THE EFFECT OF HEAT TREATMENT

ON THE

MICROSTRUCTURE AND THE CORROSION PROPERTIES OF GREY CAST IRON

BY

ALUKO, FASAKIN ISRAEL

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ABSTRACT

Investigations were carried out to study the effect of heat treatment on the microstructures and the corrosion properties of Grey cast iron. This study was carried out to determine a suitable heat treatment process which would render Grey cast iron highly resistant to corrosion in the fluids used in paper making industries. The method adopted was by total immersion of the heat treated grey cast iron samples. The media of immersion consisted of wood pulp and white liquor. The most important conclusions drawn from the results obtained were that annealing process is the most suitable heat treatment for grey cast iron; the weight-loss of the samples increased with time of exposure into the corrosion media from the annealing temperature, the rate of corrosion attack increased with the cooling rate and that the microstructure consists mainly of graphite flakes and ferrite in a pearlite matrix. The graphite flakes posed a resistance to corrosion in the Cast Iron.

DEDICATION

This thesis is dedicated to the 'ALMIGHTY GOD' for His divine assistance throughout the work.

CERTIFICATION

I hereby certify that this work was carried out by:

MR ALUKO FASAKIN ISRAEL

in the Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, and to the best of my knowledge has not been submitted elsewhere for the award of any degree.

Dr. J. O. BORODE
SUPERVISOR

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ALUKO, F. I.
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CHAPTER ONE

INTRODUCTION

According to Alagbe (1995), corrosion is the greatest enemy of Engineers. The rate at which deterioration occurs in the construction industry and equipment/machines used in paper industries are very high. This leads to a very high cost of failure, repairs and maintenance of the equipment used in such industries.

Packman (1960) explained that wood can cause corrosion of metals by direct contact and in confined spaces, also by the emission of corrosive vapour. With rare exceptions, all woods are acidic in nature, and the principal corroding agent in both types of attack is volatile acetic acid. Since wood pulp is commonly used in paper industries, the volatile acetic acid from wood will be causing a lot of corrosion on the metal containers and other metals that are used in building the equipment/machines that are used to process the chemicals used in paper industry.

Shreir (1963) defined Corrosion Engineering as the reaction of an engineering construction metal (material) with its environment with a consequent deterioration in properties of the metal (material).

Furthermore, corrosion can be defined as a destructive attack on metals which may be chemical or electrochemical in nature. Direct chemical corrosion is limited to unusual conditions involving highly corrosive environments or high temperature or both. Examples are metals in contact with strong acids or alkalis and the formation of iron oxide by dissociation of water in contact with over-heated boiler tubes. However, most of the phenomena involving corrosion of metals containing or submerged in water, or atmospheric corrosion by films of moisture, are electro-chemical in nature. (Shreir (1963)

Cast Irons, like steels, are basically alloys of iron and carbon. In relation to the Iron-Carbon diagram, cast irons contain a greater amount of carbon than that necessary to saturate austenite at the eutectic temperature. Therefore, Irons contain between 2 and 6.67 per cent carbon. Since high carbon content tends to make the Cast Iron very brittle, most commercially manufactured types are in the range of 2.5 to 4.0 per cent carbon. The ductility of Cast Iron is very low, and it cannot be rolled, drawn, or worked at room temperature. Most of the Cast Irons are not malleable at any temperature. However, they melt readily and can be cast into complicated shapes which are usually machined to final dimensions. Since casting is the only suitable process applied to these alloys, they are known as Cast Irons. Although the common Cast Irons are brittle and have weaker strength properties than most steels, they are cheap, can be cast more readily than steel.

According to Shreir (1963), Cast Iron may not be subjected to stress corrosion cracking, although it has been discovered that this can happen with ductile irons exposed to strong caustic alkali solutions. Irons exposed under conditions of cyclic stress are, however, liable to corrosion fatigue. By its nature, it is difficult to give absolute values for resistance to corrosion fatigue since this will be affected by the duration and frequency of cycling and the corrosivity of the environment. Palmer (1972) found that corrosion fatigue due to water spray could be eliminated or mitigated by using some inhibitors, but it was apparently easier to inhibit damage on grey Cast Iron than that on ductile Irons which could only be inhibited by 0.25% Potassium Chromate solution. He suggested that this was due to an inability of the other systems to maintain a continuous passive film on the Iron; grey Cast Iron is less sensitive to a notch effect in fatigue so that the presence of local sites of attack would be less important to this metal provided that the overall corrosivity of the solution was depressed.

Ethanoic acid, which is commonly known as Acetic acid, is found in wood pulp. Acetic acid is the final organic oxidation product of ethanol. The oxidation occurs in two stages: the first to ethanal , the second to ethanoic acid. Both stages can be carried out in the laboratory by heating with chromic acid (that is Potassium dichromate in concentrated sulphuric acid).

$$CH_3 . CH_2 OH_{(aq)} \longrightarrow CH_3CHO^-_{(aq)} + 2H^+_{(aq)} + 2e^- \quad \text{---1·1}$$

$$CH_3 . CHO_{(aq)} + H_2O_{(l)} \longrightarrow CH_3 . COOH_{(aq)} + 2H^+(aq) + 2e^- \quad 1.2$$

Ethanoic acid is a weak acid, that is, it is slightly ionized in dilute solution. For example, at 0.1 Mole or 6g dm^{-3}, the acid has a degree of dissociation of 1.4%.

$$CH_3COOH_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)} \quad 1.3$$

It forms a salt with an alkali or base. When it comes in contact with iron, it forms rust.

$$2CH_3COO^-_{(aq)} + Fe^{2+} + 2OH^-_{(aq)} \longrightarrow (CH_3COO)_2 Fe + 2H_2O \quad 1.4$$

Iron rusts faster in acidic environs than in aqueous neutral solution (Shreir 1963). Since this acid is present in Wood Pulp, it makes Wood Pulp dangerous to grey Cast Iron because corrosion will automatically take place.

In the paper making industries, the processing of white liquor (lime) is invariably carried out in cast irons, steel pipes, metal containers and silos. The sodium hydroxide in white liquor is very corrosive to metals including cast iron. Consequently, upon application of stress, corrosion cracking becomes a problem as it provides high stress concentration area that may lead to material failure.

In the light of above, the need to reduce the menace of corrosion and its associated problems becomes most important.

This work, therefore, sets out to determine a suitable technique of curtailing the catastrophic result likely to occur as a result of corrosion in paper industry. The method adopted is by heat treating grey cast iron

and immersing it in the white liquor and wood pulp. The effects of the corrosion of the samples were then monitored over a pre-determined period of time.

It is hoped that the study would serve as a basis for tackling likely problems that may arise from corrosion processes in pulp and paper industry.

CHAPTER TWO

LITERATURE REVIEW

Grey Cast Iron is obtained by cooling the molten metal slowly during solidification. A large portion of its carbon is present in free state as graphite flakes. The typical Grey Cast Iron contains 2.5 – 3.5% carbon, 1.4 – 2.8% silicon, 0.5 – 0.8% manganese, 0.1 – 0.9% phosphorus and 0.06 – 0.12% sulphur (Haggins (1979). Fractured surface of Grey Cast Iron appears grey because of the presence of graphite. Hence, the alloy is termed Grey Cast Iron.

Cast Iron's tensile strength can be increased by adding 0.2 – 0.3 per cent silicon. Addition of silicon to Grey Cast Iron is carried out in the form of ferro-silicon. Tensile strength of Grey Cast Iron varies from 100Mpa to 340Mpa {Chapman and Martin (1975)}. In Grey Cast Iron, graphite flakes may be present in ferritic matrix or pearlitic matrix.

Grey Cast Iron: Properties and Uses: Some unique properties of Grey Cast Iron include:

1. Cheapness: Cast Iron is cheaper than steel, as the temperature to be attained for making it is several hundred degrees lower than that for casting steel. Also, control of impurities is not critical here, as in steel making.

2. Fluidity: It has excellent fluidity and takes mould impressions quite well.

3. Wear Resistance: The wear resistance of Grey Cast Iron is very good, as graphite flakes act as lubricant.

4. Machinability: Grey Cast Iron is easy to machine, as chip formation is promoted by the graphite flakes. In addition, the flakes serve as a lubricant for the cutting tool.

6. Damping Capacity: The Grey Cast Iron has the ability to damp vibrations more than steel.

USES OF GREY CAST IRON

1. Grey Cast Iron is used as a base for erection of machinery – this is because of its good damping capacity and the high compressive strength.

2. It is used to make internal combustion engine cylinder blocks and heads.

3. It is used to make fly wheels and counter weights for lifts.

2.1 Heat Treatment:

The heat treatment given to Grey Cast Iron may be classified into:

(i) Stress relieving.

(ii) Annealing.

(iii) Normalizing.

(iv) Hardening and tempering.

These are further discussed below:

2.1.1 (i) Stress Relieving:

The purpose of stress relieving in Grey Cast Iron is to relieve residual stresses introduced during solidification, due to different cooling rates prevalent at various sections of castings. Residual stresses adversely affect the strength and cause distortion and may even result in cracking in some cases. For maximum stress relief without changing the microstructure, a temperature range of 538 – 565°C is recommended. In this temperature range, about 80 per cent of the residual stresses are removed with holding time of about one hour. When held at 590°C, more than 85 percent of the stresses can be removed.

2.1.2 (ii) Annealing:

The purpose of annealing is to soften the Grey Cast Iron and to improve its machinability by minimizing or eliminating massive eutectic carbides. This treatment reduces the tensile strength of Grey Cast Iron. For example, grade 40 Grey Cast Iron has tensile strength of

280Mpa. After annealing tensile strength comes down to about 210Mpa in this grade of Cast Iron. The extent to which the mechanical properties are reduced depends on annealing temperature, holding time, and the alloying elements present in the Iron.

Three types of annealing treatment are given to Grey Cast Iron: full annealing, graphitizing annealing and ferritizing annealing.

2.1.3 Full Annealing:

If alloy content is high in Grey Cast Iron, then it is difficult to decompose iron carbide to ferrite and graphite at 760°C. Therefore, under such conditions, full annealing treatment is adopted. For this treatment, casting is heated to a suitable temperature between 790°C and 900°C and held for about one hour. Then it is cooled slowly between 790°C and 680°C.

2.1.4 Graphitizing Annealing:

Is carried out to convert massive carbides into pearlite and graphite. The treatment is carried out at 900 – 955°C. Holding time varies from a few to several hours depending on composition, section size, the quantity and the type of the carbides. From annealing temperature to about 535°C casting is air cooled to get pearlitic structure, and from 535°C to about 285°C, it is cooled at a rate of about 110°C/hour.

2.1.5 Ferritizing Annealing:

Is carried out to improve machinability in unalloyed or low Cast Iron of normal composition. In this treatment, pearlite carbide transforms to ferrite and graphite, the ferritizing annealing temperature is kept between 700°C and 760°C, and the recommended holding time is 1 hour per 25mm of section, depending on chemical composition.

2.1.6 (iii) Normalizing:

Normalizing is done for refining the grain structure and for improving the mechanical properties. So, the purpose of normalizing treatment for Grey Cast Iron is to improve its mechanical properties which have been modified by other heating processes such as graphitizing or pre-heat and post-heat treatment of welded joints. Normalizing temperature is kept above transformation range, i.e. 885 – 925°C. Holding time recommended for Grey Cast Iron at normalizing temperature is about one hour per 25mm of maximum thickness.

Heating temperature significantly affects the mechanical properties, e.g. hardness, tensile strength and, also the micro-structure. Alloying elements such as chromium, molybdenum and nickel enhance the strengthening due to

normalizing. {According to Rajan Sharman G. P. and Sharman (1964)}

2.1.7 (iv) Hardening and Tempering

The purpose of hardening and tempering in Grey Cast Iron is to improve its strength and wear resistance. After this treatment, the wear resistance of pearlitic Grey Cast Iron is furnace or salt-bath hardened from a temperature of about 860° – 870°C. The transformation range of a particular Grey Cast Iron decides the temperature to which the casting is to be heated.

The quenching media used may be water, oil, or salt bath. But oil is the popular quenching medium for Grey Cast Iron. For furnace hardened, Grey Cast Iron, water is not preferred as quenching medium because the heat dissipation is so fast that it may cause distortion and cracking in castings. Water soluble polymer quenchants can provide the convenience of water quenching along with slower cooling rates which can reduce the effect of thermal shocks. High alloy Grey Cast Irons can be air quenched. The quenched Grey Cast Iron may be tempered by re-heating to a suitable temperature in the range 150° – 650°C. Tempering treatments increase the toughness and

relieve internal stresses which may be developed during quenching. Due to tempering, hardness decreases.

To achieve maximum toughness in Grey Cast Iron, a tempering temperature of about 370°C is recommended. After tempering at this temperature, the matrix retains a hardness level of 472 BHN. Increase in wear resistance in Grey Cast Iron is achieved by producing a structure consisting of graphite embedded in a martensitic matrix through heat treatment, soft graphite acts as a lubricant.

2.2 Iron-Carbon Diagram:

In Fe-C alloys, carbon may be present in the form of free carbon (graphite) or as iron carbide. The most frequently occuring form in steels is iron carbide known as cementite. The phase diagram in Fig.1. shows Fe and Fe_3C as the two components (Haasen, 1986). In the phase diagram, temperature is plotted against composition. Any point on the diagram, therefore, represents a definite composition at a given temperature. The iron-carbon diagram is used to determine the microstructure of an alloy, and the constituents that are present as it is slowly cooled from the liquid state to solid state. However, it must be understood that this diagram applies only to changes that occur under equilibrium conditions i.e. very slow cooling or

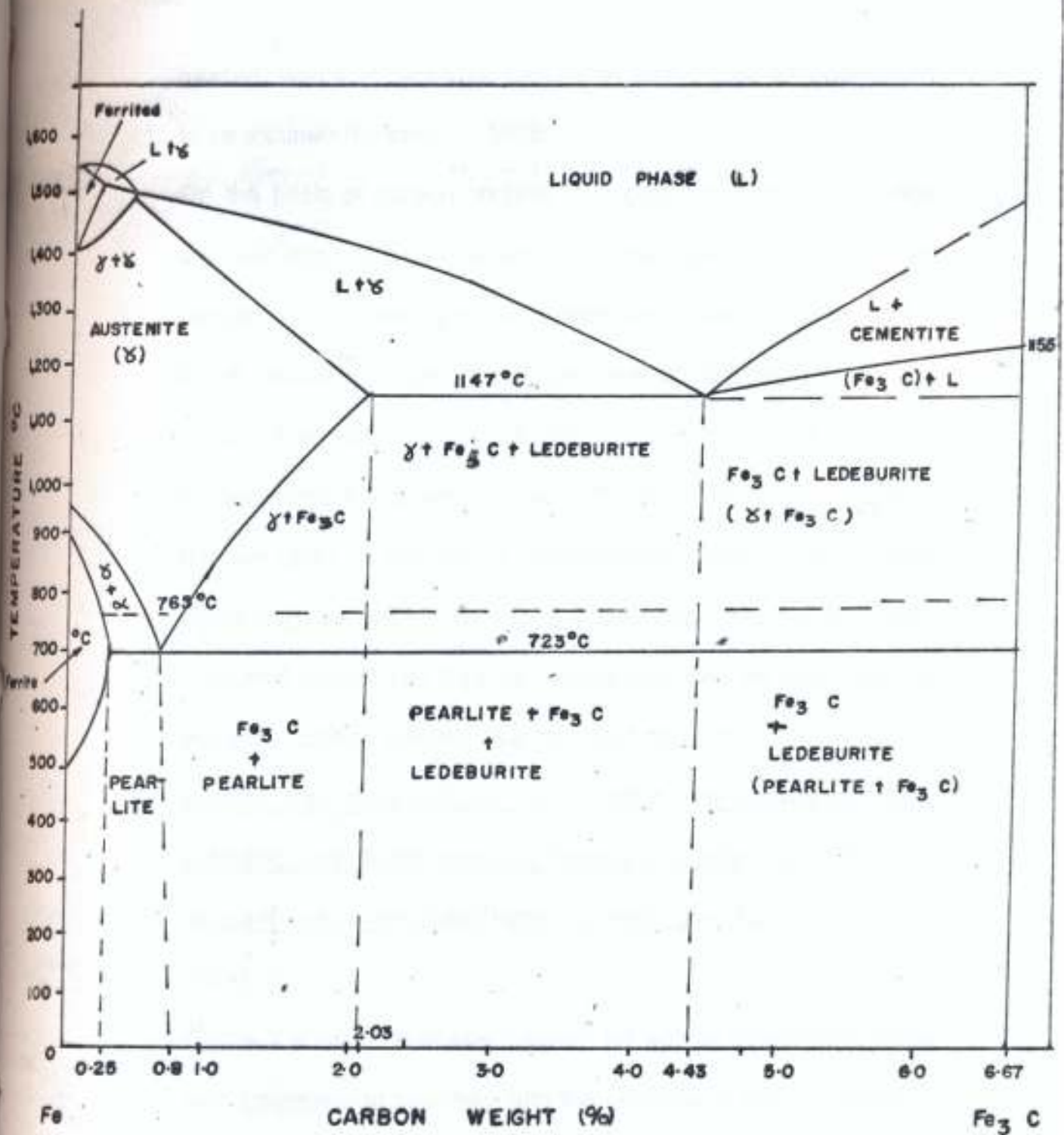


FIG.1 EQUILIBRIUM DIAGRAM OF IRON – CARBON SYSTEM

(ACCORDING TO AVNER 1964)

heating, with sufficient time allowed at each stage for equilibrium to be attained (Haasen 1986).

On the basis of carbon content, it is common practice to divide the iron-iron carbide diagram into two parts. Those alloy, containing less than 2 per cent carbon are known as steels, and those containing more than 2 per cent carbon are called Cast Irons. The steel range is further subdivided by the eutectoid carbon content (0.8 per cent carbon), steels containing less than 0.8 per cent C are called hypo-eutectoid steels, while those containing between 0.8 and 2.0 per cent are called hyper-eutectoid steels. The Cast Iron range may also be subdivided by euctectic carbon content (4.3 per cent carbon). Cast Irons that contain less than 4.3 per cent carbon are known as hypo-eutectoic Cast Irons, whereas those that contain more than 4.3 per cent carbon are called hyper-euctectic Cast Iron. (Avner 1964).

Figure 1 shows the phase diagram for Iron in equilibrium, firstly, with graphite and secondly with the reasonably stable compound cementite (Fe_3C). Fe_3C is orthorhombic in structure and has a unit cell containing 12Fe and 4 carbon atoms. The differences in the two phase diagrams are quite small except in the Cast Iron region, i.e. the region that shows the melting point of Fe – C alloys in the neighbourhood of the euctectic. The euctectic

ledeburite and the eutectoid reaction (formation of pearlite); in addition, there is a peritectic reactions at high temperatures and low carbon contents as well as a low temperature metastable phase, martensite (not shown in the phase diagram).

