enhanced by such climatic parameters as precipitation, humidity, temperature and degree of atmospheric pollutants. Sulphur dioxide causes most damage, of all the atmospheric pollutants, while in coastal regions chlorides also play a considerable role (ExternE, 1998a). The role of NO_x and ozone in the corrosion process of metals is not yet fully understood, though there is evidence (Kucera, 1994) to suggest that ozone play a significant role in quickening some reactions.

2.4 Effect of Climate Change on Parameters that Influence Corrosion
The world temperature is predicted to rise over the next century. This increase of some few degrees will be critical to many aspects of our lives and the health of ecosystems and agriculture (Brimblecombe et al., 2007). Generally, studies have shown that temperature have correlation with corrosion rates (ECE, 1984). Temperature is noted to increase the rate of reaction, though for steel the rate decrease with increase in temperature and also dry the surface.
Corrosion of metals by rainfall is dependent on the pH of the rain, intensity, duration and amount. The presence of SO₂ decreases the pH of rain, and causes faster chemical attack. As reported in (Wang et al., 1997, Misawa et al., 1974), "hygroscopic SO₂ in the industrial atmosphere often lowers the pH of water, wets rust layer and dissolves the initial corrosion products of γ-FeooH, and also promotes the phase transformation of γ-FeooH to amorphous ferric oxy-hydroxide and α-FeooH". This transformation for weathering steel is known to takes place within the first three years of exposure.

Relative humidity is one of the climate parameters included in most of the established dose-response functions. It defines the percentage of vapour density to saturation vapour density at any given time. As indicated by Brimblecombe et al., (2007) cycles of relative humidity causes crystallization and dissolution, which exert stress on structural materials in which weathering salts are present, Arroyave et al (1995); Henriksen and Rode (1986) concluded that at high relative humidity, SO₂ might form ferrous sulphate, which would attract water and be dissolved on steel surfaces, thereby accelerating the corrosion with little contribution from NO₂.

2.5 Factors Affecting Air Quality
Chemical composition of the atmosphere is of great importance to the corrosion process because of their thermodynamic and kinetic effect on corroding material. Mellanby (1988) observed that the most important pollutant that affects structural materials are sulphur dioxide and oxides of nitrogen and their oxidation products, together with chlorides and particulate matter. Ozone was also considered as its presence affects the quality of the air.

Sulphur oxide (SO₂) emissions in the UK have been in decline since 1980 due to reduction in sulphur

content of fuels, changes in fuel use patterns (e.g. to natural gas) and industrial modernisation. Estimates from Warren Spring laboratory (UKBERG, 1990) indicates that United Kingdom annual emission of oxides of nitrogen (NOx) have increased by a factor of 2 since 1945. For the United Kingdom, the average annual concentration ozone in urban areas range from 20-40μgm^{-3} while for rural area it is 40-60μgm^{-3}. The presence of carbon dioxide (CO_2) in the air does add to the acidity of rain water and thereby cause some degradation to limestone and concrete, attacks by CO_2 on calcareous stones proceeds more rapidly because the CO_2 concentration increase leading to a higher partial pressure and more decay.

2.6 Dose – Response Functions and Environmental Parameters
This is the function that determines the impact of the application of a climate data on the environment. Dose-response functions are applied to climate data such as temperature (T), relative air humidity (Rh), gaseous emissions in the air (SO_2, NO_2 and O_3) and amount of precipitation (Mikhailov, 2001). According to Melcher (1999), corrosion has many variables with uncertain nature. For this reason, the use of statistics and probabilistic models to describe the expected corrosion of structural material is appropriate. In unsheltered condition, wet deposition (through rain) of SO_2 is the most important pollutant parameter for weathering steel and zinc. Several researchers have worked on the appropriate dose-response functions that will possibly capture the adverse effect of climate and pollutant parameters on built structures. These include among others: Tidblad et al (2001), Leuenberger-Minge (2002), Mikhailov et al (2001), Lipfert (1987), Butlin et al (1992a), Kucera (1994), and BS EN ISO 9223 (2012).

