CHAPTER II

Literature Review

2.1 Background

Study on corrosion of carbon steel treated in the oxalic acid has done by (Wiersma, 2004) to determine the ratio of moles of iron corroded to moles of hydrogen evolved during the corrosion of iron in oxalic acid .The tests have focused to clean corrosion coupons in oxalic acid solutions. It is expected that most of these variables would reduce the total amount of hydrogen evolved. Further testing would need to be performed to quantify the reduction in hydrogen generation rate associated with these variables. The theory of corrosion of carbon steel in oxalic acid and experimental work were reviewed. It was concluded that the maximum ratio of moles of hydrogen evolved to moles of iron corroded is 1:1. This ratio would be observed in a de-aerated environment. Result study if oxygen or other oxidizing species are present, the ratio would be less than 1:1. If the use of lower hydrogen generation rates or total hydrogen evolved is desired, further testing to look at these variables is necessary (Wiersma, 2004).

Corrosion resistance of stainless steels in soils and in concrete by soil is a complex phenomenon due to the great number of variables involved. In principle, stainless steels should be in the passive state in soils, but the presence of water and aggressive chemical species such as chloride ions, sulphates and as well as types of bacteria and stray current, can cause localized corrosion. Result in study in soils and for selection purposes it is recommended to consider corrosion resistance of buried stainless steels firstly in relation to the preserve of chloride ions and secondly according to their resistivity and pH concentration. Specific stainless steel grade must be carefully selected according to soil conditions. In concrete, most of stainless steels with a PRE greater than 19 should be satisfactory in many cases (Cunat, P., 2001).

Study also suggests that article analyses stainless steel resistance to burning products released by heat burners. Chloride ions, existing in combustion, decrease corrosion resistance of chromic-nickel steel. It is necessary to find out for solutions how to increase corrosion resistance of welded parts **(**Kadry, 2008**).**

Study regarding carbon steel corrosion in Key West and Persian Gulf seawaters at varying oxygen concentrations and exposure conditions included the following: stagnant and sloshing, oxygenated and deoxygenated seawater, in addition to, alternating immersion and drying with oxygenated and deoxygenated seawaters and environment. The result shows that instantaneous corrosion rates increased significantly when oxygen was introduced into hypoxic or deoxygenated seawaters, the stagnant Key West seawater produced the highest corrosion rates and highest sulfide concentrations. The result also found the presence of oxygen in an anaerobic/hypoxic system as a resuttant increase of corrosion rate (Little I, *et al*. 2005).

Research work on atmospheric corrosion carried out in China describe the climate characteristics and the classification of atmospheric corrosivity across the whole country. They also describe the rusting evolution under simulated wet/dry cyclic conditions. The study use the NASCM?

technique set up a database, the NASCM to collect the atmospheric corrosion data from different stations located in the north (J Dong, *et al*. 2007). The corrosion rate increases with time in the initial stage, during which the rust consists of a large amount of amorphous FeO_2H with exiguous crystallized a-FeOOH and b-FeOOH in a low-density layer. However, the corrosion rate decreases with time in the subsequent stage, and the rust forms a high-density layer of g-FeOOH and magnetite (J Dong, *et al*. 2007).

On the other hand study of fractal characteristics and fractal dimension measurement for example study on broken surfaces of aluminum electric porcelain analyze by scanning electron microscope (SEM). The results show that the broken surface of aluminum electric porcelain is a fractal body in statistics, and the fractal dimensions of broken surfaces are different with the different amplification of multiple value . The fractal dimensions of broken surfaces were also affected by the degrees of gray . They also formed relationships between the fractal dimensions of broken surfaces and porcelain bend under strengths, shows that they are in positive correlation with the low multiples and in negative correlation with the high multiples (Yang and Zhou, 2005).

