THE SCIENCE, TECHNOLOGY AND ECONOMIC IMPLICATIONS OF CORROSION

By

PROFESSOR CELESTINE MONDE KAMMA
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- An Inaugural Lecture Delivered at the University of Lagos
  On Wednesday, July 19, 2006

PROFESSOR CELESTINE MONDE KAMMA
B.Sc., M.Sc. (Munich), Ph.D. (Bochum), FNMS
Professor of Metallurgical and Materials Engineering

Department of Metallurgical and Materials Engineering
Faculty of Engineering
University of Lagos
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Published 2006

By

University of Lagos Press
Unilag P. O. Box 132,
University of Lagos,
Akoka, Yaba – Lagos,
Nigeria.

e-mail: unilagpress@yahoo.com

ISSN 1119-4456
I. INTRODUCTION
Honestly, I feel uncomfortable when confronted with the question: What is Corrosion? "Uncomfortable" because for my answer to be meaningful to the questioner, his background has to be considered. I am unable to do that here. I, therefore, prefer that people look at corrosion as a rather complex, and often misunderstood phenomenon involved in virtually all aspects of scientific, technological and mundane processes. Because of its varied mode of operation, corrosion is known under many names, e.g. rust, tarnishing, scaling, oxidation, etc. From its nature, corrosion is known to be unavoidable, since it is a continued attempt by the material to return to its original form (e.g. ore, in the case of metallic materials).

Corrosion is often described as a "silent killer". It may remove a metal from a whole structure gradually and eventually weaken it so much that the structure fails. In other circumstances, the corrosion may attack one part of a structure preferentially, and by weakening that member, may bring destruction on the whole. In yet another case, the attack may be localized severely and bite deeply into a component. The affected part is made brittle and unable to withstand shock loads. Alternatively, the localized activity may create on the surface of the steel a fine crevice which acts as a stress-raiser and its presence may induce an early failure of the steel by fatigue.

Metallic materials, especially ferrous alloys are well-established and favoured preys of corrosion. In fact, corrosion is usually referred to as the Achilles Heels of metals and alloys.
Historically too, the impact of corrosion was felt. The great Roman philosopher, Pliny (AD23 – 79) wrote at length about ferrum corruptur (spoiled iron) [1].


Really, Pliny was vexed by the susceptibility of iron to rust. He asked himself why iron should corrode more easily than other metals. He didn’t know how to investigate problems experimentally, but he arrived at a metaphysical solution: “because iron is both the best and the worst of man’s servants. Although, very useful domestically, it is also the metal of war and slaughter.

Writing about iron arrows, Pliny said: “it is a great evil that to enable death to reach human beings more quickly, we have taught iron how to fly”. Pliny went further; “The nuisance of corrosion compensates for the advantages of the metal because the same benevolence of nature has limited the power of iron by inflicting on it the penalty of rust and the same foresight has made nothing in the world more mortal than that which is most hostile to mortality.”

Very positive records of corrosion are also in History books [3, 4]. To the fighters of old, rust was something of a mixed blessing. In the Eleventh Century, a Norman Knight, William de Lacey lost his way during a hunting expedition into the thickly wooded and swampy vale of Ewas in Wales [3]. He came across the ruins of St. David’s hermitage, where upon, overcome by an urge to mend his sinful ways, he decided to dedicate the remainder of his days to
religious contemplation and rebuilding the chapel. Legend has it that he never for the rest of his life removed his armour. One explanation for this strange behaviour was that it was a self-imposed penance.

More likely, however, is that he was prevented from doing so because of corrosion brought about by the dank atmosphere of the valley. Corrosion of arms and armour has also been advantageous. The techniques of bluing and gilding were frequently used to protect steel objects, for it was found that the application of a variety of heat treatments created highly protective films of oxide (rust) [5]. These, with skill, could turn functional weaponry into beautiful works of art.

It has always been considered by many that the green patina on copper roofs and other ornamental objects is desirable, rather than unsightly. A well-known lover of rust, Sculptor Anthony Caro, spent many years producing abstract steel sculptures. Initially, they were painted brown, the colour of rust, but he later allowed them to rust naturally and then preserved it by varnishing.

1.1 THE FACE OF CORROSION

For corrosion attack to take place, there must be favourable conditions, e.g. the presence of at least one of the following:

a) Electrolyte, e.g. water;

b) Chemicals;

c) Deformation;

d) Inhomogeneity;

e) Temperature;

f) Ignorance.
These parameters, accordingly, lead to different types of corrosion e.g.:

1. Uniform (direct) corrosion;
2. Galvanic (two-metal) corrosion;
3. Crevice corrosion;
4. Selective (dezincification) corrosion;
5. Pitting corrosion;
6. Preferential weld corrosion;
7. Fretting corrosion;
8. Intergranular corrosion;
9. Hydrogen damage;
10. Stress corrosion;
11. Corrosion fatigue;
12. Cavitations damage;
13. Bacteria corrosion (e.g. wood decay).

Each of these corrosion phenomena has its characteristic appearance and external attributes. While no attempts will be made to describe the details of each corrosion type, an effort will be made to show photographs of some of the outstanding types.

Fig. 1a A badly corroded Automobile (TOYOTA)
1.2 DEFINITION

The complexity of corrosion starts with the problem of definition. There are as many definitions as the standpoint and perception of the person trying to render the definition. The definition may be oriented towards:

a) type and mechanism of the corrosion;
b) economic aspect of the corrosion attack;
c) discipline area, e.g. chemistry, engineering, etc.;
d) the lesson of corrosion history;
e) after-effects of the corrosion attack.

Accordingly, corrosion definition can take any of the following versions:

1. Derivation from the Latin, *ordere* (to “gnaw”, in the context of rats); “corrodere”, meaning “to gnaw” to pieces;  
2. The deterioration or destruction of a material or its properties, because of its reaction with an environment;  
3. The deterioration of a material, usually a metal, due to a chemical or electrochemical reaction with its environment;  
4. A destructive attack of a metal by a chemical or electrochemical reaction with its environment;  
5. In the context of corrosion science: the reaction of a solid with its environment. In the context of corrosion engineering: the reaction of an engineering constructional metal (material) with its environment with a consequent deterioration in properties of the material with its environment with a consequent deterioration in properties of the metal (material) or wastage of the material;  
6. Deterioration and loss of material due to chemical attack, involving chemical and electronic changes;  
7. Extractive metallurgy in reverse
8. **Non-metal**: Plastics may swell or crack; wood may split or decay; granite may erode and Portland cement may leach away;

9. **Corrosion** is restricted to chemical attack of metals. **Rusting** applies to the corrosion of iron or iron-base alloys, with formation of corrosion products consisting largely of hydrous ferric oxides;

10. **Non-ferrous materials**: These corrode, but do not rust. Rusting is corrosion, but corrosion is not rusting alone.

### 1.3 CORROSION MECHANISM

For purposes of discussion of corrosion mechanism, it is convenient to limit corrosion classification into two groups:

#### 1.3.1 Electrochemical Corrosion

#### 1.3.2 Oxidation

1.3.1.1. **Conditions to be met before a corrosion cell can function**:

- **a)** There must be an anode and a cathode;
- **b)** There must be an electrical potential between the anode and cathode. (This potential can result from a variety of conditions);
- **c)** There must be a metallic path electrically connecting the anode and cathode;
- **d)** The anode and cathode must be immersed in an electrically conductive electrolyte which is ionized (meaning that some of the water molecules - $H_2O$ -
are broken down into positively charged hydrogen ions \((H^+)\) and negatively charged hydroxyl ions \((OH)\). [The usual soil moisture or water, surrounding pipelines normally fulfills this condition]. Once these conditions are met, an electric current will flow and metals will be consumed at the anode.

![Diagram of Aqueous galvanic corrosion system](image)

Fig 1b Aqueous galvanic corrosion system (6)

![Diagram of Electrochemical Process occurring during gaseous oxidation](image)

Fig 1c Electrochemical Process occurring during gaseous oxidation (6)

The pressure exerted by the potential difference between the anode and cathode results in the migration of electrons from the anode to the cathode. At the anode, with the loss of electrons, positively charged iron atoms remain, which
combine with negatively charged \((0H^-)\) ions in the environment to form, usually, a ferrous hydroxide \((Fe(OH)_2)\), which may react further later to form ferric hydroxide, \(Fe(OH)_3\), which is the familiar rust.

At the cathode, a surplus of electrons has arrived from the anode. These surplus negatively charged electrons combine with positively charged hydrogen ions from the environment (electrolyte) to form hydrogen \((H_2)\). When \(H^+\) is converted to \(H_2\) and hydrogen gas at the cathode, a surplus of hydroxyl ions \((0H^-)\) is created at the cathodes. This surplus operates to increase the alkalinity of the electrolyte in the vicinity of the cathodes.

The conventional concept of current flow is from plus (+) to minus (-). This can be confusing, being in the opposite direction to the flow of electrons.

- Conventionally, + will be from cathode to the anode in the metallic circuit.
- Conventionally, + will be from anode to the cathode in the electrolyte.
- Metal is consumed where current leaves it to enter the surrounding electrolyte.
- Metal receiving current from the surrounding electrolyte does not corrode (except certain materials, e.g. Al and Pb.), called amphoteric which can corrode if receiving excessive amount of current.