2.3 Phases in Fe-C System

- Ferrite: is an interstitial solid solution of carbon in BCC Iron. It is stable over the temperature range of 273 to 910°C. It is the softest structure that appears on the diagram. (Haasen 1986)

Average properties are:

Tensile strength, 400 N/mm^2 elongation, 40 per cent in 2 inches hardness, less than Rockwell B90. (Avner 1964)

Ferrite BCC: Is stable from 1294°C to 1535°C, the melting point of iron. The maximum solubility of carbon is 0.09 wt%. (Haasen, 1964)

Cementite: Is an intermetallic compound with the formular, Fe_3C. The atom per cent of carbon in cementite is 25 but the weight per cent is 6.67. It is a typical hard and brittle intestitial compoundd of low tensile strength (approx 4,000N/mm^2) but high compressive strength. It is the hardest structure that appears in the diagram. Cementite has a complex orthorhombic crystal structure, with twelve iron atoms and four carbon atoms in the unit cell. (Avner 1964) and (Haasen 1986)

Austenite: Is the name given to the γ-solid solution. It is an interstitial solid solution of carbon dissolved in γ (F.C.C.) Iron. Maximum solubility is 2 per cent at 1146°C.

Average properties are:

Tensile strength, 1,500N/mm^2 elongation 10 per cent in 5 centimetres hardness, Rockwell C40 approximate, and it has a high toughness. It is normally not stable at room temperature, under certain conditions, it is possible to obtain austenite at room temperature.

Pearlite: Is the eutectoid mixture containing 0.8 per cent C and is formed at 723°C on a very slow cooling. It is a very fine plate-like or lamella mixture of ferrite and cementite. Average properties are: Tensile strength, 1,200 N/mm^2 elongation, 20 per cent in 2 inches; hardness – Rockwell C20, or Rockwell B95 – 100 or BHN 250 – 300.

Ledeburite: It is the eutectic mixture of austenite and cementite. It contains 4.3 per cent carbon and is formed at 1146°C. (Avner, 1964)

Graphite: Has a hexagonal lattice structure, in which sheets of primarily bonded carbon atoms are held together by secondary bonds. (Avner 1964)

2.4 STRUCTURAL CHANGES DURING TRANSFORMATION

In almost all the heat-treating procedures, iron alloys are heated to temperatures corresponding to the region in which it exists in the form of austenite. Where there is a diffusion process which adheres to the general principles of crystallization theory. (Alan 1975)

Structural changes during transformation can be best described by considering a portion of iron-carbon diagram relevant to heat-treatment of iron alloys.

Considering the transformation of a ferrite cementite mixture (pearlite) into austenite. When steel (eutectoid steel, 0.8%C) is heated to a temperature of 727°C, a certain amount of cementite is dissolved in the ferrite. As the temperature is raised above 727°C, the carbon content in certain portions of the ferrite increases. Such portions of the ferrite are unstable and undergo transformation into austenite which is stable at the given temperature. Austenite nuclei are formed at the interfaces between the ferrite and cementite as shown in fig. 2. (Alan 1975)

If iron alloys with an austenite structure, obtained by heating to a temperature above 850°C is super cooled to a temperature below 727°C, the austenite is in a metastable state and undergoes a transformation. The kinetics of super cooled

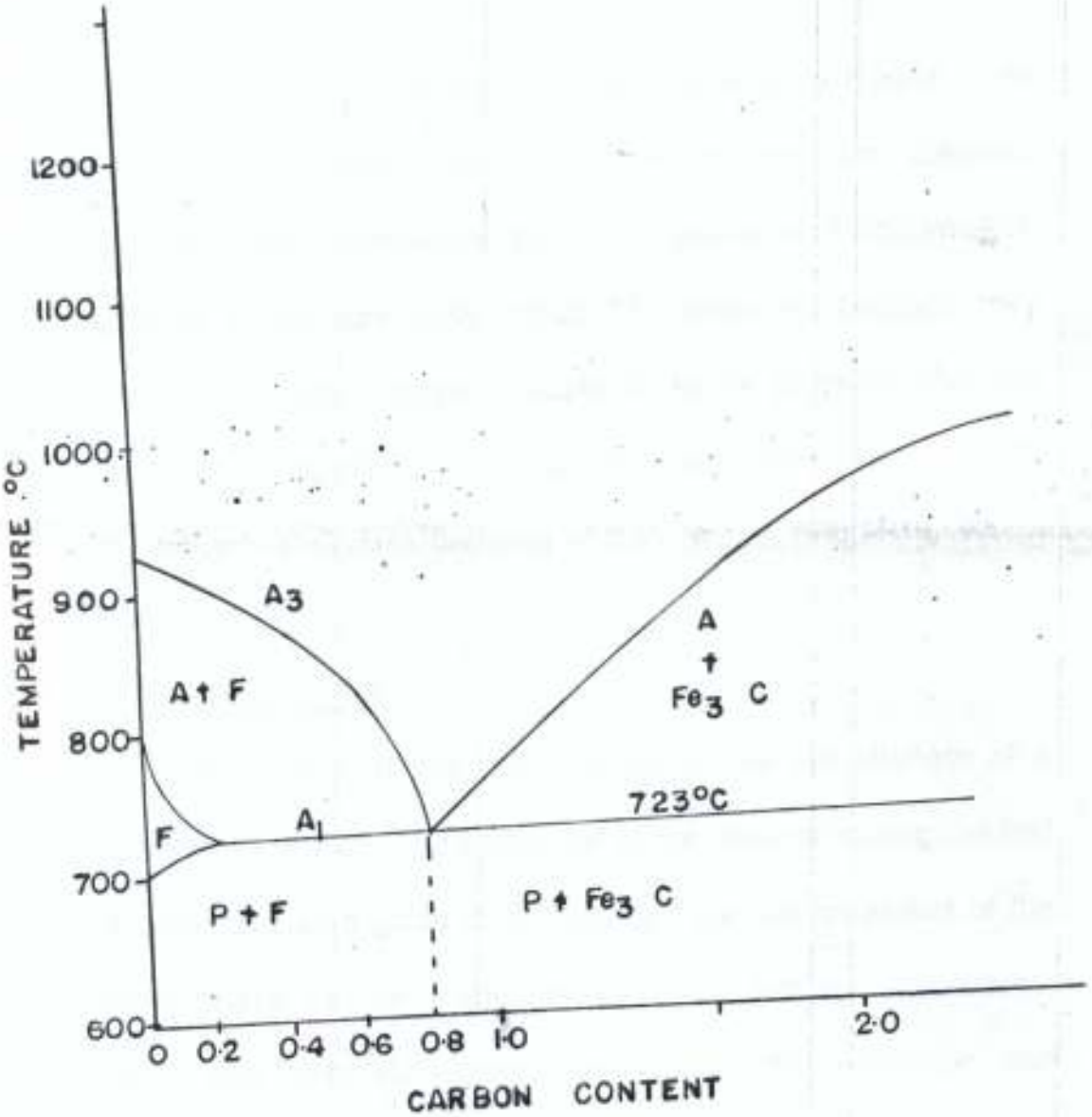


FIG. 2 IRON – CARBON DIAGRAM
(ACCORDING TO CHAPMAN AND MARTINS) (1975)

A — AUSTENITE

C — CEMENTITE

P — PEARLITE

F — FERRITE

austenite transformation can best be described by means of an experimentally plotted time-temperature transformation diagram, or isothermal (constant-temperature) austenite transformation diagram (more commonly called TTT diagrams because they relate the transformations of austenite to the pertinent time and temperature conditions). Such diagrams are also called S-Curves and C-Curves because of their shape. (Fig.2B) (Alan 1975)

2.5 THE TENSILE TEST

The object of this test is to determine the strength of a material in tension. The behaviour of the material during the test is also used as a guide to its ductility. Various properties of the material that can be determined by tensile test are yield stress, upper and lower yield points, tensile strength, elongation, and reduction in area.

The test is carried out in a tensile testing machine on a specimen (test piece) previously prepared from the material to be tested. The dimensions and form of the specimen vary according to the size and shape of the material to be tested; flat test pieces being used from strip or flat bars and round specimens from round – section bars, etc.

The gauge length bears a fixed relationship to the test area, i.e. gauge length = $5.65\sqrt{A}$.

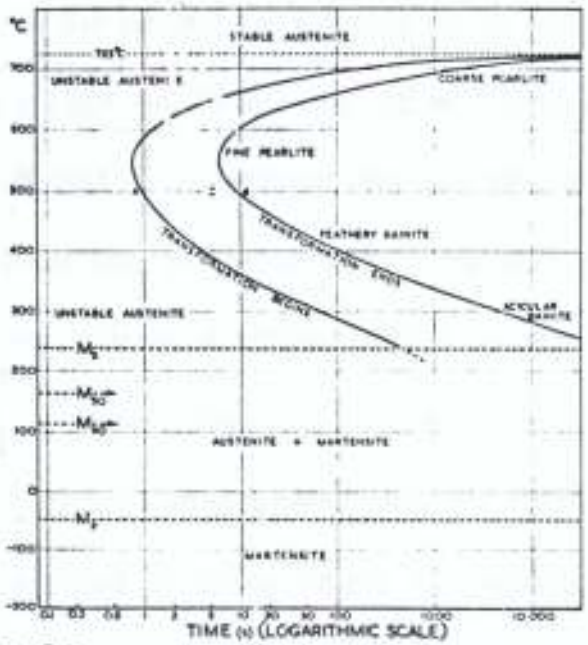


FIG. 2.8—Time–Temperature–Transformation (T.T.T.) Curves for a Plain Carbon Steel of Eutectoid Composition.

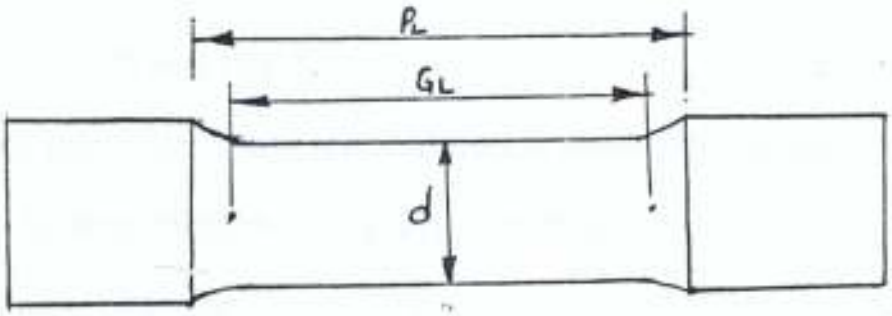


FIGURE 3: Tensile test piece.

(Chapman and Martin 1975)

d = Diameter

P_L = Parallel Length

G_L = Gauge Length = $5.65\sqrt{A}$.

Where A = $\frac{\pi d^2}{4}$

The reduced centre portion is the test part proper, the ends being for the purpose of gripping in the machine. The extremities of the gauge length are marked with centre-punch dots so that, when a test is completed and the specimen is stretched, the elongation can be measured. The test diameter is joined to enlarged ends by a smooth radius because, if the corners were sharp, a concentration of stress might occur at this point of sudden change in diameter, and the fracture would take place there instead of some where the gauge-length points. This occurrence would prevent any accurate reading of the elongation and might also give a false reading for the breaking load (Higgins 1979 and 1991)

The results generally required from a commercial tensile test are as follows: (Higgins (1979) and (1991)

(a) Tensile Strength:

This is found by dividing the maximum load by the original cross-sectional area of the specimen. (Note that for ductile materials, the maximum load maybe greater than the breaking load.

(b) Elongation Percentage

This is given by expressing the stretch as a percentage of the original test length.

$$\text{i.e. } \frac{\text{Stretch}}{\text{Original length}} \times \frac{100}{1}$$

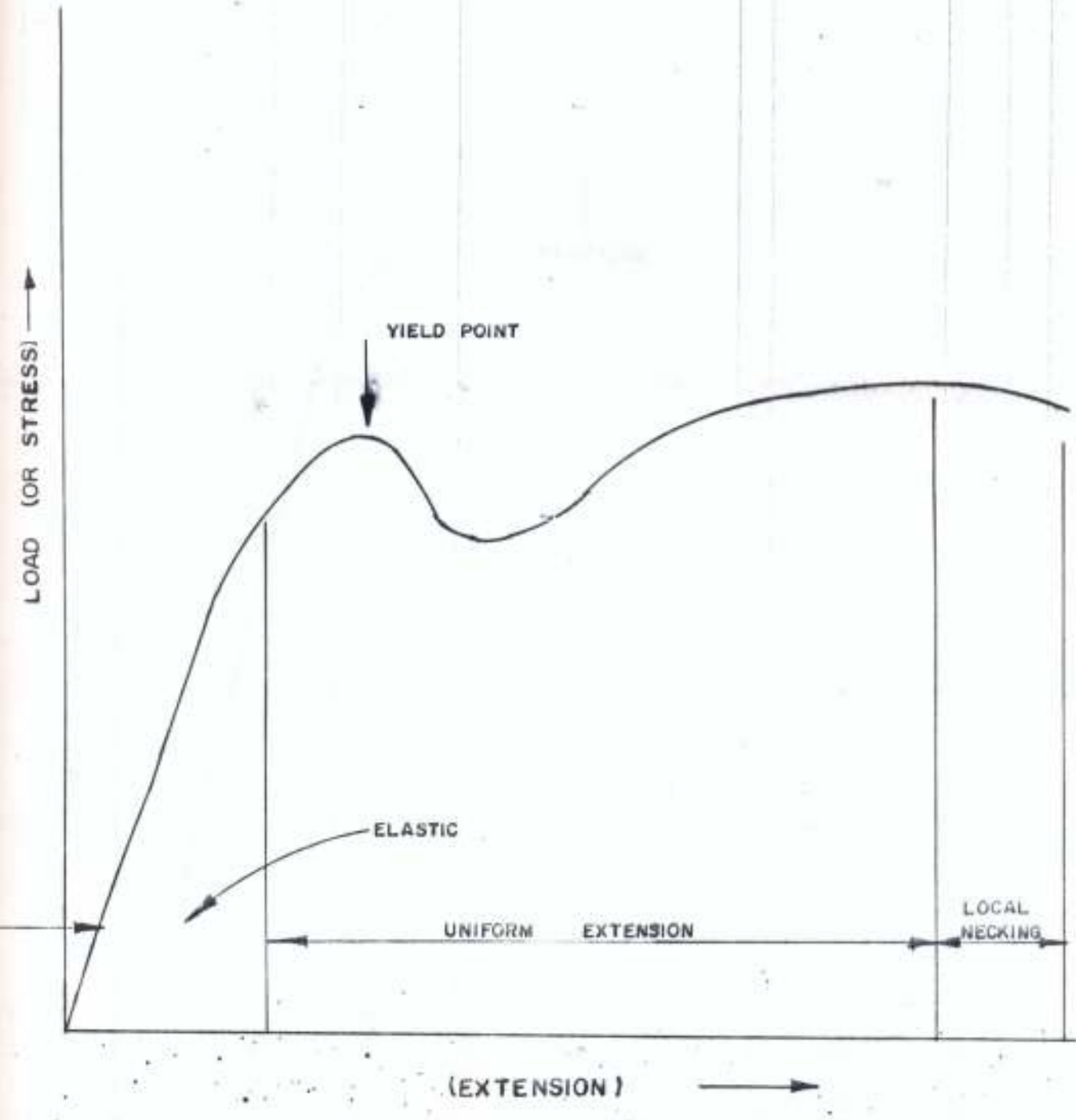


FIG. 4 LOAD (OR STRESS) Vs. EXTENSION GRAPH (FOR DUCTILE STEEL)
(ACCORDING TO CHAPMAN (1975))

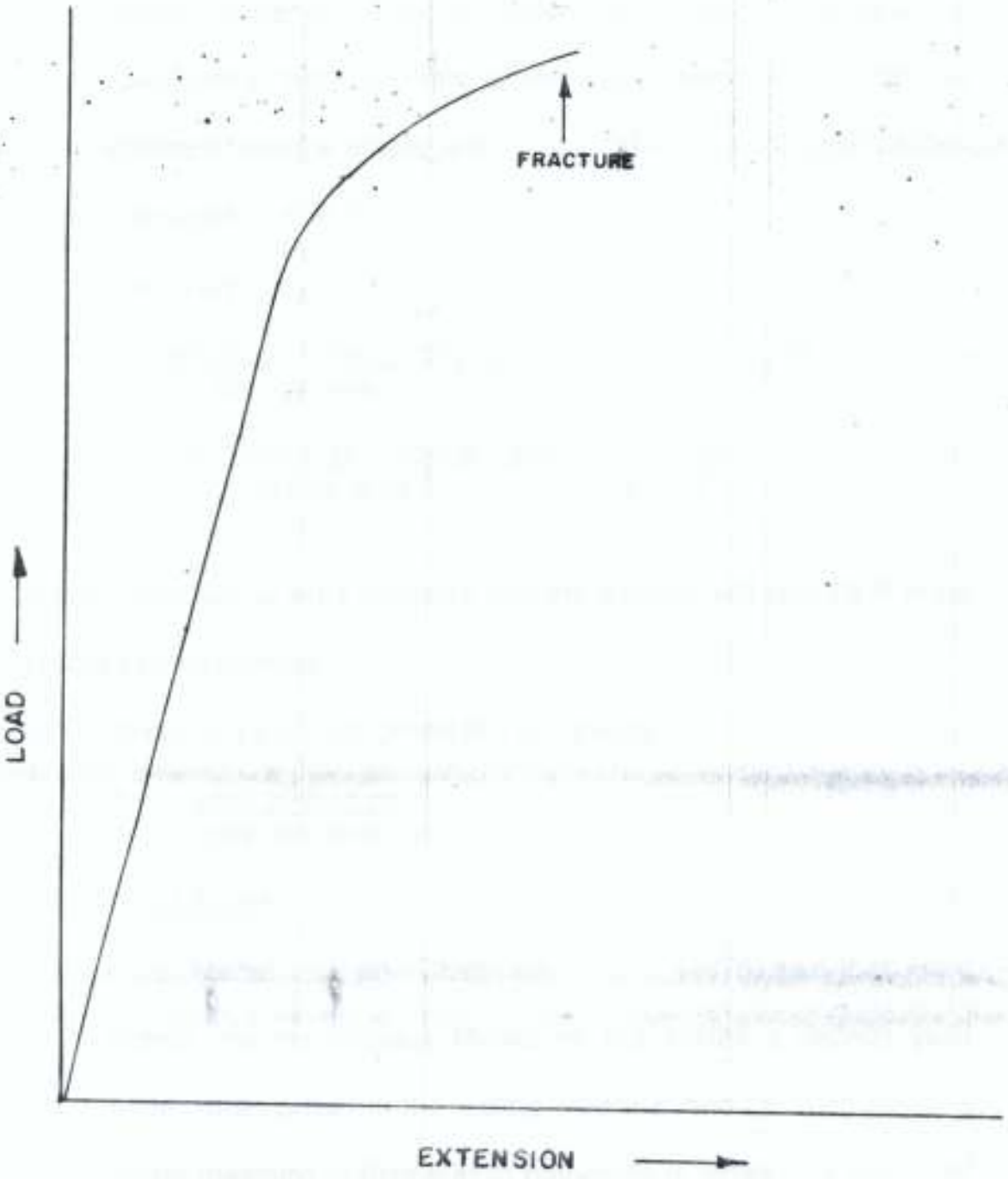


FIG. 5 LOAD VERSUS EXTENSION GRAPH
(FOR HARD STEEL)
(ACCORDING TO CHAPMAN)
(1975)

Good elongation combined with a reasonable strength indicates a ductile material. Besides these two main properties, a specification may stipulate other requirements which may be obtained from the tensile test:

(c) Reduction in area %

This is given by

$$\frac{\text{reduction in area at fracture}}{\text{original area}} \times \frac{100}{1}$$

$$= \frac{\text{Original area} - \text{area at fracture}}{\text{original area}} \times \frac{100}{1}$$

A high reduction of area indicates that the material will lend itself more readily to cold working.

