

FROM DUST TO DUST: THE CHEMISTRY ALTERNATIVE



AN INAUGURAL LECTURE

By

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FROM DUST TO DUST: THE CHEMISTRY ALTERNATIVE

By the sweat of your brow you will eat
your food until you return to the ground,
since from it you were taken; *for dust you
are and to dust you must return.* (Gen. 3:19)

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Ladies & Gentlemen

1.0 INTRODUCTION

It is with joy, honour, privilege and deep sense of humility that I stand before you all today to deliver this Inaugural Lecture of this great University. Of course, having by the Grace of the Almighty God been elevated to the enviable scholarship position of a professor, it could be justifiably argued that it is a binding duty for one so elevated to defend the action of the university authorities and academic peers who adjudged my humble contributions to scholarship worthy of recognition.

An inaugural lecture affords the individual an opportunity to define his new standing, while at the same time; he outlines his goals for attainment of objectives. In the case of academics, an inaugural lecture, enables the professorial entrant to publicly review his field of expert knowledge, present his academic credentials and relate his contributions in that field to the needs and challenges of his immediate and/or larger society.

At the interment of departed Christians, the priest often quotes the sobering words in Gen. 3:19. This verse informs us that our bodies are products of the earth, and at death we return to it. Most metals occur in the form of ores in the earth's crust. The ores are mined from the earth. We observe that the metals in their interaction with the immediate environment **seek** to return to the combined state (ore) from which they were initially obtained. It is this cycle and their eventual corrosion to form metallic compounds and so return to the earth that am referring to as "Dust to Dust". In short, my INAUGURAL LECTURE is about the **LIFE CYCLE OF METALS** and how chemistry has been employed to inhibit/reduce the corrosion of metals and prolong their life span. In retrospect, I observe that most of my research has had a lot of connection with metals, alloys and related materials.

In the last fifteen years or more, I have worked with some of my colleagues and students on corrosion inhibition processes. Mr. Rector, permit me to acknowledge some of my former PhD students who are now my colleagues and lecturers in some universities in Nigeria. They are Dr. Saviour Umoren, Dr. Nabuk Eddy and Dr. Okon Abakedi. The first has applied for the position of Associate Professor with over 40 publications and he is currently the Head of Department of Chemistry at the University of Uyo, Nigeria. The second is presently a Lecturer but has applied for the position of Senior Lecturer with over 30 publications at the Ahmadu Bello University, Zaria, Nigeria. Am still in contact with them and we still publish some good papers together. These are a few of my academic ambassadors and am really proud of them. In the early 18th century, Isaac Newton (1642-1727) summed up the process of scientific research when he said: **"I keep the subject of my inquiry constantly before me, and wait till the first dawning opens gradually, by little and little, into a full and clear light."** For me this speaks to a journey of consistent hard work and focus. The concept of parallel journeys arose from my reflection on the extraordinary developments in the field of corrosion science over the past two decades and how this has shaped my career as a scientist. This journey has been possible because of the people who have walked with me or crossed my path at critical times during my development and I dedicate this lecture to them. *Nature's* guide for mentors by Lee et al [1] states: **"Having a good mentor early in your career can mean the difference between success and failure in any field."** At this juncture, firstly, I want to specially acknowledge, my mentor, Prof. CNR Rao, an emeritus professor, a renowned Physical / Solid State / Materials chemist, Linus Pauling Professor of Chemistry and former president of the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India. He actually contributed immensely to what I am today and I cannot forget my stay at JNCASR, India under his tutelage. Going to Prof. Rao's office with my head down, armed with a plot or calculation showing that the project seemed to be going nowhere, I will leave believing that I solved the mysteries of the Universe. On many occasions I remember walking to his office convinced that I had been wasting my time, and then ten minutes later walking out with a smile and the sure knowledge that what was a bad result was indeed just what I needed in order to proceed with the project. Secondly, Prof. U.J. Ekpe (professor of Applied Physical Chemistry) of the Department of Chemistry and the Dean of Graduate School, University of Calabar, Nigeria for believing in me that I could attain whatever status I want in life from hard work, perseverance and being focused. I cannot remember them cancelling any appointments with them despite the tremendous demands on their time. I greatly admire their attitude and skill.

Mr. Rector, academic /non academic colleagues, students and distinguished ladies & gentlemen, before I start my lecture proper, I want to inform you all that the year 2011 is the **INTERNATIONAL YEAR OF CHEMISTRY** in partnership with the United Nations Educational, Scientific and Cultural Organization (UNESCO) and International Union of Pure and Applied Chemistry (IUPAC) and am glad that am presenting my Inaugural lecture this year. This recognition for Chemistry was made official by the United Nations in December 2008. The International Year of Chemistry – 2011 (IYC2011) is meant to celebrate the achievements of Chemistry and its contributions to the well-being of mankind under the unifying theme **“Chemistry – our life, our future”**. The goals of IYC2011 are to increase the public appreciation of Chemistry in meeting world needs, to encourage interest in chemistry among young people and to generate enthusiasm for the creative future of Chemistry. The year 2011 also coincides with the 100th anniversary of the Nobel Prize awarded to Madame Marie Curie (recognizing her discovery of the elements radium and polonium) – an opportunity to celebrate the contributions of women to science. “If it stinks, it’s Chemistry – that’s one memory trick some smart-aleck high-school students might recommend to identify core sciences. But Chemistry goes far beyond noxious fumes. It serves as the backbone of our modern society and is essential for a sustainable future and improved standard of living. South Africa is a resource rich country, and it’s not surprising that Chemistry plays a dominant role in the success of several of the main industrial sectors, such as mining, petrochemical, energy, polymer, food, water, pharmaceutical, fertilizer and agrochemical, cement and construction materials, and in addition is the core science in the analytical service laboratories. Therefore, Chemistry remains the core of South Africa’s economy. I will therefore like to crave your indulgence to take you through a few lines of what the subject, Chemistry is and what chemist do.

2.0 WHO IS A CHEMIST?

Chemists are people who understand the behavior of the constituents of matter – atoms, molecules and ions which determine everything around us in the world, including how we feel on a given day. They are well equipped to tackle many of the problems faced by the modern society. A chemist may choose to study the mechanism of recombination of DNA molecules, measure the amount of insecticide in drinking water, compare the protein content of meat, develop a new antibiotic or analyze moon rock etc. He is capable of designing a synthetic fibre, a life saving drug, or analyze a space capsule. To understand why an autumn leaf turns red, or why a diamond is hard, or why soap gets us clean, requires first, a basic understanding of chemistry. It is also obvious that a chemistry background is important if one plans to teach chemistry or to work in the chemical industry, developing chemical commodities such as polymeric materials, pharmaceuticals, flavorings, preservatives, dyestuffs or fragrances. A significant knowledge of chemistry is often required in a number of related professions such as engineering, medicine, pharmacy, medical technology, nuclear medicine, molecular biology, biotechnology, pharmacology, toxicology, paper science, waste management, art conservation, forensic science, patent law. Thus, a chemistry degree with cognate working experience and possible possession of an advanced degree either in a business related discipline such as Business Administration or even Law will effectively equip an individual to function effectively in a higher management level in an industry.

2.1 WHY STUDY CHEMISTRY?

Chemistry is an incredibly fascinating subject because it is so fundamental to our world. It plays a role in everyone's life and touches almost every aspect of our existence in some way by meeting our essential basic needs of food, clothing, shelter, health, energy, clean air, water and soil. Chemical technologies enrich quality of life in numerous ways by providing new solutions to problems in health, materials and energy usage. Thus, studying chemistry is useful in preparing us for the real world. Chemistry is often referred to as the **central science** because it joins together physics and mathematics, biology and medicine, and the earth and environmental sciences. Knowledge of the nature of chemicals and chemical processes therefore provide insight into a variety of physical and biological phenomena. Knowing chemistry is worthwhile for every human being because it provides an excellent basis for understanding the physical universe we live in. **FOR BETTER or FOR WORSE, EVERYTHING IS CHEMICAL.**

This lecture will attempt to bring to limelight the contribution of chemists and Chemistry to the emancipation of mankind. To some, Chemistry is a myth, whereas it is not so. In Genesis 2:1-2, the Bible says that "God created the heaven and the earth ----- and He rested from his works". Due to his insatiable nature, man has perpetually requested for many more materials that will satisfy his dynamic lifestyle. God having rested from His works, decided to entrust the continuation of his work of creation to chemists.

Mr. Rector, I want to now begin my lecture proper by highlighting my fascination for chemistry of materials (metals and alloys) and to demonstrate its character building capabilities.