### 1.3.1.2 Corrosion Reactions

Corrosion reactions involved in corrosion mechanism are two-fold:

- **a) Chemical Reaction:**
  
  \[
  2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \\
  \]

  \(Fe(OH)_2\) undergoes further reactions to form rust.

Rusting is corrosion; but corrosion is not rusting alone.
b) Electrochemical Mechanism:

i.) Anodic reaction (metallic oxidation)

\[ 2Fe \rightarrow 2Fe^{++} + 4e^- \text{ (electrochemical oxidation)} \]

ii) cathodic reaction (reduction of oxygen)

\[ 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \]

With corrosion regarded as an Electrochemical Reaction, we have the following situation:

Corrosion of Fe in oxygenated water:

\[ Fe \rightarrow Fe^{++} + 2e^- \text{ (anodic reaction)} \]

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (cathodic reaction)} \]

Overall: \[ 2Fe + O_2 + 2H_2O \rightarrow 2Fe^{++} + 4OH^- \rightarrow 2Fe(OH)_2 \]

However, Fe(OH)_2 is unstable and in the absence of low oxygen, it decomposes to magnetite (Fe_3O_4).

\[ 3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \]

Fe_2O_4 If it is adherent and compact, a passivating situation ensues.

In the presence of O_2, Fe(OH)_2 oxidizes to rust by dissolving in oxygen:

\[ 2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow Fe_2O_3 \cdot H_2O \text{ (reddish brown)} \]

Formation of magnetite (Fe_3O_4) in most operation is very important as it determines the passivity or otherwise of the metal.

1.3.1.3 Factors Affecting Corrosion

Major factors:

- Water;
- pH;
- Ionic species;
- Fluid.
Corrosion, as a process, depends on a complex interaction between the material, its environment and the circumstances of exposure.

1.3.1.4 Requirements For Corrosion

a) Metal capable of undergoing anodic reaction (all metals can);

b) Environment capable of oxidizing the metal to a chemically combined state;

c) An electrolytic ally conducting environment;

d) Metal/Environment interface that allows the transfer of electrons from the metal to the incoming $O_2$ and $H_20$ in the corrosion cell.

1.3.1.5 Control of Corrosion

- Design
- Material selection
- Coating
- Chemical Treatment
- Electrochemical Protection

1.3.2 Oxidation of Metals and Alloys

1.3.2.1 Oxidation refers to an electron producing reaction in the absence of water or an aqueous phase. Directly related to oxidation are Scaling, Tarnishing and dry corrosion.

All metals except gold, silver and the members of the platinum group experience oxidation reactions, to some degree, even at room temperatures. At normal, ambient temperatures the rate of dry oxidation is usually extremely low, by corrosion standards. The rate increases with temperature.

Iron does not oxidize in dry air at room temperatures; it does so readily at elevated temperatures and forms on itself a film of oxide which is loosely adherent only. In
most cases, this oxide can be detached from the underlying metal quite easily. Oxidation of this kind takes place freely during the hot working of iron and steel. The metals become covered with a layer of oxide, which is generally known as Mill-scale. Some metals when exposed to ordinary air at room temperature form oxides which attach themselves so firmly that the resulting skins act as protective films against further chemical action on the metals.

1.3.3 Tarnishing
This is a peculiar type of corrosion attack which occurs when a metal is exposed to ordinary air or to some gaseous atmosphere. It is the result of a simple chemical reaction between the surfaces of the metals and some component of the ambient gas. A typical example of tarnishing is seen in the blackening of silver when it is exposed to an atmosphere which contains either $\text{H}_2\text{S}$ or some equivalent, organic sulphur compound. It can be assumed for all practical purposes that no action of this kind takes place with ordinary iron; metal and alloys corrode readily, but they do not tarnish in dry air at normal atmospheric temperatures. On the other hand, some of the stainless steels tarnish, though they also do not corrode.

1.3.4 Corrosion of Plastics and Elastomers
Polymeric materials corrode by processes quite different from those associated with metallic corrosion. Physico-chemical processes, rather than electrochemical reactions, are responsible for the degradation of plastic and elastomers.

Polymeric materials are attacked by:

a) Swelling
b) Dissolution
c) Bond rupture due to:
   i) Chemical reaction (e.g. oxidation)
   ii) Heat
   iii) Radiation (e.g. sunlight).

These reactions can occur singly or in combination.

Swelling and dissolution, with and without chemical – bond breaking, are the chief causes of attack during exposure to liquids.

II 2.0 ECONOMIC ASPECTS OF CORROSION

Corrosion is undesirable because of its negative impact on the economy. How much corrosion costs is usually expressed as a percentage of a nation’s economy.

In 1949 the estimated corrosion cost per year in the United States of America was $5 billion. This was 2.1% GNP [7]. By 1975 the estimated cost of corrosion in the US had risen to $70 billion, 4.2% of GNP [8, 9].

In the UK alone, for instance, 1 tonne of steel is completely converted into rust every 90 seconds. Cost of corrosion prevention by the use of paints has been estimated $35 x 10^9 per year in the USA; that of coating bridges is $110 – 130 x 10^6 per year; cost of corrosion protection of oil production installations in one major Nigerian petroleum company amounts to $31 million per year. [11]

With this percentage of GNP spent on corrosion, one can appreciate the enormity of the impact of corrosion on a nation’s economic growth; no wonder people have wondered why the treatment of corrosion has not been pursued as earnestly as a cure for AIDS.

In 1997, NEPA recorded 21 failed transformers in just one town, Warri. This was due to stress corrosion cracking. NEPA had to fund a N5 billion scheme to
replace worn-out equipment in order to boost power supply [10].


Investigations have shown that the total annual costs of floods, hurricanes, tornadoes, fires, lightning and earthquakes are less than the costs of corrosion. [13]

In fact, it has been observed that about 10% of total world's metal output is being lost due to the destructive action of corrosion. [14].

2.1 INDIRECT CORROSION COSTS

It is unfortunate that, in modern usage, the term "cost" usually implies only financial penalty. In fact, corrosion costs society in three ways:

- It is extremely expensive, financially;
- It is extremely wasteful of natural resources at a time of increased concern over damage to the environment;
- It causes considerable inconvenience to human beings and sometimes loss of life.

2.2 THE EXPENSE OF CORROSION

In most cases expense of corrosion involves a combination of direct and indirect corrosion costs. There are six main ways corrosion can be incurred:
2.2.1 Corrosion in Oil Industry

This industry contains a wide variety of corrosive environments. Corrosion problems occur in the petroleum industry in at least four general areas:

a) **Products**

Oil and gas fields contain tremendous amounts of iron and steel pipes, tubing, casing, pumps, valves and sucker rods; leaks cause loss of oil and gas and also permit infiltration of water, thus increasing corrosion damage.

b) **Transportation and Storage**

Petroleum products are transported by tankers, pipelines, railways, tank cars and trucks. The outside submerged surface of underground pipelines are protected with coatings and by using cathodic protection. Cathodic protection is also applied to the sea-water used for washing.
c) **Refinery Operations**

Most of the corrosion difficulties in refineries are due to inorganics such as waters $\text{H}_2\text{S}$, $\text{CO}_2$, $\text{H}_2\text{SO}_4$ and $\text{NaCl}$ and not the organics themselves.

Corrosion agents may be classified into two general categories:

i) Those present in feed stock or crude oil;

ii) Those associated with process or control.

d) **Maintenance**

Usually, maintenance, with respect to oil industry includes overhauling of pipes, etc. During this period, production, distribution along the affected networks are temporarily stopped. Less petroleum products are produced and distributed. Both local consumption and exports suffer. Turn Around Maintenance of the four Nigerian refineries is estimated to cost over N900 billion, i.e. close to the nation's average annual budget.

2.3 **SOCIAL IMPLICATIONS OF CORROSION**

2.3.1 It has been postulated that the downfall of the Roman empire can be attributed in part to corrosion problems, especially the storage of wine in lead-lined vessels.

It was established that lead dissolved in wine consumed by the Roman hierarchy. This resulted in insanity (lead poisoning) and contributed to the subsequent eventual downfall.

2.3.2 It is interesting to also realize that lead and alcoholic beverages date back to the era of Benjamin Franklin. One manifestation was the “dry bellyache” with accompanying paralysis which was mentioned by
Franklin in a letter to a friend. This malady was actually caused by the ingestion of lead from corroded lead coil condensers used in making brandy. The problem became so widespread that the Massachusetts Legislature passed a law in the late 1700s that outlawed the use of lead in producing alcoholic beverages. [8]

2.3.3 Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion.