According to Spicer, *et al* (1994), about the Surface morphology for corrosion detection using patterned heat sources, roughness of the back surface was investigated for specimens that treated by using different heat source. The result shows that the surface roughness exhibiting corrosion, and for prepared samples with milled channels of varying geometry. An area with heating source is used initially to provide one dimensional heating of the specimen which allows plate thinning, disbanding, or presence of Corrosion to be rapidly detected. Conclusion of his study, a thermographic nondestructive evaluation technique, for corrosion in aging aircraft is proposed, in which implements both area. The area heating source provides one dimensional heating of the specimen and allows suspect areas to be rapidly detected. Of this study, a localized heating source is then used to further characterize the suspected regions by monitoring the variation in lateral heat flow produced by variations in the back of the surface roughness which would be indicative of corrosive action on the underside of the skin. The physical basis for implementation of this technique was investigated by studying the temperature time signatures for a series of prepared specimens with different back surface morphologies (Spicer, *et al*.1994).

2.2 Overview on corrosion

2.2.1 Define corrosion

Corrosion is defined as the deterioration of material by reaction to its environment. The corrosion occurs because of the natural tendency for most metals to return to their natural state; e.g., iron in the presence of moist air will revert to its natural state, iron oxide. Metals can be corroded by the direct reaction of the metal to a chemical, e.g., zinc will react with dilute sulfuric acid, and magnesium will react with alcohols' (John, 1994).

2.2.2 Theory of corrosion

Corrosion causes huge losses, which rise yearly with the increased usage of metals in industrial development. The usual concept of corrosion is that it is a result of an electrochemical reaction taking place on the surface of the metal where the metal is converted into metal oxides or other corrosion products. With some metals, they produce a tight skin on the metal surface, which hinders further corrosion, and if this surface layer is broken, it is self-healing. These metals are said to be passivated and include lead, nickel, cadmium, chromium and aluminum. Zinc corrosion products form a fairly tight layer on zinc and further corrosion is slow. A tight layer of iron and chromium oxides forms on the surface of stainless steel and is the reason for the resistance of this metal. Iron and steel, however, form rust as a corrosion product, which is porous, and is not firmly adherent and does not prevent continued corrosion (Knoy and P.E, 1999).

2.2.3 Corrosion mechanism

The transmission of the current, in anode reaction by iron goes into solution as ferrous ions viz (http//:resense.co.nz, 1999).

Fe----------------------> Fe+2 + 2e-

Iron Ferrous ions Electrons …………….. (Anode reaction)

This reaction is the basis for the corrosion of iron. Electrons generated as shown above are consumed at the cathode area, and react there in various ways depending on the availability of oxygen. In normal Atmospheric corrosion there is an ample supply of oxygen and the following reaction occurs.

Fe----------------------> Fe+2 + 2e-

Iron Ferrous ions Electrons ……………… (Anode reaction)

H2O + 1/2 O2 + 2e- ------------------> 2OH

Water Oxygen Electrons Hydroxyl Ions ……………… (Cathode reaction)

The hydroxyl ions (OH-) from the cathode combined with the ferrous ions (Fe+2) from the anode to form ferrous hydroxide, which is precipitated. This further reacts with oxygen and water to form hydrated ferric oxide, which is known as rust. This is shown as:

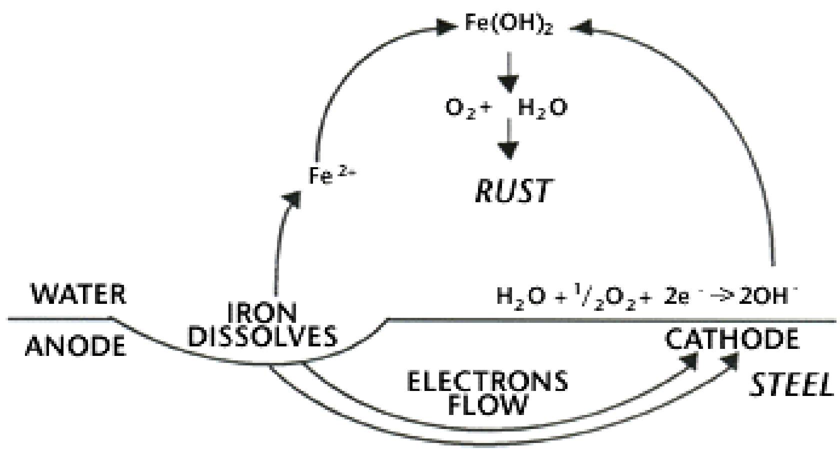


Figure 2.1 Corrosion mechanism (Source: http//:resense.co.nz, 1999)

