CORROSION AND STRESS CORROSION CRACKING OF PLAIN CARBON STEEL IN WOOD PULP AND WHITE LIQUOR

BY

JOJOLOLA OLADIMEJI OYETUNDE

BEING A THESIS SUBMITTED TO THE

SCHOOL OF POSTGRADUATE STUDIES

IN PARTIAL FULFILLMENT

FOR THE AWARD OF
MASTER OF ENGINEERING

IN

METALLURGICAL AND MATERIALS ENGINEERING

OF

FEDERAL UNIVERSITY OF TECHNOLOGY
AKURE ONDO STATE

1996

ii

CERTIFICATION

I certify that this work was carried out by Mr. **JOJOLOLA OLADIMEJI OYETUNDE** in the department of Metallurgical and Materials Engineering, Federal University of Technology Akure, and to the best of my knowledge it has not been submitted elsewhere for the award of a degree.

O. O. JOJOLOLA
Student

J. O. BORODE
Supervisor

iii

ABSTRACT

Experimental investigations have been carried out to study corrosion and stress corrosion susceptibility of plain carbon steel in wood pulp and white liquor with or without the addition of Hg^{++} and Sn^{++} ions under the influence of heat treatment by using weight loss and stress corrosion test methods. Result obtained showed that susceptibility to corrosion and stress corrosion cracking is a function of the cooling rate from the austenitising temperature. Potential measurements revealed potentials at which corrosion will occur and where passivity will occur while pH values decrease with exposure time which implies increasing acidity with or without the addition of Hg^{++} and Sn^{++} ions in both wood pulp and white liquor.

iv

DEDICATION

THIS WORK IS DEDICATED TO THE GLORY OF GOD

AND

TO MY PARENTS, MR AND MRS JOJOLOLA

ACKNOWLEDGEMENT

First and foremost, I am grateful to the Almighty God for His abundant mercy and protection since my first day on earth till this day.

I acknowledge the effort of my supervisors, late Prof. O. T. Adepoju, Dr. R.C. Agarwala, and Dr. J. O. Borode. I am also grateful to all my departmental lecturers, for their assistance during the period of this programme.

A friend in need, they say is a friend indeed, thus I acknowledge the contribution of the following people; 'Lola Olatunji, Deji Filani, Taiwo Oke, Tina Olatunji, 'Yinka Ajeigbe, Akeem Ogunyemi and Foluso Jolade for their unflinching support during this programme.

I am also grateful to all those who have contributed one way or the other to the success of this thesis. I say a big thank you.

TABLE OF CONTENTS

ix

LIST OF TABLES

CONTENTS PAGE

LIST OF FIGURES

CONTENTS PAGE

CONTENTS PAGE

CONTENTS PAGE

CHAPTER ONE
INTRODUCTION

The significant role of corrosion in industrial processes cannot be over emphasised. This is because corrosion of materials has a destructive effect on many production processes and thus the need to monitor and control it in order to minimise its damaging consequences.

Corrosion can therefore be defined as the destruction or deterioration of a material due to its reaction with its environment. The scope of destructive nature of corrosion is very wide and it covers practically all classes of materials used for engineering application.

The significance of corrosion studies can be viewed in the light of its effect on the national economy. The primary objective therefore is to reduce the enormous losses resulting from the corrosion damages and its attendant or associated problems.

Another significance of corrosion studies is associated with improved safety and reliability of operating equipment in production processes which through corrosion may lead to serious catastrophic consequences and in effect high production loss.

Fontana (1986) estimated that the annual cost of corrosion in the United States is about $30 billion, while Hoar (1971) estimated the cost of corrosion on the national economy in the United Kingdom to be 1.365billion pounds (1971) prices, the survey does not include the agricultural sector. These costs arise as a result of actual cost of replacement (direct cost) of corroded material and indirect costs, which may be due to lost production during shut down, high maintenance costs e.t.c.

Molozink et al (1979), Ohtani et al (1974) and Wilde (1986) all agreed that among the many factors that control the tendency of a material

to corrode, material properties and nature of the environment are probably the most important.

One area of significant industrial prodution is the paper making industry in which the pulp and white liquor are extensively used. It is therefore pertinent to examine the corrosion susceptibility of carbon steel in the media involved in paper making.

To date, little or no work has been done to study corrosion in wood pulp and white liquor, hence this work was carried out to ascertain the extent to which addition of extraneous ions and heat treatment operation of normalising, annealing, water quenching and tempering can affect the corrosion and stress corrosion susceptibility of plain carbon steel in wood pulp and white liquor.