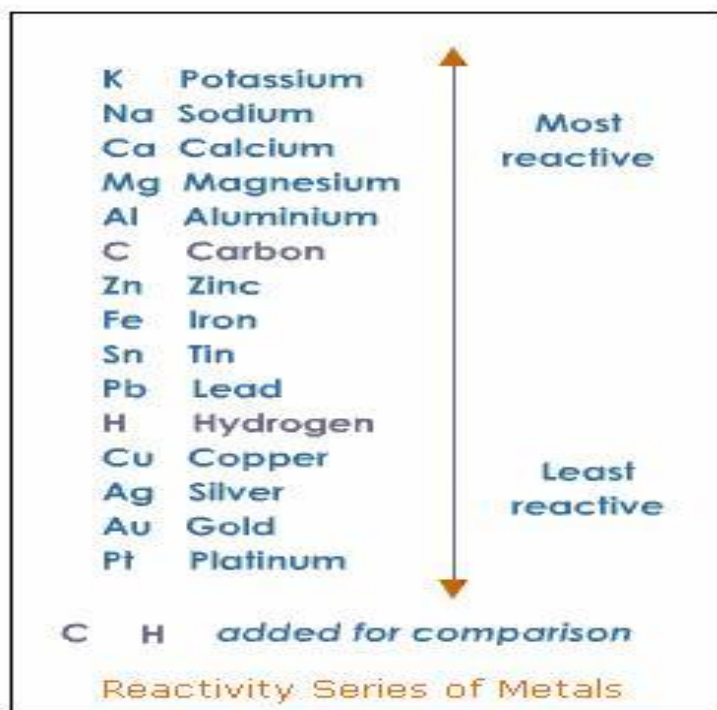
3.0 OCCURRENCE & EXTRACTION OF METALS

Metals occur as minerals in the earth's crust in the following chemical states: oxides, sulphides and to a lesser extent, in 'native' form. A mineral from which the metal of interest can be extracted at a profit is called an 'ore'. Chemically, an ore may contain three classes of minerals, namely: (a) Value minerals (b) Secondary Value minerals and (c) Gangue minerals.

Ore preparation is a two-part process consisting of beneficiation and agglomeration. Beneficiation involves the separation of value mineral from the gangue while agglomeration is the process of reforming fine particles into larger lumps of appropriate size and strength. The main methods of agglomeration are sintering, nodulising, pelletizing and briquetting [2].

One of the outstanding properties of a metal is its tendency to ionize. This tendency is measured by means of electrode potentials. If the metals are arranged in a decreasing order of their electropositivities (reactivities), we have an '**activity or electrochemical series**'. In this arrangement the metals may be sub-divided into three categories namely most electropositive, moderately electropositive and least electropositive. Very reactive elements exist mainly in the form of chloride, trioxo-carbonate (IV) and oxide ores. Moderately electropositive metal ores exist in the form of oxides, tetraoxo-carbonate (IV) and sulphides while ores of least electropositive metals exist in the form of sulphides and native (free) elements. The method of extraction (reduction) of a particular metal depends on its electropositivity or its position in the electrochemical series. Most electropositive metals are extracted by electrolysis of molten ores (electrometallurgy) while moderately electropositive metals are obtained by reduction of oxides (pyrometallurgy). Ores of least electropositive

metals are extracted by thermal or chemical methods (hydrometallurgy). The diagram below shows the reactivity series of metals.



3.1 METALS AND CORROSION

Metals are opaque, lustrous elements that are good conductors, malleable and ductile. In Chemistry, metals may be defined as elements that readily form cations (positive ions) and form metallic bonds with other metal atoms and ionic bonds with non-metals. Metals may also be described as a lattice of positive ions surrounded by a cloud of localized electrons. The metallurgist considers metals as elements that have overlapping conduction bands and valence bands in their electronic structure. They react with oxygen in the air to form basic oxides. Metals constitute over 80% of the elements in the periodic table. Metals are widely used in;

- i. Construction – farming tools, bridges, household conveniences, building, communication etc.
- ii. Transportation – cars, buses, trucks, ships, airplanes etc.
- iii. Electric power generation and distribution.
- iv. Biomedical applications.

- v. Ornaments and cooking utensils.

3.1.1. Definition of corrosion

The process whereby a material breaks into its constituents atoms because of the chemical reactions with its surrounding is called **Corrosion**. Rusting of a metal is a commonly known type of electrochemical corrosion. In rusting, the metal actually undergoes electrochemical oxidation with oxygen as an oxidant. The metal oxide (rust) is then formed. This metal oxide (rust) is the damage that is of serious concern to most industries all over the world. Corrosion is not only limited to metals, it can also take place on other materials such as polymers and ceramics. Nevertheless, in polymers it is more often than none explained as degradation than corrosion although they are referring to a similar process. Amongst many metals, corrosion is experienced strongly in iron and steel. This is because the oxide that is formed during the process of oxidation does not hold firmly to the surface of the metal, as a result it moves off the metal easily. In the case of aluminum metal, an oxide coating that aluminum forms assist in bringing the oxide to strongly bond the surface of the metal thereby slowing down the corrosion (or stop further exposure to oxygen).

Corrosion is a natural process driven by energy considerations. The process of extraction of metals from their ores stores up vast quantity of energy in the metal. Corrosion is therefore a means of releasing this stored – up energy. The metal because of its high energy is in an excited state / state of high energy. The corrosion process is a means of going to the lower energy state (the combined state).

The electrochemical reaction that causes corrosion consists of four factors namely;

- i. Anode
- ii. Cathode
- iii. Electrolyte
- iv. Electronic circuit

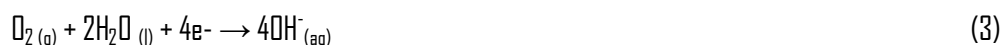
The process of rusting or corrosion takes place in multisteps. Firstly, iron is oxidized to ferrous (Fe^{2+}) ions, according to the reaction 1 given below;



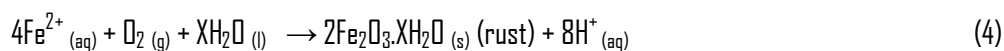
Then the (Fe^{2+}) ions are oxidized to ferric ions (Fe^{3+}), as indicated by reaction 2;



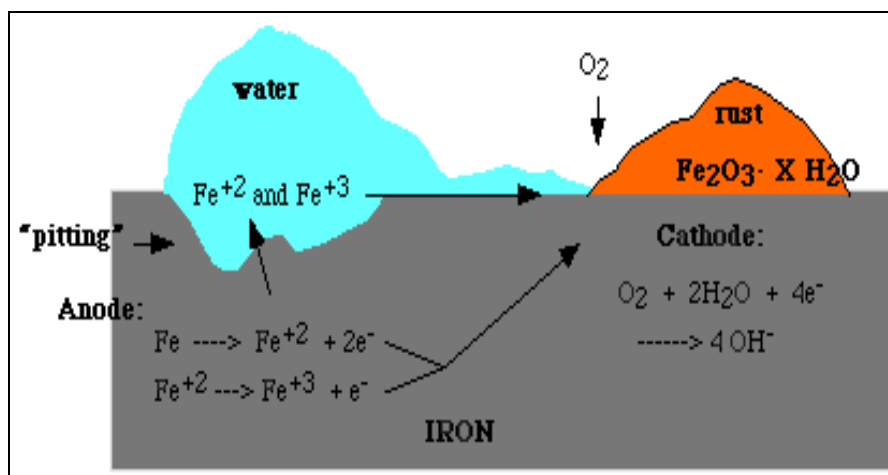
The third step is the reduction of oxygen by the electrons from reactions (1) and (2). This reduction is summarized by reaction (3) below;



The last step involves the reaction between Fe^{2+} and O_2 to produce ferric oxide [iron (III) oxide]. Equation (4) illustrates this;



Iron can serve as an anode and oxygen gas as the cathode in an electrochemical cell with the salt bridge as an aqueous solution of ions. The processes involved in this electrochemical cell can be further illustrated by the figure below.



Processes involved in the electrochemical cell to form Iron oxide (Rust)

In dry conditions (where there is no moist) such as in places like desert, corrosion is much less slower than in a moist area where there is moisture carrying oxygen (O_2). There are many other factors that influence the rate of corrosion of mild steel, including the presence of salt. This is true because the molten salt increases the conductivity of the aqueous solution that is formed at the surface of the metal. Because the conductivity is increased, the rate of electrochemical corrosion increases. The temperature of the system also affects the rate of corrosion of mild steel.

3.1.2. Types of Corrosion

There are many different types of corrosion that are known today namely;

- i. **Uniform corrosion:** which is also known as general corrosion since the corrosion is caused by direct chemical attacks on the substance.
- ii. **Galvanic corrosion:** when two different metals are placed in contact under electrochemical action.
- iii. **Concentration cell corrosion:** when two metals or more are allowed to come into contact with different concentration of the same solution.
- iv. **Pitting corrosion:** this type of corrosion takes place at microscopic defects on a metal surface.

- v. **Crevice corrosion:** also known as contact corrosion. It takes place right at the point of contact of the metal with the other metal or a metal with a non metal.
- vi. **Filiform corrosion:** this type of corrosion takes place on substances that are painted. When moisture finds its way in the coating of the surface that is painted, the result is likely to be a filiform corrosion.
- vii. **Intergranular corrosion:** the grain boundaries of a substance are attacked perhaps by a strong acid.
- viii. **Stress corrosion cracking:** this type of corrosion is also commonly abbreviated as SCC. The simultaneous effects of stress and the environment cause SCC.
- ix. **Erosion corrosion:** the harsh chemical environment combined with high fluid surface speeds lead to a corrosion known as erosion corrosion.
- x. **Dealloying:** although this type of corrosion is not commonly encountered, it remains problematic. This process occurs when the alloy loses its atomic component of the metal and retains its corrosion resistance component on the metal surface.
- xi. **Corrosion in concrete:** self explanatory type of corrosion. In the concrete material, there is a carbon steel among the components therein. While the steel is a very crucial component of the concrete for the strength purposes of the building, it is also important to note that steel is capable of undergoing corrosion.
- xii. **Refinery corrosion:** this is the type of corrosion that results from the equipment surface that has been attacked by the strong acid.
- xiii. **Microbial corrosion:** also abbreviated as MIC, is caused by the activities of microbes.