(d) Stress at yield point (when this is present)

$$= \frac{\text{Load at yield point}}{\text{cross-sectional area}}$$

2.5.1 Proof Stress

Martin and Chapman (1975) said that: Hard Steels and non-Ferrous Metals do not exhibit a definite yield point, when pulled in the testing machine, and for such cases a better measure of their elastic properties is defined by the Proof Stress.

This is the stress necessary to cause a certain permanent elongation to the test piece (generally about 0.1%), and the method of determining it is shown in Figure 6.

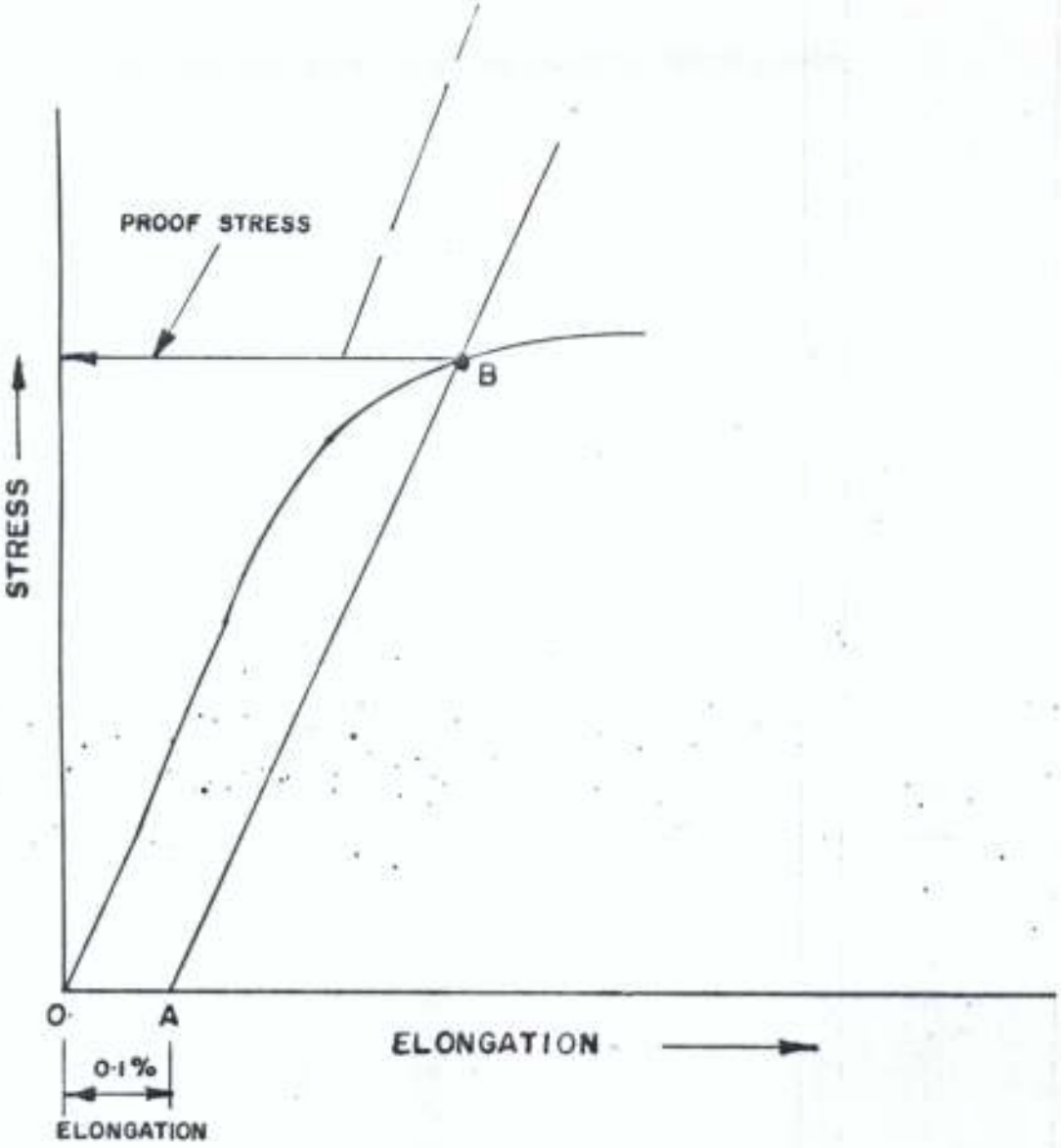


FIG.6 PROOF STRESS

(ACCORDING TO CHAPMAN)
(1975)

From the figure, point A is first determined, where OA represents the percentage elongation, and then from A, a line AB is drawn parallel to the elastic line of the stress strain diagram. The point B where this line cuts the curve gives the proof stress.

2.6 CORROSION OF METALS

Corrosion may be described as a destructive attack on metals which may be Chemical or electro-chemical. Under most ordinary conditions of exposure, the corrosion products comprise mainly of oxides (more or less hydrated), carbonates, and sulphides. At high temperatures the products consist mainly of oxides, though indications are that corrosion of this type also progress more rapidly when some mo sture is present. Corrosion may be entirely superficial or may attack the inter-crystalline boundaries and cause disintegration in the metal, as dezincification of brass or so called caustic embrittlement in boiler steel.

2.6.1 Mechanism of Corrosion

Every metal when placed in water has the tendency to go into solution. The acidity of the water determines the initial speed of attack. As in all electrochemical couples which form over the surface of the metal, become polarized due to the accumulation of hydrogen on cathodic surfaces. This action may stop corrosion process. In the case of iron in acqueous media, ferrous hydrated film forms on the metal, retards the rate of dissolution of the metal.

2.7 Factors Controlling Corrosion

The main factors influencing corrosion are listed below:-

(a) Primary factors – Having to do mainly with the metal

1. Effective electrode potential of the metal in solution.
2. Chemical and physical homogenity and texture of its surface.
3. Its inherent ability to form an insoluble protective film.
4. Over voltage of hydrogen on the metal surface.

(b) Corrosion Factors which vary with Environment

1. Hydrogen – ion activity pH in the solution.
2. Effective supply of oxygen in the solution adjacent to the metal.
3. Distribution of available oxygen on the metal surface.
4. Specific nature, concentration, and distribution of other ions in the solution.
5. Effective rate of flow of the liquid past the metal surface.
6. Presence of solid particles (dirt), or a coating of any kind, as mill scale, on the metal surface, or contact with other conducting material in the presence of an electrolyte.
7. Temperature.

8. Whether the metal is under static stress or cyclic alternating stress – i. e corrosive fatigues.
9. The ability of environment to build up protective films on the metal.
10. Biological influence.

2.8 WOOD

Wood is particularly valuable for certain conditions which are corrosive to common metals (acids, external exposure) and for contact with food stuffs or beverages. Wood is not subject to corrosion in the electro-chemical sense of the term applied to metals, but it can be attacked by chemicals (particularly alkalis and oxidizing agents) and is subject to biological attack, a hazard not encountered with most other structural materials. (Packman 1960)

2.8.1 COMPOSITION, STRUCTURE AND NOMENCLATURE

Wood is a naturally formed organic material consisting essentially of elongated tubular elements called cells arranged in a parallel manner for the most part. These cells vary in dimensions and wall thickness with position in the tree, age, conditions of growth, and kind of tree. The walls of the cells are formed principally of chain molecules of cellulose, polymerized from glucose residues and oriented as a partly crystalline material. These chains are aggregated in the cell wall at a

variable angle, roughly parallel to the axis of the cell. The cells are cemented by an amorphous material called lignin. The complex structure of the gross wood approximates a rhombic system. The direction parallel to the grain and the axis of the stem is longitudinal (L), the two axes across the grain are radial (R) and tangential (T) with respect to the cylinder of the tree stem. This anisotropy and the molecular orientation accounts for the major differences in physical properties with respect to direction which are present in wood. (Packman 1960)

Timber is classified broadly as hardwood, which is produced by the broad-leaved trees (angiosperm), such as oak, maple, ash: soft wood, which is the product of coniferous trees (gymmosperms), such as pines, larch, spruce, harmlock.

Standard Nomenclature

The standard nomenclature of timber is based on commercial practice which groups woods of similar technical qualities but separate botanical identities under a single name.

The chemical composition of woody cell walls is generally about 40 to 50 per cent cellulose, 15 to 35 per cent lignin, less than 1 per cent mineral, 20 to 35 per cent hemicellulose, and the remainder extractable matter of a variety of sorts. Soft woods and hard woods have about the same cellulose content.

2.8.2 MOISTURE RELATIONS

Wood is a hygroscopic material which contains water in varying amounts, depending upon the relative humidity and temperature of the surrounding atmosphere. The standard reference condition for wood is ovendry weight, which is determined by drying at 100 to 105°C to constant weight.

Resistance of wood to chemical action

The resistance of wood to chemical action is best in the less permeable heartwood of the conifers. Aqueous solutions of sodium hydroxide, sulphuric, hydrochloric, and nitric acids cause most damage, since swelling and degradation are simultaneous. Temperature changes for a given solution act roughly with the logarithm of time.

Submersion of timber in water

This will prevent fungus action as noted but will eventually cause deterioration of wood due to hydrolysis of the cellulose. This change correlates with strength tests in bending and compression.

2.9 The Corrosion of metals by Wood

Wood can cause corrosion of metals by direct contact and, in confined spaces, also by the emission of corrosive vapour. With rare exceptions, all woods are acidic, and the principal corroding agent in both types of attack is volatile acetic acid.

{Shreir 1963 (Vol.2)} Acetylated polysaccharides form part of the structure of wood, the acetyl radical constituting some 2 – 5% by weight of the dry wood. Hydrolysis to free also known as ethanoic acid occurs in the presence of moisture at a rate varying from one species to another; a wood of lower acetyl content can liberate acetic acid much faster under given conditions than another wood of higher content. Small quantities of formic, propionic and butyric acids are also formed, but their effect can be neglected in comparison with that of acetic acid. (Shreir (Vol.2) 1963)

2.9.1 Chemical Nature of Acetic Acid

Ethanoic acid is commonly known as acetic acid. It is the final organic oxidation product of ethanal. The oxidation occurs in two stages: the first to ethanol, the second to ethanoic acid. Both stages can be carried out in the laboratory by heating with chromic acid. (That is, potasium dichromate in concentrated sulphuric acid). (Holderness and Lambert 1978)

$$CH_3.CH_2OH_{(aq)} \rightarrow CH_3.CHO_{(aq)} + 2H^+_{(aq)} + 2e^- \quad 2.1$$

$$CH_3.CHO^-_{(aq)} + H_2O \rightarrow CH_3.COOH_{(aq)} + 2H^+_{(aq)} + 2e^- \quad 2.2$$

Ethanoic acid is a weak acid, that is, it is slightly ionized in dilute solution. For example, at 0.1 mole or 6g dm^{-3}, the acid has a degree of dissociation of 1.4%;

$$CH_3\,COOH_{(aq)} \longrightarrow CH_3\,COO^-_{(aq)} + H^+_{(aq)} \quad 2.3$$

It forms a salt with an alkali or base.

$$2CH_3COOH^- + Fe^{2+} + 2OH^-_{(aq)} \rightarrow (CH_3COO)_2Fe + 2H_2O \quad \text{---} \quad 2.4$$

When it comes in contact with iron, it forms rust.

Contact corrosion may be reduced by the presence of natural inhibitors, such as tannins, in the wood, and will be promoted by sulphates and chlorides in it, especially if mineral preserving processes involving these ions have been applied.

2.10 Less and More Corrosive Woods

Table 1 shows the list of woods whose aggressiveness by vapour corrosion has been quoted in a survey (according to Rance and Cole 1950), together with typical pH values of the aqueous extracts of these woods as reported in another investigation. (Gray 1958)

While certain reservations must be kept in view (i.e. there is necessarily no correlation between pH and corrosivity, and of pH values, which might well be even wider if differences in duration of seasoning were taken into account), the results of vapour corrosion tests nevertheless indicate a general correlation between pH values and the corrosiveness of wood vapours. It may reasonably be concluded that a strongly acid wood, pH less than 4.0, is

TABLE 1: Relative Corrosivity of Wood by Vapour Corrosion

Wood	Classification in Defence Guide - 3A	Typical pH values
Oak	most corrosive	3.35,3.45,3.85,3.9
Sweet chestnut	most corrosive	3.4,3.45,3.65
Steamed European beech	moderately corrosive	3.85,4.2.
Birch	" "	4.85,5.05,5.35
Douglasfir	" "	3.45,3.55,4.15,4.2
Gahoon	" "	4.2,4.45,5.05,5.2
Teak	" "	4.65,5.45
Western red cedar	" "	3.45
Parana pine	Least corrosive	5.2 to 8.8
Spruce	" "	4.0,4.45
Elm	" "	6.45,7.15
African	Least corrosive	5.1,5.4,5.55,6.65
Mahogany Walnut	" "	4.4,4.55,4.85,5.2
Iroko	" "	5.4,6.2,7.25
Ramin	" "	5.25,5.35
Obeche	Least corrosive	4.75,6.75

Ref: Gray, (1958)

potentially dangerous, and a less acid wood, pH more than 5.0, is likely to be relatively safe.

Heat treatments of wood are dangerous, (Chapman and Martin 1975) for although existing acid vapours may be expelled, further vapours are formed by accelerated hydrolysis. Volatile acid hardeners such as hydrochloric acid and formaldehyde (which oxidises to formic acid) present in glues and plywood contribute to vapour corrosion, as can varnishes and paints.

Wood preservatives appear not to affect emission of corrosive vapours from wood, suggesting that the hydrolysis of acetyl polysaccharides is chemical, not biochemical. Some copper base preservatives can give enough leachable copper ions to cause galvanic corrosion of other metals, notably aluminium and steel.

2.11 Metals Affected by Corrosion from Wood

The metals most susceptible to corrosion by wood are steel, zinc, cadmium, magnesium alloy and lead. The susceptibility of zinc and cadmium is no argument against the galvanising or cadmium plating of steel, since these coatings reduce the rate of corrosion of steel by contact with wood or wood vapours, although they will not give the high degree of protection

which they provide in open exposure to marine or tropical atmospheres.

Aluminium is relatively resistant. So also are copper, brass, tin and stainless steel, but these metals should not be used as thin coatings on mild steel as they promote rusting at any point of breakdown.

2.12 Practical Conclusions

Contact Corrosion – Nails and Fastenings in many non-durable wooden articles exposed to damp will outlive the useful lives of the articles, and their corrosion is of no great importance.

Corrosion is, however, important in life and pattern nails in roofs, fences and other more permanent structures. Unprotected steel should never be used. Galvanized steel is much better, and brass, copper, the more corrosion-resistant alloys of aluminium, and stainless steel, are likely to give even longer service.

Vapour Corrosion: The best way to pack articles made of metals susceptible to vapour corrosion is in boxes made of metal or of those plastics which do not themselves emit corrosive vapours. (Rance and Cole 1958)

2.13 Effect of Structure and Composition on Corrosion Resistance

An essential difference may be observed between the behaviours of steel and cast iron components immersed in an environment in which rust is precipitated at some distance from the corroding

surface. (Shreir, 1963) The steel will waste away at a steady rate and its overall dimensions will steadily diminish, whereas cursory examination of the cast iron may suggest that it has not corroded at all, since its dimensions appear to be substantially unchanged. This difference arises from the fact that the cast iron contains in its microstructure several more or less corrosion – resistant components which are largely or completely absent from the microstructure of steel. The most important of these corrosion resistant micro-constituents, are graphite, phosphide eutectic, and, to a lesser extent, carbide. When the cast iron corrodes in such a way that the corrosion product is deposited at some distance from the corroding surface, a stiffened, in the case of phosphorous irons, by phosphide eutectic cells and plugged by the carbonaceous debris resulting from the decomposition of the pearlite, silicic acid derived from the oxidation of the silicon dissolved in the iron, and whatever rust is precipitated relatively close to the metal. This skeleton, although much inferior in strength to the original iron, nevertheless retains sufficient strength to resist moderate erosion and may preserve the original contour of the component quite well.

The amount of graphitic residue retained on a corroding surface depends partly on the morphology of the graphite and partly on the corrosivity of the medium. In general, a coarse flake

graphite tends to give a more permeable and less strong residue than a finer graphite.

For example, while flake graphite iron retains virtually all the graphitic residue when corroded in 0.5% sulphuric acid, the residue from a nodular graphite iron is largely detached; in 0.05% sulphuric acid, however, there is little difference in the amounts retained by the two irons. The effect of the graphite in the iron on the corrosion process depends on the residue thickness, thus in 0.5% acid, graphite stimulates attack on the nodular graphite iron because of its ability to act as an efficient cathode for hydrogen evolution, but in 0.05% acid, once the residue thickness reaches about 0.1mm the attack tends to become stiffed. An interesting side light on this aspect is that flake graphite irons exposed in hot 70% sulphuric acid often do not evolve hydrogen, but in 0.5% acid, once the residue thickness reaches about 0.1mm the attack tends to become stiffed. This surprisingly is apparently absorbed by the graphite, presumably because of the high surface tension forces involved in bubble formation in this medium.

2.14 Corrosion by Waters

The corrositivity of a natural water depends on the concentration and type of impurity dissolved in it and especially on its oxygen content. Waters of similar corrosivities, e.g.. well-aerated quiescent sea-water corrodes cast iron at the rate of 0.05

– 0.1mm/y while most well-aerated quiescent 'fresh' waters corrode iron at 0.01 – 0.1mm/y.

Those waters in which the carbon dioxide content is in excess of that required as bicarbonate ion to balance the bases present are among the most dangerous of the 'fresh' waters. Hard waters usually, though not invariably, deposit a carbonate scale and are generally not appreciably corrosive to cast iron, corrosion rates of less than 0.2mm/y being frequently encountered. Water-softening processes do not increase the corrosivity of the water provided that the process does not result in the development of an excess of dissolved carbon dioxide.

Waters of pH less than 6 may be expected to be corrosive, but, because any weak acids present in the solution may not be fully ionised, it does not follow that water of pH greater than 7 will not be corrosive. Mine waters are particularly corrosive to cast iron, often to such an extent as to preclude their use, because of their relatively high acid content, derived from the hydrolysis of ferric salts of the strong acids, mainly sulphate, and because the ferric ion can act as a powerful cathodic depolariser.