2.2.4 Protection from rusting

There are a few basic methods for protecting metals from corrosion:

One is to slow down the process. Slowing the corrosion process was done with protective coatings such as paint or tar. These help to keep out the oxygen, water, and electrolyte salts. The presence of small salt compound crystals in the air is the major reason why metal corrodes more rapidly at seacoasts. The cathodic protection from corrosion occurs when a metal to be protected is coupled with a metal more easily oxidized than itself or coated by zinc. Instead of Fe2+ ions going into solution, Zn2+ ions are lost from the zinc. The iron remains unaffected. From the other side, anodic protection, the metal to be protected is briefly made positive to form a stable oxide film on its surface. The stable oxide film then protects the underlying metal from corrosion **(**Knoy and P.E, 1999**).**

2.2.5 Basic causes of corrosion

2.2.5.1 Condition necessary for corrosion

Four conditions must exist before the electrochemical reaction

- Corrodes surface (in anode),
- Cathode,
- Conductive liquid path (electrolyte, usually condensate and salt or other contaminations),
- Conductor to carry out the flow of electrons from the anode to the cathode.

(The elimination of any one of the four conditions will stop corrosion). The coating on the surface of the metal will prevent the electrolyte from connecting the cathode and anode so the current cannot flow. Therefore, no corrosion will occur as long as the coating is unbroken (John, 1994).

2.2.5.2 Effect of material selection

One of the fundamental factors in corrosion effect is the nature of the material. Most materials are usually selected primarily for structural efficiency, and corrosion resistance is often a secondary consideration in design. The use of corrosion-resistant alloys is not a cure-all for corrosion prevention. Corrosion-resistant metals by nature passive (more noble) and can cause severe galvanic corrosion of active (less noble) materials. A common occurrence is to replace a corroded part with a corrosion-resistant alloy only to find that the corrosion has shifted to another location and increased in severity (John, 1994).

2.2.5.3 Water intrusion

Moreover (John, 1994) gave us an idea about the water intrusion is the principal cause of corrosion problems encountered in the field with the use of equipment. Water can enter an enclosure by free entry, capillary action, or condensation. With these three modes of water entry acting, and with the subsequent confinement of water, it is almost certain that any enclosure will be susceptible to water intrusion. As a general rule, assume that water enters any unit except the hermetically sealed or pressurized designs. Swamp like areas, enclosures, accumulation areas should be provided with drain holes at their lowest point or wherever water may collect. The size of the drain holes should be large enough to permit proper application of a protective coating (John, 1994).

2.2.5.4 Environment effect

At normal atmospheric temperatures, the moisture in the air is enough to start corrosive action to take place. Oxygen is essential effect for corrosion to occur in water at ambient temperatures. Other factors that affect the tendency of a metal to corrode are Stability of the corrosion products, Acidity or alkalinity of the conductive medium (pH factor), Biological organisms (particularly anaerobic bacteria), Variation in composition of the corrosive medium, and Temperature. The corrosion problem at KSC is complex. The presence of salts and acids on metal surfaces greatly increases the electrical conductivity of any moisture present and accelerates corrosion. Moisture tends to collect on dirt particles. The maintenance of clean surfaces on passive metals or alloys and alloys plated with more noble metals can be of even greater importance than for plain carbon steel. If small corrosion areas develop, the combination of small active anodes in relation to large passive cathodes causes severe pitting. This principle also applies to metals that have been passivated by chemical treatments as well as for metals that develop passivation due to environmental conditions. Corrosive attack begins on the surface of a metal exposed to a corrosive environment. If allowed to progress, the corrosion works down into the core of the material. Because corrosion never originates in the core, there will always be evidence on the surface whenever an attack is in progress. The most common visible manifestations of corrosion are pitting on stainless steel or aluminum, rust on carbon steel, and intergranular exfoliation on aluminum (John, 1994).