Generally, these different forms of corrosion can be divided into three categories namely;

- i. GROUP I – Those which can be observed by the naked eye (general, localized and galvanic corrosion).
- ii. GROUP II- Those which can be recognized with the assistance of some means of examination (velocity related intergranular, dealloying corrosion).
- iii. GROUP III- Those which can only be identified by using microscopes.

3.1.3. Rate of Corrosion

The process of corrosion involves a weight loss of the material or substance. This loss per unit time is used to express the rate of corrosion. The rate of corrosion depends on the material being corroded. There are materials that are not capable of producing a passive film and those that are capable. The rate of corrosion in those substances that have the ability to form a passive film is much slower in comparison to those that do not have the capability to produce the passive film. When a thin protective layer oxide (passive film) is formed on the surface of the metal, the phenomenon is known as passivation.

Most of the passive films are within the size range of 10 nm in thickness. The passive films assist in preventing corrosion of a particular metal. In harsh environmental conditions, the passive film tend to become unstable and hence breakdown.

3.1.4. Effects of Corrosion

The effects of corrosion are experienced by many human beings if not all. Lives, jobs and health of the human beings are amongst the other things that are affected by the effects of corrosion. Some of the effects of corrosion are briefly discussed:

- i. **Health effects:** Human beings continuously make use of metals or metal products. These include the metal piercing on their bodies. The other known example is the applications of metallic plates and cups by human beings. When the metallic plates and cups are affected by corrosion, the human health can be at a gross risk.
- ii. **Safety effects:** In this world there are so many crucial means of transportation that are made of metals. These include cars, airplanes and ships. If any of the metals that is used in the construction of a car is attacked by any type of corrosion, the safety of the passengers may not be guaranteed. The use of metals in the construction industries such as construction of bridges and even buildings is one more crucial example. If these metals are attacked by corrosion the safety effects are likely to be experienced.
- iii. **Economic effects:** The economy of each and every country has a share in the industries of that particular country. Petroleum industries continue to make use of metals for their fluid carrying pipes and tanks. These industries find themselves spending a great amount of money in their attempts to minimize corrosion. If a pipe or a tank breaks as result of corrosion, there will be a loss of production which in turn affects the economy.
- iv. **Cultural effects:** Many nations pride themselves in their heroes. These heroes include political heroes, religious heroes and many more. In South Africa alone, there are a number of statues of many political heroes. These statues are mostly made up of metallic products which can be attacked by corrosion. Corrosion attacks these precious statues thereby affecting the cultural beliefs of a particular nation.
- v. **Technological effects:** Most of the technological gadgets are constructed from metallic products. These include electricity power stations and solar energy systems. When corrosion damages these metallic substances, the technological effect is experienced.

In the light of all the above mentioned effects of corrosion, control measures / procedures needs to be implemented in order to **reduce or inhibit** corrosion thereby prolong the life span of the metals or materials and preventing the return to the combined state (ore) from which they were initially obtained ("dust to dust" or "earth to earth").

3.1.5. Corrosion Inhibition

An inhibitor is a substance that slows down or retards a chemical reaction. A corrosion inhibitor is a substance which when added to an environment, reduces the rate of attack by the environment. The use of corrosion inhibitors is one of the best methods of combating corrosion. In order that they can be used effectively, three factors must be considered, namely:

- (i) Identification of the corrosion problems,

- (ii) The economics of the inhibition process.
- (iii) The compatibility of the inhibitor with the process being used.

Generally, three of the four components of a corrosion cell (anode, cathode, electrolyte and electronic conductor) may be affected by corrosion inhibitors in order to reduce corrosion. The inhibitor may cause:

- (i) Anodic inhibition by increasing the polarization of the anode
- (ii) Cathodic inhibition by increasing the polarization of the cathode
- (iii) Resistance inhibition by increasing the electrical resistance of the circuit while forming a thin or thick deposit on the surface of the metal, and
- (iv) Diffusion restriction by restricting the diffusion of depolarizers (eg. Dissolved oxygen) to the surface of the metal. By so doing the inhibitors play a dual role.

3.1.5.1. Types of Inhibitors

There are six classes of inhibitors namely:

- (i) Passivating (anodic),
- (ii) Cathodic,
- (iii) Ohmic,
- (iv) Vapour phase, and
- (v) Organic/Inorganic.

For the purpose of this lecture, I will concentrate only on the Organic/Inorganic type of inhibitors which happens to be the ones I have studied in the past 15 years. Organic and inorganic compounds constitute a large class of corrosion inhibitors, which as a general rule; affect the entire surface of a corroding metal when present in sufficient concentration. Most of the organic/inorganic compounds containing elements of Groups VB, VIB or functional groups of the type $-NH_2$, $=CO$ and $-CHO$ are known to be effective inhibitors. The principal mechanism suggested by several researchers in the field of corrosion inhibition studies is 'adsorption'. The inhibitor is adsorbed on the entire surface of the corroding metal and by so doing prevents attack from the corrodent. Organic inhibitors are adsorbed according to the ionic charge of the inhibitor on the metal's surface. Cationic inhibitors e.g. amines (positively charged) or anionic inhibitors e.g. sulphonates (negatively charged) will be adsorbed preferentially, depending on whether the metal is charged positively or negatively.

The inhibitors may therefore be considered as two fundamental types [2] namely:

- (i) Type A: Those which form a protective barrier film on anodes or cathodes by reaction between the metal and the environment. The Type A inhibitors functions in neutral or in some cases, alkaline solution in which the main cathodic reaction is an oxygen reduction reaction in which the corroding metal surface is covered by a film oxide or hydroxide. Type A inhibitors tend to produce a protective film or stabilize an already existing ore.
- (ii) Type B: Those which are initially adsorbed directly onto the metal surface by interaction between surface charges and ionic and/ or molecular dipole charges. This division of inhibitor types results principally from the pH of the solution where they operate.

Inhibitors must be present in a minimum concentration for them to be fully effective. When the inhibitor falls below a specified minimum amount, the cover it provides is inadequate and the exposed area becomes a centre for more active corrosion. This is very common with anodic inhibitors. It has been observed that at certain concentrations, inhibitors lose their efficiency and become corrosion promoters [3]. The efficiency of organic inhibitors can be improved in the presence of certain halogen ions. Halogen ions alone are also known to inhibit corrosion to some extent in acid solutions. The efficiency of the corrosion inhibition is in the order; $I^- > Br^- > Cl^-$. Fluoride does not show inhibition characteristics. Synergism of halogen ions can be attributed to the fact that the metal adsorbs halogen ions whose charge shifts the surface in a negative direction, thereby increasing adsorption of the cationic organic inhibitor [4 – 8].

Mr. Rector, being able to discover possible compounds that can be used as corrosion inhibitors requires a lot of hard work, innovation and laboratory analysis / synthesis and can only be done when God allows it. It is not all those who work and want to synthesize these compounds that succeed. Psalm 127: 2 states: "It is in vain you wake up early to sleep late, to eat the bread of sorrow because God gives all these things to his beloved even while they are sleeping" (Amplified Bible). The revelation of what to do and the direction to go about it is given by God as in **Isaiah 45:3 – " And I will give thee the treasures of darkness, and hidden riches of sweet places, that thou mayest know that I, the Lord, which call thee by thy name, am the God of Israel"**. I have been rather lucky and blessed. I give glory to the Almighty God.

As I mentioned earlier, my research work has been centered on metals but for the purpose of this lecture I will concentrate on corrosion and corrosion inhibition. The problem of corrosion has been a subject of concern for several years and this happens to be one of the major problems facing many industries in the world today ranging from the petroleum industries, mining industries and even to our everyday life. Several countries and industries all over the world have spent and allocated huge sums of money into the possibility of combating this corrosion menace. A lot of researches and researchers have been investigating the issue of how to reduce (if not combat) the problem of corrosion. A lot of compounds have been studied as possible corrosion inhibitors by several groups and this area of research continues to generate a lot of more interest over the years.