While well-aerated near-neutral waters are normally much more corrosive than less-well-aerated waters, waters with near zero oxygen contents may cause high rates of corrosion if active sulphate reducing bacteria, which can act as very efficient

depolarising agents, are present. A corrosion rate of 1.5mm/y has been observed on cast iron exposed to such a water. (Shreir 1963)

2.15 Corrosion by Acids

Unalloyed grey or white cast irons possess no useful resistance to dilute mineral acids. In very dilute acids the presence of air, or other oxiding agents such as ferric salts, appreciably increases the corrosion rate. If corrosion rates are to be held below 0.22mm/y in moderately aerated solutions, it is unwise to exceed a total acid concentration of 0.001M, irrespective of the acid concerned.

2.16 Corrosion by Alkalis

Dilute alkali solutions do not corrode cast iron at any temperature, but hot solutions exceeding about 30% concentration will attack it, with an accompanying evolution of hydrogen, to form a ferrite. Its corrosion rates are to be held below 0.2mm/y the temperature should not exceed 80°C. Corrosion rates may range as high as 1.25 – 2.5mm/y in boiling solutions of more than 50% concentration. Molten caustic soda (650°C) may attack cast iron initially at rates around 20mm/y, but it is probable that this figure decreases somewhat after a few days. In spite of these high corrosion rates, caustic-concentration and fusion pots are made from cast iron, since the material is relatively cheap, and the thick

wall necessary for mechanical strength also gives the pot long life. It is of the utmost importance to ensure that concentration and fusion pots are cast in sound metal, as any unsoundness, particularly at the bottom of the pan, will lead to pitting attack and premature failure. The addition of 1 to 3% nickel to metal for these castings is said to be beneficial. Indeed the addition of Ni and Cr to grey cast iron gives a high resistant than when the gray cast iron is unalloyed.

2.17 Effects of Metalurgical Structure on Corrosion

(a) Effect of Crystal Defects on Corrosion

There are two quite distinct ways in which crystal defects can affect corrosion behaviour. Firstly, they might be expected to have an effect when corrosion occurs under conditions of active (film-free) anodic dissolution and is not limited by the diffusion of oxygen or some other species in the environment. But the effect of crystal defects might be expected to be minimal if the rate of active dissolution is controlled by the rate of oxygen diffusion.

Secondly, crystal defects might be expected to affect the corrosion behaviour of metals which owe their corrosion resistance to the presence of thin passive or thick protective films on their surface. Finally, it should be noted that in both cases, the effect of crystal defects and

microstructural features must, in general, tend to make the corrosion less uniform and more localized. (Standard Handbook for Mechanical Engineers, 1916)

2.18 The Microstructure of Cast Iron

Higgins (1991) stated some structures which are possible for Cast Irons of different compositions and treatments. Among these are:

(a) Primary Cementite and Pearlite

(b) Primary Cementite, Graphite and Pearlite

(c) Graphite and Pearlite

(d) Graphite, Pearlite and Ferrite

(e) Graphite and Ferrite.

(a) Primary Cementite and Pearlite

A cementite-austenite eutectic structure forms at 1131°C and as the alloy cools to 723°C the austenite transforms to pearlite. The primary cementite and pearlite structure which is hard, white, low-silicon irons is found also in other types of iron which have been chilled.

(b) Primary Cementite, Graphite and Pearlite

These are mottled irons of such compositions that cause small changes in either composition or cooling rate. They will favour the formation of either cementite or graphite. The remaining austenite present at 723°C transforms to pearlite.

(b) Graphite and Pearlite

This structure contains a high-duty Grey Cast Iron which has solidified as a graphite ausenite eutectic and the austenite in it has transformed to pearlite at 723°C.

(d) Graphite, Pearlite and Ferrite

This is a coarser Grey Iron which is weaker and softer. The silicon content is high. Here the graphite austenite eutectic has cooled slowly enough through the eutectoid temperature (723°C) for some of the carbon which has dissolved in the austenite to deposit on to the existing graphite flakes leaving a matrix of ferrite. Some of the austenite has also transformed to pearlite.

(e) Graphite and Ferrite

This variety of iron usually has a very high silicon content. The graphite-austenite eutectic has cooled slowly enough for the whole of the carbon dissolved in the austenite to diffuse on to existing graphite flakes leaving a matrix entirely of ferrite. Such a Cast Iron is very soft and easily machined. The ferrite present will contain dissolved silicon and manganese.

In addition to the phases mentioned above, iron phosphide, Fe_3P, may be present in the microstructure. In white or mottled iron, it will be present as a ternary eutectic with

cementite and ferrite, whilst in coarse Grey Irons of the type (e) above, a binary eutectic with ferrite will be formed. This binary eutectic contains only 10% phosphorous, so that an overall 1% phosphorus in the Iron may produce sufficient phosphide eutectic to account for 10% by volume of the resulting structure. The embrittling effect of the phosphide eutectic network will then be evident.

2.19 Effect of Grain Structure on Corrosion

The grain structure of alloys can markedly affect their corrosion behaviour. For example, the corrosion resistance of certain wrought metals may be less on surfaces perpendicular to the hot – or cold – working direction than on surfaces parallel to this direction. Typically, there may be severe localised corrosion starting on the faces perpendicular to the working direction and proceeding into the metal in the working direction which remain relatively unattacked. Such end-grain attack, which is basically the result of the grain structure being elongated in the working direction, has been observed in austenitic stainless steels, titanium alloys and mild steel.(Pritchard (1971))

2.20 Layer Corrosion

Shreir (1978), stated that the most marked effect of grain structure on corrosion is observed in wrought aluminium alloys. These alloys generally do not recrystallise during heat treatment

after rolling, extrusion, etc mainly because their grain boundaries are pinned by inclusions. They, therefore, exhibit the elongated shaped grain structure. As a result of this structure, these alloys may be susceptible to exfoliation (also known as layer or lamellar) corrosion. The corrosion products formed force the layers apart and cause the metal to swell and, in severe instances, to disintegrate into separate sheets of metal (i.e. to exfoliate). Since the exfoliation is normally intergranular, it is clear that exfoliation is usually affected by intergranular precipitation and hence by heat treatment. Shreir (1963); Cowan and Tedman (1973)

2.21 Graphitisation

Cast Irons, contain complex alloys – the iron carbon phase diagram exhibits a eutectic reaction at 1420K and 4.3 Wt % carbon. One product of this eutectic reaction is always austenite, depending on the cooling rate and the composition of the alloy, the other product may be cementite or graphite. The graphite may be in the form of flakes which are all interconnected (although they appear separate on a metallographic section), or spheroids, which are all separatee. The resultant alloys are known as white, grey and spheroidal graphite Cast Irons, respectively. During subsequent cooling the austenite may transform (as already mentioned) to ferrite, pearlite or martensite,

or it may, in the case of high-nickel irons, be retained at room temperature. In Grey Cast Irons, the matrix, therefore, corrodes preferentially, leaving behind the network of inter-connected graphite flakes; this is, of course, very porous and weak. The attack is often not readily apparent on superficial inspection. White Cast Irons are not susceptible to graphitisation since they contain no graphite; spheroidal graphite Cast Irons are also not susceptible to graphitisation, since they do not contain graphite it is in the form of discrete spheroids which have a limited effect, instead of the inter-connected graphite flakes in Grey Cast Iron.

2.22 METALLOGRAPHY

Metallography is the study of the internal structure of metals and alloys at different magnifications under a microscope. Useful information on grain size, shape and distribution and on percentage of various constituents in the structure can be obtained by metallographic techniques.

Preparation of the sample is necessary for revealing the micro-structure of a given specimen. There are two types of metallographic examinations:

(i) macro-examination; where the structure is observed with naked eye or under low magnification (times 5); and

(ii) micro-examination; where small areas at high magnification (50 to 2000 times) are observed for this purpose

Macro-examination reveals the following:

(i) segregation of impurities (for instance, antimony in bearing metals and sulphur and phosphorous in steel).

(ii) presence of non-metallic inclusions, e.g. sulphides and oxides.

(iii) Grain size

(iv) Fabrication techniques (for instance, casting, rolling, forging and welding).

(v) Casting defects (e.g. blowholes, pipe formation seams and laps).

2.22 Macro-etching

Macro-etching of metals involves deep etching with a suitable reagent that reacts selectively with metal structure. The structure so revealed can be examined by naked eyes at a low magnification. The surface of metal to be examined is ground and polished with the help of emery paper. After this, the metal is immersed in the reagent until the structure is clear. Alternatively, the metal surface may be swabbed with the reagent for a few minutes. The metal surface is then washed in water and methylated spirit and finally dried.

CHAPTER THREE

3.0 EXPERIMENTAL TECHNIQUES

3.1 MATERIALS AND PREPARATION

(a) Cast Iron

The material used in this study is Cast Iron. This was obtained by using a conventional sand casting technique to cast the iron in a standard foundry workshop. The scraps used were obtained from local sources. Melting was carried out in an induction furnace at the Federal Polytechnic, Ado-Ekiti. The chemical composition of the samples used are given in table 2 below.

Carbon	Silicon	Manganese	Phosphorus	Sulphur
2.75	1.5	0.35	0.70	0.10

Table 2: Composition of Grey Cast Iron

(b) Oil

Standard grade SAE 40 was used and this was obtained from a local dealer.

(c) Corrosive Media

The Corrosive Media used are:

(i) Wood Pulp.

(ii) White Liquor.

These two Corrosive Media were obtained from Nigeria Paper Mill, Jebba. The Media were kept at room temperature throughout the duration of the experiment.

3.2 Equipment

In this study, a number of equipment were used during experimentation. Such equipment include:

(a) Induction Furnace – for melting scrap metal required to produce the Cast Iron needed for the study

(b) Carbolite Electric Furnace – Used for the heat-treatment of samples.

(c) Lathe Machine – Used to machine test-specimens.

(d) Tensiometer – Used for measuring the tensile properties of the specimens.

(e) Wotpert Hardness Testing Machine – Used to obtain the hardness of the specimens.

(f) Laboratory Mounting Machines – Used for mounting the samples on EPO mould.

(g) Laboratory Grinding and Polishing Machines – Used in grinding and polishing the samples surfaces to a mirror-like surface.

(h) TH3 Olympus Optical Microscope – Used to take the photomicrograph of the specimens.

3.3 EXPERIMENTAL METHOD

3.3.1 Tensile Test

The Cast Iron Rod was machined to the tensile piece standard size. (See fig. 7 below)

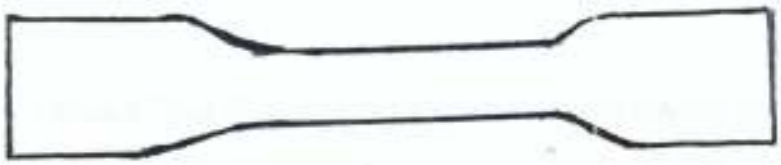


Fig.7 – Tensile Test Specimen.

The Cast Iron was so soft and brittle, so great care was taken in the machining of this test pieces with regard to both dimensional accuracy and quality of test specimens were produced.

The specimen was clamped on the tensiometer. The machine was switched on into operation, with a graph sheet fixed on the rotating drum. The machine plotted the graph of the load against extension curve. The machine was switched off immediately when the test piece broke. The broken pieces of the test specimen were then removed, joined together and the new diameter as well as the new length were determined.

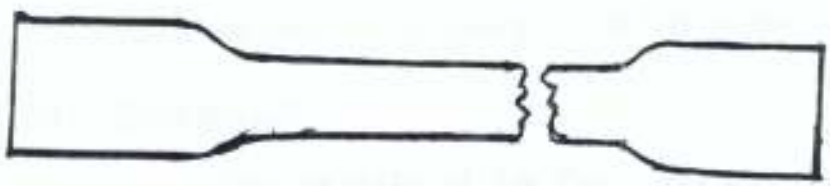


Fig.8 – Tensile Test Piece, after experiment, showing no neck region.

3.3.2 Heat Treatment Processes Used

The Cast Iron used was subjected to the following heat treatment processes:

(i) Annealing

(ii) Normalizing

(iii) Stress Relieving

(iv) Quenching

(v) Tempering.

(i) Annealing

Ten pieces of the Cast Iron specimens were put inside the carbolite furnace and heated gradually up to 900°C. At this temperature, the pieces were held for one hour. This is a sufficiently high temperature to ensure that fully homogenised phase is reached by all the samples according to the iron-carbon diagram.

The furnace was then switched off and the samples were allowed to cool slowly inside the furnace.

(ii) Normalizing

Ten samples of the Cast Iron was put inside the furnace and heated gradually until it attained a temperature of 925°C. This is because the normalizing temperature is usually kept above the transformation temperature range. They were held at this temperature for one hour for proper homogenisation. The recommended holding time for Grey Cast Iron during normalizing is one hour per 25mm of maximum section thickness. The thickness of the sample is just 20mm in diameter. The specimen were then brought out of the furnace to cool in still air.

(iii) Stress Relieving

Another ten specimens were heated in the furnace for up to a temperature of 560°C. These were held at this temperature for one hour. They were then removed from the furnace and allowed to cool in still air.

(iv) Quenching

Another ten test samples were heated up to a temperature of about 870°C. Immediately this temperature was reached, the samples were removed, five were quenched in oil (SAE 40), while another five were quenched inside water held at room temperature.

(v) Tempering

The samples quenched in oil and water, were then removed and cleaned to make sure they were dry and free from either oil or water. Two of each set were selected and transferred back to the furnace. These were later re-heated up to 370°C held at this temperature for 1 hour and subsequently cooled in air.

3.4 WEIGHT LOSS EXPERIMENT

The test to evaluate the corrosion rate of Grey Cast Iron was set up as shown in fig.9 below:

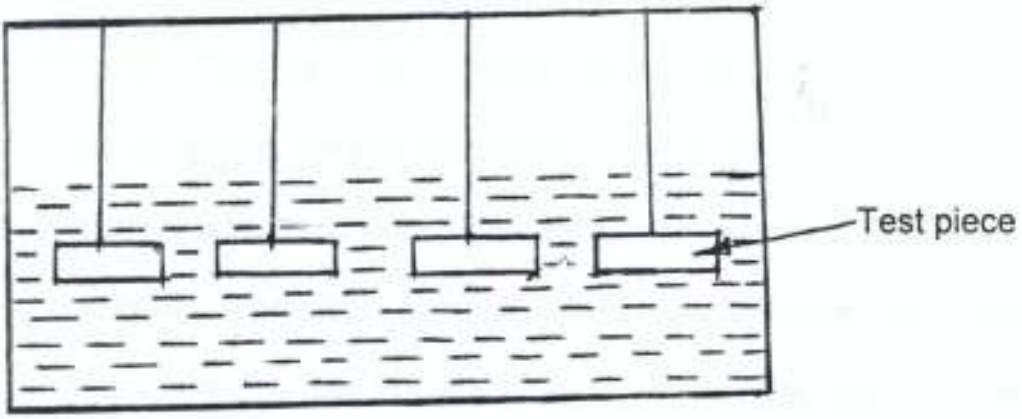


Fig.9 Schematic View of the Set up for Weight Loss Test

The surface area of the test pieces were measured with their initial weights before they were suspended in various solutions as shown in fig. 9. Mercury-Chloride ($HgCl_2$) was added in the main environments at 3% by weight.

Five pieces of annealed, normalized, stress relieved, tempered and as Cast specimens were selected. They were then cleaned, rinsed with alcohol and later air dried.

Four troughs were prepared. One containing the Wood-Pulp dissolved in water, another contained white liquor, while the third contained Wood-Pulp contaminated with 3% by weight of mercury chloride and the last contained white liquor contaminated with 3% by weight of mercury chloride.

The immersed samples were withdrawn after every four days. Then they were cleaned by washing them under running tap to remove dirts of the corrosive parts, followed by rinsing with alcohol and air drying. The samples were then weighed on a sensitive chemical balance. The weights were recorded to determine any loss in weight due to corrosive action of the media under study. The results are given in below:

Tables (3 – 14). The corrosion was determined by the weight loss per unit surface area of the specimen. The steps followed above were repeated for every four day intervals for twenty days expiration.

3.5 PRE-EXPOSURE TEST

Four troughs were also used, each contained the following fluids:

(i) Wood Pulp dissolved in water

(ii) White liquor

(iii) Wood Pulp plus Mercury Chloride

(iv) White liquor plus Mercury Chloride

The set up for this study is as shown in fig.10

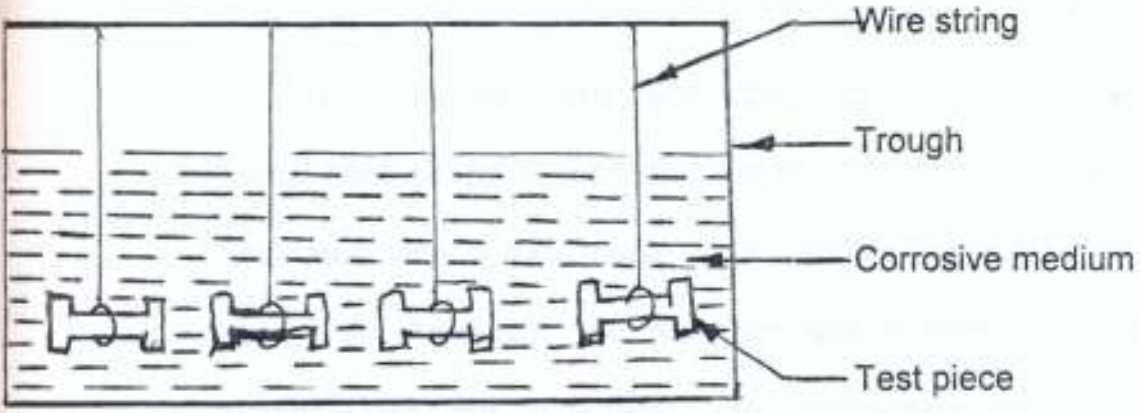


Fig.10: Pre-Exposure Test

The immersed test samples were removed later and pulled in tension to fracture to test for their tensile properties. Fracturing was done with the aid of a tensiometer. The percentage elongation was obtained for each sample. The results obtained are recorded in Tables 15 – 23

3.6 METALOGRAPHY

Some samples of the Cast Iron were selected and studied metalographically. They were cut into sections, grounded, polished to mirror-like on the surface. They were later etched by using 4% picral. This etching reagent is very good for etching pearlite and spheroidised structures, but does not attackt the ferrite grain boundaries, picral is the most suitable reagent for all Cast Irons, with the exception of alloy and completely ferritic Cast Irons.

The samples were then observed under an Olympus Optical Microscope at magnification of 100. The samples were illuminated with a data cable quartz iodine lamp (120V, 1000 watts). An Arwo-pan 100 ASA film was loaded in the canon camera which was attached to the frequency photolude of the microscope. This was used to take the photomicrograph of the samples one after another until the photomicrograph of all the specimens were taken. The film was removed, developed and printed (see photo plates 1 – 5).

CHAPTER FOUR

4.0 RESULTS

4.1 VISUAL OBSERVATIONS

The following visual observations of the specimens were noticed when carrying out the experiments.

(i) Annealed Samples:

The annealed samples were covered with reddish scales of oxides. The oxide scales were removed prior to experimentation.