It is hoped that the result of this work will help to reduce general corrosion rate and failure due to corrosion of digester, storage tanks and connecting pipes in a paper mill.

CHAPTER TWO
LITERATURE REVIEW

2.1 REVIEW OF CORROSION PRINCIPLES

Corrosion resistance depends on many factors. Thermodynamics and electrochemistry are of great importance in understanding and controlling corrosion.

Thermodynamic studies and calculations indicate the spontaneous direction of a reaction and can reveal whether or not the corrosion is theoretically possible.

Metallurgical factors frequently have a pronounced influence on corrosion resistance. In many cases the metallurgical structure of alloys can be controlled to reduce corrosion attack.

2.2 ELECTROCHEMICAL CORROSION

2.2.1 ELECTROCHEMICAL REACTIONS

This can be illustrated by the attack on iron by hydrochloric acid.

The reaction is

$$Fe + 2HCl \text{ ----> } FeCl_2 + H_2 \quad \text{.... (1)}$$

Noting that the chlorine ion is not involved in the reaction, this equation can be written as

$$Fe + 2H^+ \text{ ------> } Fe^{2+} + H_2 \quad \text{..... (2)}$$

This equation (2) can be conveniently divided into two reactions, the oxidation of iron and the reduction of hydrogen ions, the reduction takes place at the cathode, thus it is called cathodic reaction while the oxidation which takes place at the anode is called anodic reaction.

$$Fe \text{ ----> } Fe^{2+} + 2e \quad \text{(anodic reaction)} \quad \text{..... (3)}$$

$$2H^+ + 2e \text{ ----> } H_2 \quad \text{(cathodic reaction)} \quad \text{..... (4)}$$

An oxidation reaction is indicated by the increase in oxidation number. A decrease in oxidation number signifies reduction reaction.

Equations (3) and (4) are partial reactions - both must occur spontaneously and at the same rate on the metal surface. Thus it can be emphatically stated that during metallic corrosion, the rate of oxidation equals the rate of reduction (in terms of electron production and consumption).

The anodic reaction in every corrosion reaction is the oxidation of metals to its ion. This can be written in the generalized form :

$$M \longrightarrow M^{n+} + ne \quad \text{..... (5)}$$

There are several cathodic reactions that are frequently encountered in metallic corrosion. The most common are :

Hydrogen evolution : $2H^+ + 2e \longrightarrow H_2$ ..... (6)

Oxygen reduction (acid solutions): $O_2 + 4H^+ + 4e \longrightarrow 2H_2O$ .... (7)

Oxygen reduction (neutral or basic solutions) :

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$ ... (8)

Metal ion reduction: $M^{3+} + e \longrightarrow M^{2+}$

Metal deposition: $M^+ + e \longrightarrow M$

Hydrogen evolution is a common cathodic reaction since acid or acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of producing this reaction. Metal ion reduction and metal deposition are less common reactions and are not frequently found in chemical process streams. More than one oxidation or reduction reaction can occur simultaneously. For example, during corrosion of zinc in aerated HCl, cathodic reactions are both oxygen reduction and hydrogen evolution.

2.2.2 POLARIZATION

An electrochemical reaction is said to be polarized when a decrease in the driving force (electrode potential difference) for corrosion reactions at the electrodes is observed with time. It can be conveniently

divided into two different types; activation polarization and concentration polarization.

Activation polarization refers to an electrochemical process that is controlled by the reaction sequence at the metal -electrolyte interface. The reaction sequence which occurs during hydrogen evolution might be the electron transfer step or the formation of hydrogen molecules. The relationship between reaction rate and overvoltage for activation polarization is:

$$\eta_a = \beta_a \log i_a/i_0 \quad \ldots\ldots (9)$$

where

η_a = overvoltage

β_a = constant = $\frac{2.303RT}{\propto ZF}$

i = current density

Equation (9) is called the Tafel equation

Concentration polarization refers to electrochemical reactions that are controlled by the diffusion in the electrolyte.