4.0. MY CONTRIBUTIONS TO CORROSION INHIBITION STUDIES USING SYNTHETIC ORGANIC/INORGANIC INHIBITORS.

My research over the years has been focused on corrosion and corrosion inhibition studies using different metals / materials and compounds as inhibitors in different media (acidic, basic and neutral) via weight loss, hydrogen evolution and

thermometric methods. The application of the principles of physical chemistry (like kinetics, thermodynamics, adsorption, quantum chemical concepts and calculations) and materials science (chemistry and physics) has been used and reflected in my research over the years. During the period I have completed and published several studies in peer reviewed international and local journals of wide readership. My completed researches are broadly divided into five categories (but are not limited to) namely:

- (i) The use of synthetic organic and inorganic compounds such as thiosemicarbazones and its derivatives, dyes (methyl red, methylene blue, methyl orange, thymol blue, solochrome black T etc), acetylphenothiazine, acetamidoaniline etc as corrosion inhibitors and the effect of halides in different media. A few of the publications resulting from these researches are below:
 - (1) U. J. Ekpe, U. J. Ibok, B. I. Ita, O. E. Offiong and **E. E. Ebenso**, (1995). Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in HCl. **Material Chemistry and Physics 40; 87 - 93. [9]**
 - (2) **E. E. Ebenso**, (1998). Inhibition of aluminium (AA3105) Corrosion in HCl by acetamide and thiourea. **Nigerian Corrosion Journal. 1(1); 29 - 44. [10]**
 - (3) **E. E. Ebenso**, U. J. Ekpe, B. I. Ita, O.E.Offiong and U. J. Ibok, (1999). Effects of molecular structure on the efficiency of amides and TSC used for corrosion inhibition of mild steel in HCl. **Materials Chemistry and Physics 60; 79 - 90.[11]**
 - (4) **E. E. Ebenso**, (2001). Inhibition of corrosion of mild steel in HCl by some Azo dyes. **Nigerian Journal of Chemical Research. 6; 8 - 12. [12]**
 - (5) U. J. Ekpe, P. C. Okafor, **E. E. Ebenso**, O. E. Offiong and B. I. Ita (2001). Mutual effects of TSC derivatives on the acidic corrosion of aluminium. **Bulletin of Electrochemistry 17(3); 131 - 135. [13]**
 - (6) **E. E. Ebenso**, P. C. Okafor, O. E. Offiong, B. I. Ita, U. J. Ibok and U. J. Ekpe (2001). Comparative investigation into the kinetics of corrosion inhibition of aluminium alloy (AA 1060) in acidic medium. **Bulletin of Electrochemistry 17(10); 459 - 464. [14]**
 - (7) **E. E. Ebenso**, P. C. Okafor and U. J. Ekpe (2003) Studies on the inhibition of aluminium corrosion by 2-acetylphenothiazine in chloroacetic acids. **Anti-Corrosion Methods & Materials 50(6); 414 - 421. [15]**
 - (8) **E. E. Ebenso**, (2003a). Effect of halide ions on the corrosion inhibition of mild steel in H₂SO₄ using methyl red. Part I. **Bulletin of Electrochemistry 19(5); 209 - 216. [4]**
 - (9) **E. E. Ebenso**, (2003b). Synergistic effect of halide ions on the corrosion inhibition of aluminium in H₂SO₄ using 2-acetylphenothiazine. **Materials Chemistry and Physics 79(1); 58 - 70. [5]**
 - (10) P. C. Okafor, **E. E. Ebenso**, U. J. Ibok, U. J. Ekpe and M. I. Ikpi (2003) Inhibition of 4-acetamidoaniline on corrosion of mild steel in HCl solution. **Transactions of SAEST 38 (3); 91 - 96. [16]**

- (11) **E. E. Ebenso**, P. C. Okafor, U. J. Ekpe, U. J. Ibok and A. I. Onuchukwu (2004). The joint effects of halide ions and methylene blue on the corrosion inhibition of aluminium and mild steel in acid corrodent. **Journal of Chemical Society of Nigeria**. **29(1)**; 15 – 25. [7]
- (12) E. E. Oguzie, B.N. Okolue, **E. E. Ebenso**, G. N. Onuoha and A. I. Onuchukwu (2004) Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in HCl solutions. **Materials Chemistry and Physics** **87(2-3)**; 394 – 401. [17]
- (13) P. C. Okafor, **E. E. Ebenso** and U. J. Ekpe (2004). Inhibition of aluminium corrosion by some derivatives of thiosemicarbazone. **Bulletin of Chemical Society of Ethiopia**. **18(2)**; 181- 192. [18]
- (14) **E. E. Ebenso**, (2004). Effect of methyl red and halide ions on the corrosion of aluminium in H₂SO₄. Part 2. **Bulletin of Electrochemistry**. **20(12)**; 551 - 559. [6]
- (15) **E. E. Ebenso** and E. E. Oguzie (2005) Corrosion inhibition of mild steel in acidic medium by some organic dyes. **Material Letters** **59 (17)**: 2163 – 2165. [19]
- (16) E. E. Oguzie and E. E. Ebenso (2006) Studies on the corrosion inhibitive effect of Congo red dye – halides mixture. **Pigment and Resin Technology** **35(1)**: 30 – 35. [20]
- (17) Alfred I. Onen, B.T. Nwufu, **Eno E. Ebenso** and Mbuthi R. Hlophe (2010) Titanium (IV) oxide as corrosion inhibitor for aluminium and mild steel in acidic medium. **International Journal of Electrochemical Science** **5**: 1563 – 1573.[21]
- (18) **Eno E. Ebenso**, Ime B. Obot and L.C. Murulana (2010) Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium. **International Journal of Electrochemical Science** **5**: 1574 – 1586. [22]
- (19) **Eno E. Ebenso**, Ime B. Obot (2010) Inhibitive Properties, Thermodynamic Characterization and Quantum Chemical Studies of Secnidazole on Mild Steel Corrosion in Acidic Medium. **International Journal of Electrochemical Science** **5**; 2012 – 2035. [23]
- (20) I.B. Obot, N.O. Obi- Egbedi, S.A. Umoren and **E. E. Ebenso** (2011) Adsorption and kinetic studies of fluconazole for the corrosion of aluminium in HCl solution. **Chemical Engineering Communications** **198**; 711 – 725. [24]
- (ii) Synergistic, kinetics, adsorption and thermodynamic studies using synthetic polymers such as polyvinyl chloride (PVC), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyacrylamide (PAA) and polyvinyl pyrrolidone (PVP) as corrosion inhibitors and the effect of halides in different media. Most of the published papers in this category results from the PhD Thesis work I supervised of one of my good students (Dr. Saviour A. Umoren). A few of the publications resulting from these researches are listed below:
- 1) S.A. Umoren, O.Ogbobe, **E.E.Ebenso** and U.J.Ekpe (2006) Effect of halide ions on the corrosion inhibition of mild steel in acidic medium using polyvinyl alcohol. **Pigment and Resin Technology** **35 (5)**: 284 – 292. [25]

- 2) **E. E. Ebenso**, U.J. Ekpe, S. Umoren, Ekerete Jackson, O.K. Abiola and N. C. Oforka (2006) Synergistic effect of halide ions on the corrosion inhibition of aluminium in acidic medium by some polymers. Journal of Applied Polymer Science **100(4): 2889 - 2894. [8]**
 - 3) S.A. Umoren, **E.E.Ebenso**, P.C.Okafor and O.Ogbobe (2006) Water soluble polymers as corrosion inhibitors of mild steel in acidic medium. Pigment and Resin Technology **35 (6): 346 - 352. [26]**
 - 4) S.A. Umoren, O.Ogbobe and **E.E.Ebenso** (2006) The adsorption characteristics and synergistic inhibition between polyethylene glycol and halide ions on the corrosion of mild steel in acidic medium. Bulletin of Electrochemistry **22 (4): 155 - 167. [27]**
 - 5) S.A. Umoren, **E.E.Ebenso**, P.C.Okafor, U.J.Ekpe and O.Ogbobe (2007) Effect of halide ions on the corrosion inhibition of aluminium in alkaline medium using polyvinyl alcohol. Journal of Applied Polymer Science **103(5): 2810-2816. [28]**
 - 6) S. A. Umoren, O.Ogbobe, P.C. Okafor and **E. E.Ebenso** (2007) Polyethylene glycol and polyvinyl alcohol as corrosion inhibitors of aluminium in acidic medium. Journal of Applied Polymer Science **105(6): 3363 - 3370.[29]**
 - 7) S.A. Umoren and **E.E.Ebenso** (2007) The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄. Materials Chemistry and Physics **106: 387- 393. [30]**
 - 8) S.A. Umoren, O.Ogbobe , I.O. Igwe and **E.E.Ebenso** (2008) Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives. Corrosion Science **50(7): 1998 - 2006. [31]**
 - 9) S. A. Umoren and **E. E. Ebenso** (2008) Blends of polyvinyl pyrrolidone and polyacrylamide as corrosion inhibitors for aluminium in acidic medium. Indian Journal of Chemical Technology **15(4): 355 - 363. [32]**
 - 10) S.A. Umoren, **E.E.Ebenso** and O.Ogbobe (2009) Synergistic effect of halide ions and polyethylene glycol on the corrosion inhibition of aluminium in alkaline medium. Journal of Applied Polymer Science **113: 3533 - 3543.[33]**
- (iii) The use of some quantum chemical ,molecular modeling , theoretical and Quantitative Structure Activity Relationship (QSAR) studies of compounds used as corrosion inhibitors [e.g. some sulphonamides (namely sulfaacetamide , sulfapyridine , sulfamerazine, sulfathiazole, sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine); some antibiotics / antimicrobial drugs e.g rhodanine azo sulpha compounds (namely 5-sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidinone,5-sulphamethazineazo-3-phenyl-2-thioxo-4-thiazolidinone, 5-sulphadimethoxineazo-3-phenyl-2-thioxo-4-thiazolidinone, 5-sulphamethoxazoleazo-3-phenyl-2-thioxo-4-thiazolidinone] using density functional theory (DFT) at the B3LYP/6-31G (d,p) and BP86/CEP-31G* basis set levels and other semi empirical methods and ab initio calculations using the RHF/6-31G (d,p). Most of the published papers in this category results from the PhD Thesis work I supervised of one of another of my good students (Dr. Nabuk O. Eddy). A few of the publications resulting from these researches are listed below:
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- 1) Taner Arslan, Fatma Kandemirli , **Eno E. Ebenso**, Ian Love and Hailemichael Alemu (2009) Quantum chemical studies on the corrosion inhibition of some sulphonamides on mild steel in acidic medium . **Corrosion Science 51 (1): 35 - 47. [34]**
- 2) Nnabuk O. Eddy, Udo J. Ibok, **Eno E. Ebenso**, Ahmed El Nemr and ElSayed H.El Ashry (2009) Quantum chemical study of the inhibition of the corrosion of mild steel in H₂SO₄ by some antibiotics. **Journal of Molecular Modelling 15: 1085 - 1092. [35]**
- 3) **Eno E. Ebenso**, Taner Arslan, Fatma Kandemirli , Necmettin Caner, Ian Love (2010) Quantum chemical studies of some rhodanine azosulpha drugs as corrosion inhibitors for mild steel in acidic medium. **International Journal of Quantum Chemistry 110 (5): 1003 - 1018. [36]**
- 4) **Eno E. Ebenso**, Taner Arslan, Fatma Kandemirli, Ian Love, Cemil Ogretir, Murat Saracoglu and Saviour A. Umoren (2010) Theoretical studies on some sulphonamides as on corrosion inhibitors for mild steel in acidic medium. **International Journal of Quantum Chemistry 110(5) : 2614 - 2636. [37]**
- 5) Nnabuk O. Eddy, **Eno E. Ebenso** and Udo J. Ibok (2010) Adsorption, synergistic effect and Quantum chemical studies on ampicillin and halides for the corrosion of mild steel in H₂SO₄. **Journal of Applied Electrochemistry 40(2): 445 - 456. [38]**
- 6) Nnabuk O. Eddy and **Eno E. Ebenso** (2010) Quantum chemical studies on the inhibition potentials of some penicillin compounds for the corrosion of mild steel in 0.1M HCl. **Journal of Molecular Modelling 16: 1291 - 1306. [39]**
- 7) **Eno E. Ebenso** , David A. Isabirye and Nabuk O. Eddy (2010) Adsorption and Quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium. **International Journal of Molecular Sciences 11; 2473 - 2498. [40]**
- 8) Nnabuk O. Eddy and **Eno E. Ebenso** (2010) Adsorption and Quantum chemical studies on cloxacillin and halides for the corrosion of mild steel in acidic medium. **International Journal of Electrochemical Science 5; 731 - 750. [41]**
- 9) Nnabuk O. Eddy, Stanislova R. Stoyanov and **Eno E. Ebenso** (2010) Fluoroquinolones as corrosion inhibitors for mild steel in acidic medium; experimental and theoretical studies. **International Journal of Electrochemical Science 5; 1035 - 1058. [42]**
- 10) **Eno E. Ebenso**, Ime B. Obot (2010) Inhibitive Properties, Thermodynamic Characterization and Quantum Chemical Studies of Secnidazole on Mild Steel Corrosion in Acidic Medium. **International Journal of Electrochemical Science 5; 2012 - 2035. [23]**