2.7 Pathway to Corrosion
The EternE (1998a) project identified metals (steel) as one of the pathways of acidic emissions and precursors of photo-oxidants effect on materials. The impact pathway follows the following routes: discoloration, protective film formation, corrosion stress and cracking leading to materials loss and structural failure. Structural failure from pollutant exposure is more noticeable where there is fundamental flaw in design or adequate protection.
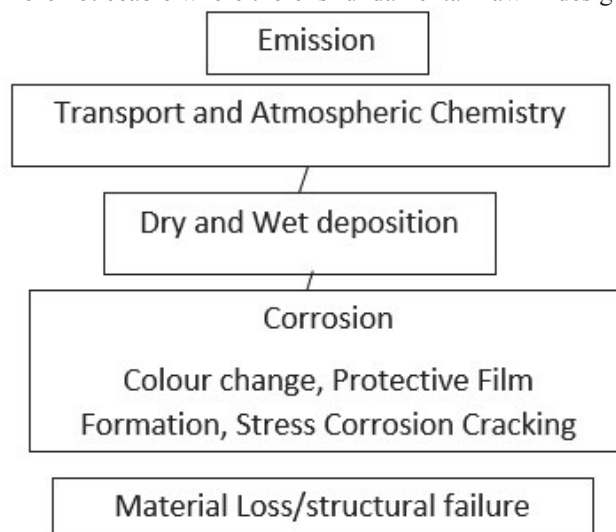

Figure1: Impact pathways for effect of acidic deposition in metals (adapted from EternE Project – 1998a).

3.   METHODOLOGY
In this research, efforts will be made to look at the effects of climate change pollutants on the corrosion rates of steel in rural, urban and industrial environment using the dose-response function approach. The data for this work were obtained from the work of Brimblecombe et al (2008) on the climate around London region.
 The analysis of corrosion requires the use of statistics and probabilistic models. The mean and standard deviation of the pollutant data are obtained and from the mean, a dose-response value of the annual material loss is calculated for weathering steel. For this reason, it is important to present some descriptive statistics of pollutants that will be needed for climate parameters.

3.1   Descriptive Statistics of Pollutants and Climate Parameters
Mean of Pollutants and Climate Parameters
The mean of each pollutant and climate parameter record is calculated using the following:

$$X = \frac{1}{N}\sum_{i=1}^{N} X_i$$

(2)

where X_i is the random variables of pollutants or climate parameter and N is the total number of observations.

Standard Deviation

This is a measure of variability. It indicates the dispersion or variation from the mean. Low value shows data points are close to mean whereas high value point to a spread out from mean values.

$$\sigma_X = \sqrt{\left[\frac{1}{N}\sum_{i=1}^{N}(X_i - X)^2\right]} = \sqrt{\left[\frac{1}{N}\sum_{i=1}^{N}X_i^2 - \left(\frac{1}{N}\sum_{i=1}^{N}X_i\right)^2\right]} \tag{3}$$

Variance (σ^2)

Variance measures the degree of spread out of a set of numbers.

$$Var(X) = E[X^2] - X^2 = \sigma_X^2 \tag{4}$$

Coefficient of Variation

This is defined as the ratio of the standard deviation σ_{sX} to the mean X. It is a normalized measure of dispersion of a sample data which is expressed as a percent.

$$C_v = \frac{\sigma}{X} \tag{5}$$

where σ is the standard deviation of the set of numbers or variables and X is the mean.

3.2 Dose-Response Function and Estimation of Material Loss

For this research, the dose-response function adopted is BS EN ISO 9223 (2012). ISO 9223 is the code for the classification, determination and estimation of corrosion of metals. Based on comparative estimation of the various dose-response function thickness losses, the function for this code was chosen for the analysis. This function is expressed as

$$r_{corr} = 1.77.[SO_2]^{0.52}.\exp^{(0.020RH+fst)}+0.102[CL^-]^{0.62}\exp^{(0.033RH+0.040T)} \tag{6}$$

where fst=0.150 (T-10) when T≤10°C, otherwise -0.054 (T-10), r_{corr}= first year corrosion rate of carbon steel in μm/year. The reason for the choice of this dose-response function for the analysis is because of the critical influence of the parameters in the corrosion rate of metals. This code classifies the atmospheric corrosivity of the environment by categories based on the one year corrosion rate experiment on standard specimens. From this test, the numerical values of the first year corrosion rate of different metals under various corrosivity categories were estimated. The principal elements in the corrosion of metals are temperature, humidity, pollution by sulphur and the acidity of the air.