If there is no activation polarisation at the electrode, then the concentration polarisation is given as ;

$$\eta_c = \frac{2.3RT}{nF} \log (1 - i/i_L) \quad \ldots\ldots (10)$$

where

η_c = concentration polarisation

R = gas constant

i = current density

i_L = limiting diffusion current density

T = absolute temperature

n = number of electrons transferred

F = Faraday constant

Usually both activation and concentration polarisation occur at an electrode, in this situation activation polarisation usually controls at low reaction rates whereas at higher reaction rates concentration polarisation becomes controlling. The total polarisation is the sum of the combinations of activation polarisation and concentration polarisation:

$$\eta_T = \eta_a + \eta_c \qquad \ldots\ldots (11)$$

where

η_T = total overvoltage

During anodic dissolution, the equation for the kinetics of anodic dissolution is given by:

$$\eta_{diss} = \beta \log i/i_o \qquad \ldots\ldots (12)$$

During reduction processes such as hydrogen evolution or oxygen reduction, concentration polarisation becomes important as the reduction rate approaches the limiting diffusion current density. The overall reaction for a reduction process is given by combining equations (9) and (10) with appropriate signs:

$$\eta_{red} = -\beta \log i/i_o + \frac{2.3RT}{nF} \log (1 - i/i_L) \ldots\ldots (13)$$

The importance of equations (12) and (13) lies in the fact that they are basic equations of all electrochemical reactions. Equation (13) applies to any reduction reaction equation (12) applies to almost all anodic dissolution reactions except in metals which demonstrate active - passive behaviour. Thus using β, i_L , i_o,the kinetics of virtually every corrosion reaction can be precisely described.

The magnitude of polarization is termed overpotential. It is a measure of polarization with respect to the equilibrium potential of an electrode. That is, the equilibrium potential of an electrode is considered as zero and the overpotential is stated in terms of volts or millivolts plus or minus with respect to this zero reference.

2.2.3 PASSIVITY

Passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environment conditions. It is a result of formation of adherent protective oxide film that is stable in the electrolyte. The metals become inert and behave as if they were noble metals such as platinum and gold.

Fontana (1986) reported that when a small piece of steel was immersed in 70% trioxonitrate V acid at room temperature, no reaction was observed. Weight loss determinations indicate that the corrosion rate of the steel was approaching zero. When water was added, diluting the trioxonitrate V acid approximately one to one no change occurs. The steel remains innert. However, when the steel was scratched with a glass rod or when the beaker was shaken violently so that the sample strikes the sides, a violent reaction occurs resulting in the iron going into solution; and large volume of hydrogen oxide gases were released.

From this experiment, it can be seen that in the passive state, the corrosion rate of a metal is very low, the pasive state is relatively unstable and subject to damage by the effect of scratching.

Iron, chromium, nickel, titanium and alloys containing major amounts of these elements demonstrate active - passive transitions.

2.3 THERMODYNAMICS OF AQUEOUS CORROSION

All interactions between elements and compounds are governed by the free energy changes available to them. The change in free energy ΔG is a direct measure of the maximum electric energy available from a system.

The free energy of an electrochemical reaction can be calculated by the following equation;

$$\Delta G = -nFE \quad \ldots\ldots (14)$$

where

n = number of electrons involved in the reaction

F = Faraday constant

E = cell potential

If the reactants are at unity, the cell potential can be obtained from the table of standard electrode potentials.

If the reactants are not at unity, the Nernst equation can be used to obtain the cell potential;

$$E = E_o + \frac{2.3}{nF} \log \frac{a_{oxid}}{a_{red}} \quad \ldots\ldots (15)$$

where

E = half cell potential

E_o = the standard half cell potential

R = gas constant

T = absolute temperature

n = number of electrons transferred

F = Faraday constant

a_{oxid} and a_{red} are activities (concentrations) of oxidized and reduced species.

The actual magnitude of the free energy change is relatively unimportant in corrosion applications, the most important factor is the sign of the free energy change for a given reaction, since this indicates whether or not the reaction is spontaneous.

From equation (14), it can be stated that in any electrochemical reaction, the most negative or active half cell tends to be oxidised, and the most positive or noble half cell tends to be reduced.

From this rule, it follows that all metals with reversible potentials more active (negative) than hydrogen will tend to be corroded by acid solutions.

Thermodynamics or, more specifically, half cell potentials can be used to state a criterion for corrosion. *Corrosion will not occur unless the spontaneous direction of the reaction indicates metal oxidation.*

The applications of thermodynamics to corrosion phenomena have been further generalised by means of potential-pH plots. This is called Pourbaix diagram. The potential-pH diagram for iron is shown in figure 1. The diagram is constructed based on calculations from Nernst equation and solubility data for various metal compounds. As shown, it is possible to delineate areas in which iron, iron hydroxide, ferrous ions, etc., are thermodynamically stable.

The diagram helps in predicting the spontaneous direction of reactions, estimating the composition of corrosion products, predicting environmental changes that will prevent or reduce corrosive attacks.