(ii) Stress Relieved Specimens:

The Stress Relieved Specimens appeared dark-blue in colour after cooling.

(iii) Tempered Samples:

It was observed that the oil quenched samples appeared very dark after it had been tempered while the water quenched samples had some reddish scale covering their surface after tempering.

(iv) Normalized Samples:

The normalized specimens were brought out of the furnace after it had been heated to 925°C and held for one

hour for proper homogenisation. By the time the samples were brought out of the furnace, they were red hot. As they cooled rapidly in still air, a reddish scale covered the surface.

4.2 Weight Loss

It was observed that small bubbles of gases were evolved from the solution after about 2 – 5 hours of exposure of the Cast Iron samples to Wood Pulp and white liquor.

Although no test was carried out to ascertain the nature of the gas evolved, evidence from similar studies has shown that the gas evolved contained hydrogen. (Alagbe . 1995) Even though, it is not the principal cathodic reaction. The cathodic reaction may be a combination of hydrogen and oxygen reduction.

The quality of the evolved gas was smaller in wood pulp than in white liquor. This later stopped after about 3 hours.

(i) White Liquor

It was also observed that the specimens that were immersed in white liquor was covered with a film that was relatively black in colour. When they were removed and washed under running tap, it was observed that the surface was very slippery and even difficult to remove from one's finger.

(ii) Wood Pulp

The samples that were dipped inside the wood pulp looked reddish on removal. After washing them, they turned black. In this case, the surface was not slippery.

(iii) White Liquor plus the Mercury Ion

It was also observed that almost the same visual observations that were seen in the white liquor was also obtained in this case.

(iv) Wood Pulp plus $HgCl_2$

The specimens that were immersed in wood pulp contaminated with the mercury ion (Hg^{2+}) was covered with bubbles of the water on the surface.

4.3 OTHER OBSERVATIONS

(i) Annealing Process

The samples had been softened and the internal stresses had been removed. The percentage elongation was improved. It increased from 7.50% for the as received to 13.48% for the specimen immersed in white liquor and 10.81% for the annealed specimens immersed in wood pulp. This process also softened the Grey Cast Iron and improved its machinability by minimizing or eliminating massive eutectic carbides.

(ii) Stress Relieved Specimens

The main purpose of this process is to remove the residual stresses that were introduced into the Cast Iron during solidification, due to different cooling rates at various section of the castings. It was found that the heat treatment process increased the tensile strength of the material from 327.35N/mm^2 for the as received to 329.68N/mm^2 for the specimen dipped in white liquor and wood pulp respectively. The hardness was improved from B76.20 to B78.30 Brinell hardness testing machine.

(iii) The Normalized Samples

The result here is similar to that of the annealed component but the mechanical properties are somewhat better than an annealed component. The surface finish of a normalized specimen is better than that of an annealed ones when machined, since the high ductility of the annealed makes the surface to tear.

4.4 Record of Tables

Tables 15 and 16 show the tensile properties for hardened specimens while Table 17 indicates the tensile properties for quenched specimens. The tensile properties for the stress relieved specimens were shown in Tables 18 and 19. Tables 20

and 21 contain the tensile properties for the annealed specimens while tables 22 and 23 are for the normalized specimens.

The results obtained from the weight loss experiments are listed in tables 3 and 4 show the weight of specimen inserted in white liquor and the weight loss due to corrosion respectively. While table 5 indicates the weight loss per unit area (g/dm^2) for the specimen dipped in white liquor. Tables 6 and 7 show the weight of specimens dipped in wood pulp and the weight loss per unit area (g/dm^2) of the specimen dipped in wood pulp. The weight of the specimen dipped in white liquor with the Mercury Ion (Hg^{++}) added and the weight loss are indicated in Tables 9 and 10 respectively. Table 11 contains the weight loss per unit area (g/dm^2) of white liquor with the Mercury Ions (Hg^{++}). Table 12 shows the weight of the specimen dipped in wood pulp with Mercury Ions (Hg^{++}) added. While the weight loss is recorded in Table 13, Table 14 shows the weight loss per unit area ((g/dm^2).

4.5 Microscopic Examination of the Specimens

The photomicrograph of each specimen taken were examined after the film had been developed and printed (see photo plates 1 – 5 pages). The micro-structure of the Cast Iron that was observed is as stated below:

(i) Grey Cast Iron as-received:

It consists of graphite flakes (dark) and ferrite (light) in a matrix of Pearlite (see photo Plate 1).

(ii) The annealed specimen's structure is also in form of graphite flakes (black) with ferrite (white) (see photo Plate 2)

(iii) The structure of the Normalized Grey Cast Iron was completely pearlitic with dark regions of inter-dendritic graphite. (see photo Plate 3)

(iv) The structure of the quenched Grey Cast Iron was completely graphite and pearlite (see photo plate 4).

(v) The structure of the stress relieved contains (white) patches of phosphide eutectic or cementite (light) in a matrix of pearlite (dark). (see photo plate 5).

TABLE 3: WEIGTH OF SPECIMEN INSERTED IN WHITE LIQUOR

TIME DAYS	SPECIMEN WEIGTH (g)				
	A	B	C	D	E
0	22.3005	20.5000	21.3000	23.600	18.0800
4	22.2690	20.4860	21.2870	23.589	18.0140
8	22.2270	20.4270	21.2620	23.567	17.8600
12	22.1260	20.3070	21.1980	23.535	17.7220
16	22.0160	20.1480	21.1380	23.513	17.6770
20	21.9300	20.0470	21.0870	23.485	17.6340

SPECIMEN

A - Annealed Specimen piece
B - Normalized " "
C - Tempered " "
D - As cast " "
E - Stress relieved specimen piece

SPEC. SURFACE AREA (dm^2)

A = 0.0689 dm^2
B = 0.0945 dm^2
C = 0.0909 dm^2
D = 0.0926 dm^2
E = 0.0456 dm^2

TABLE 4 : SPECIMEN WEIGTH LOSS DUE TO CORROSION

TIME DAYS	WEIGTH LOSS (g)				
	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0315	0.0144	0.0126	0.0108	0.2010
8	0.0789	0.0734	0.0377	0.0323	0.2199
12	0.1736	0.1930	0.1019	0.0645	0.3582
16	0.2840	0.3520	0.1623	0.0861	0.4022
20	0.3692	0.4530	0.2126	0.1141	0.4460

TABLE 5 : WEIGHT LOSS PER UNIT AREA g/dm^2 FOR SPECIMEN DIPPED IN WHITE LIQUOR

TIME DAYS	WEIGHT LOSS PER UNIT AREA (g/dm^2)				
	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.4570	0.1522	0.1386	0.1166	0.9203
8	1.1451	0.7767	0.4147	0.3488	2.8072
12	2.5195	2.0423	1.1210	0.6965	3.0712
16	4.1219	3.7248	1.7854	0.9298	5.0020
20	5.3584	4.7936	2.3388	1.2321	5.6217

TABLE 6 : WEIGTH OF SPECIMEN IMMERSED IN WOOD PULP

TIME	SPECIMEN WEIGTH (g)				
DAYS	A	B	C	D	E
0	17.8000	18.0000	19.0500	21.0000	18.8000
4	17.7465	17.9250	19.0208	20.9462	18.6954
8	17.6574	17.8500	18.9469	20.9107	18.6564
12	17.6163	17.7990	18.8984	20.8924	18.6187
16	17.5147	17.7015	18.8256	20.8902	18.5504
20	17.4647	17.6730	18.7820	20.8482	18.4695

A - Annealed - 0.1238dm^2
B - Normalised - 0.0838dm^2
C - Tempered - 0.08317dm^2
D - As cast - 0.0532dm^2
E - Strenth relieved specimen - 0.0776dm^2

TABLE 7 : SPECIMEN WEIGTH LOSS IN WOOD PULP

TIME	SPECIMEN WEIGTH LOSS (g)				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0535	0.0750	0.0291	0.0538	0.1046
8	0.1426	0.1500	0.1031	0.0893	0.1436
12	0.1837	0.2010	0.1516	0.1076	0.1813
16	0.2853	0.2985	0.2244	0.1098	0.2496
20	0.3353	0.3270	0.2680	0.1518	0.3305

TABLE 8 : WEIGTH LOSS PER UNIT AREA (g/dm^2) OF SPECIMEN IMMERSED IN WOOD PULP

TIME	WEIGTH LOSS PER UNIT AREA (g/dm^2)				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.4321	0.8949	0.3500	1.0113	1.3479
8	1.1519	1.7899	1.2396	1.6786	1.8605
12	1.4838	2.3986	1.8227	2.0226	2.3363
16	2.3045	3.5620	2.6981	2.0639	3.2165
20	2.7084	3.9021	3.2223	2.8534	4.2590

TABLE 9 : WEIGTH OF SPECIMEN IMMERSED IN WHITE LQUOR WITH MERCURY (Hg^{++}) ION

TIME	SPECIMEN WEIGTH (g)				
DAYS	A	B	C	D	E
0	18.2000	16.6000	20.2000	16.5000	17.1000
4	18.1490	16.5510	20.1720	16.4640	17.0680
8	18.0770	16.4890	20.1310	16.4010	16.9330
12	17.9650	16.3420	20.0350	16.3530	16.8130
16	17.8960	16.2940	20.0010	16.2960	16.6640
20	17.8420	16.2570	19.9590	16.2010	16.5610

Surface Areas

A - Annealed - 0.0939dm^2
B - Normalised - 0.0694dm^2
C - Tempered - 0.0855dm^2
D - As cast - 0.1355dm^2
E - Stress relief - 0.0756dm^2

TABLE 10 SPECIMEN WEIGTH LOSS IN WHITE LIQUOR CONTERMINATED WITH Hg^{++}

TIME	SPECIMEN WEIGTH LOSS				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0510	0.0489	0.0275	0.0351	0.0320
8	0.1225	0.1102	0.0686	0.0983	0.1668
12	0.2349	0.2571	0.1647	0.1474	0.2870
16	0.3033	0.3060	0.1989	0.2036	0.4365
20	0.3574	0.3428	0.2401	0.2991	0.5393

TABLE 11; WEIGHT LOSS PER UNIT AREA (g/dm^2) OF WHITE LIQUOR WITH MERCURY ION Hg^{++})

TIME	WEIGHT LOSS PER UNIT AREA (g/dm^2)				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	1.1612	0.7054	0.3210	0.2590	0.4233
8	2.7893	1.5876	0.8024	0.7253	2.2063
12	5.3488	3.7037	1.9264	1.0877	3.7962
16	6.9062	4.4085	2.3265	1.5025	5.7738
20	8.1380	4.9386	2.8084	2.2072	7.1335

TABLE 12:WEIGHT OF SPECIMEN IMMERSED IN WOOD PULP WITH MERCURY IONS (Hg^{++})

TIME	SPECIMEN WEIGHT (g)				
DAYS	A	B	C	D	E
0	19.1000	21.8000	15.4000	16.3000	18.2000
4	19.0155	21.7096	15.2510	16.2602	18.1255
8	18.9550	21.6118	15.1460	16.1370	18.0044
12	18.8460	21.5228	15.0650	16.0580	17.8930
16	18.7740	21.4360	14.9130	16.0315	17.7430
20	18.7002	21.3230	14.7490	15.9310	17.6876

Surface Area

A - Annealed - 0.07913dm^2
B - Normalised - 0.06246dm^2
C - Tempered - 0.11420dm^2
D - As cast - 0.08470dm^2
E - Stress relief - 0.08254dm^2

TABLE 13.: SPECIMEN WEIGHT LOSS (g) FOR WOOD PULP WITH MERCURY IONS

TIME	SPECIMEN WEIGHT LOSS (g)				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	0.0845	0.0903	0.1486	0.0378	0.0745
8	0.1449	0.1881	0.2535	0.1626	0.1956
12	0.2537	0.2772	0.3349	0.2420	0.3066
16	0.3261	0.3637	0.4867	0.2685	0.4568
20	0.3998	0.4766	0.6510	0.3681	0.5124

TABLE 14: WEIGHT LOSS PER UNIT AREA (g/dm^2) FOR THE WOOD PULP WITH MERCURY (Hg^{++})

TIME	WEIGHT LOSS PER UNIT AREA (g/dm^2)				
DAYS	A	B	C	D	E
0	0.0000	0.0000	0.0000	0.0000	0.0000
4	1.0678	1.4458	1.3012	0.4462	0.9021
8	1.8311	3.0121	2.2197	1.9197	2.3697
12	3.2061	4.4380	2.9325	2.8571	3.7145
16	4.1210	5.8229	4.2618	3.1696	5.5342
20	5.0524	7.6305	5.7005	4.3459	6.2078

TABLE 15: TENSILE PROPERTIES FOR TEMPERED SPECIMENS

Corrosion media used	Specimen diameter (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Extension (mm)	% Elongation
White liqour	10.00	286.48	40.05	42.01	1.96	4.89
Wood pulp	10.10	296.45	40.08	41.78	1.70	4.29
As cast	10.02	327.35	39.12	43.46	4.34	11.09
_	9.80	364.25	38.30	39.60	1.30	3.39

TABLE 16; TENSILE PROPERTIES FOR TEMPERED SPECIMENS WITH CORROSIVE MEDIACONTAMINATED WITH Hg^{++} ION

Corrosion media used	Specimen diameter (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Extension (mm)	% Elongation
White liqour plus Hg^{++}	10.01	266.85	40.00	42.00	2.00	5.01
Wood pulp plus-Hg^{++}	10.02	277.41	40.21	41.94	1.73	4.30
As cast	10.02	317.35	39.12	43.46	4.34	11.09
_	9.80	364.20	38.30	39.60	1.30	3.39

TABLE 17: TENSILE PROPERTIES FOR QUENCHED SPECIMEN.

Type of heat treatment	Test piece dia(mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Ext. (mm)	% Elongation
Oil quenched	10.01	314.49	40.00	41.05	1.05	2.62
Water quenched	10.00	302.39	40.00	41.00	1.00	2.50
As cast	10.02	327.35	39.12	43.46	4.34	11.09
Oil quenched	9.80	319.48	41.20	41.68	0.48	1.17

TABLE 18: TENSILE PROPERTIES FOR STRESS RELIVED SAMPLES

Corrossion media	Test piece dia. (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Extension (mm)	% Elongation
White liquor	10.02	324.68	39.80	42.11	2.31	5.80
Wood pulp	10.01	333.56	39.91	41.91	2.00	5.01
As cast	10.02	327.35	39.12	43.46	4.34	11.09
_	10.04	349.73	41.70	42.89	1.19	2.85

TABLE 19: TENSILE PROPERTIES FOR STRESSRELIEVED SAMPLES IMMERSED IN A CORROSIVE MEDIA CONTERMINATED WITH Hg^{++} IONS

Corrosive media used	Test piece dia. (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Extension (mm)	% Elongation
White liqour with Hg^{++} ion	10.01	309.73	40.01	42.35	2.34	5.85
Wood pulp with Hg^{++}	10.06	326.27	40.05	42.45	2.40	5.99
As cast	10.02	327.35	39.12	43.46	4.34	11.09
-	10.04	349.73	41.70	42.89	1.19	2.85

TABLE 20 : TENSILE PROPERTIES FOR ANNEALED SAMPLES

Corrosion media used	Test piece dia.(mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Ext. (mm)	% Elongation
White liqour	9.98	319.59	38.05	43.18	5.12	13.48
Wood pulp	10.01	309.72	39.02	43.24	4.22	10.86
As cast	10.02	327.35	39.12	43.46	4.34	11.09
-	9.89	322.05	37.00	38.80	1.80	4.86

TABLE 21: TENSILE PROPERTIES FOR ANNEALED SAMPLES IMMERSED IN CORROSIVE MEDIA CONTERMINATED WITH MERCURY CHLORIDE

Corrosion media used	Test piece dia. (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Ext. (mm)	% Elongation
White liquor + Hg^{++}	9.87	277.74	40.02	43.25	3.23	8.06
Wood pulp + Hg^{++}	10.10	257.43	40.12	43.86	3.74	9.32
As cast	10.02	327.35	39.12	43.46	4.34	11.09
-	9.89	322.05	37.00	38.80	1.80	4.86

TABLE 22 :TENSILE PROPERTIES FOR NORMALIZED SAMPLES

Corrosión media used	Test piece diam. (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Extension (mm)	% Elongation
White liquor	9.96	340.14	40.01	42.41	2.40	5.99
Wood pulp	10.03	284.76	40.70	41.85	1.19	2.83
As cast	10.02	327.35	39.12	43.46	4.34	11.09
—	9.50	387.51	38.20	39.17	0.91	2.38

TABLE 23: TENSILE PROPERTIES FOR NORMALIZED SAMPLES IMMERSED IN CORROSIVE MEDIA CONTERMINATED WITH MERCURY CHLORIDE

Corrosion media used	Test piece dia. (mm)	Tensile strength N/mm^2	Original length (mm)	New length (mm)	Ext. (mm)	% Elongation
White liquor + Hg^{++}	10.00	270.56	40.01	41.35	1.35	3.32
Wood pulp + Hg^{++}	10.03	287.76	40.01	41.41	1.40	3.50
As cast	10.02	327.35	39.12	43.46	4.34	11.09
/	9.50	387.51	38.20	39.17	0.91	2.38

CHAPTER FIVE

5.0 DISCUSSION

5.1 Effect of Heat Treatment on Load Versus Extension Graphs:

(1) Annealing:

Figure 18 shows a decrease in tensile strength of annealed specimen as compared with the as-received specimen. This can be attributed to the purpose of annealing process which is to relief the internal stresses within the cast iron. Since the material was cast initially, so it must have enclosed some hot gasses and inclusions (impurities) which led to a set up of internal stresses. When all the stresses had been removed, the material became free from stress. This observation agreed with the reason for the experiment because all of the annealed samples have less tensile strength when compared with the as-cast specimen.

Usually, it takes one hour for a complete re-crystallization to take place in Cast Iron (Byrne , 1965). The structure formed during crystallization is exactly the

same as the structure that existed before casting, the result is in agreement with the above statement.

(2) Normalizing:

From Figure 19, it is clear that the tensile strength of normalised Cast Iron is higher than the annealed Cast Iron. The tensile strength would have been greater than that of as-cast but due to the corroding effect of the corrosive media that the specimens were immersed. This would have weakened it somehow. That notwithstanding, the normalised Cast Iron is tougher, and has a higher tensile strength than the annealed Cast Iron.

(3) Hardening

Hardening is the process of heat treatment by which the Cast Iron is made hard by rapid quenching from high temperature. This consists of:

(i) Water quenched; and

(ii) Oil quenched samples.

(4) Quenching

The result of Figure 16 showed that the rate of cooling in water is faster and non-uniform than the rate of cooling in oil because the specimen that was quenched in water showed a very hard structure which did not fail at maximum load due to the martensitic structure that is

present within the specimen. This is in agreement with the idea that martensitic structure is very hard and brittle. The hardness and brittleness of martensite is due to the fact that martensite is a super saturatedd solid solution of carbon trapped in a body centred tetragonal structure, which is a metastable condition. (Gordon and Philips 1965) This highly distorted lattice is the prime reason for the high hardness of martensite.