3.3   Depth of Corrosion

Steel corrosion rate with time for outdoor exposure is not constant. From ISO 9223, it is shown to decrease with exposure by the relation:

$$D = r_{corrosion} * t^b \tag{7}$$

where t is the exposure time in years, $r_{corrosion}$ is the rate in the first year expressed in um/a and b is the metal-environment-time exponent, which for carbon steel is 0.026.

4.   RESULTS AND DISCUSSIONS

4.1   Climate Change Predictions

The summary of the results of this research can be seen in table 1. The decrease in the volume of SO_2 and other pollutants after the 1970's is indicative of the effect of regulation and monitoring. First the use of coal for domestic and industrial purposes was minimized, then regulation on smoke abatement was developed and following the era of European Union, monitoring activities were improved. Based on Houghton's temperature rise projection, the continuous average rise up to 2070 is evident in table 1. Based on the projected rainfall and evaporation decrease in summer and autumn, the reduction in relative humidity is shown in table 1. From table 1, it is evident that the policy on pollution abatement of SO_2 embarked upon since the 1970's has given rise to a reduction in sulphate concentration in the United Kingdom. As shown in in table 1, emission of carbon dioxide is increasing rapidly and becoming larger with time.

Table 1. Estimate of mean values of parameters using future projection records

Year	PM_{10}	SO_2	NO_2	O_3	HNO_3	Temp.	pH	RH	Rain	CO_2
	$(\mu g)m^{-3}$					(^0C)		(%)	(mm)	ppm
2010	30	17	40	40	1.15	11.8	5.2	72	582	383
2030	15	15	20	30	0.71	12.3	5.5	71	590	430
2050	14	14	20	30	0.73	12.9	5.5	71	604	530
2070	13	13	20	30	0.77	14.4	5.5	70	574	610
2090	12	12	20	30	0.73	13.4	5.5	68	551	730
Mean	16.80	14.20	24.00	32.00	0.82	12.96	5.44	70.40	580.20	536.60
Variance	44.56	2.96	64.00	16.00	0.03	0.81	0.01	1.84	311.36	15558.24
Std Dev.	6.68	1.72	8.00	4.00	0.17	0.90	0.12	1.36	17.65	124.73
Coeff. Of Var.	0.40	0.12	0.33	0.13	0.20	0.07	0.02	0.02	0.03	0.23

4.2 Spatial Variation of Parameter

In this regard, it is observed that location affects the rate of loss of materials from steel exposed to the climate change. Materials exposed to the rural area is least affected while those in industrial environment is most affected as seen in figures 2, 3, and 4 below. To obtain these values, the SO_2 is varied for the rural, urban and industrial areas while the temperature and relative humidity is kept constant. A plot of the thickness loss against time for various environments gives the rate of corrosion.

The expressions for the $r_{corrosion}$ used for the determination of the depth of corrosion for the various environments of rural, urban and industrial according to ISO 9223 are:

Rural area: $r_{corrosion}(2 < SO_2 < 15) = 3259.8 In(X) - 2473$ (9)

Urban environment: $r_{corrosion}(5 < SO_2 < 100) = 5281.9 In(X) - 40104$ (10)