2.2.6 Types of corrosion

2.2.6.1 Surface corrosion

Surface corrosion is the most common form of corrosion and the results from a direct chemical attack on a metal surface and involves only the metal surface. Surface corrosion usually occurs over a wide area and is more or less equal in dispersion .On a polished surface, this type of corrosion is first seen as a general dulling of the surface, and if allowed to continue, the surface becomes rough and possibly frosted in appearance. The discoloration or general dulling of metal created by exposure to elevated temperatures is not to be considered general surface corrosion (John, 1994).

2.2.6.2 Filiform corrosion

This type of corrosion is when oxygen concentration cell are formed, and it occurs on metal surfaces. It occurs when the relative humidity of the air is between 78 and 90 percent and the surface is slightly acidic. This type of corrosion usually attacks steel and aluminum surfaces. It makes the damage deeper and more severe for aluminum, which leads to intergranular corrosion, see figure 2.2 (http://tech.purdue.edu, 1998).

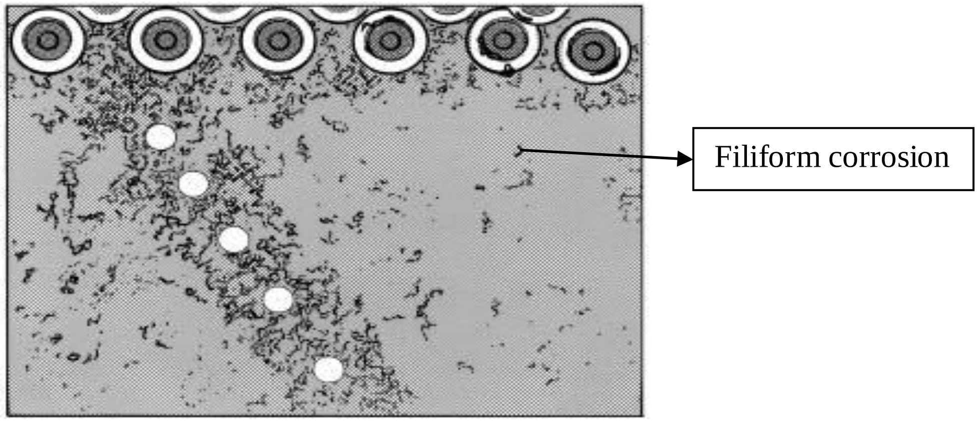


Figure 2.2 Filiform corrosion (Source:http://tech.purdue.edu, 1998)

2.2.6.3 Consolation cell corrosion.

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cell corrosion: (1) Metal ion concentration cells, (2) Oxygen concentration cells, and (3) Active passive cells (John, 1994).

2.2.6.4 Fatigue corrosion

This type of corrosion is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. Fatigue corrosion failure occurs in two stages, the combined action of corrosion and cyclic stresses damages the metal pitting and crack formation to such a degree that it fractures by cyclic stressing. This occurs, even if the corrosive environment is completely removed. The second stage is essentially a fatigue stage in which failure proceeds by propagation of the crack due to stress effect (John, 1994).

2.2.6.5 Galvanic corrosion

Galvanic corrosion occurs when two dissimilar metals make contact in the presence of an electrolyte. It is usually recognizable by the presence of a build-up of corrosion at the joint between the metals (John, 1994). As show in Figure 2.3.