A similar example of this is the sudden collapse, because of corrosion fatigue, of the Silver Bridge over the Ohio River at Point Pleasant 0H in 1967. This resulted in the loss of 46 lives and cost millions of dollars. [6]

2.4 SOME CONSEQUENCES ARE ECONOMIC AND CAUSE THE FOLLOWING:

- Replacement of corrosion equipment;
- Over-design to allow for corrosion;
- Preventive maintenance, e.g. painting;
- Shutdown of equipment due to corrosion failure;
- Contamination of product;
- Loss of efficiency, e.g. when over-design and corrosion products decrease the heat-transfer rate in heat exchangers;
- Loss of valuable products, e.g. from a container that has corroded;
- Inability to use otherwise desirable materials;
- Damage of equipment adjacent to that in which corrosion failure occurs.
2.5 Of Special Mention are the following Social Consequences:
- Safety, e.g. sudden failure can cause fire, explosion, release of toxic product and construction collapse;
- Health, e.g. pollution due to escaping product from corroded equipment or due to a corrosion product;
- Depletion of natural resources, including metals and the fuels used to manufacture them;
- Appearance as when corroded material is unpleasing to the eye.

2.6 ECONOMIC CORROSION CONTROL PRACTICES
An overview of the most usual economic corrosion practices is hereby briefly given:

2.6.1 Methods of Protection Against Corrosion
For practical purpose, protection could be classified as preventive or curative.

2.6.1.1 Preventive Protection
Here, the effects of corrosion are foreseen and steps taken to minimize losses at the designed stage. Even if the normal corrosion process is allowed to occur (due to the relatively high cost), it is still a preventive measure since it was envisaged from inception and considered less detrimental than the trouble and cost to be incurred by protecting the structure from the onset.

2.6.1.2 Curative Protection
This is applied when corrosion has already begun. It could be that corrosion was not initially envisaged or due to changes in the nature of electrolyte or inadequate survey, etc.
2.6.1.3 Design and Materials Selection
The fight against corrosion should be embarked upon at the inception of the project as a preventive measure.

2.6.1.4 Coating
Coatings act in two ways to provide protection for the metal:
(i) It could be sacrificial to the protected metals;
(ii) Provide electrical insulation between the metal and electrolyte.

The various ways of achieving coated surface are: painting, electroplating, vitreous enamellings, galvanizing, phosphating, plastic (polymer).

2.6.1.5 Electrolyte Treatment
It is the presence of the electrolyte at the surface of the metal that sets up corrosion cells, the anode and cathode reactions operating distinctly. Any possibility of hindering or inhibiting any of the reactions (cathodic or anodic) will definitely resist the operation of the cells.

2.6.1.5.1 Poisoning of anodic and cathodic reactions.

2.6.1.5.2 Filming inhibitors: Films formed isolate the metal from the corroding environment: anodic inhibitor, and cathodic inhibitor.

2.6.1.6 Insulation
This isolates the metal from corrosion current.

2.6.1.7 Cathodic Protection
This is achieved in two ways:
(a) Sacrificial anodic system
(b) Power impressed current system

2.7 CORROSION MONITORING
This process is defined as the systematic measurement of corrosion or degradation of an item of
equipment, with the objective of assisting understanding of the corrosion process and/or obtaining information for use in controlling corrosion and its consequences. Implicit in this statement is the possibility of being able to measure the changes in corrosion rate with time and then make use of this information in a feedback loop as a means of controlling the corrosion process. Any method which provides an assessment of equipment of the process environment can be considered for use in corrosion monitoring.

2.8 PEOPLE FACTORS
Corrosion failure is an engineering problem. To engineer is human [15]. People being inextricably linked to engineering, follows that people are also inextricably linked to corrosion. From this, the human influence on corrosion failures can easily be appreciated.

We have four kinds of people who affect the lifetime of engineering systems: the procurer, the designer, the manufacturer and the user or maintainer. Three elements are present in corrosion failures: the materials, the environment in which they operate and the people who interact with the system.

In summary, we have seen that most times the effects of corrosion are catastrophic and thus result to deaths. The effects of corrosion permeate nearly every aspect of human endeavour, including deaths.

The cost of corrosion is put at between 3.5 - 4.0% of GNP in industrialized nations. This value is expected to be higher in developing countries where the effects of corrosion are more devastating. In the U. K. alone, for instance, 1 tone of steel is completely converted into rust every 90 seconds. With this percentage of
GNP spent on corrosion, one can appreciate the enormity of the impact of corrosion on a nation's economic growth.

III. CORROSION CONSIDERATIONS IN THE SERVICE OF TECHNOLOGY

Section I of this lecture was aimed at creating a background knowledge for the appreciation of the contents of section III; in other words, a prerequisite for section III. In fact, it treated the relevant, scientific and economic aspects of corrosion. The aim of the present section, III, is to try to see the extent of involvement of corrosion in engineering applications, vis-à-vis technology.

From section II, it was clear that corrosion seemed to rear its ugly head in virtually all aspects of human endeavour. This was made clear from the various experimental work carried out in our engineering workshops and laboratories. We have decided to select four of the works for this task. The choice was made as representative as possible, ranging from appliances of daily use (e.g. automobile vehicle, fridges, washing machines, family planning instruments, like copper in uterine devices, etc.) to physical metallurgical researches. In each case, the problems involved were identified and at the end, our contribution to knowledge established.

The following four cases are discussed:

(a) Corrosion Problems in Automobile Vehicles;
(b) Corrosion in Domestic Appliances;
(c) Aspects of Corrosion in Family Planning;
(d) Design of Corrosion Resistant Microstructures.
3.1 CORROSION PROBLEMS IN AUTOMOBILE VEHICLES

ANAMCO, an automobile company in Enugu, Enugu State, spends about N8 billion yearly for painting steel used for auto body to prevent rusting. The actual cost of corrosion of automobile - fuel systems, radiators, exhaust systems and bodies are in billion of dollars. [20] On December 13, 1983 an article in the Times International magazine published in America stated "Six hundred new pickup trucks worth nearly $5 million have been junked because they rusted while packed at a Tampa, Florida Port awaiting shipment for up to a year". The trucks (made in Japan) were crushed and sold for scrap (about $50 each). It is also known that corrosion in automobile fuel system alone costs 100 million dollars yearly in USA. [15] Auto radiators account for about 52 million dollars. [16] Corrosion involvement in the treatment of exhaust systems is estimated to cost 500 million dollars in the USA [15].

In this work, special attention is given to corrosion problems in:

(i) Auto body
(ii) Exhaust system
(iii) Radiator system

The three parts are the most corrosion susceptible areas of the automobile, and will therefore, be treated in detail.

3.1.1 Auto Body

When corrosion consideration is given to auto body, the following aspects are noteworthy:

Auto Bodywork: - made of sheet steel;
- prone to atmospheric corrosion;
receives rough treatment from external influences, e.g. moisture, road dirt,
Auto Body Corrosion
The corrosion process in auto body is identified to occur in 3 phases:

(a) Initial Phase: Here, the auto body just begins to lose some of its brand new attraction. The first signs of pitting due to scratches, embedded dirt, dissimilar welded joints and other deposits on the body start to show. These pits harbour moisture and combined with air, the corrosion process is initiated.

(b) Second Phase: By now, the pits have grown into holes. The body becomes visibly corroded and the presence of concentration cells makes the corrosion process rapid at this stage. Extensive coating and spraying would still restore the body work at this phase. Here, most people are forced to do something about this advanced stage of deterioration. It would make more sense at this stage to buy new body panels for the automobile.

Care of Bodywork
1. Thorough washing of bodywork using recommended detergent.
2. Thorough rinsing of the bodywork after washing
3. Periodic bodywork inspection for pits, dirts and deposits.
4. When observed, dirts and deposits should be removed, pits cleaned up and re-coated.
5. Vehicle, as much as possible, should be packed in a cool, dry place.
6. When first signs of phase II are observed, extensive coating and spraying should be applied immediately.
3.1.2 Automobile Exhaust System

A typical exhaust system is shown in Fig. 3.1. This is a long hollow metallic structure consisting of connected pipes with special compartment that collects, treats and safely discharges the waste products of combustion of automobile engine. Whatever the engine type, it is attached to the engine combustion chamber by the manifold and leads to the outside by the tail-pipe.

Fig. 3.1a A new exhaust pipe (steel-coated at tail end)

Fig. 3.1b A badly corroded exhaust pipe

3.1.2.1 Functions of Exhaust System

Exhaust system collects, treats and discharges two main components from the engine:

(i) Gaseous chemical products
(ii) Energy (Heat and sound energy).
Following the combustion of the fuel in the automobile engine, \( \text{CO}_2 \), steam, unburnt hydrocarbon, soot, \( \text{CO} \), \( \text{SO}_2 \) are produced as gaseous fumes. These substances, most of which are poisonous to human health, are safely discharged to the rear side of the car by the exhaust system.

The sound energy produced in the engine fuel combustion comes out as continuous explosive noise. This is absorbed by the muffler and the resonator of the exhaust system reduces the noise to the mild sound we hear.