A comparison of the tensile strength for the water quenched sample and the oil quenched sample showed that the oil quenched sample, exhibited both the plastic and elastic regions distinctively. This can be attributed to slow, uniform cooling which allows the formation of graphite and pearlite in its micro-structure. This reduces the hardness and makes it possible for the specimen to be ductile. This is the reason why we have a plastic range in the load extension curve of the oil quenched sample.

5.2 Effect of Heat-Treatment on Percentage Elongation

The annealed samples have the highest percentage elongation (10.86% to 13.48%), while the quenching samples have the least percentage (2.50% - 2.62%) elongation

Annealing

The annealing process was applied in order to refine the structure of the Cast Iron. The Cast Iron was heated to just above its upper critical temperature (900°C), so that the coarse grain structure was replaced by fine-grained austenite. On cooling, this gave rise to a structure of fine-grained ferrite and pearlite.

5.3 Effect of Corrosion on the Heat Treatment Samples

(i) Annealling

From tables 20 & 21 the maximum tensile strength of the annealed specimens was obtained from the specimen that was heat treated but was not immersed in any of the corrosive fluids. This gave 322.05N/mm^2 while the highest tensile strength that was obtained from the ones immersed in white liquor is 319.59N/mm^2.

This shows that the material (Cast Iron) has corroded. It, therefore, has a great effect on the tensile strength. The corrosion attack on the Cast Iron therefore tends to weaken the metal. It is also clear that the annealed Cast Iron is quite okay in white liquor since there is a little variation in the samples immersed in the corrosive media as compared with the Cast Iron in as-cast state.

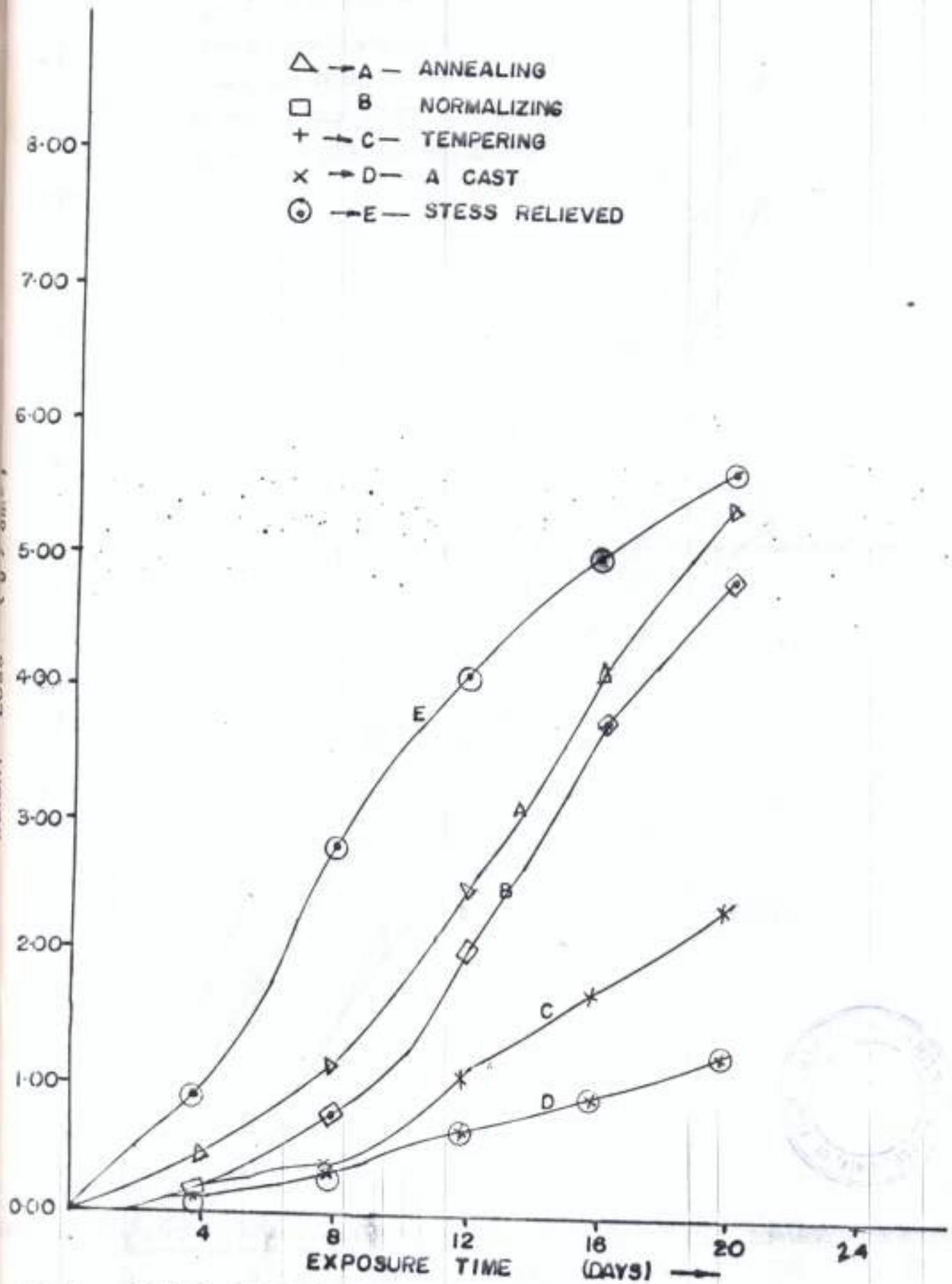


FIG. 11 EFFECT OF HEAT TREATMENT ON CORROSION OF CAST IRON WHITE LIQUOR.

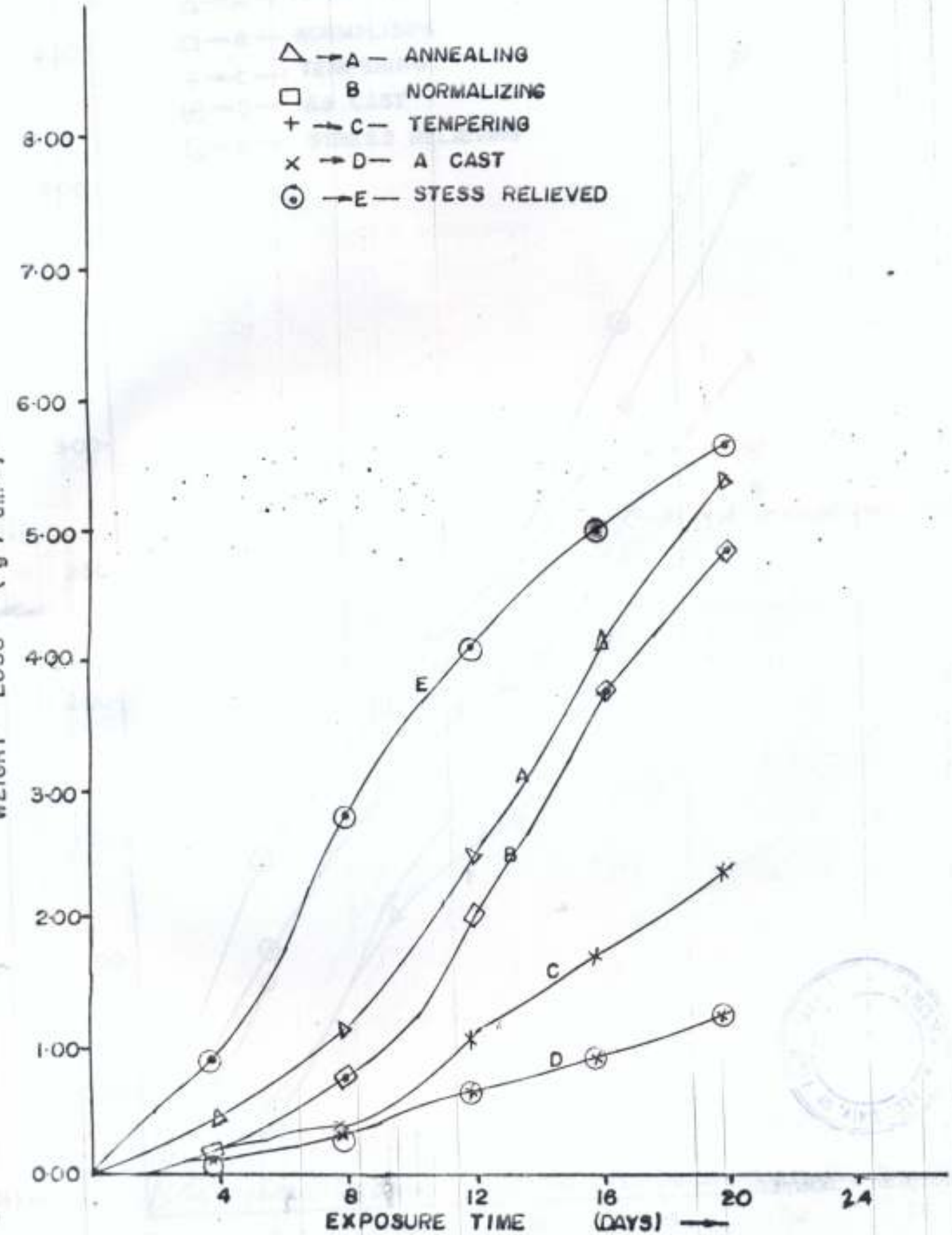


FIG.11 EFFECT OF HEAT TREATMENT ON CORROSION OF CAST IRON WHITE LIQUOR.

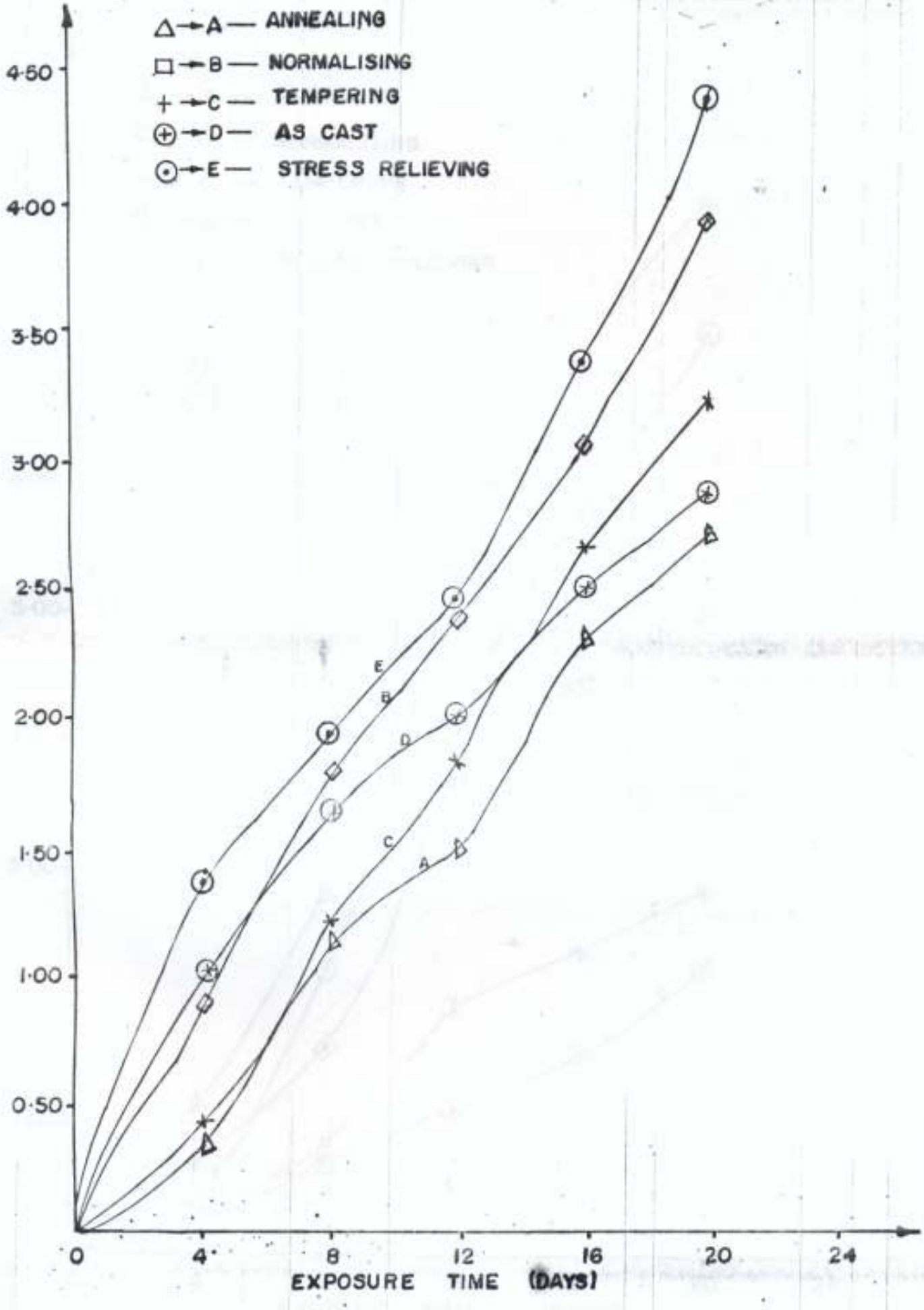


FIG. 12 EFFECT OF HEAT TREATMENT ON CORROSION OF CAST IRON IN WOOD PULP.

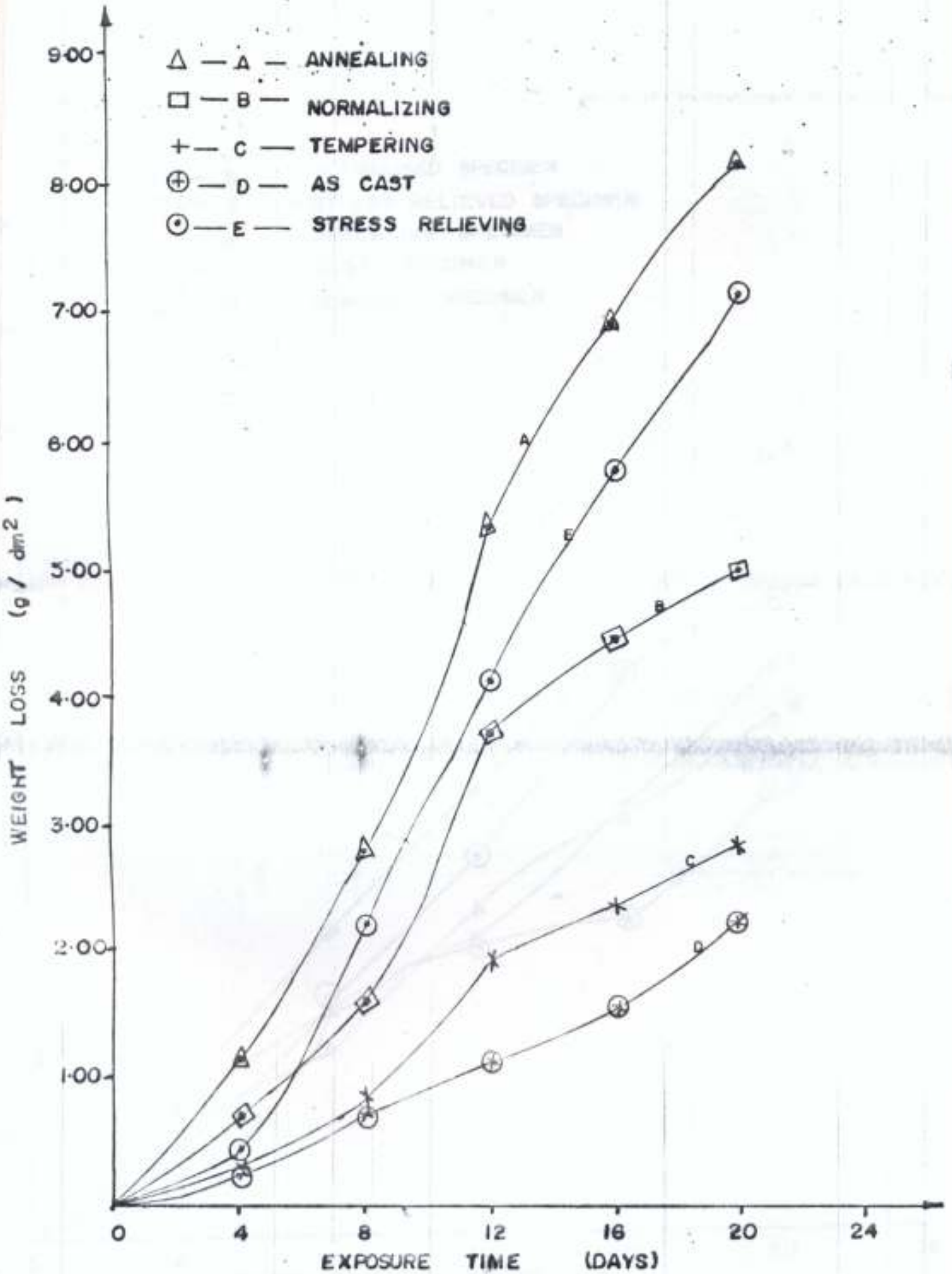


FIG. 13 EFFECT OF HEAT TREATMENT ON CORROSION OF CAST IRON IN EXTRANEOUS IONS IN WHITE LIQUOR.