- 11) N.O. Eddy, B.I. Ita, N.E. Ibisi and **E.E. Ebenso (2011)** Experimental and Quantum Chemical studies on the Corrosion Inhibition Potentials of 2 – (2- Oxindolin-3-ylideneamino) Acetic acid and Indoline- 2,3-dione. **International Journal of Electrochemical Science 6; 1027 – 1044. [43]**
 - 12) V.F. Ekpo, P.C. Okafor, U.J. Ekpe and **E. E. Ebenso (2011)** Molecular Dynamics Simulation and Quantum Chemical Calculations for the Adsorption of some thiosemicarbazone (TSC) derivatives on mild steel. **International Journal of Electrochemical Science 6; 1045 – 1057. [44]**
 - 13) N.O. Obi-Egbedi, K.E. Essien, I.B. Obot and **E. E. Ebenso (2011)** 1, 2 – Diaminoanthraquinone as Corrosion Inhibitor for mild steel in hydrochloric acid: Weight loss and Quantum Chemical study. **International Journal of Electrochemical Science 6; 913 – 930. [45]**
 - 14) N.O. Eddy, F.E. Awe, C.E. Gimba, N.O. Ibisi and **E.E. Ebenso (2011)** QSAR, Experimental and Computational Chemistry Simulation studies on the Inhibition potentials of some Amino Acids for the corrosion of mild steel in 0.1M HCl. **International Journal of Electrochemical Science 6; 931 – 957. [46]**
- (iv) The use of plant extracts (green and environmentally friendly) - (*Carica papaya, Azadirachta indica, Phyllanthus amarus, Garcinia cola, Delonix regia, Ocimum basilicum, Piper guinensis, Musa sapientum, Allium cepa, Allium sativum*) and naturally occurring polymers (exudates gums namely *Raphia Hookeri, Pachylobus edulis, Gum Arabic, Dacryodes edulis etc*) as corrosion inhibitors. The publications generated from this category will be discussed in section 4.1 on Chemistry, Sustainable Development and Corrosion Inhibition.

Most of my research results from the above studies showed that the compounds used as corrosion inhibitors can be efficient in either acidic or basic medium. We have recorded and reported over 70% inhibition efficiency with most of the studied inhibitors which is a clear indication that the compounds really inhibited the corrosion of the materials and hence prolong their life span. The studies too has been able to propose the type of adsorption mechanism and adsorption isotherm that the corrosion inhibition process obeyed (i.e.) whether physical or chemical adsorption, Langmuir, Freundlich, Temkin etc adsorption isotherms. The synergistic, kinetics and thermodynamic studies of the reactions were also exhaustively reported. The studies showed that most of the compounds used as corrosion inhibitors which contained oxygen, nitrogen and sulphur atoms in their structure were good corrosion inhibitors and show potential for industrial application. It is pertinent to mention here that most of my completed researches are from single authored papers, master's and doctoral students' supervision and research collaboration that I have with some colleagues in other universities in Nigeria, Turkey, Lesotho, Germany and India. The results obtained in these studies have considerably reduced the rate of corrosion of the materials and increased the life span of the metals/ materials thereby decreasing considerably the time it takes for the metals/ materials to return back to the earth or dust.

- (v) At a certain time in the course of my researches, I delved into the area of Chemistry and Physics of Materials which involved the deposition of thin films of some ferromagnetic oxides showing metallic conductivity with perovskite structure (e.g. SrRuO_3), ordered double perovskites, $\text{A}_2\text{B}'\text{B}''\text{O}_6$ (A being alkaline earth or rare-earth ion; transition metals B' and B'' occupy the transitional metal sites perovskite B sites) (e.g. $\text{Sr}_2\text{FeMoO}_6$), rare-earth cobaltates with perovskite structure exhibiting metal-insulator transition e.g. $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ series (where Ln = La, Nd and Gd; x = 0.0, 0.1, 0.3 and 0.5; A = Sr) and rare-earth manganate with perovskite structure e.g. $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

series ($x = 0.3$ and 0.4) using nebulized spray pyrolysis technique. The thin films were characterized using XRD, EDAX and SEM. Further studies were done on the resistivity, magnetization and magnetoresistance properties of the thin films. These researches formed the basis of some of my collaboration with some scientist in India and Germany. The results of these researches were published in:

- 1) S. Parashar, **E. E. Ebenso**, A. R. Raju and C. N. R. Rao (2000) Insulator-metal transitions induced by electric and magnetic fields in thin films of charge-ordered $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$. **Solid State Communication** **114**: 295 - 299. [47]
- 2) **E. E. Ebenso**, Kripasindhu Sardar, M. Chandrasekhar, A.R. Raju and C.N.R. Rao (2000). Thin films of $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ ($\text{Ln} = \text{La, Nd and Gd}$) and SrRuO_3 by nebulized spray pyrolysis. **Solid State Sciences** **2**: 833 - 839. [48]

4.1 CHEMISTRY, SUSTAINABLE DEVELOPMENT AND CORROSION INHIBITION

The challenge of meeting human development needs while protecting the earth's life support systems continues to confront scientists, technologists, policy makers and communities from local to global levels. Many believe that science and technology (S&T) must play a more central role in sustainable development, yet little systematic scholarship exists on how to create institutions that effectively harness S & T for sustainability.

4.1.1 What is Sustainability?

- “Sustainability is the ability to provide a healthy, satisfying and just life for all people on earth, now and for generations to come, while enhancing the health of ecosystems and the ability of other species to survive in their natural environments”.
- Sustainability is system-based.
- However, the concept of sustainability dates back to history. As the challenge of living in harmony with the earth becomes increasingly difficult, more than ever, society needs education and high quality cutting-edge research to meet these challenges.

4.1.2. What is Sustainable Development?

- “Sustainable development” is a process of change during which societies and their citizens learn to deal with the tension between ecological sustainability and economic development while doing justice to interests at both local and global level.
- This general definition can be interpreted differently depending on locality and geographical location.
- Sustainable development balances three principal requirements namely:-
 - ❖ The needs of society (the social objective);
 - ❖ The efficient management of scarce resources (the economic objective);

- ❖ The need to reduce the load on the eco-system in order to maintain the natural basis for life (the environmental objective).