### 3.1.2.2 Corrosion Problems In Exhaust System

(a) Exhaust system parts are actively subjected to rust and other forms of corrosion attack. This leads to leaks in the exhaust system. Consequently, poisonous fumes and pollution from the engine combustion chamber find their way into passenger compartment. This could cause ill health and death;

(b) Also, the sound of the vehicle is noisy when exhaust system is damaged in the corrosion process. The exhaust-pipe loses its silencing abilities also;

(c) Increased leaks of the exhaust fume from the damaged holes result also to malfunctioning of the engine because it affects the stroke, pressure and breath of the engine and indirectly reduces speed and power output, of the vehicle [17, 18];

(d) Corroded exhaust pipe leads to an increase in the level of fuel consumption.
3.1.2.3 Factors Affecting Corrosion of Exhaust System

Factors that promote corrosion in the exhaust system:
Temperature, pressure, combustion, efficiency of the engine, vibration of the system, corrodent nature of exhaust fumes, handling and road environment.

Temperature: High temperature of the exhaust gases counts as one of the major factors that increase the rate of corrosion in the exhaust system. Combustion in the engine produces enormous heat, which in addition to the function of the radiator, is removed from the engine by exhaust gases.

The temperature of the exhaust gases is influenced by: speed, load, efficiency of the radiator.

3.1.2.4 Forms of Corrosion Attack in Exhaust Systems.
1. Uniform Corrosion: This takes place at the completely exterior part of the system; occurs also in the interior of the system and is mostly gaseous oxidation process.

2. Galvanic Corrosion: This is commonly encountered in the exterior of the system when the moisture from the air condenses and mixes up with other minerals from the exhaust fume to form galvanic cell. It could also result from temperature difference in the pressure of water.

3. Corrosion Fatigue: When the exhaust system is not firmly fastened to the body, the vibration of the car and galloping motion generates cyclic stress that results to fatigue failure at corrosion sites.

4. Fretting: The loose attachment of exhaust pipes to hangers could generate friction of the system with the point of attachment and cause corrosion as fretting corrosion.
5. Crevice Corrosion: The various points of attachment of fastening of the different parts of the exhaust system provides crevices which retain impurities, water or mud to initiate corrosion.

6. Pitting: Due to the pressure of various acid solution that results from the combination of condensed moisture with corrodent of the exhaust – fumes, small holes are most times formed which weaken the exhaust components as pits.

3.1.2.5 Corrosion Mechanism in Exhaust System

Three types of Mechanism:

(a) High Temperature Oxidation

In this mechanism, the exhaust gases entering the exhaust pipes cause high temperature oxidation, or corrosion process occurring without an aqueous environment. In this process, metallic ions and their electrons diffuse through the oxide film where the electrons help to produce the oxide ions. Growth of the oxide film takes place at the oxide/environment interface.

(b) Internally Nucleated Corrosion

Combustion of petrol produces water along with lead salts and acids which pass as gas or vapour into the exhaust system. H$_2$SO$_4$ and HNO$_3$ in the exhaust gases can shorten the life of a steel exhaust system.

The acids include H$_2$SO$_4$ and H$_2$SO$_3$ derived from sulphur in the fuel, but also HC$_1$ and HB$_r$; the latter is derived from C$_2$H$_4$Br$_2$, present as an additive. If the silencer or pipe is cold, as in the first start of the day, these corrosive elements will condense on the interior surface of the exhaust system.

26
They act as weak acid, eventually eating through the metal. Every time a car starts from the cold, a minute amount of internal corrosion takes place. This is why a car used for short trips needs more frequent exhaust replacement than one used regularly for long journeys. The condensate from exhaust gases produces a very corrosive mixture of acids.

(c) Externally Nucleated Corrosion
This occurs by virtue of the external road deicing salt, where the paintwork or coating of the exhaust pipe has been chipped away by a stone particle carrying salt. This would set up fairly rapid corrosion, leading ultimately to perforation. The continuous blasting of the paint work or coating of exhaust system by mud and grit at the velocity of the car will initiate a corrosion attack.

Atmospheric corrosion also aids the external corrosion of the exhaust pipe. Sea-salt particles and especially salt-water constitute relatively severe corroding environment for automobile. It is on record that automobile vehicles in Nigeria corrode faster in the south (Lagos) than in the north.

3.1.2.6 Design Considerations for Exhaust Development
The following recent contributions to the knowledge of corrosion specific findings about exhaust systems are vital to their future development and are hereby recommended:

1. Materials: aluminized or stainless steels.

2. Design: Larger silencer diameter. This would lead to metal temperature reduction. As temperatures are reduced, the likelihood of condensation at a given speed increases. Condensation has been linked directly to corrosion; the dew point of the gases being
55 - 60°C and maximum corrosion being measured in the range 45 - 50°C.

3. Compression Ratio: One of the major limits to efficiency is the compression ratio allowed before detonation knocking occurs in the cylinder. This (compression ratio) limits the maximum cylinder pressure and therefore, the power recoverable from the explosion. To increase power output, smaller engines must run faster and this obviously increases the mean gas velocity in the exhaust system. Noise output increases approximately the 4th or 5th power of engine speed [19]. It is observed that corrosion plays a significant, if not decisive, role in the failure of exhaust systems.

4. Internal Corrosion: in the exhaust system is linked directly to the dew point of the exhaust gases; corrosion may therefore, be assessed by measuring the temperatures of various points on the exhaust systems. Internal corrosion arises from the products of combustion; these are typically H₂SO₄ from sulphur in the fuel, HN0₃ from dissociation of nitrogen at the high temperature of the combustion and HCl.

5. Insulators: Use of insulators to prevent internal condensation in the assessed through exhaust system is assessed temperature surveys. Insulating the silencer quickly raises the metal temperature, thereby reducing the exhaust life. This is because temperatures in operation were increased into the corrosion zone.

6. Exhaust System Corrosion: Corrosion of the exhaust silencer is the total of both the internal and external wastages. Internal wastage is usually far greater than the external corrosion.
3.1.2.7 Metallurgical Approach
Metals during production are conferred with characteristics that enhance their performance. One of such qualities is corrosion resistance. To achieve this, metallurgists either alloy the metal, apply appropriate heat treatment or coat the metal with corrosion resistant material, which could be either a metal, organic resin or paint. A good number of exhaust systems are [21] hardened Cr-Ni Austenitic steel which is alloy of Fe, C, Cr, Mn, Ni and Ti that has been properly heat-treated. This has the desired corrosion resistance quality needed by the system. The manifold region is normally made of cast iron which withstands the temperature and resistance concurrently. The whole system is often covered with paints or bitumen to prevent external corrosion.

Modern exhaust systems especially those of expensive cars are made of stainless steel which is corrosion resistant to a high degree.

3.1.2.8 Conclusion
High temperature of the exhaust system coupled with the various corrodents that pass out through the system as well as its location which exposes it to splash of water and contaminants from the roadside add up to make corrosion in exhaust system proceed in an alarming high rate that keep the car-user uncomfortable.

The most active corrosion occurs when the engine gets cold, especially at night and air that diffuses into the system condenses the moisture content which combines with sulfur dioxide and nitrogen oxide or even carbon dioxide to give a mild acidic solution which then sets up galvanic attack on the system materials.
Any effort directed at regulating temperature, water or corrodent from touching the materials of the exhaust system would reduce corrosion to the barest minimum. In consequence, the following recommendation can be advanced:

Due to the active role which moisture plays in the corrosion of exhaust system and knowing that this moisture condense from the air that enters the system when the engine is cold, especially at night, it is very important to keep the exhaust interior dry. It is here suggested to introduce an air-drying mechanism into the exhaust system. This could be a chamber similar to muffler with hygroscopic material that will be replaceable when saturated. This chamber will continuously absorb the moisture content of the air in the exhaust.

More modification of the system to close when the engine is off, could be additional mechanism to restrict more atmospheric air from entering. For this device to be more efficient, the compartment of the drying chamber should open each time the engine is off and the exhaust system closed from the tail pipe. The closing of the tail pipe will therefore stop more air from entering.

3.1.3 Aspects of Corrosion in Automobile Radiators

Automobile radiator is one of the min components susceptible to corrosion. It is an automobile cooling system whose function is to dissipate heat from the hot water circulating in the cooling system. When it corrodes, it does not dissipate as much heat as when not corroded.
3.1.3.1 Material: Cast-Iron, Steel, Al-alloy, Brass, Copper, Solder.

3.1.3.2 Types of Corrosion Present in the Radiator:

1. Stress – Corrosion Cracking

In the radiator there exists large temperature changes (high temperature when engine is in operation; low temperature when engine is not in operation). Stresses may therefore, be developed in the metal tubes due to continuous expansion and...
contraction of these tubes; these may eventually lead to cracking of the tubes.

2. Erosion: The erosion is achieved by the continuous contact between the suspended matter, e.g. sand, abrasive products, etc., in the flowing water and the inner surface of the metal tubes.

3. Impingement Corrosion: This type of corrosion occurs when corrosion damage is accelerated by the mechanical removal of corrosion products (e.g. oxides) which would otherwise tend to stifle the corrosion reaction from the inner surface of the tube.

4. Corrosion Fatigue: This is a reduction of the ability of a metal to withstand cyclic repeated stresses. The corrosion of the inner surface of the tube will lower fatigue resistance, and stressing of the surface will tend to accelerate corrosion.