Since the diagram represents equilibrum conditions, it should not be used to predict the velocity of a reaction.

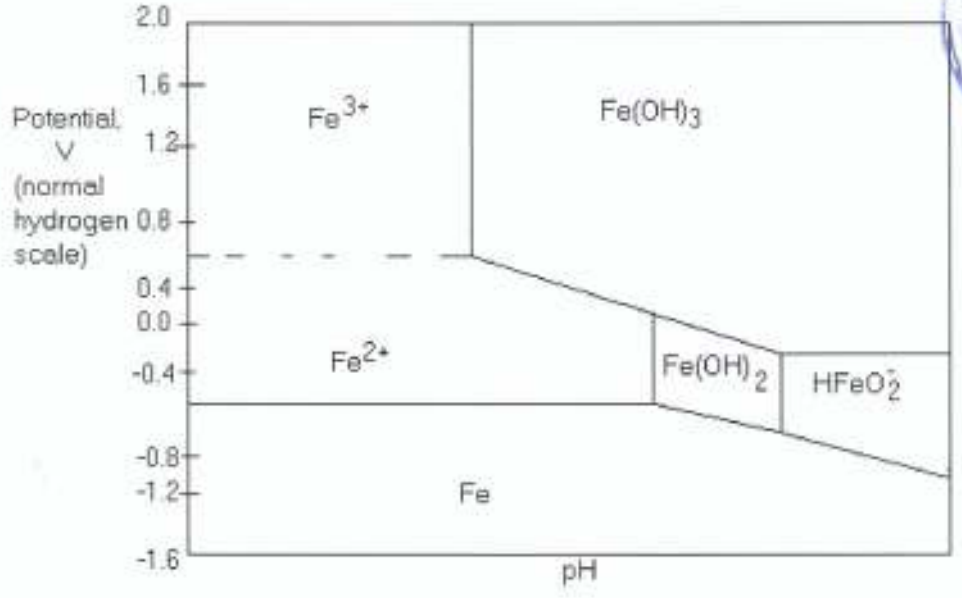

Figure 1: Simplified potential pH diagram for the iron-water system (Fontana 1986)

2.4 EFFECT OF ENVIRONMENTAL FACTORS ON CORROSION

Most often, process variables in industrial processes do affect significantly the corrosion of materials. Some of these variables are:

1. Effect of oxygen and oxidizers: the effect of oxidizer additions or the presence of oxygen on corrosion rate depends on the medium and the metals involved. The corrosion rate may be increased by the addition of oxidizers, oxidizers may have no effect on the corrosion rate, or a very complex behaviour may be observed.

2. Effect of velocity: some metals owe their corrosion resistance in certain mediums to the formation of massive bulk protective films on their surfaces, for example both lead and steel are protected from attack in tetraoxosulphate VI acid by insoluble sulphate films. When materials like these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack.

3. Effect of temperature: corrosion rate rapidly increases with temperature. In some materials, an almost negligible effect at lower temperature is followed by a very rapid rise in corrosion rate at higher temperatures. Fontana (1986) reported that when 18-8 stainless steel was immersed in trioxonitrate V acid at low or moderate temperatures, the stainless steel was in the passive state very close to the transpassive region but on increasing the temperature of trioxonitrate V acid, its oxidizing power is increased resulting in rapid increase in corrosion rate of the stainless steel.

2.5 REVIEW OF FORMS OF CORROSION

It is convenient to classify corrosion in the forms in which it manifests itself, the basis for this classification is the appearance of the corroded metal. Some of the basic forms of corrosion are unique, but all of them are more or less interrelated. They are:

1. Uniform corrosion: it is characterised by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface area. The metal becomes thinner and eventually fails. This form of corrosion represents the greatest destruction of metal on a tonnage basis.

2. Galvanic corrosion: this form of corrosion occurs between two dissimilar metals joined together in a corrosive or conductive solution. It is an electrochemical corrosion in which the less important metal becomes anodic and the more resistant metal cathodic.

3. Crevice corrosion: it is an intensive localised corrosion that occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. It is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits and crevices under bolt and rivet heads. Example of deposits that may produce crevice corrosion are sand, dirt, corrosion products and other solids. Contact between metal and non metallic surfaces can cause crevice corrosion as in the case of a gasket.

4. Filiform corrosion: it is a special type of crevice corrosion. It occurs under protective films and does not weaken or destroy metallic components but only affects surface appearance. A typical example is the attack of enamelled or lacquered surfaces of food and beverage cans that have been exposed to the atmosphere. The red brown corrosion filaments are readily visible.