Sustainable development depends on providing goods and services for a growing population without sacrificing environmental quality. Since the Rio Earth Summit in 1992, sustainable development has been increasingly accepted *as a way to run businesses by balancing economic, environmental and societal responsibilities. Within the industry, it is called the strategy of the 3Ps, namely **Profit, Planet and People**. With the ‘profit’ dimension, businesses are expected to make robust profit while allowing their customers to make profits as well. The ‘planet’ responsibility calls for efficient management of available resources and protection of the environment from waste disposal. Finally, the ‘people’ dimension requires respect for the people and communities the businesses are in contact with.*

In 1987, a UN report defined “sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their needs” . Sustainability development can also be defined as “meeting the worlds demand for energy, food, water and medicine – in a sustainable way, while protecting the environment – requires development of new technologies and advanced materials.” Sustainable development therefore is required to help meet the worlds need for:

- Energy - energy technologies
- Resources - use strategies
- Food
- Water
- Medicine
- Protection of the environment

Considering the fact that I have presented several papers on sustainable development in science and technology at several conferences and forum over the years and bearing in mind that this is a very broad area, my focus is on the contribution of research in chemistry to sustainable development with particular emphasis on CORROSION & ENVIRONMENTALLY FRIENDLY (GREEN) CORROSION INHIBITORS. Therefore, given societal needs in the 21st century and beyond, the question now is what science and technology innovations do we need to achieve the goal of sustainable feature? **SURE THE ANSWER IS CHEMISTRY!!!!**

- Chemistry is a specific discipline in science that tries to understand and explain the makeup and changes of all things that have mass and occupy space. Over the years, chemistry has steadily advanced into the study of complete molecular structures in science and related areas. **A subject as all-encompassing as chemistry plays a very big role in sustainability.**
- One of the reasons for studying chemistry is “As a means for improving the condition of mankind by ameliorating his environment” .

- Chemistry, a branch of science that deals with the structure, composition, energetic, properties, and reactive characteristics of substances at atomic, molecular, and nanometer-length scales, is uniquely suited to contribute in positive and meaningful ways to sustainable life. Chemists are uniquely qualified to provide a molecular-level approach to and understanding of sustainability.
- Some areas of sustainability namely energy, green chemistry, processing and environment are very important to the chemist. These are areas in which basic chemistry research and educational initiatives can play a pivotal role in driving innovations that will help achieve a sustainable feature.

Chemistry is a central science in energy conversion, storage and utilization. Most of our widely used forms of energy come from combustion of fossil fuels that are clearly not sustainable. Society requires new energy sources that can be sustainably created, stored, interconverted and used. Chemistry plays a crucial role in making all these to take place. In the area of green chemistry and processing, change will come about when chemists have the tools to use renewable resources with few by products produced by simpler, less energy-intensive and more efficient processes to power our society. Chemistry advances in sustainability research addresses the importance of the environment. The application of chemistry and allied sciences can play a significant role in the attainment of sustainability when the broader issues of sustainability are integrated at the technology development phase. Chemistry can make important contributions to the conservation of resources by the development of:-

- ✓ More efficient and environmentally more benign chemical processes;
- ✓ Chemical products that are based on renewable resources;
- ✓ Chemical products that are environmentally more benign, and enhance the efficiency of production processes and products in other areas significantly;
- ✓ Products that allow the consumer to use resources more efficiently;
- ✓ A product design that fits into a recycling concept.

Sustainable chemistry is closely related to “green chemistry” ; but with a slight difference in the definition: while green chemistry indicates that a not risky and polluting chemical production process may exist, the sustainable chemistry concepts links eco-efficiency, economic growth and quality of life in terms of the cost/benefit analysis. The sustainable chemistry approach emphasizes the concept of sustainable risk. The role of the chemist is to minimize this risk and reduce the impact on the environment to a level sustainable by the environment, assuring a good quality of life. Green chemistry is used to indicate technologies for which a careful cost/benefit or assessment study has not been made. “Sustainable chemistry” is thus the natural trend of chemistry, but not an independent factor from economic growth, quality of human life and health care. The evaluation of new “green” chemical processes and products follows a rigorous assessment in terms of eco-efficiency, risk minimization and socio-environmental impact which quantitatively evaluates the costs and benefits of the new process and alternative solutions. **There is no doubt that our lives have been enhanced by chemistry. The importance of green chemistry as an alternative in the developing world and Africa is really a blessing and its gains should be exploited. Sustainability depends largely on the twelve principles of green chemistry namely:-**

- ❖ **Prevention** - It is better to prevent waste than to treat or clean up waste after it has been created.
- ❖ **Atom Economy** - Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- ❖ **Less Hazardous Chemical Syntheses** - Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- ❖ **Designing Safer Chemicals** - Chemical products should be designed to effect their desired function while minimizing their toxicity.
- ❖ **Safer Solvents and Auxiliaries** - The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- ❖ **Design for Energy Efficiency** - Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- ❖ **Use of Renewable Feed stocks** - A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- ❖ **Reduce Derivatives** - Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- ❖ **Catalysis** - Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- ❖ **Design for Degradation** - Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- ❖ **Real-time analysis for Pollution Prevention** - Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- ❖ **Inherently Safer Chemistry for Accident Prevention** - Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Mr. Rector, academic /non academic colleagues, students and distinguished ladies & gentlemen, for the past 15 years, I have sacrificed my life working and doing research in the area of corrosion , synthesizing/preparing compounds that could function as potential corrosion inhibitors for materials in different media. Most have been tested and have industrial applications. Corrosion can be minimized by employing suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reaction or both. Among the several methods of corrosion control such as cathodic protection , anodic protection , coating and alloying, the use of chemical inhibitors is often considered as the most effective and practical method of corrosion prevention. A corrosion inhibitor can also be defined as a “chemical” additive which

when added to a corrosive aqueous environment reduces the rate of metal wastage. It is widely accepted that inhibitors especially the organic ones work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino ($-\text{NH}_2$), carboxyl ($-\text{COOH}$) and phosphate ($-\text{PO}_4^{3-}$) although other functional groups or atoms can form coordinate bonds with metal surfaces. Inhibitors function by adsorption of ions or molecules onto metal surface. They reduce the corrosion rate by:

- ✓ Increasing or decreasing the anodic and/or cathodic reaction
- ✓ Decreasing the diffusion rate for reactants to the surface of the metal
- ✓ Decreasing the electrical resistance of the metal surface.

Inhibitors are often easy to apply and offer the advantage of *in-situ* application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor namely:

- ✓ Cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge.
- ✓ Toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species.
- ✓ Availability of the inhibitor will determine the selection of it and if the availability is low, the inhibitor becomes often expensive.
- ✓ Environmental friendliness.

A number of heterocyclic compounds have been reported as corrosion inhibitors and the screening of synthetic heterocyclic compounds is still being continued. Though many synthetic compounds showed good anticorrosive activity, **most of them are highly toxic to both human beings and environment.** The safety and environmental issues of corrosion inhibitors arisen in industries has always been of global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system *viz.* kidneys or liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications. **These toxic effects have led to the use of natural products/ plant extracts as anticorrosion agents or inhibitors which are eco-friendly and harmless. THIS HAS BEEN ONE OF THE FOCUSES OF MY RESEARCH IN CHEMISTRY OVER THE PAST 15 + YEARS.** Recently, many alternative eco-friendly corrosion inhibitors have been developed / studied by many research groups in many parts of the world. A few number of research groups in Africa (including mine) are currently engaged in this area of research focusing on the use of plant extracts as corrosion inhibitors. This is a case study of the use of our resources for sustainable development and research. A series of reports have been highlighted in our laboratories on studies of other natural products (exudate gums) as corrosion inhibitors of mild steel and aluminium in acidic and basic media. The corrosion inhibition activity in many of these plant extracts is due to the presence of heterocyclic constituents like alkaloids, flavonoids *etc.*, Even the presence of tannins, cellulose and polycyclic compounds normally enhances the film formation over the metal surface, thus reducing corrosion. The natural

products are available and also biodegradable in nature, hence safe to the environment. They are practical examples of renewable sources of energy which enhance sustainability. Their extracts contain a large variety of organic compounds rich in p-electrons, donor atoms namely O-, N-, S-, P-, etc with which they get adsorbed on the metal surface by displacing water/ solvent molecules and form a compact barrier film. The recent trend of reporting plant extracts as corrosion inhibitors is very encouraging. It is certain that natural compounds will emerge as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability and non-toxic nature. I have used several plant extracts as corrosion inhibitors in my research due to the phytochemical constituents of the plants. The plants are also green and environmentally friendly compared to the synthetic compounds which most of the time are hazardous. I have contributed a lot to this area of research and my articles have been cited severally by other researchers in this field.