Under cyclic stress conditions, rupture of protective oxide films that prevent corrosion takes place at a greater rate than at that which new protective film can be formed. Such a situation frequently results in formation of anodic areas at the points of rupture; these produce pits that serve stress concentration points for the origin of cracks that cause ultimate failure.

5. Cavitation: Cavitation is present in the radiator. Formation of transient voids or vacuum bubbles in a liquid stream passing over a surface is called cavitation. When these bubbles collapse on a metal surface, there is a severe impact or explosive effect that can cause considerable mechanical damage, and corrosion can be greatly accelerated because of the destruction of protective films.
3.1.3.3 Factors Affecting Corrosion in an Automobile Radiator

1. Temperature
   (i) Corrosion increases with rising temperature.
   (ii) Secondary effect: solubility of air (oxygen), the most common oxidizing substance influencing corrosion.

2. Flow
   Hot water flowing through the radiator, the relative movement of the hot water over a metallic surface tends to accelerate corrosion by carrying away protective corrosion products.

3. Suspended Matter
   Sand, salt and abrasive particles in suspension in water, especially when dirty water is used to fill the radiator can aggravate deterioration by water, in the motor. This includes the scouring effects of mechanical abrasion and the frequently greater effect of the removal or prevention of formation of what would otherwise be protective corrosion products or scales.

4. Handling
   If the radiator is malhandled, it will increase the rate of corrosion; using dirty water can increase the rate of corrosion in the radiator. Corroded particles accumulate in the tubes and with time cause blockage in the radiators.

5. Materials
   The type of metal the radiator is made of is also one of the factors affecting corrosion in radiators. The material should be of adequate thermal conductivity, resistance to corrosion.
6. Environment
The gases, moisture and pollutants, in the atmosphere affect the corrosion of the radiator, when the moisture and dust content of the atmosphere are high.

7. Knocking
Knocking is abnormal — turbulent — violent combustion taking place at an uncontrolled rate. Knocking can occur in various ways, one of which is when the engine overheats (due to a corroded or faulty radiator) and the gasket gets burnt, water from the radiator starts to mix with the engine oil; with time, the engine oil will change colour and start to lose its lubrication values, which eventually results in seizures in the engine.

8. Effect of Anti-rust Solution
An important means of combating corrosion is the use of anti-rust. This is generally very attractive in closed circulation systems (such as the radiator). In the radiator, the inhibitor used in the anti-rust solution lubricates the system and also increases the boiling temperature of the radiator fluid (water). The concentration of the anti-rust in the radiator is also important because if it is too high, it may reverse its function and aid corrosion. The anti-rust solution increases the working life of the radiator and reduces corrosion to a minimum.

9. Fuel Tank
This component is indirectly associated with aspects of radiator problem and therefore, deserves mention here. When water condenses in the fuel tank, it mixes with the fuel and leads to the corrosion of the steel fuel tank. Corrosion products clog the fuel filter and carburetor jets. In
recent times, the best way of corrosion prevention in the radiator is the use of plastic tanks. If fuel tanks are corroded, vehicle owners are advised to wash their tanks and always keep the tanks half-filled to avoid condensation of water when temperature drops at night. The cladding of steel with an alloy is another corrosion prevention technique. Also the use of organic coating as linings of steel tanks solves the problem of corrosion.

3.1.3.4 Heat – Transfer and Corrosion Relationship In Radiator System

It is known that heat-transfer phenomenon in automobile radiator is a major issue in corrosion considerations. Materials selection is equally very important. An investigation was carried out to establish the effect of corrosion on the heat-transfer efficiency of iron and aluminum as materials for automobile radiator. [21] the methodology used is hereby summarized. Test Materials: Cast-iron and Aluminum. Test Procedure: Weight-loss of test material after a specified exposure period in corrodent (water at room temperature (20°C).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pure Water</th>
<th>Aluminum</th>
<th>Cast - Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>985.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific-Heat</td>
<td>4.179</td>
<td>0.896</td>
<td>0.452</td>
</tr>
<tr>
<td>Capacity (Cp) (Kg/Kg.0C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity Kg/ms</td>
<td>5.13 x 10^-4</td>
<td>To be evaluated</td>
<td>To be evaluated</td>
</tr>
<tr>
<td>Conductivity (Thermal)</td>
<td>0.649</td>
<td>204</td>
<td>73</td>
</tr>
</tbody>
</table>

Table: 3.1. Properties of Pure Water, Aluminum Iron [22]
Calculations

The temperature at which an engine works best is about 80°C. We will assume in this study that the temperature of water entering the radiator from the engine is 80°C and that the temperature of water leaving the radiator is equal to the ambient temperature 20°C.

The mean temperature \( T_m \) across the radiator will be

\[
T_m = \frac{80°C + 20°C}{2} = 50°C
\]

The property of pure water, aluminum and iron given in Table 3.1. are at 50°C. The rate of corrosion for aluminum in water in 28 days is 0.006 gm.

Assuming a multiplication factor of 2 is used to estimate the actual weight loss in a radiator, therefore, weight-loss of aluminum = 0.0012 gm

Assuming the rate of corrosion in a period of 5 years, the rate of corrosion will be 0.0042 gm. Aluminum

Similarly, for cast iron 0.282 gm cast – iron

For this investigation, the cooling system of a Mazda bus was used.

Results

Total heat transferable = 853.06W (\( A\lambda \)) value of heat transferred for fluid Y (water and \( A\lambda \)) after 1 year and 5 years are 844.1 Watts and 816.1 Watts.

For 1 year and 5 years (water and Fe), 837.16 Watts and 767.48 Watts respectively.

The efficiency of the radiator after 1 year can be computed as follows:
Al - Radiator: $844.19 \times 100 = 98.9\%$
\[
\text{Efficiency after 5 yrs.}
\]
Al - radiator $= 815.17 \times 100 = 95.6\%$
\[
\text{Fe - Radiator: of } = 837.16 \times 98.1\%
\]
Fe - radiator $= 767.48 \times 100 = 89.9\%$

These results show that:

a) The efficiency of the radiator in transferring heat decreases with increasing degree of corrosion;

b) Aluminum is a better radiator material than cast iron.

The result in (a) implies too that for a given radiator material, the efficiency in heat-dissipation decreases with increasing age of the material, vis-à-vis increasing degree of corrosion.

Conclusion
From the investigation, it is clear that corrosion has side effects on both the automobile and its user. It is also evident that the quality of the material used in the construction of automobile parts should be high. A high quality material guarantees a longer life for an automobile. Since cost is a vital issue, the manufacturer should go for a metal that would not cost him so much but at the same time satisfy his design requirements. The manufacturer should also take into consideration the anticipated life of the equipment.
3.2 CORROSION IN DOMESTIC APPLIANCES

A study of the corrosion phenomenon in domestic refrigerators and washing machines was carried out. Thirty samples of refrigerators and eight washing machines of different makes and at different locations were used in the study. The study looked into the various factors affecting corrosion, the environmental conditions, etc. Pictures of practical cases of corrosion occurrence in the equipments were taken for analysis.

3.2.1 Results

The study revealed many facts about corrosion in domestic refrigerators and washing machines. The various corrosion damages prominent in the samples of refrigerators and washing machines were studied and locations of the attacks were identified as follows:

a) the outer metallic body;
b) the door hinges;
c) metallic shelves;
d) condenser, compressor;
e) around the edges of the adhesive rubber on the inside of the door. Usually, no single refrigerator will experience corrosion attack on all the parts mentioned. The outer metallic body made of mild steel is the most susceptible to corrosion attack; because of the low temperature; the air inside the refrigerator is readily condensed. The condensed water vapour can combine with any gaseous pollutants to initiate corrosion attack on the inside of the refrigerator, especially the metallic shelves. Also, leakages in the refrigerant flow tube network might result in the compressor sucking in water vapour which on condensation can cause knocking, leading to eventual packing up of the compressor without which the whole refrigerator is useless.
3.2.2 Factors Favouring Corrosion in Refrigerators

The following are the factors responsible for corrosion attack on refrigerators:

1) Atmospheric factors, such as gases, dust, temperature and relative humidity influences on corrosion have been earlier explained in section 1.3.

2) Internal or applied stress
The material used in making the refrigerator outer body is usually procured as mild steel coils. During the process of transformation, the coils into flat sheets of required shapes and sizes by cold rolling, bending and cutting, stresses are trapped inside the metals which are concentrated at the bends and sharp corners. Because these stresses are not eliminated by proper heat treatments, the stressed regions serve as points for the initiation of corrosion attack.

This factor is responsible for the observation in plate 1, where the corrosion attack is more pronounced at the top-left hand corner and the base of the refrigerator.

Plate 1
They affect paint adhesion; hence paint peeling always starts from these regions in the absence of scratching or indentation.

(c) Corrosion Propagation at Point of Paint Discontinuity. Fig. 3.2 shows the effects of forces acting on a stressed part, resulting in poor paint adhesion at the surface and paint discontinuity.

![Diagram showing stresses acting at the edges of refrigerators’ and washing machines.]

Because of the paint discontinuity, a galvanic cell is set up in which the exposed metal is the anode and the remaining protective coating the cathode. By means of osmotic pressure, the material under the coating is attacked gradually while its surface paint remains in place until the adhesion is destroyed by corrosion.
product formation and the paint peels freely, thus exposing the corrosion attack underneath it.