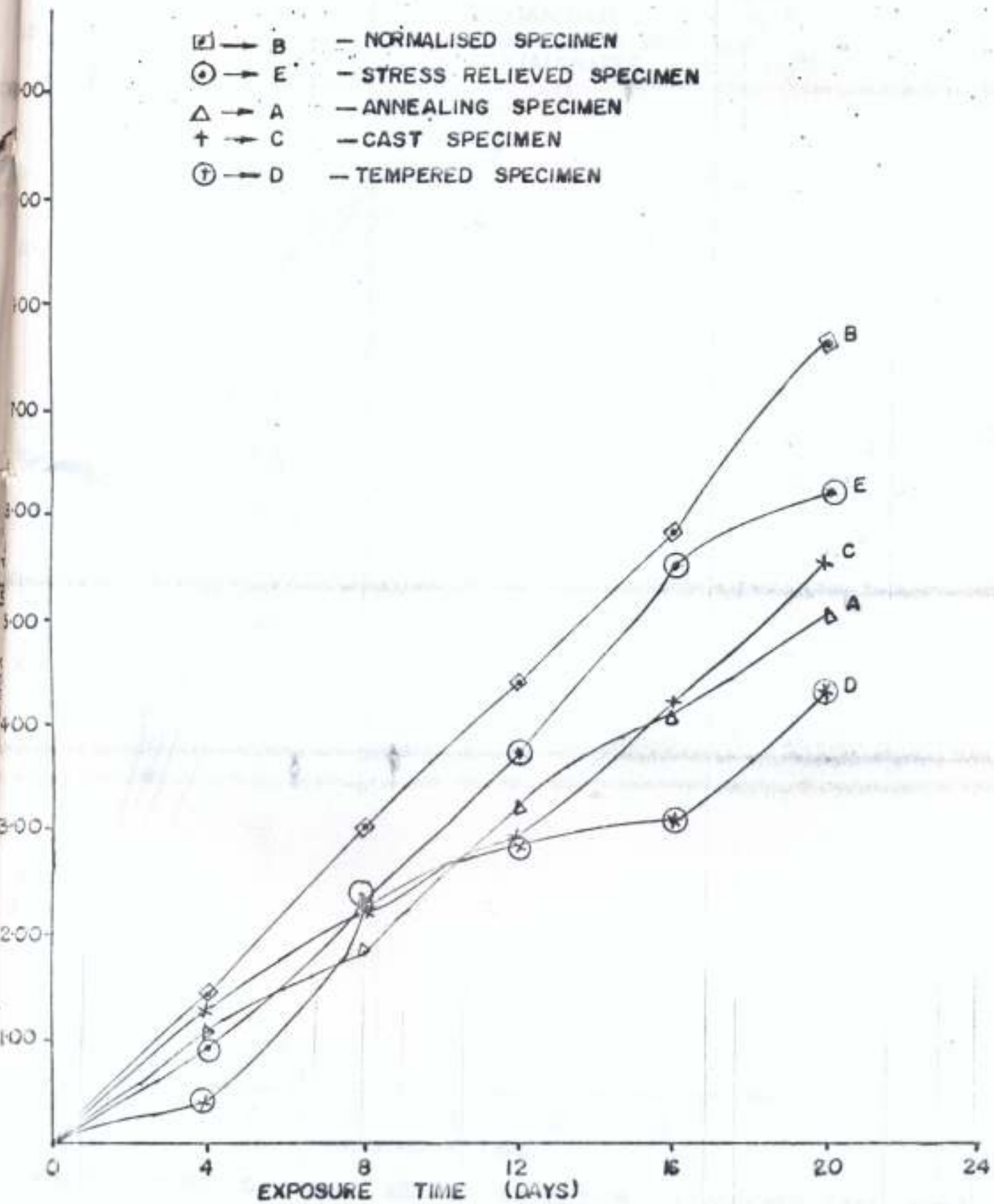


FIG.14 EFFECT OF HEAT TREATMENT ON CORROSION OF CAST IRON IN

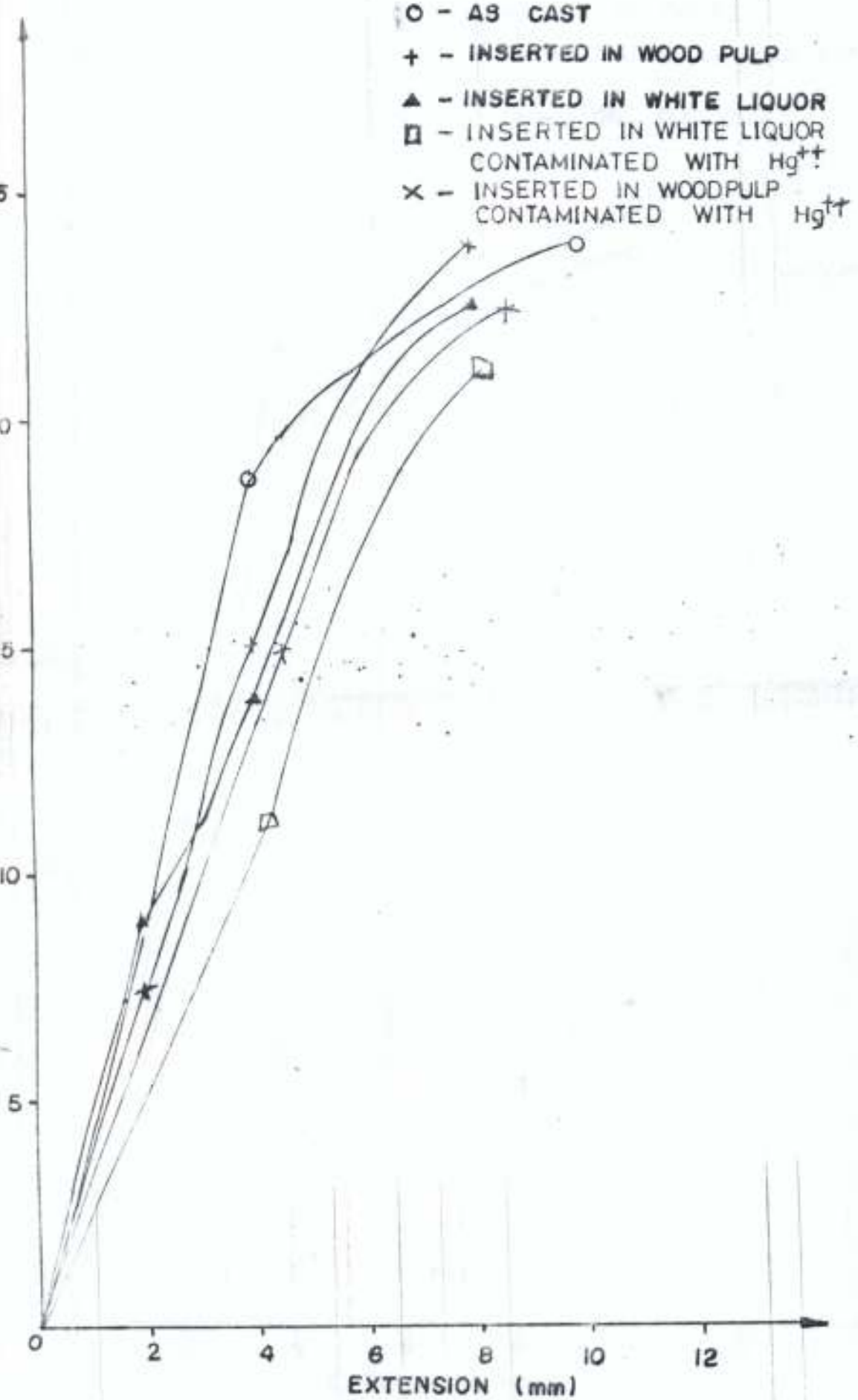


FIG. 15 GRAPH OF LOAD AGAINST EXTENSION (HARDENED CAST IRON)

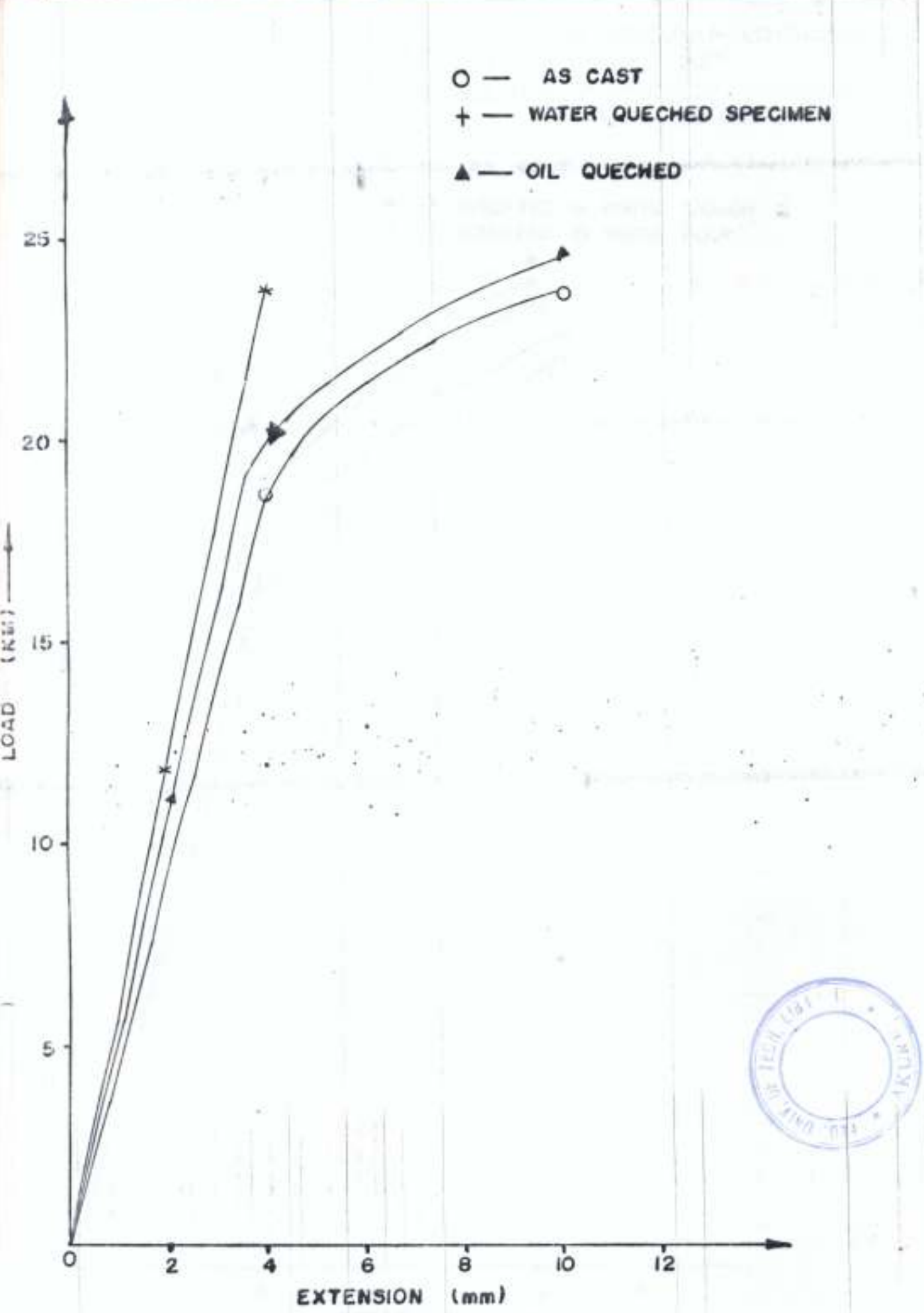
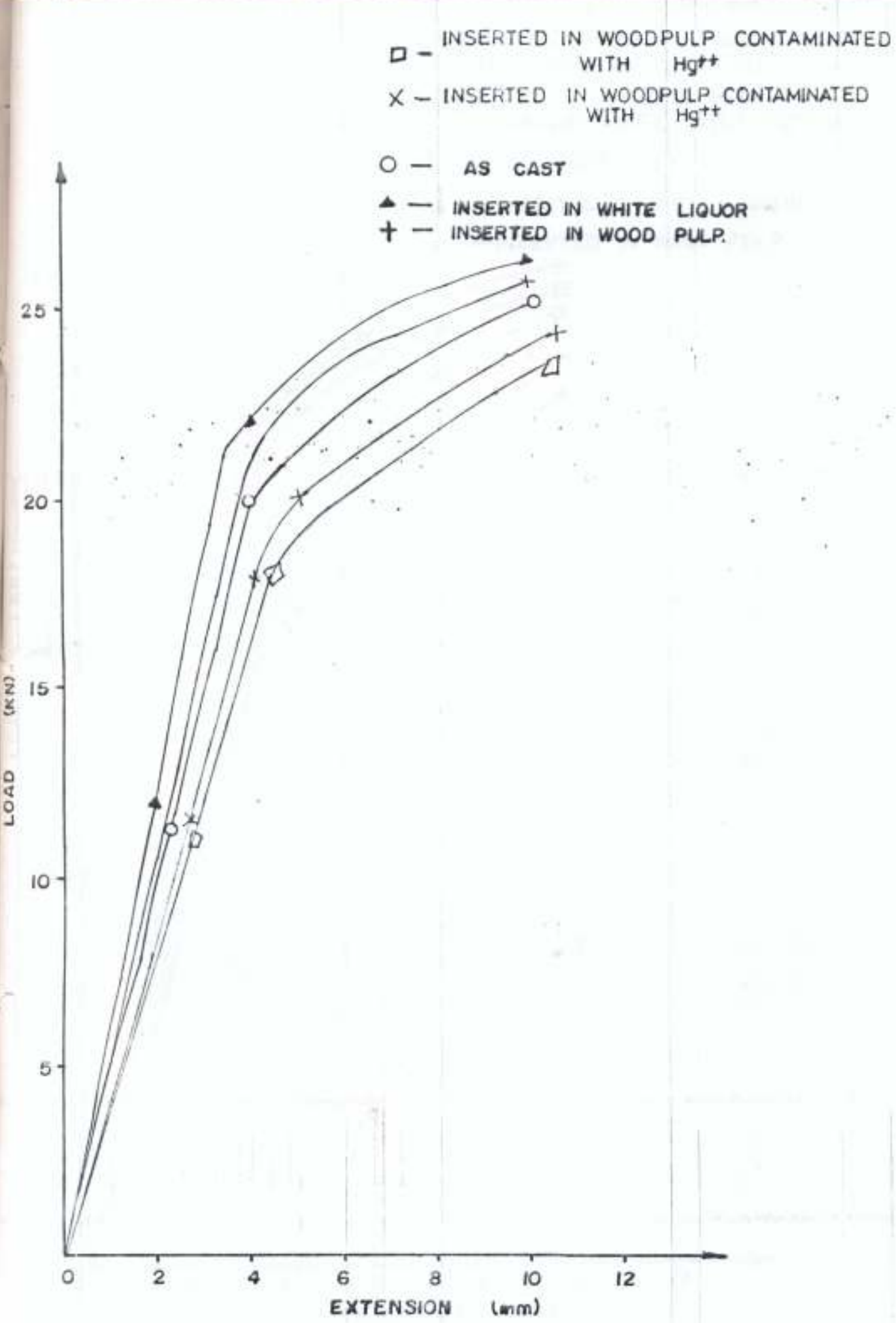


FIG. 16 GRAPH OF LOAD AGAINST EXTENSION (WATER AND OIL QUENCHED SPECIMENS)



F.G.17 GRAPH OF LOAD AGAINST EXTENSION FOR STRESS RELIEVED (SPECIMEN)

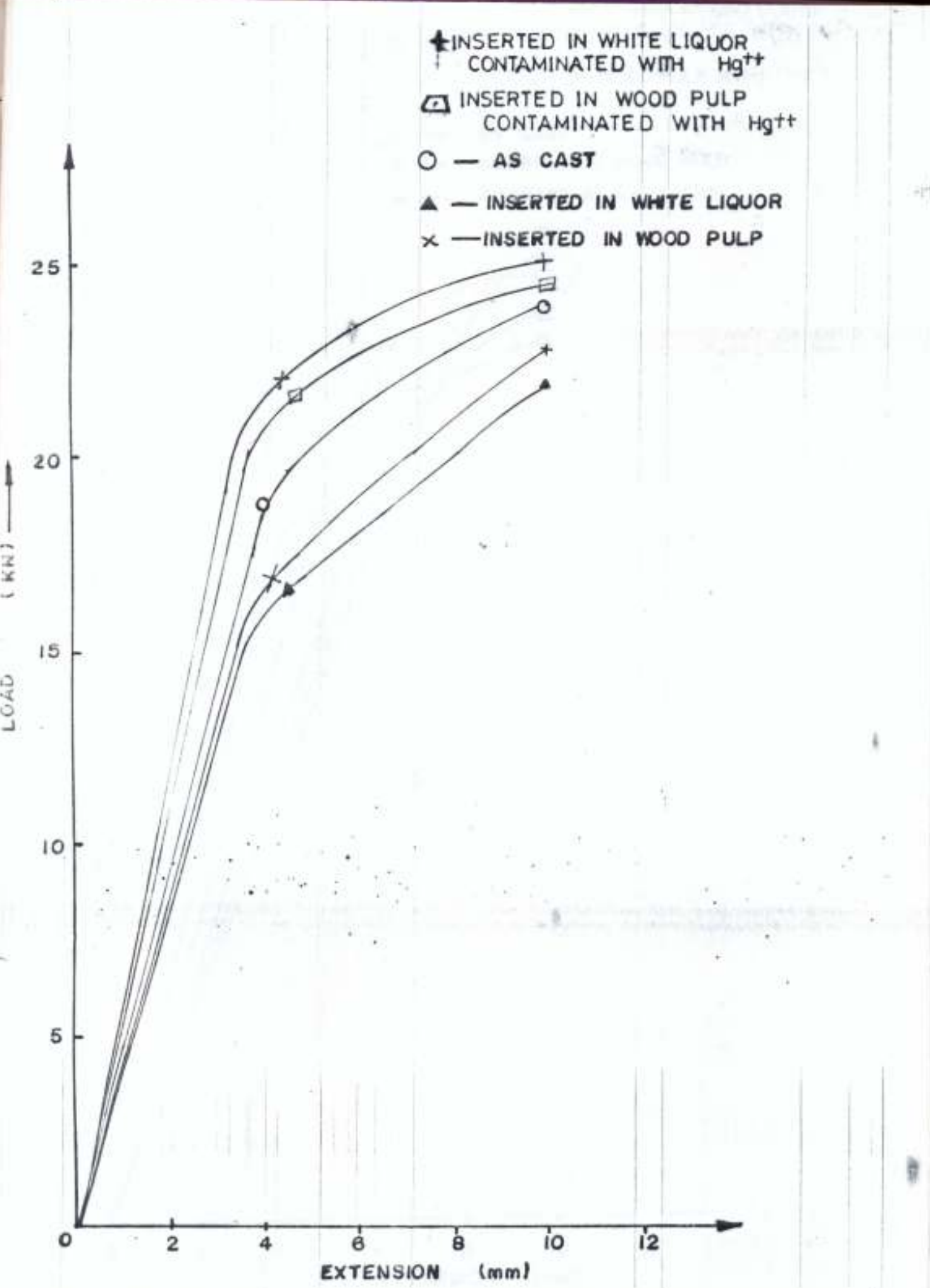


FIG. 18 GRAPH OF LOAD AGAINST EXTENSION (ANNEALED SPECIMEN)

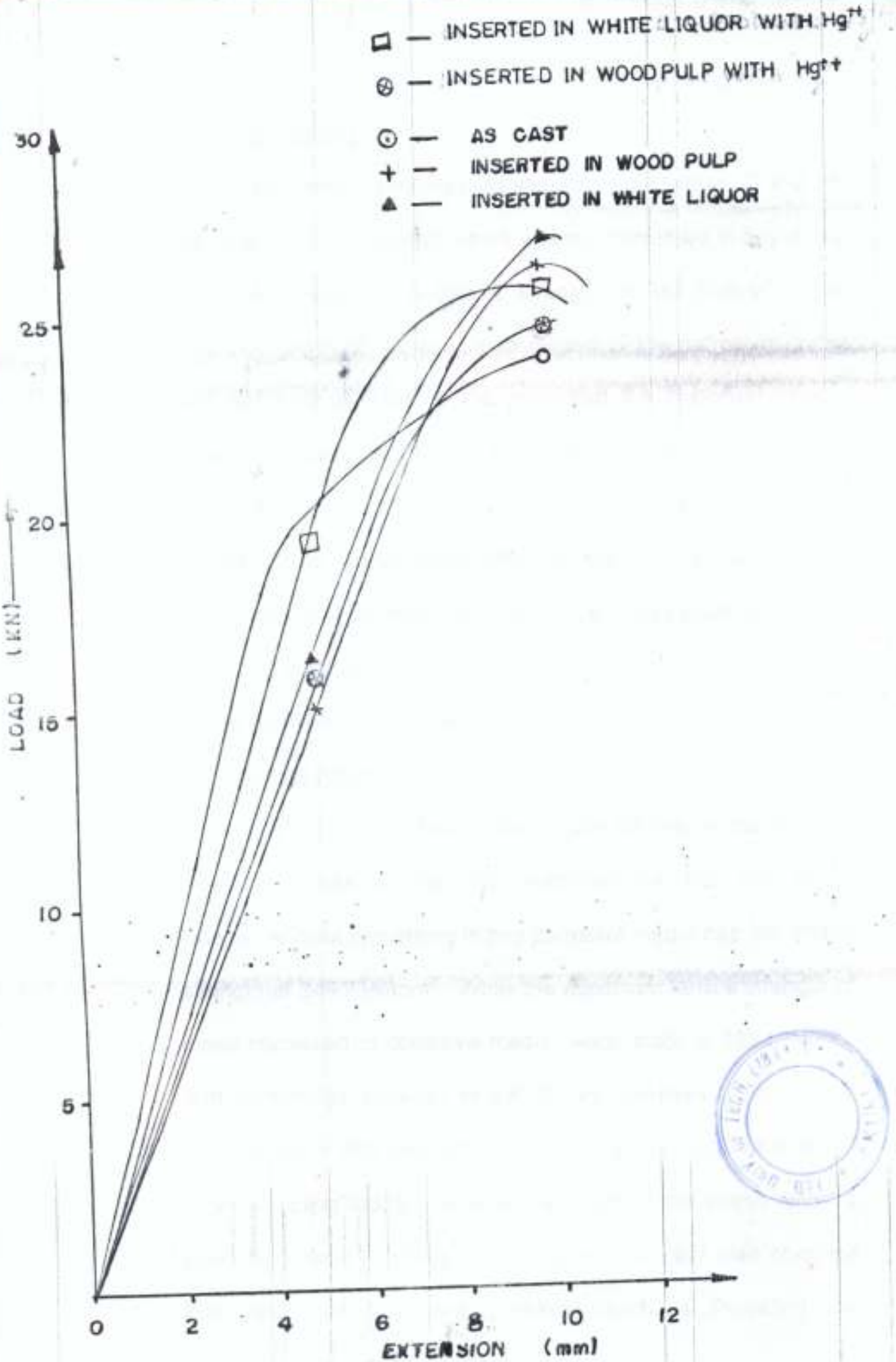


FIG. 19 GRAPH OF LOAD AGAINST EXTENSION FOR THE NORMALIZED SPECIMEN.