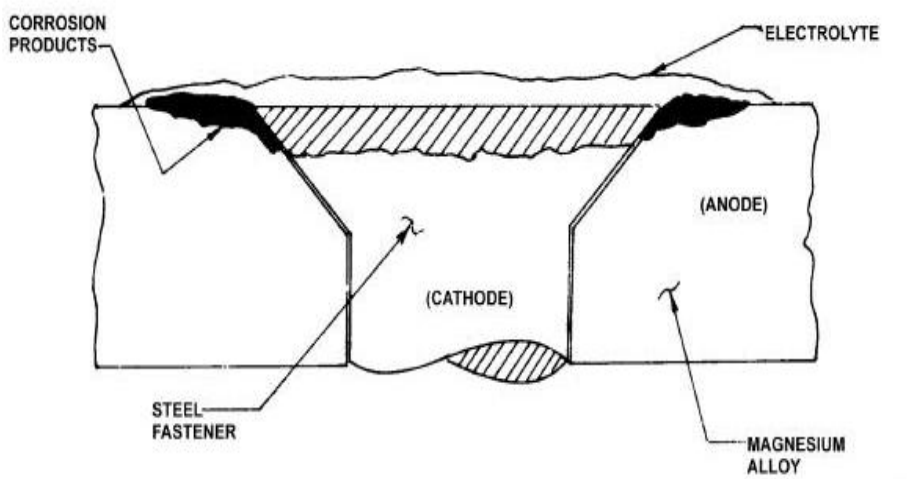


Figure 2.3 Galvanic corrosion of magnesium adjacent to steel fastener,

(Source: http://tech.purdue.edu, 1998)

2.2.6.6 Crevice corrosion

Crevice or contact corrosion is the corrosion produced at the region of contact of metals with metals or metals with non-metals. It may occur at washers, under barnacles, at sand grains, under applied protective films, and at pockets formed by threaded joints. Whether or not stainless steels are free of pit nuclei, they are always susceptible to this kind of corrosion. First corrosion occurs when surfaces of metals are used in contact with each other or with other materials and the surfaces are damped by the corrosive medium or when a crack or crevice is permitted to exist in a stainless-steel (John, 1994).

2.2.6.7 Pitting corrosion

Pitting corrosion is one of the most destructive and intense forms of corrosion Figure 2.4. It can occur in any metal but is most common on metals that form protective oxide films, such as aluminum and magnesium alloys. It is first noticeable as a white or gray powdery deposit, similar to dust, which blotches the surface (John, 1994).

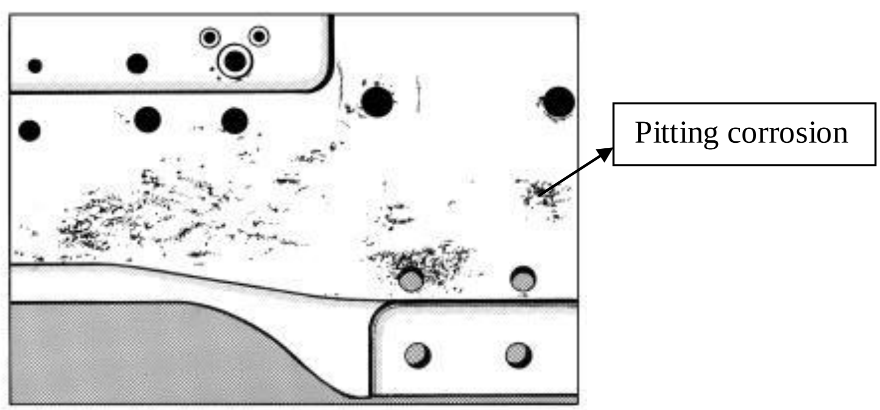


Figure 2.4 Pitting corrosion (external view) (Source: http://tech.purdue.edu, 1998)