Industrial area: $r_{corrosion}(50 < SO_2 < 400) = 11623 In(X) - 88252$ (11)
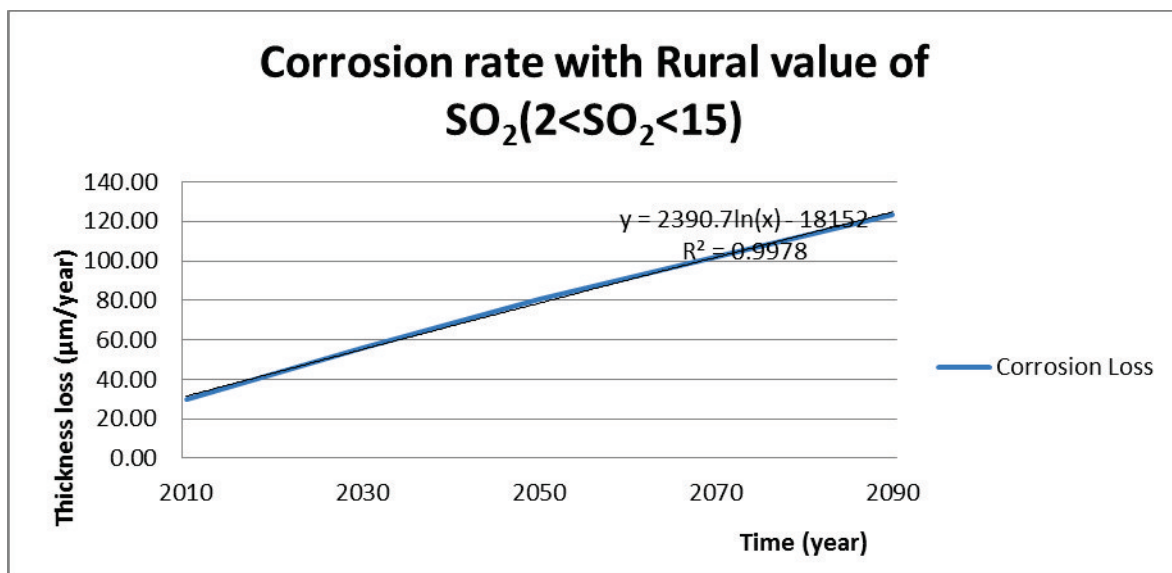

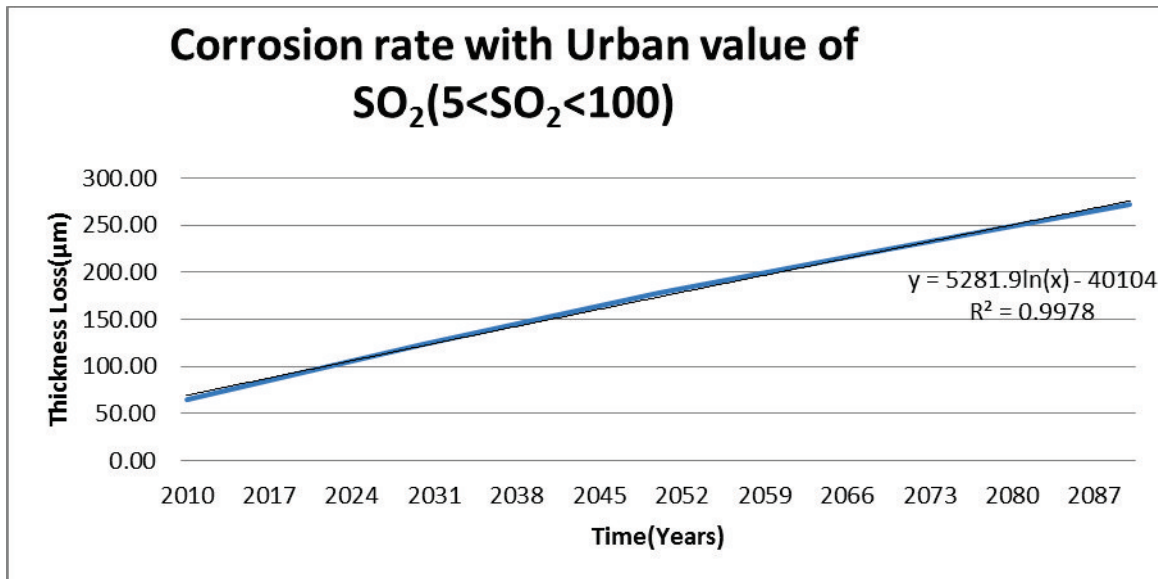
Figure2 : Corrosion rate for rural environment