(3) Dissimilar Material in Contact

In refrigerators, name-plates, locks, door hinges, bolts, nuts, wooden or metallic stand, etc., come in contact with the mild steel body. These points serve as spot of initiation of corrosion attack galvanic cell in a suitable environment.

The observations in plates 8 and 2 are due to this factor. In plate 8, the use of a non-metallic covering introduces crannies which serve as crevices or pits, and localized corrosion attack sets in areas of dissimilar materials are seen in contact with each other are shown.

Plate 8
Mishandling and Maintenance Habit

Maintenance habit and mishandling are among the important factors contributing to corrosion in refrigerators. Instances of mishandling involve situations such as that found in kitchens where oil, pepper and salt due to cooking activities stain or smear the body of the refrigerator, and these contaminants allowed to stay there accumulating dust and moisture. The stained regions serve as spots for the initiation of corrosion attack, because they are preferentially attacked because of oxygen starvation in those regions. The attack usually takes a few days or weeks to start, depending on the surrounding atmosphere, but as soon as it starts, it easily spreads over the body of the refrigerator. Other examples of mishandling include banging the door, and this weakens the door support and the paint adhesion; scratching the freezer floor with sharp objects and situations where kids hit or scratch the body of the refrigerator either in annoyance or during playing. All these results in corrosion attack.

The habit of cleaning the refrigerator with liquid solutions that do not evaporate quickly (e.g. kerosene) attracts dust particles to the refrigerator, giving rise to localized attack around the dust spot, especially if the dust particles are hygroscopic as a result of oxygen exclusion effect.

Also the habit of leaving the refrigerator surrounding wet, favours corrosion attack at its base where it is usually in contact with wooden or metallic stand. The combined effect of the refrigerator weight and water absorption weakens the wood fibres causing it to decay. Decaying results in the evolution of corrosive acidic vapour which attacks the base of the refrigerator. In the case of a metallic stand, due to wetness, galvanic cell formation results in corrosion attack. Plate 5 shows a good example of this situation.
Another example of mishandling is covering the top of the refrigerator with nylon or plastic material and placing of trays or other domestic utensils on the refrigerator. The materials trap moisture in the space...
between them and the refrigerator, due to low oxygen content in the enclosed space; the spots are attacked in preference to other parts. The attack is more prevalent under a nylon or plastic covering as depicted by plates 5 and 4.

These two materials have the ability to provide additional heat in conjunction with the moisture and oxygen exclusion effect, thereby accelerating the rate of corrosion product formation.

Defrosting
The effect could be ascribed to the observation, where the melted ice flowing out of the freezer compartment is trapped between the adhesive rubber and the space between the freezer floor and the refrigerating section, as in plate 2b and 7a. This happens also when the freezer door is not tightly closed. Due to the presence of dissimilar material in contact and low oxygen content in that region compared to the inside of a refrigerator and the surrounding atmosphere, a differential aeration cell results and that part will be preferentially attacked.
In the single door type, defrosting as a result of power failure or user’s need causes water to flow into the catch basin under the freezer compartment. Where defrosting takes place repeatedly without emptying the basin, it can result in the water flowing out and bathing the base of the refrigerator, giving rise to serious corrosion attack at the base of the refrigerator.

Overcharging the compressor with refrigerator also results in large volume of melted ice and the attendant corrosion attack, as seen in plate 9b.

6) Installation
Many refrigerators are installed very close to the wall such that there is little or no space for heat convection between the wall and the condenser where the refrigerator loses the heat conducted from the refrigerated space. This results in conduction and transmission of heat between the wall and the refrigerator causing the refrigerator experience thermal stresses. Thermal stress has the effect of aiding rapid peeling of the paint coating such that both the condenser and the back of the refrigerator are endorsed to further corrosion attack which will be aqueous in mechanism. The development also reduces the amount of heat transfer by the condenser causing the refrigerator to defrost easily whenever there is any slight break in power supply.

7) Uses: Where the different foods and fruits and beverages are not properly packed before being kept in the refrigerator, they give off juice and fluid that are very corrosive, especially fruits and vegetable, thereby making the metallic shelves and floor of the refrigerator susceptible to corrosion attack. Again, a commercial refrigerator will corrode at a rate proportional to its usage, i.e. it will corrode more than a domestic refrigerator.
3.2.3 Practical Cases of Corrosion in Refrigerators

Presence of cold rolled stresses: The top left hand corner and the base section show extensive corrosion damage. They are regions of high stress concentration; an effect that reduces paint adhesion in those regions.

Corrosion of the stressed regions and pits developing from points of paint discontinuities due to scratching, etc. are aided by atmospheric factors, e.g. moisture condensing and sticking to the body of the refrigerator on a still night.

This attack can be eliminated through proper design and stress annealing heat-treatment to relieve the steel cabinet of the induced stresses and also shielding the refrigerator to protect it from wet or damp atmospheric corrosion attack. Also noticeable are corrosion attacks around the door handle – an example of galvanic corrosion – and at the base of the door.

Plate 3: This is an old refrigerator bought in 1976, showing crevice corrosion at the top door hinge, above the freezer compartment and at the top of the refrigerator where the adhesive rubber is in contact with the metallic body. The attack on the shelves is the
result of dirt accumulation inside the rubber groove and crannies usually present whenever a non-metal is in contact with a metallic body.

From the information gathered, the refrigerator shows little or no appreciable corrosion attack between 1976 and 1984 when it was placed in the sitting room but from 1985 when it was transferred to the kitchen, which was poorly maintained, it started corroding gradually and progressively both on the inside and the outside, especially at the base where it is in contact with a wooden stand which is always damp or wet, due to the absence of melted ice catch basin.

Plate 6

This is a case of mishandling where the painting on the top surface of the refrigerator has been eroded away by the mechanical action of drawing soft drink crates on top of the refrigerator; stress concentration effect is also noticeable.
This shows a serious case of mishandling and poor maintenance habit, it is a typical situation commonly found among the low-income group and some rich
illiterates. The refrigerator is converted into a cupboard for keeping any material which causes pollution or contamination thereby promoting corrosion attack both inside and outside the refrigerator.
Picture 9b shows a refrigerator used in a canteen for storing food items like pepper, tomatoes, fish, vegetables and leaves. The freezer compartment shows excessive ice formation due to refrigerant overcharging. The corrosion attack, noticeable on the door, can be attributed to the combined effect of concentrated stress and moist human palm which is very corrosive when opening and closing the door.

3.2.4 Conclusion
Based on the results of the investigation, we can make the following conclusions:

i. The quality of the mild steel outer body, the type of paint employed as well as the process of painting greatly affect the corrosion tendencies of the refrigerator.

ii. Handling of the refrigerator, which has a correlation with the education and social status of the users; cases of mishandling are more prominent is among the illiterate and the poor.

iii. Corrosion associated with defrosting problem is more rampant in the double door type than the single door type.

iv. Incessant breaks in power supply resulting in frequent defrosting contributes to the corrosion problems in refrigerators, especially in the absence of an effective drainage system.

v. The use of a non-metallic top, like ply wood formical, etc., to prevent corrosion arising from placing foreign body on the refrigerator’s top can only be effective, if the coupling is done in such a way that crannies are not present at the joints.
vi. The presence of induced cold worked stresses, especially around bends and sharp corners aggravate the corrosion of refrigerators.

vii. The effectiveness of using a wooden or metallic stand to protect the base of the refrigerator from water, depends on the extent to which water is kept away from the interface of the refrigerator and the stands as well as the elimination of relative movement.
3.3 CORROSION APPLICATION IN FAMILY PLANNING

An attempt to delve into studies in family planning is a great and magnanimous venture. The practice and application of family planning techniques have helped the society a lot in various ways:

a) to control birth;
b) to regulate population;
c) to reduce pressure on the limited available resources and eventually predict the future of the environment.

One conspicuously misses one aspect of this list, namely, an analysis of the various reactions that best define the complexity of the human body. This is seen as added advantage for this novel idea of the utilization of corrosion principles in the practice of family planning. To this end, the Copper Intra Uterine Device, popularly known as CuluD, is chosen for investigation.

3.3.1 Biomaterials Technology

Biomaterials are those that can survive in the natural ambience of the human body environment with a gradual degradation in their physical, chemical and mechanical properties. Biomaterials technology is dedicated to providing better health care and improve quality of life.

For a material to survive in the body environment, it must possess certain characteristics:

- **Biocompatibility:** interplay between the characteristics of the material and those of the particular environment considered.
- **Low level of reactivity,** i.e. quite chemically stable, depending on its function.
The human body environment is quite aggressive, associated with a variety of salt and varying pH conditions.

3.3.2 Test Material

The Biomaterial chosen for this investigation was an IUD (an intra uterine device, which serves as a contraceptive for preventing pregnancies). The special test material for the investigation was Cu T 380 A.