2.2.7 Monitoring corrosion

There are multiple ways for following up and the monitoring of pipeline corrosion in the oil and gas. These roads would be able to know what type of erosion and modification, and what are the reasons for the basis of this information can be obtained to identify ways for prevention for example if we take a sample of the tube wells used for injection wells or pipelines alsors, crisis would be the work of the analysis. It shows that there are bacteria, and determines the type of bacteria present in it. It will be used to identify the type of chemical that are commensurate with the type of bacteria thus causing the erosion . Thus, after determining the type and cause of corrosion, is to identify ways of protection and control. In this way the loss of road segment of the mineral coupon is the method of electrical resistance and the method of polarization. There are many ways to identify and determine the rate of erosion within the pipes and tanks, installations and vessels used in the different mineral transport and storage of petroleum products (oil - gas - water).

There are also technical options such as cathodic and anodic protection, materials selection, chemical dosing and the application of internal and external coatings. Corrosion measurement X employs a variety of techniques to determine how corrosive the environment is and at what rate metal loss is being experience. Corrosion measurement is the quantitative method by which the effectiveness of corrosion control and prevention techniques can be evaluated and provides the feedback to enable corrosion control and prevention methods to be optimized. A wide variety of corrosion measurement techniques exists, including, such as Non destructive, Testing analytical

Chemistry, Operational data, Fluid electrochemistry, and another to Corrosion monitoring: Weight loss coupons, Electrical resistance, Linear polarization, Hydrogen penetration, Galvanic current. Some corrosion measurement techniques can be used on-line, where it is constantly exposed to the process stream, while others provide off-line measurement, such as that of determined in a laboratory analysis. Corrosion monitoring is the practice of measuring the corrosively of process stream conditions by the use of "probes" which are inserted into the process stream and which are continuously exposed to the process stream condition. Corrosion monitoring "Probes" can be mechanical, electrical, or electrochemical devices. Corrosion monitoring techniques alone provide direct and online measurement of metal loss/corrosion rate in industrial process systems. Provided by the four combinations of on-line/off-line, direct/indirect measurements are corrosion monitoring direct, On-line, Non destructive testing direct, Off-line, Analytical chemistry indirect, Off-line, Operational data indirect, and on-line methods.

Corrosion monitoring techniques

A large number of corrosion monitoring techniques exist. The following list details the most common techniques which are used in industrial applications: Corrosion Coupons (weight loss measurements (Britton, 2009**).** Other techniques exist, but almost all require some expert operation, or otherwise are not sufficiently rugged or adaptable to plant applications. Of the techniques listed above, corrosion coupons, ER, and LPR form the core of industrial corrosion monitoring systems. These corrosion monitoring techniques have been successfully applied technique and are used in an increasing range of applications: due to these following reasons:

• Easy to understand and implement.

• Equipment reliability has been demonstrated in the field environment over many years of operational application.

• Results are easy to interpret.

• Measuring equipment can be made intrinsically safe for hazardous area operation.

• It is economic benefit through reduced plant down time and plant life extension (Britton, 2009).

2.3 Properties of steel

2.3.1 Carbon steels.

Carbon steels or unalloyed steels are materials made up of iron and carbon. The percentage of carbon has a dramatic effect on the properties of the material and therefore is suitable for use.

Table 2.1 Carbon steels may be classified into 3 major groups, carbon steel content

AMG	Type of steel	% of carbon	Properties
1.1	Magnetic soft steel (mild steel)	Low 0.03 – 0.25%	Ductile and easily cold worked
1.2	Structural steel/case carburising steel	Medium 0.15- 0.40%	Wear resistant
1.3	Plain carbon steel	High 0.4 - 1.2%	Wear resistant and tough

2.3.2 Corrosion in steel

Corrosion is the deterioration of essential properties in a material due to reactions with its surroundings. Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well. The problem with iron as well as many other metals is that the oxide formed by oxidation does not firmly adhere to the surface of the metal and flakes off are easily causing "pitting". Extensive pitting eventually causes structural weakness and disintegration of the metal. Although one of the main reasons why carbon steel is used in corrosion resistance, they do in fact suffer from certain types of corrosion in some environments and care must be taken to select a grade which will be suitable for the application (C.Garcia, *al et*. 2008).