4.2. MY CONTRIBUTIONS TO CORROSION INHIBITION STUDIES USING ECOFRIENDLY (GREEN) INHIBITORS - CASE STUDY OF SUSTAINABLE DEVELOPMENT IN RESEARCH

Several reports have been published by us on the use of plant extracts as corrosion inhibitors (to mention but a selected few) – see Table I below:

Table I: Corrosion inhibition studies using ecofriendly (green) inhibitors from our research group

S.No	Ecofriendly(green) corrosion inhibitor (plant extracts)	Corrodent/ Material	Maximum% inhibition efficiency/Type of adsorption	References
1.	<i>Azadirachta Indica</i> leaves	Acid/ mild steel	75.75	U. J. Ekpe, E. E. Ebenso and U. J. Ibok (1994). Inhibitory Action of <i>Azadirachta indica</i> Leaves extract on the corrosion of mild steel in H ₂ SO ₄ . <i>Journal of West African Science Association</i> . 37; 13 – 30. [49]
2.	<i>Carica Papaya</i> leaves	Acid/ mild steel	87.90/Physical adsorption	E. E. Ebenso and U. J. Ekpe (1996). Kinetic study of corrosion and corrosion inhibition of mild steel in H ₂ SO ₄ using <i>Carica papaya</i> leaves extract. <i>West African Journal of Biological and Applied Chemistry</i> . 4; 21 – 27. [50]
3.	<i>Azadirachta Indica/ Carica Papaya</i> leaves	Acid/ Aluminium	AI 68.92 CP65.08/ Chemical Adsorption	E. E. Ebenso , U.J.Ibok, U.J. Ekpe, S. Umoren, Ekerete Jackson, O.K. Abiola, N. C. Oforka and S. Martinez (2004) Corrosion inhibition studies of some plant extracts on aluminium in acidic medium. <i>Trans. SAEST39(4)</i> ; 117 – 123. [51]
4.	<i>Citrus Paradisi</i> (fruit juice)	Acid/ mild steel	45.60	Olusegun K. Abiola, N.C. Oforka and E. E. Ebenso (2004) Inhibition of mild steel corrosion in an acidic medium by fruit juice of <i>Citrus Paradisi</i> . <i>Journal of Corrosion Science & Engineering</i> . 1(1); 75 – 78. [52]
5.	<i>Allium Sativum</i> leaves	Acid/ mild steel	67.68/ Physical Adsorption	P. C. Okafor, U. J. Ekpe, E. E. Ebenso , E. M. Umoren and K. E. Leizou (2005) Inhibition of mild steel corrosion in acidic medium using <i>Allium Sativum</i> extracts. <i>Bulletin of Electrochemistry</i> 21(8): 347 – 352.[53]

6.	<i>Ocinum Basilicum</i> leaves	Acid/ Aluminium/ halides	94.80/ Physical Adsorption	E. E. Oguzie, A.I. Onuchukwu, P.C.Okafor and E.E.Ebenso (2006) Corrosion inhibition and adsorption behaviour of <i>Ocinum basilicum</i> extract on aluminium. <i>Pigment and Resin Technology</i> . 35(2): 63 - 70. [54]
7.	<i>Allium Cepa and Allium Sativum</i> leaves	Acid/ mild steel	AC 84.26 AS 84.91/ Physical Adsorption	P. C. Okafor, U. J. Ekpe, E. E. Ebenso , N. S. Umo and A. R. Etor (2006) Extracts of <i>Allium Cepa</i> and <i>Allium sativum</i> as corrosion inhibitor of mild steel in HCl solution. <i>Trans.SAEST</i> . 4(2): 82 - 87.[55]
8.	Gum Arabic (exudates gum)	Acid/ Aluminium/ halides	84.76/ Physical Adsorption	S.A.Umoren, O.Ogbobe and E.E.Ebenso (2006) Synergistic Inhibition of aluminium corrosion in acidic medium by Gum Arabic and halide ions. <i>Trans.SAEST</i> 4(2): 74 - 81. [56]
9.	Gum Arabic (exudates gum)	Alkaline/ Aluminium	74.16/ Chemical Adsorption	S.A. Umoren, I. B. Obot, E.E.Ebenso , P. C. Okafor, O.Ogbobe and E. E. Oguzie (2006) Gum Arabic as potential corrosion inhibitor for aluminium in alkaline medium and its adsorption characteristics. <i>Anti-Corrosion Methods & Materials</i> 53 (5): 277 - 282.[57]
10.	<i>Carica Papaya</i> (leaves, seeds, heartwood and bark)	Acid/ mild steel	Leaves 93.88 Seed 84.53 Wood 71.49 Bark 54.59/ Physical Adsorption	P. C. Okafor and E. E. Ebenso (2007) Inhibitive action of <i>Carica papaya</i> extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. <i>Pigment and Resin Technology</i> 36(3): 134 - 140. [58]
11.	<i>Garcinia Kola</i> seeds	Acid/ Aluminium	85.04/ Physical Adsorption	P. C. Okafor, V.I. Osabor and E. E. Ebenso (2007) Eco friendly corrosion inhibitors: Inhibitive action of ethanol extracts of <i>Garcinia Kola</i> for the corrosion of aluminium in acidic medium. <i>Pigment and Resin Technology</i> 36(5): 299 - 305. [59]
12.	<i>Delonix Regia</i> (Leaves and seeds)	Acid/ Aluminium	93.60/ Physical Adsorption	Olusegun K. Abiola, N. C. Dforka, E. E. Ebenso and N. M. Nwinuka (2007) Eco friendly corrosion inhibitors: Inhibitive action of <i>Delonix regia</i> extract for the corrosion of aluminium in acidic medium. <i>Anti-Corrosion Methods & Materials</i> 54(4): 219 - 224.[60]
13.	<i>Dacryodes edulis</i> (exudates gum)	Acid/ Aluminium	62.40/ Physical Adsorption	S.A. Umoren, I.B. Obot, E.E. Ebenso and N. Obi-Egbedi (2008) Studies on the corrosion inhibition of <i>Dacryodes edulis</i> exudates gum for aluminium in acidic medium. <i>Portugaliae Electrochimica Acta</i> . 26(2): 199 - 209. [61]
14.	Naturally Occurring exudates gums (<i>Pachylobus edulis</i> , <i>PE</i> and <i>Raphia</i> <i>hookeri</i> , <i>RH</i>)	Acid/ Aluminium	PE 51.00 RH56.30/ Physical Adsorption	S.A. Umoren, I.B. Obot, E.E. Ebenso and P.C. Okafor (2008) Eco-friendly Inhibitors from Naturally Occurring Exudates Gums for Aluminium Corrosion Inhibition in Acidic Medium <i>Portugaliae Electrochimica Acta</i> . 26(3): 267 - 282. [62]
15.	<i>Pachylobus edulis</i> (exudates gum)	Acid/ Aluminium/ halides	63.00/ Physical Adsorption	S.A. Umoren, I.B. Obot and E.E. Ebenso (2008) Corrosion inhibition of aluminium using exudate gum from <i>Pachylobus edulis</i> in the presence of halide ions in HCl. <i>E-Journal of Chemistry</i> . 5 (2): 355 - 364.[63]
16.	<i>Raphia hookeri</i> (exudates gum)	Acid/ Aluminium/ halides	70.50/ Physical Adsorption	S.A. Umoren and E.E.Ebenso (2008) Studies of anti-corrosive effect of <i>Raphia hookeri</i> exudates gum - halide mixtures for aluminium corrosion in acidic medium. <i>Pigment and Resin Technology</i> . 37 (3):173 - 182.[64]
17.	<i>Musa sapientum</i> peels	Acid/ mild steel	71.06/ Physical Adsorption	N.O. Eddy and E.E. Ebenso (2008) Adsorption and inhibitive properties of ethanol extracts of <i>Musa sapientum</i> peels as a green corrosion inhibitor for mild steel in H ₂ SO ₄ .

<i>African Journal of Pure and Applied Chemistry</i> 2 (6): 46 – 54. [65]				
18.	Naturally occurring polymers and synthetic	Acid/ mild steel/ halides	64.30/ Chemical Adsorption	S.A. Umoren, O.Ogbobe , I.O. Igwe and E.E.Ebenso (2008) Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives . <i>Corrosion Science</i> 50(7): 1998 – 2006. [31]
19.	<i>Phyllanthus amarus</i> (Leaves, seeds, Leaves+seeds)	Acid/ mild steel	Leaves 94.10 Seeds 84.10 LV+SD 87.2/ Chemical Adsorption	P. C. Okafor, M. E. Ikpi , I. E. Uwah, E. E. Ebenso , U. J. Ekpe and S. A. Umoren (2008) Inhibitory action of <i>Phyllanthus amarus</i> extracts on the corrosion of mild steel in acidic media. <i>Corrosion Science</i> 50(8) : 2310 – 2317. [66]
20.	<i>Raphia hookeri</i> (exudates gum)	Acid/ mild steel/ halides	70.00/ Physical Adsorption	S.A. Umoren, I.B. Obot, E.E. Ebenso and N. Obi-Egbedi (2008) Synergistic Inhibition between Naturally Occurring exudates gum and halide ions on the corrosion of mild steel in acidic medium <i>International Journal of Electrochemical Science</i> 3 : 1029 – 1043. [67]
21.	<i>Piper guinensis</i> (leaves)	Acid/ mild steel	92.11/ Physical Adsorption	E. E. Ebenso , N.O.Eddy and A.O. Odiogenyi (2008) Corrosion inhibitive properties and adsorption behavior of ethanol extract of <i>Piper guinensis</i> as a green corrosion inhibitor for mild steel in H ₂ SO ₄ . <i>African Journal of Pure and Applied Chemistry</i> 2 (11): 107 – 115. [68]
22.	<i>Raphia hookeri</i> (exudates gum)	Acid/ Aluminium	56.30/ Physical Adsorption	S.A. Umoren, I.B. Obot, E.E. Ebenso and N. Obi-Egbedi (2009) The inhibition of aluminium corrosion in HCl solution by exudates gum from <i>Raphia hookeri</i> . <i>DESALINATION</i> 247: 561 – 572. [69]
23.	<i>Gongronema latifolium</i> (leaves)	Acid/ mild steel	90.00/ Physical Adsorption	N.O.Eddy and E.E. Ebenso (2010) Corrosion inhibition and adsorption properties of ethanol extract of <i>Gongronema latifolium</i> on mild steel in H ₂ SO ₄ . <i>PIGMENT AND RESIN TECHNOLOGY</i> 39(2): 77 – 83. [70]
24.	<i>Ananas sativum</i> (Leaves)	Acid/ Aluminium	96.09/ Chemical Adsorption	E. I. Ating, S. A. Umoren, I.I. Udousoro, E. E. Ebenso and A.P. Udoh (2010) Leaves extract of <i>Ananas Sativum</i> as green corrosion inhibitor for aluminium in HCl. <i>GREEN CHEMISTRY LETTERS AND REVIEWS</i> 3(2): 61-68. [71]

Other articles not mentioned above include refs [72 – 78]. Most of the articles I have published in this field have been cited over 100 times and are published in ISI rated journals as recorded by the SCOPUS search engine of Elsevier Science. This shows strong evidence of the impact of how my research relates to others in my field. The work done in this area has been well received by the corrosion community and efforts are being made to patent some of the results of the studies for industrial application. I also collaborate with some other research groups in other parts of the world where similar researches are going on. My research is contemporary and has potential industrial application to the local, national (South Africa) and the international community.