![Photo of copper-T IUD](image)

This is a T-shaped device with a polyethylene frame holding 380mm of exposed area of Cu. Shelf life is about 10 years.
Fig 3.4 Descriptive photo of copper-T IUD

Fig 3.5a
3.3.3 **Methodology**

(a) **Eligibility to use an IUD:**

An IUD can be used by a patient, if:
the patient has had a baby and wants a space of 2 or more years between pregnancies;

(2) the patient wants a reliable method of contraception that can be removed easily;

(3) The patient has a low risk of contacting STDs (sexually transmitted diseases).

(b) Not eligible to use an IUD:

1. a patient with more than one sexual partner;
2. a patient that had a partner who has other partners;
3. a patient with a vaginal or pelvic infection;
4. a patient with very painful menstrual period;
5. a patient who has not had children and wants to have children in the future;
6. a patient who had an ectopic pregnancy in the past, i.e. pregnancy in the fallopian tube;
7. a patient who is anaemic, i.e. has very little concentration of iron in her blood;
8. a patient who has a medical condition, e.g. rheumatic heart diseases or treatment with other drugs that stop one's immune system from working properly;
9. a patient who has fibroid or other conditions that change the shape of the uterus or cervix.

3.3.4 Choice of Test Samples

Used samples, (used Copper Intra Uterine Device) were collected from various hospitals and family planning clinics across the Lagos metropolis. These hospitals include:

(i) Lagos University Teaching Hospital (LUTH);
(ii) Planned Parenthood Federation of Nigeria (PPFN);
(iii) General Hospital, Ikeja (Ayinke House);
(iv) General Hospital, Lagos Island (Island Maternity).
On the whole, 25 samples were collected at different intervals, 5 of the 25 samples were resident in different hosts for precisely 1 year, 3 samples were resident in hosts for about 2 years, 9 samples resident in hosts for less than 1 year, while the remaining 8 were resident in different hosts for durations that ranged from 2 to 5 years. Five (5) samples that were resident in their hosts for exactly one year and one control (neutral) sample were subjected to the tests. These 6 samples were labelled A (control sample), B,C,D,E,F.

3.3.5 Testing of Samples

The testing procedure was actually carried out to sample the results obtained from A, with those obtained from B,C,D,E,F (used samples). The tests carried out include:

(i) **Visual and Colour Test**: aimed at determining the colour and physical appearance of the used samples in comparison with the control sample as a result of the reaction that occurred between the samples and the uterine environment in different hosts.

(ii) **Potential Difference Test**: This was carried out to determine the potential difference across 2 of each of the 6 Copper ends on the specimen. Great importance was attached to this parameter, since the p.d. of a material represented the driving force for a reaction. A digital voltmeter was used to determine the voltage. The voltage values ranged between 0.03 - 0.10 mV.

(iii) **Resistance Test**

This test determined the resistance of the specimens to the flow of the current. A digital multimeter with calibrations was used. The values of the resistance obtained ranged between 0.80 and 1.10 M .......
Current Evaluation
From the measured voltage and resistance, the current values were calculated (Ohm’s Law). The current gave an indication of the dissociation of the uterine acidic fluid.

The voltage values were plotted against the log values of the current, as in the case of the activation-polarization curve [23]

3.3.6 Mechanism of Action of CuiUds
The CUIUD can be used to prevent conception following unprotected intercourse. The egg reaches the uterine cavity 6 days after fertilization in the fallopian tube. Since the CuluD acts to prevent implantation, it can be inserted up to 5 days after the unprotected intercourse. Thus, it prevents fertilization by decreasing and inactivating the number of sperms reaching the fallopian tube. The primary mode of action of IUDs is interference with fertilization rather than implantation because the prevention of implantation only plays a minor role.

Once the IuD is inserted into the uterus, it interacts with the uterine environment gradually. This uterine environment is of a constantly acidic nature and a reaction between it and the copper on the CUIUD takes place leading to the release of products, fig. 3.3.6(a, b, c).

The acidic composition of the uterine environment is not particular due to secretions from different glands in the neighbouring areas around the uterus.

The products, as a result of the reaction between the Cu metal and the acidic uterine environment help prevent fertilization by:
1. inhibiting zinc containing metalloenzymes in the uterus;
2. Reducing activity in the endometrial steroid receptor;
3. Producing low levels of human chorionic gonadotropin in the buteal phase;
4. Depressing ovum transportation of the cervical mucus by sperms;
5. Elevating the fibrinolytic activity of the endometrial;
6. Bringing about certain enzymatic changes in the endometrial that is not suitable for implantation of the fertilized ovum;
7. Interfering with mobilities and survival of sperms;
8. Producing an inflammatory reaction in the uterus; making the environment hostile for sperms to survive. Thus, since the copper which is a metal reacts with acidic environment, it is more reactive than its plastic counterpart and the most obvious interpretation is corrosion. Corrosion of the Cu occurs in the uterus; the loss of Cu, vis-à-vis, rate of release varying during the time the device remains in the uterus; declining exponentially during the 1st year of use and then increasing as a result of destabilization and fragmentation of the accumulated layer of copper-corrosion products.

It is estimated that the loss of Cu for various types of IUDs is about 0.25 micro mol/day which has been known not to reduce the efficiency of the IUD. The IUD is seen as a reversible but potentially permanent method.

### 3.3.7 Advantages of CulUD

1. It is a very long lasting contraception method;
2. It is highly effective;
3. It does not require a lot of attention on the user's part;
4. It is inexpensive if used long term;
5. It reduces the risk of unwanted pregnancies limits abortions and regulates population;
6. It reduces risk of endometrial and cervical cancer;
7. It is convenient, does not interfere with normal activities, sexual desire and sexual intercourse;
8. The effectiveness of the CuIUD is about 99% and so, the risk of getting pregnant is 1%.

3.3.8 Disadvantages of CuIUD
1. Heavier and more painful periods than before the use of IUD;
2. Short term use is very costly;
3. They do not prevent sexually transmitted infections;
4. The IUD must be inserted by a trained provider, which may delay insertion;
5. Recommended infection prevention practices must be followed during the insertion procedure;
6. The patient must be carefully screened for risk factors for IUD use, e.g. increased risk of sexually transmitted diseases, multiple partners, etc.

3.3.9 Conclusion
The Copper IUD is a device which consists of copper wound/coupled with plastic to produce an anode-cathode system. This anode-cathode device placed into the corrosive medium (electrolyte), leads to the corrosion reaction. It can thus be deduced that the type of corrosion associated with the use of copper intra-uterine device can be hypothesized to be galvanic corrosion due to the two dissimilar materials.

The inflammatory reaction brought about by the use of copper IUD in the uterus as suggested by the medical experts can further be interpreted by the materials engineers as corrosion reaction.
The check-ups to be followed up by the IUD user consists of cleansing the partly used specimen with dettol. This cleansing action is a chemical reaction outside the uterine environment which can be hypothesized to break down the tenacious oxide layers which would ordinarily induce passivity.

From past works and medical research, there has been no proof of after-effect with the use of copper IUD despite its corrosion products formed, which are actually responsible for inactivating the sperm.

From the colour-test, the colour changes indicate that corrosion reaction had taken place based on the fact that copper, as a metal, has the tendency to corrode.

### 3.3.10 Recommendation

1. From the study, there should be a continual use of the Intra Uterine Device because of its high efficiency and effectiveness.
2. The regular check-ups suggested by the medical experts should be followed regularly and be made more often. The cleansing action with dettol helps to break down the passive tenacious oxide layers that can result during use.
3. This form of contraception is recommended for the eligible female individuals, i.e. those with good medical history, single partners, mothers, etc., to adopt. This promotes one-sex partnership.
4. Metallurgists, and materials scientists and corrosion engineers have a wonderful role to play in this field of study. At the moment, there exists misconceptions among medical experts and metallurgical/materials engineers with respect to the interpretation of mechanisms involved in the contraception theory of the copper IUD. While the metallurgist believes definitely that the galvanic corrosion process taking place in the uterus environment leads to changes in pH in the
uterus-electrolyte and consequently gives rise to the inactivation of the sperms, the medical experts are yet to advance a concrete justification for the contraceptive action.

The materials scientists need to research more into the biomaterials aspect of this field in order to solve the problem of long-lasting materials and compatibility.
3.5 DESIGN OF CORROSION RESISTANT MICROSTRUCTURES

3.5.1 Our discussions so far centred on:

(a) Corrosion attack on structures (automobile components, domestic appliances, biomaterials, in fact every imaginable device).
(b) The great need to quest for corrosion resistant engineering materials.
(c) One must add too that the materials should have the requisite mechanical properties, especially, hardness, hardeability and ductility.

It is almost impossible to achieve all these requirements simultaneously; often it is rational and perhaps more economical to allow a certain measure of corrosion; to try to avoid every bit of corrosion in a given project could be unnecessarily expensive. To try to have optimal values of each mechanical property may not be possible, if corrosion is to be fully eliminated. Ductility, for instance, cannot coexist with high hardness values, e.g. the situation in a martensitic structure.

It has been established that certain factors affect the microstructure of material and hence its ability to corrode. [24] Deviation from stoichiometry produces excess vacancies within intermetallic compounds e.g. FeAl, vacancies assist in diffusion of atoms to the surface to participate in corrosion process.