Corrosion can cause a variety of problems,

• Perforation such as of tanks and pipes, (Corrosion analysis of stainless Steel 509).

• Loss of strength where the cross section of structural members is reduced by corrosion, leading to a loss of strength of the structure and subsequent failure,

• Degradation of appearance, where corrosion products or pitting can detract from a decorative surface finish.

• Finally, corrosion can produce scale or rust which can contaminate the material being handled; this particularly applies in the case of food processing equipment. Corrosion of stainless steels can be categorized into the following: General corrosion, Pitting corrosion, Crevice corrosion, Stress Corrosion Cracking, Sulfide Stress Corrosion Cracking, Intergranular Corrosion, Galvanic Corrosion, Contact Corrosion **(**Kadry, 2008**).**

2.3.3 Production steel

1. Materials used to produce pig iron

2. Coal as coke used to supply carbon. In a blast furnace, ore is heated in the presence of carbon which allows oxygen in the ore to react with carbon to form gases

3. Mestone helps to remove impurities

4. On ore processed ore at the start of the process has about 65% iron

5. Requires about 3.2 tons of raw materials to produce

6. Impurities (slag) float on the top of melt. Produce 1.0 ton of steel

Three types of furnaces have been used for refining pig iron (or scrap steel) into refined steel, are: open hearth (no longer used in the US), Basic oxygen, and Electric arc.

2.4 Overview fractal

2.4.1 Fractal dimension

The term fractals refers to the mathematical concept of how vastly different objects can be described using the same mathematical statement. Fractal term for fractional dimension was first used by Benoit Mandelbrot, who proposed the concept as an approach to the scale of problems in the real world (Battat and Ros, 2000) and (Barnsley, 1988). Fractal properties of porous media have attracted considerable attention, and many theoretical including, computer simulations, and experimental studies, have been under which are taken in attempt to understand it. There are six basic methods of measuring fractal properties, the box counting methods, adsorption studies, chord-length measurement, correlation function measurement, small angle scattering and spectral methods (Sahimi, 1995). Fractal can be used to analyze surface that were formed though physical process such as a deposition processes and, the recession process where surface shrinks through erosion and etching, by combination of growth and recession etc. Fractals can be used to characterize porous fractal structure, and is also a useful tool to understanding the fabrication and characterization of microelectro mechanical system (mems), microchip and the DNA surface that is the result of a one to one mapping of the genetic code and a self affine surface, (Battat and Rose, 2000). The fractal dimension is a measure of roughness of a surface (Hayashi, J, *et al*. 2002) where that; able to used several methods of measuring the roughness of material example, image processing can be used as a guide to setting the threshold field existence of a preferred orientation in a thin film (Dannenberg, 2002).

Image analysis

Image analysis process for material, employs a wide variety of techniques to perform morphological study as well as textual analysis in order to rapidly count, measure, and /or classify features such as particles size, fibers, or structural elements through counting the number of several domains, converting these numbers to areas, and finally averaging. Moreover, the rough pore configuration was observed across the fracture surface (Ghorbani, *et al*. 2006). Method of measuring the fractal dimension of a fractured surface is described by image j software. The computer can mechanically computer the offset at many places in the two images and calculate their height on the basis of the parallax angle. The sum of the area of all planes formed by an array of three-dimension points is an approximation of the area true surface area.(Friel and Pande ,2000).

2.4.2 Fractals Application

In fact, there are hundreds of applications of fractal from different aspects, such as generating computer aided mammography, creating realistic image, producing fractal music and etc. Here, we are only going to describe some of these practical applications.