Mr. Rector, you will notice that I publish with most of my students and colleagues. I am a devout disciple of joint authorship although a lot of people have abused it. It is pertinent to point out, that Science has become so all embracing and multi disciplinary that no one individual can singularly hope to consummate meaningful science just alone. It is the confluence of ideas and the pulling of resources that is very important. What counts in the final analysis is that good service is done to Science. Indeed, it must be mentioned that apart from review articles and the like, single authorship in Science is virtually completely being out of vogue in more developed laboratories in the world and in fact tacitly discouraged. The sheer complexity, sophistication and multidisciplinary nature of the techniques and equipments available for modern day science

makes it mandatory that collaborative effort now reign supreme. Perhaps, it may even be argued that some of the most celebrated cases of fraud in Science (falsification of data) have been perpetuated by solo efforts. For my younger colleagues, I say get together, pool ideas and make your mark. Never mind that they are going to assign ¼ etc marks for each paper. **The international community of Science (and that is what counts ultimately) only judges you by the quality of the paper.**

5.0. ONGOING AND FUTURE RESEARCH

My ongoing research and aim over the next ten years will be concentrated on four core areas with smaller – explanatory projects. The core themes are as follows though some work is ongoing on some of them:

- (a) **Quantum chemical, theoretical and Quantitative Structure Activity Relationship studies** of the corrosion inhibition efficiencies of some compounds namely penicillin compounds, thiosemicarbazides, furfural hydrazone derivatives, fluoroquinolones, some triazole and imidazoline derivatives used as corrosion inhibitors. The methods of density functional theory (DFT) at the B3LYP/6-31G (d,p) and B3LYP/6311G(d,p) basis set levels and some semi empirical methods will be used to determine the relationship between the molecular structure of the compounds and their corrosion inhibition efficiencies (%IE). The quantum chemical parameters, namely E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} , dipole moment (μ), electron affinity (**A**), ionization potential (**I**), the absolute electronegativity (χ), absolute hardness (η), softness (σ), polarizability (α), the Mulliken charges and the fraction of electrons (ΔN) transfer from inhibitors to iron, would be determined and correlated with the experimental %IE. Quantitative Structure Activity Relationship (QSAR) approach will be used and a composite index of some quantum chemical parameters performed in order to characterize the inhibition performance of the studied molecules. The aim of the studies is to find good theoretical parameters to characterize the inhibition property of the inhibitors and the correlation between the inhibition efficiency and the electronic properties using different methods and basis sets. This research project will be done in collaboration with my research collaborators at the Department of Chemistry, Kocaeli University in Turkey through the support of the Scientific Research Fellowship (TUBITAK) of the government of Turkey.
- (b) **Industrial applications of some of the compounds used as corrosion inhibitors** – the overall aim of the work is to commission some graduate students in collaboration with CSIR to review the properties of the compounds we have used as corrosion inhibitors over the years and see the possibility of their industrial applications and to patent the work. Plans are already in progress. The project has great potential of strong growth given the local and national relevance and opportunity to expand the work in other areas.
- (c) My third emerging / new area of research that is developing is **“thermodynamics and excess molar volume studies of solutions”**. The importance of this area is to study the thermodynamic properties of the solutions of the compounds we intend to use as corrosion inhibitors before doing the electrochemical studies and experiments.

- (d) Research on the potential use of **IONIC LIQUIDS** as corrosion inhibitors. This project is on already in our laboratories where a master's student (Mr. Chester Murulana) is carrying out the investigations. The project is part sponsored by the Corrosion Institute of South Africa.

6.0. CONCLUSION

In today's Inaugural lecture, Mr. Rector, I hope I have shown that various compounds that God has allowed me to prepare / synthesize have been useful as corrosion inhibitors for potential use by man to increase the life span of the metals and materials instead of allowing them to go down mother earth because of corrosion.

The use of natural products, which are renewable resources, can be seen as a long term contribution to sustainable development. The prudent exercise of advanced manufacturing technologies within Africa represents an opportunity for us to initiate sustainable, regional production and potentially create markets for export. Africa has an advantage over global industries in this regard by virtue of the ability to implement truly novel technologies without abandoning existing investments in outmoded or less than optimal manufacturing facilities, and by lowering fixed costs in human capital and construction. The elements of achieving sustainable regional production therefore include:

- Coupling indigenous knowledge with good process and manufacturing practices.
- Identifying technologies that are elegant by virtue of their simplicity.
- Designing a “Green footprint” for advanced technology manufacturing and green / sustainable chemistry which includes such concepts as waste minimization, solvent selection, atom utilization, intensive processing and alternative synthetic routes from sustainable resources. The challenge for chemists is to develop products, processes and services in a sustainable manner, to improve quality of life, the natural environment and industry competitiveness.
- Green / sustainable chemistry issues are here to stay. The most successful chemical companies of the future will be those who exploit its opportunities to their competitive advantage, and the most successful chemists of the future will be those who use green chemistry concepts in research and development, innovation and education.
- Industries are also discovering that ‘green’ approaches to chemical processes are not only beneficial to the environment but can boost profits too. It is also a fertile ground for collaboration between academic and industrial scientists.

7.0. RECOMMENDATIONS

Mr. Rector, based on my experience over the years and as a research chemist, I wish to humbly make the following recommendations:

1. I would not be what I am today or standing in front of you to give this lecture if I did not have access to very good equipments/ facilities in good and well furnished laboratories; I therefore strongly recommend that more priority should be placed on acquiring standard up to date teaching and research equipments for the department of Chemistry and the sciences in general.
2. Ample laboratory space is of paramount importance for teaching and research to grow in the sciences. The ideal situation is for a professor to have a laboratory where he carries out his research with his students. A situation where a professor in any of the sciences does not have a laboratory dedicated to him with equipments is abnormal. I humbly recommend that this be looked into. By so doing, we will have more research outputs that will elevate the North West University in general and the Mafikeng Campus in particular to higher ranking institution in research and teaching.
3. The amount of funds allocated for research activities should be increased geometrically.

I am not saying nothing has been done but I recommend that more should be done in this direction.

Mr. Rector, academic /non academic colleagues, students and distinguished ladies & gentlemen, this is my sermon. Perhaps, I should end by making reference to Holmes and Allwood [79] thus:

**“As life is action and passion, it is required of man
that he should share the passion and action of the
time, at the peril of being judged not to have lived”.**

Yes, we have struggled over the years, to live our footprints, our actions; the passions, notwithstanding. And that is no idealism.

8.0. ACKNOWLEDGEMENTS

First and foremost, I thank the Almighty God who has made me what I am today. Without Him I can do nothing but with Him I can do all things. I give Him my unreserved glory, honour and adoration.

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the Department of Chemistry and the Dean of Graduate School, University of Calabar, Nigeria for making sure I get the best attention throughout my period of tutelage in their laboratories.

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I want to specially thank Prof. M. Maselesele, the Dean of Faculty of Agriculture, Science and Technology (FAST) for all the support she has given to me since I was employed in this University. To all my colleagues in FAST, I say thank you for accepting me as one of you and believing that we can work together to strengthen the FAST family. To my colleagues in the Department of Chemistry (academic, non-academic staff and students), you all are incredibly humane, friendly and supportive and you have made the department become my academic home. I am really humbled by your show of brotherhood. According to Desmond Tutu - Africans believe in something that is difficult to render in English. We call it "ubuntu" or "botho". It means the essence of being human. You know when it is there and when it is absent. It speaks about humanness, gentleness, hospitality, putting yourself out on behalf of others, being vulnerable. It embraces compassion and roughness. It recognizes that my humanity is bound up in yours, for we can only be human together,

To my dear wife, Glory and son, Emmanuel, you both are the best gifts God gave to me. I thank you sincerely for enduring the life of having an academic as husband and father resulting in absence from home many times. Glory, I thank you for choosing to sacrifice, your constant prayers, support, allowing me to pursue my dreams and for the wonderful complementary role at home.

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I thank all of you wonderful people and friends too numerous to mention individually who have come from far and near to grace this occasion.

Mr. Rector, academic /non academic colleagues, students and distinguished ladies & gentlemen, when I began this lecture, I was full of trepidation, but now, my nerves are sequestered as I come to the end. There would be no lecture without all of you good people being present.

I thank you most sincerely for your patience, listening to what I had to say and most importantly for attending this inaugural lecture.

Thank you and God bless you all richly. Amen.

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