(ii) Normalizing

Examining the normalized samples, (see tables 22 and 23 the heat-treatment sample which was not immersed in any of the corrosive media has a tensile strength of 387.51/mm^2. The tensile strength of the specimen dipped in the corrosive media was seriously affected to the point that the maximum tensile strength obtained is 340.4N/mm^2 in white liquor, while the least was obtained from white liquor plus mercury ion as 270.56Nmm^2. In other words, the corrosion attack on the samples was much in white liquor with the mercury ion than in ordinary white liquor.

It is clear here that the corrosive media had a serious effect on the normalized specimens.

(iii) Stress Relieving

The effect of the heat treatment can be seen in the samples that were stress relieved. The specimen that was only stress relieved without immersing in any corrosive media has the tensile strength of 349.73N/mm^2. While the maximum tensile strength of those immersed in corrosive media (wood pulp) is 333.56Nmm^2 with percentage variation of 4.62%, and the least (white liquor plus $HgCl_2$) is 309.73N/mm^2 having the percentage variation of 11.44%. Even though the tensile strength of the stress relieved specimens were not very high compared to what was obtained from other heat treatment processes (such as annealing and

normalizing), the tensile strength of the material tends to be a bit stable. This shows that the internal stresses that were relieved made the corrosion attack on the samples to be very little.

(iv) Tempering

From Tables 15 and 16, the variation of the tensile strength of the tempering specimens can be seen on these tables. The maximum tensile strength is 296.45N/mm^2 while the minimum is 266N/mm^2. Although, the specimen that were quenched either with oil or water have a very high tensile strength than the tempered ones. Since the purpose of tempering the Grey Cast Iron is to obtain the maximum toughness.

5.4 Photomicrographic Examination and the Interpretation of Corroded Specimens

The photomicrographs of the Grey Cast Iron showing the microstructure of the Cast Iron are shown in Plates 1 – 5).

5.4.1 Structure of the as-cast Grey Cast Iron

The structure of the as-cast Grey Cast Iron consists of the flakes of graphite (dark) and patches of ferrite (light) in a matrix of pearlite. Dendritic structure can also be seen (see micrograph 1)

5.4.2 Structure of the Annealed Grey Cast Iron

The structure of the annealed Grey Cast Iron consists of graphite flakes (black) with ferrite (white). It is seen here that in

PLATE 1: MICROGRAPH OF THE AS-CAST GREY CAST IRON

It consists of graphite flakes (dark) and ferrite (light) in a matrix pearlite

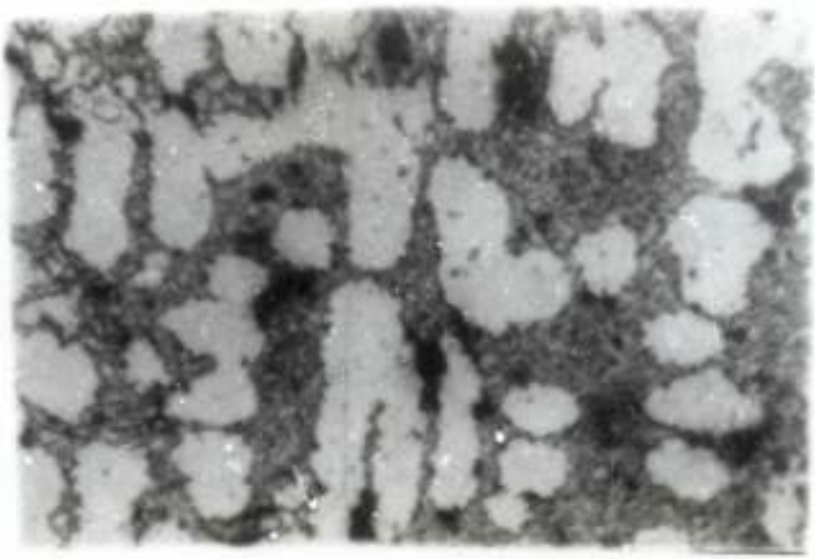


PLATE 2: MICROGRAPH OF THE ANNELED GREY CAST IRON

The annealed specimen's structure is in form of graphite flakes (black) with ferrite (white)

PLATE 3: MICROGRAPH OF THE NORMALIZED GREY CAST IRON

The structure of the Normalized Grey Cast Iron was completely pearlitic with dark regions of interdendritic graphite.

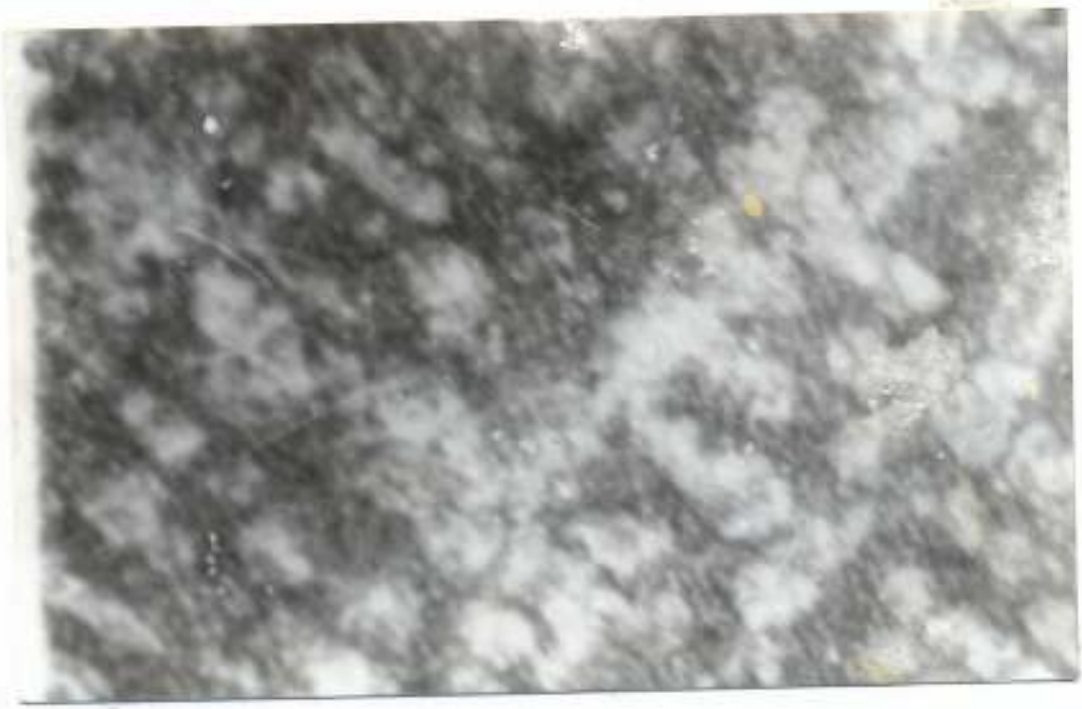


PLATE 4: MICROGRAPH OF THE QUENCHED GREY CAST IRON

The structure of the oil quenched Grey Cast Iron is in form of graphite and pearlite.

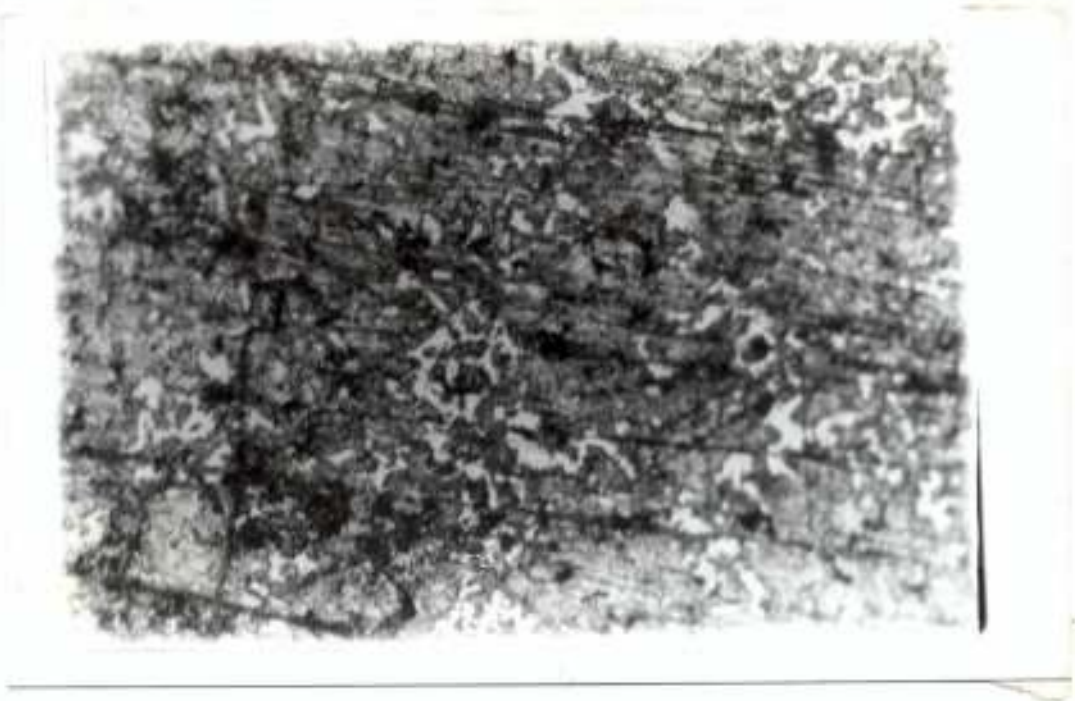


PLATE 5: MICROGRAPH OF THE STRESS RELIEVED GREY CAST IRON

The structure of the stress relieved contains (white) parches of phosphide eutectic or cementite (light) in a matrix of Pearlite (dark)

annealing for one hour at 900°C it broke down to spheroidal graphite Cast Iron.

The cementite in the original pearlite has been decomposed into fine grained ferrite and carbon which has diffused into the inter-dendritic graphite flakes. This is shown in micrograph 2.

5.4.3 Structure of the Normalized Grey Cast Iron

The structure shown in normalized Grey Cast Iron is purely pearlitic with dark regions of inter-dendritic graphites. No ferrite is seen in this structure. The dark portion could be attributed to the corroding effect of the corrosive media in which the specimen was immersed. (See photo plate 3).

5.4.4 Structure of the Quenched Grey Cast Iron

Examining the quenched specimen in micrograph 4, it shows a purely graphite and pearlite structure. Graphite can be identified in the inter-dendritic section.

5.5 Effect of Corrosive Media in the Specimens

The chemical attack of metals with resultant deterioration, destruction and loss of material is known as corrosion. The attack may be internal as well as external. The rate at which corrosion takes place is a function of factors such as the composition of the metal, the degree of exposure to humidity and

temperature, the presence of voids, stresses, and types of surface films. (Gordon and Philips 1965)

5.5.1 Wood Pulp

Wood Pulp contains Cellulose $(C_6H_{10}O_5)_n$ which is hydrocarbon and when dissolved in water it forms volatile acetic acid. This acid is the principal corroding agent in the solution. It attacked the Cast Iron samples that were immersed in the Wood Pulp solution for corrosion to take place. From table 8, the weight loss per unit area (g/dm^2) of the specimen dipped in wood pulp is reflected.

Annealed sample had the least corroding effect when exposed to the wood pulp solution. The corrosion effect of the wood pulp solution is of this order: tempering, normalizing, as-cast and stress relieving. It is least in the annealing specimen because of the slow cooling of the process and much in the process whereby they were rapidly cooled. The sample that were cooled had fine grain structure but the samples that were rapidly cooled had coarse grains. Corrosion attack is usually much on the coarse grains than on fine structures.

5.5.2 White Liquor

White liquor contains mainly sodium hydroxide and some other constituents. Hydroxides are less aggressive to metals attack than acids because:

(1) The consumption of H^+ ion reduces the cationic conductivity of the sodium which in turn reduces the conductivity of the solution.

(2) Formation of H_2O can be looked upon as ionic association with attendant reduction in conductivity.

(3) Formation of H_2O can lead to dilution.

When the samples were exposed to white liquor (contains sodium hydroxide which is a base), the metal surface was covered by the hydroxide which reduces the rate of corrosion in the solution compound.

$$OH^- + H^+ \ldots\ldots\ldots\ldots\ldots\ldots H_2O \quad - - - - - 5.1$$

From Figure 10, the graph of the weight loss against the exposure time. The weight loss is minimal compared to that of figure 15. The stress relieved was most attacked by the corroding effect of the white liquor while the as-received was most favoured in this case.

5.5.3 Wood Pulp plus Mercury Ion

When Wood Pulp was contaminated with the Mercury Chloride and this dissolved in solution as:

$$HgCl_2 \text{ ---------- } Hg^{++} + 2Cl^- \quad - - - - - 5.2$$

There is going to be low rate of dissolution and low rate of Hydrogen evolution. But there is high rate of crack propagation (hydrogen embrittlement). This determines the rate of corrosion in the fluid. Since the contaminated solution changes, the over

potential of corrosion reaction, the overall rate of corrosion was faster than that of the Wood Pulp alone. The annealed sample and the as-cast were least attacked while the tempered, normalized and stress relieved samples were greatly affected by corrosive medium.

5.5.4 White Liquor plus Mercury Ion

The solution of white liquor contaminated with Mercury Chloride. The Chloride Ion destroyed passivity. This enhances corrosion by reducing the passive region. The oxide film that was found covering the white liquor was removed by the chloride ion and hydrogen embrittlement takes place. The metal then corrodes greatly as can be seen in figure 13.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Studies have been undertaken to examine the effect of heat treatment on the micro-structure and the corrosion properties of Grey Cast Iron. The following conclusions are drawn from the studies carried out.

1. The tensile strength of the annealed sample (309.72 N/mm^2) was less than that of the as-cast sample (327.35 N/mm^2). This shows that annealing process removed the internal stresses of the Cast Iron. The tensile strength of the Cast Iron was also affected by the corrosive media in which the samples were immersed.
2. As for the percentage elongation, better ductility was obtained from the annealed samples than other heat treated samples. The least percentage elongation was obtained from the quenching samples.
3. The weight loss of the samples increases with time of exposure. This shows that the Cast Iron corroded in the immersed media.

4 The rate of corrosion attack increased with the cooling rate. This is the reason why corrosion was less in the annealed samples, which was slow cooled in the furnace, than other heat treated samples that were cooled rapidly either in still air or quenching media.

5 From the photo-micrograph observations, the following micro-structure of the Cast Iron were observed:

(i) Grey Cast Iron (as-cast) – Consists of graphite flakes (dark) and ferrite (light) in a pearlite matrix. The matrix corroded differentially, leaving behind the network of inter connected graphite flakes, this is, of course, very porous and weak.

(ii) The annealed structure is also in form of graphite flakes (black) with ferrite (white). The graphite flakes posed resistance to corrosion. The rate of corrosion in the annealed structure was very minimal compared to other heat treated specimens.

(iii) The structure of normalized Grey Cast Iron was completely pearlitic with dark region of inter-dendritic graphite. The pearlitic structure corroded leaving a dendritic graphite stiffened.

(iv) The structure of the quenched Grey Cast Iron consisted of graphite and pearlite. Generally, some

dark spots are seen in some of the micrograph showing the effect of corrosion on such areas.

From the analysis of the photomicrograph above, Cast Iron contains graphite in its micro-structure. Graphite is corrosion resistant.

If annealed Cast Iron is used for the constructional metals and equipment machines used in paper industries to process wood pulp and white liquor – less will be spent in repairs and maintenance of these equipment. This is because the rate at which deterioration takes place will be very minimal since corrosion effect on the annealed Cast Iron is very small.

Also, from the mechanical properties obtained and the micro-structure analysis carried out in this research work, one can deduce that Grey Cast Iron when annealed is a good metal that can be used in making machines and equipment for paper mill industry.

6.2 RECOMMENDATIONS

Based on the results obtained from the research work, the following recommendations are made:

(1) This type of research can be carried out using white Cast Iron and other alloy of Cast Iron such as Chromium, nickel and silicon Cast Iron to know whether their resistance to corrosion in paper industry may be better than that of Grey Cast Iron.

(2) The silicon content of the Grey Cast Iron could be varied and a similar research work is carried out on them to see what the result will be.

(3) The same research work can be carried out but this time, we can use alkali and 3% sodium chloride instead of the wood pulp and white liquor to see the effect of corrosion generally on the Grey Cast Iron.

(4) The research work can be carried out, instead of using full annealing method of heat treatment we can use ferritizing, intercritical and sub-critical annealing method. These can be used to compare the result of the full annealing method.

(5) The carbon content of the Grey Cast Iron can be varied and will then carry out the research work.

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