Hardening by heat treatment results in microstructural changes and in heterogeneity. This leads to decrease in corrosion resistance.

Martensite: This indicates internal stresses and high degree of dislocation. These features are well-known catalysts for corrosion attack.
Normalized Structures: a well-known equilibrium structure, devoid of internal stress and low corrosion susceptibility.

Tempered Martensite: Lies mid-way between Martensite and Normalized structure with regard to internal stress. It has a minimal corrosion susceptibility.

Heterogeneity: Heterogeneous alloys are a mixture of two or more phases which differ in composition and structure. The phase difference within the microstructure gives rise to galvanic effect which leads to corrosion in a corrosive medium. Heterogeneity also arises due to segregation and precipitation of different phases within the microstructure. Substantial potential difference between one phase and the adjacent phase makes them susceptible to inter-granular corrosion. Precipitation of a phase from a super saturated solution occurs along grain boundaries.

This makes the grain boundaries differ in composition from the other regions of the microstructure. Since grain-boundaries are high energy areas, they are more susceptible to corrosion.

Heat Treatment: Hardening by heat treatment results in changes in microstructure and heterogeneity and generally decreases resistance to corrosion. Martensite transformation is a diffusion less solid-state transformation. Because of the high rate of quenching, dislocation and defects are trapped within the microstructure in disordered form, thus increasing its heterogeneity. The hardness and brittleness of the material are increased while the corrosion resistance is decreased. A compromise is achieved by tempering to increase ductility and corrosion resistance.
3.5.2 Deformed Heterogeneous Metals

Recrystallization is the best tool for the design of microstructures. The occurrence of recrystallization requires that energy be stored in the material in the form of defects. [25] These can be obtained by thermal or radiation treatments. The most common way, however, is the introduction of defects by plastic deformation. If they provide the driving force for recrystallization, the average energy density (i.e. dislocation density) is of primary importance.

For the formation of new crystallites, the local defect structure becomes very significant. The following sites are listed in the sequence of their effectiveness in aiding the formation of recrystallized grains:

(a) (1) Original grain boundaries, (2) transformation bands, (3) intersections of twins and bands of concentrated slip, (4) coalescing subgrains, and (5) continuously growing subgrains.

If a second phase is dispersed in the alloy, the defect structure is modified, depending on whether:

(a) coherent particles are deforming with the matrix;
(b) small particles are by-passed by dislocations; and
(c) large particles act as dislocation sources.

Characteristic for case (a) is that the plastic strain becomes confined to small planar portions of the volume, because of a local decrease in critical sheer stress due to cutting of particles. [29] Workhardening of particular slip planes in case (b) favours an even distribution of dislocation across the volume. If the particles of the second phase become large and widely...
spaced, the dislocation distribution again becomes inhomogeneous, but different from case (a).

The interfaces of the particles act as dislocation sources, and flow around the particles lead to a high amount of lattice curvature in their close environment. [30] This leads to the establishment of an additional nucleation site for recrystallized grains.

The incoherent interface of large particles and a high dislocation density and lattice curvature favour the formation of recrystallization fronts. An additional requirement for this to occur is a particle spacing above a critical value - as a rule, 2 to 3 times the dislocation cell size – so that a sufficient number of dislocations cell rearrange.

3.5.3 Recrystallization of Supersaturated Solid Solutions

This problem is characterized by the fact that in addition to the defects, the alloy contains atoms that have a tendency to precipitate. Therefore, sequential and simultaneous precipitation and recrystallization reactions occur, by which a wide variety of different microstructures, can be obtained.

This leads to different shapes of the functions \( t_R = f(T) \) and \( t_A = +(r) \)

\[
\begin{align*}
C_0 &= \text{Constant} \\
A &= f(T) \\
P_0 &= \text{Constant}
\end{align*}
\]

\( T_R \): start of recrystallization (particle free); \( t_p \): start of precipitation (dislocation free); \( t_pr \): start recrystallization after proceeding precipitation; \( t_{pr} \): start of precipitation at a dislocation density so.

From this, four temperature ranges can be defined.

\[ T > T_E = T_l \] recrystallization in the solid solution,
3.5.4 Design of Corrosion Resistant Microstructure

A novel microstructure (Fig. 3.5.4a) was designed by a systematic choice of recrystallization parameters [26, 27, 28], as follows:

Carbon Steel (0.23%) containing round Fe₃C particles of size 130nm; pre-recrystallization deformation 90%; recrystallization annealing temperature 55°C for 20 mins and cooled in water at room temperature.
Recrystallization was rather sluggish, having taken place via *in-situ* recrystallization followed by (discontinuous) primary recrystallization. Owing to the dispersed Fe₃C, the deformed structure was rendered homogeneous and therefore a rather homogeneous transformation process took place during the heat treatment. This gave a recrystallized structure that was hard and rather coarse grained. This structure satisfied the ideal structure for corrosion resistance and relatively high strength and ductility.

This is a novel contribution in the field of physical metallurgy. This was the first time, Recrystallization annealing treatment can justifiably be regarded, in physical metallurgical parlance, as a hardening thermomechanical treatment. The typical structure (Fig. 3.5.4b) is hard owing to the homogeneous dispersed Fe₃C particles over the grains; the corrosion resistance of this structure explained by the relatively coarse and stress-free grains. This research work has been published in virtually all over the world (USA, Canada, France, Australia, Britain, Germany, Japan and Nigeria).

![Fig. 3.5.4b Physical Metallurgy (550°C, 20min)](image_url)
IV. CONCLUDING REMARKS

At the end of this lecture a few points remain unforgettable in our minds:

- Corrosion is everywhere among us with its attacking force.
- Unfortunately, the economic effects for individuals and the nation appear to be unbearable.
- Exact economic figures for Nigeria are difficult to come by because of the Nigerian situation, namely, companies not being prepared to supply meaningful information on corrosion problems.
- The general lack of awareness of the serious impact of corrosion on our lives is stifling developmental progress in our country. Who could imagine such positive aspects of corrosion like its contribution to family planning!! The adverse effects of corrosion are not limited to financial considerations: wastage of materials, adverse effects on materials and engineering properties are equally serious.

Apart from the sections considered in this lecture, there are other areas in our daily life where corrosion effects are colossal: petroleum, agriculture and aviation industry.

Infact, corrosion is aptly comparable to corruption. If both are left uncontrolled, they eat deep into the very fabric of our nation’s economy in an irreversible manner that recovery most often becomes an unrealizable mirage. It is therefore imperative for the survival of our nation to prevent corrosion and corruption rather than embark on the futility of curing them. The government of Nigeria should articulate policies that address corrosion in the same manner as it has done for its “cousin” corruption.
ACKNOWLEDGMENTS

Where do I start? Where do I end? It is wise to start with God. I know very many things God has done for me and I sincerely believe that there are more things I don't know he has done for me. For all this, I am very sincerely grateful to Him. I request everybody who loves me to help me to thank Him for the so many good things he did for me. I pray to Him too to bless all of you wonderful people, without exception.

I remember my very loving parents. I will always practise what they taught me. I owe everything I have or do to them. My eldest brother (Papa), who didn’t “die” until he died two months ago. This was his motto; it was then that I ceased to have a father.

My immediate late elder brother, “A. U”. All my other brothers and sisters (living and dead) passionately love/loved me. God knows how I feel when I think of them. I remember with special gratitude the contribution of Rev. Monsignor Dr. B. O. Onwumere to my life. My academic career is full of sweet memories.

I never one day spent a minute thinking of what next: primary to secondary school, to Higher School, to Germany and back to Nigeria; while waiting for the Higher School exam result, my principal sent his vice (all Irish) from C. K. C. Onitsha to my village in Mbaise, Imo State, to relate to me news of my German University Education (with scholarship, of course) and two days later, I left for Germany.

Everything went smoothly for me everywhere. I am grateful to all those that God used to make me happy.

My friends - in fact, to give glory to God, I try not to have enemies – are too numerous to mention: playmates in my village, school mates, in B.S.C. Orlu, C.K.C. Onitsha, colleagues in UNILAG. I feel fine, when they call me in their
usual humorous way; Prof. Talabi ("Chief"), Prof. S.A. Balogun ("C. M.") Prof. Susu ("Chief Kamma"), our Vice-Chancellor ("C. M. K.") Prof. Ndiokwere ("Chike", for the famous Chikeobi"), etc. etc., For all this, I say "thank you". This is naturally extended to UNILAG and its principal and non-principal officers, for bringing me to a level, worthy to deliver an inaugural lecture.

I remember all my town’s men and women in Lagos; my Eziudo Citizen – club members, I say "CITIZEN". Everybody is hereby remembered and thanked.

Finally, I will close by mentioning two only important groups: my very immediate family with the MD/CEO - my wife, the "Oriaku"; She is "First" (but after me), then the others ("Thatcher", "Engineer", and other Mbaise - "clan’ members). Everybody in my family is a director, but I am the Director. Well, Kunle and his family are included here; "stole" one family member. I promise him a return match, directly or indirectly; our OBJ will be the referee. God is the last and Biggest, Amen.
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