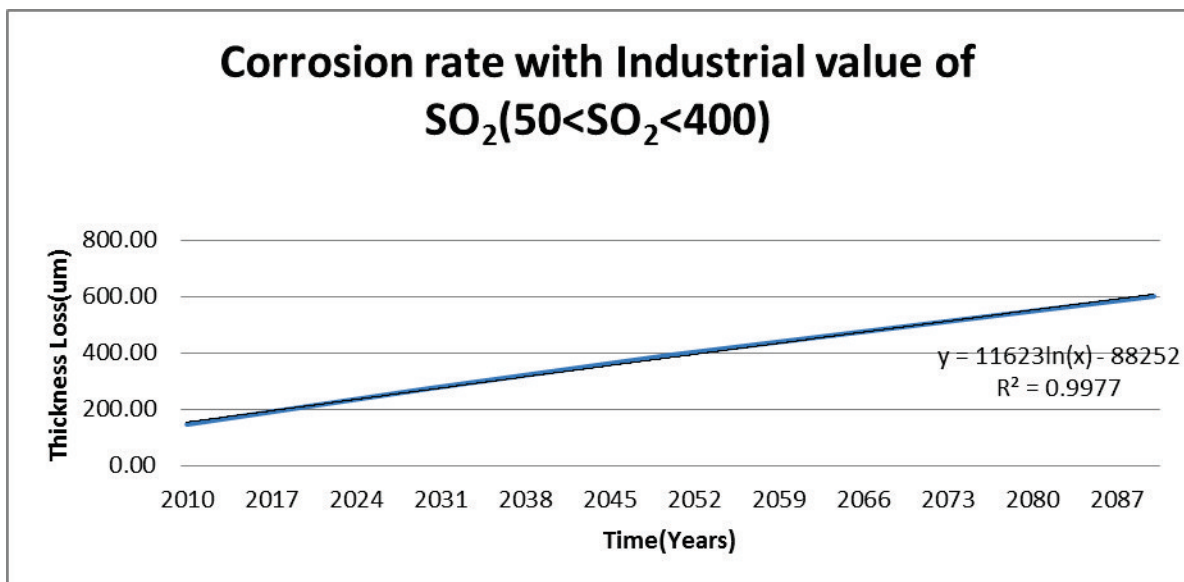Figure 3: Corrosion rate for urban environment

Figure 4: Corrosion rate for Industrial environment

From the figures, it is shown that sulphur dioxide corrosion is much high for industrial area than in rural environment. The effect is therefore a higher thickness loss in the industrial area than in the rural. The rate of corrosion $r_{corrosion}$ is shown to be $1.17\ um/a$, $2.58\ um/a$ and $5.68\ um/a$ for rural, urban and industrial areas respectively. This shows that SO_2 corrosion rate compared for rural to industrial is approximately five times while urban compared to industrial and rural compared to urban rate is slightly above two times for each.

5. CONCLUSIONS

The work reviewed the current efforts to study the impact of natural and anthropogenic factors on climate and the effect of change on climate and air quality on building materials. It was observed from the study that the climate/weather will continue to change due to the damaging influence of human activities, due to burning of fuels containing sulphur, such as coal and heavy oils used by power plants and refineries, on the earth.

Building materials affected by climate change were identified and the impact of climate change as it affects the urban/industrial areas more than rural environment was noted.

The pollutant SO_2 is projected to continue to fall if regulatory efforts are intensified. The presence of SO_2 and water is noted to be the major cause of corrosion of materials. Carbon dioxide which causes greenhouse effect on the other hand is estimated to increase due to increased use of various energy resources and other human activities.

The results obtained show that SO_2 corrosion rate of industrial environment is about five times that of

rural environment while that of industrial to urban and urban to rural corrosion rates are slightly above two times for each.

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