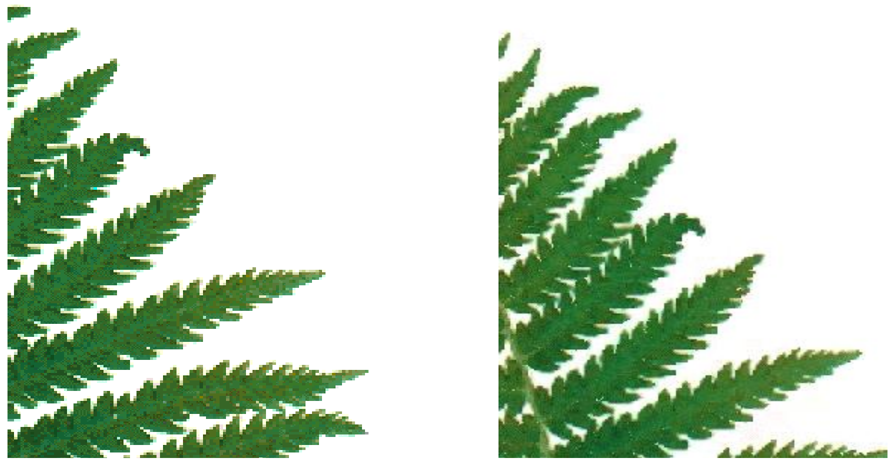
2.4.2.1 Natural fractal objects:

Fractal bronchial trees in mammals, Growth of fractal trees in nature, Optimal fractal distribution, Absolute limitations of tree distributive structures River Networks, Fractals and algometry. There some applications of fractal concepts to the study of complex systems:

Image analysis and compression, multiracial signal analysis, scaling topology of the internet, fractal aviation communication network (Abdul Salam, 2004).

2.4.2.2 Fractal compression

The fractal compression can be used to resemble real-life object, and we've discussed how it works as well. However by the goal of compressing real images into fractal images the advantage of using fractal compression is to enlarge the fractal without getting a blocky picture. That is because fractals are infinitely detailed and enlarge causes it to "smooth" the rough spots, as between two pictures of ferns below (Figure 2.5)



(a) **(b)**

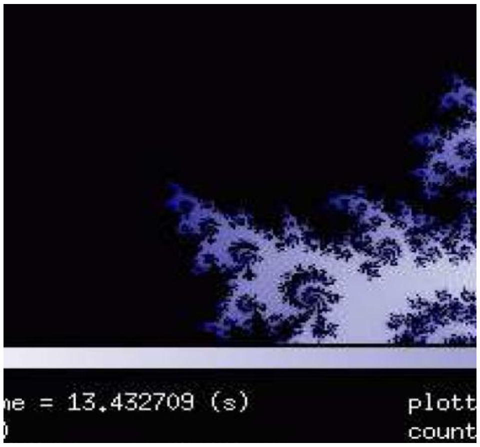
Figure 2.5 (a) Enlargement of a bitmap (left), (b) The compressed image (right)

(Chen ting and Huang liming, 2001)

The pictures show that the one on the right has more details. The one on the left is just an enlargement of a bitmap.

2.4.2.3 Fractals and procedural terrain

Fractals are naturally recursive shapes they are defined by rules that specifies how to make the shape from smaller and simpler copies of itself. Hand-crafted models of trees, buildings etc can, be made more lifelike by using recursive algorithms for placement, and to introduce slight differences between each instance of a model. Procedural generation of terrain can dramatically reduce the workload on artists responsible for the design of 3D world's e.g. video games and movies (Clem, *et.al*. 2009).



(a) **(b)**

Figure 2.6 The graph(a) and graph (b) Package application fractals, (Clem, *et.al*. 2009)

Some application of fractal theory

According to the chaos theory and fractal geometry, scientists have been able to understand how systems once thought to be completely chaotic. The most significant contributions of fractal geometry is its "capability" to model natural phenomena, such as plants, clouds, geological formations and atmospheric phenomena. Fractal theory has also contributed in such diverse fields as linguistics, psychology, image compression technology, superconductivity, circuitry and other electronic applications (Juan, 2000).