5. Pitting corrosion: it is an extremely localised attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or very close together that they look like a rough surface. Pitting is highly destructive and an insidous form of corrosion that results in equipment failure due to perforation with only a small percent weight loss of the entire structure.

6. Intergranular corrosion: it occurs as a result of localised attack at and adjacent to grain boundaries with relatively little corrosion of the grains. The alloy disintegrates and/or loses its strength. It can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain boundary areas. Depletion of chromium in the grain boundary regions results in intergranular corrosion of stainless steels.

7. Erosion corrosion: it occurs as a result of the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally this movement is very rapid and mechanical wear effects or abrasion are involved. Erosion corrosion is characterised in appearance by grooves, gullies, waves, rounded holes and valleys and usually exhibits a directional pattern. Gases, aqueous solutions, organic systems and liquid metals are some of the corrosive mediums that could cause erosion corrosion. Metals that form protective films for protection also suffer erosion corrosion when the films are damaged or worn and the metal and alloy are attacked at a rapid rate.

8. Selective leaching: it is the removal of one element from a solid alloy by corrosion processes. The most common type is the selective removal of zinc in brass alloys (dezincification). Similar processes occur in other alloy systems in which chromium, aluminium, iron, cobalt and other elements are removed.

9. Stress corrosion: stress corrosion cracking (SCC) refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium.

2.6 STRESS CORROSION CRACKING

Stress corrosion cracking is a term given to the intergranular or transgranular cracking of a metal by the conjoint action of a static tensile

stress and a specific environment. Trethwey and Chamberlain (1992) said that this form of corrosion is very common throughout industry and despite decades of intensive research, after which workers are only now beginning to understand the processes involved, measures adopted to control it are still frequently unsuccessful.

Pure metals are more resistant to SCC than alloys of the same base metal but are not immune. Agrawal et al (1979) reported that pure copper has been induced to crack in slow strain rate tests, but these conditions are quite severe in comparism to service conditions.

SCC may be either transgranular or intergranular, but the crack follows a general macroscopic path that is always normal to the tensile component of stress. Liu et al (1980) said that in transgranular failures, the cracks propagate across the grains usually in specific crystal planes, usually low indices such as [100], [110] and [210]. The intergranular mode suggests some inhomogenuity at the grain boundaries. For example, segregation of sulphur and phosphorous at the grain boundaries is the possible cause of intergranular SCC of low alloy steels. According to Parkins (1990) intergranular SCC may be as a result of stress assisted intergranular corrosion since most alloys showing such failures also show at least weak evidence of intergranular corrosion without stress.

Carbon steels are susceptible to SCC in many corrosive environments and the most common environments are in nitrates and cyanides which are often present in chemical process streams. The SCC in intergranular carbon and low alloy steels failures have been reported by Korbin (1987) in aqueous solutions and moist gases containing moistures of CO_2 and CO. Long et al (1983) have reported the segregation of carbon and nitrogen at the grain boundaries thus causing cracking, so also is Jones and Ricker (1987) for phosphorous.

Fontana (1986), said that many investigators have classified all cracking failures occurring in corrosive media as stress corrosion cracking,

including failures due to hydrogen embrittlement. However these two type of cracking failures respond differently to environmental variables.

During stress corrosion cracking, the metal or alloy is virtually unattacked over most of its surface, while fine cracks progress through it. One feature of SCC which occurs repeatedly is the unexpectedness of such cases . Often a material ,chosen for its corrosion resistance in a given environment , is found to fail at a stress level well below its normal fracture stress . Rarely , is there any obvious evidence of an impending failure ,and because it can occur in components which are apparently unstressed, it is even more of a surprise when components are found defective. Not all metal environment combinations are susceptible to cracking. Stainless steel crack in chloride and caustic environments but do not crack in sulphuric acid, nitric acid, acetic acid or pure water. In the oil industry, where pipes in deep, high pressure wells require the use of high strength steels which are known to be susceptible to SCC, particularly in the presence of hydrogen sulphide. MCreynolds and Vennet (1975) reported that an inhibitor has been used consistently in an attempt to alleviate corrosion problems in such situations, yet failures in the presence of the inhibitor were still been reported 10 years after the inhibitor had been proved ineffective.

Ford (1984) reported that it is now generally agreed that there is no single mechanism for SCC . Any combination of a number of significant factors may contribute to a given SCC failure.

The failure of metal components can be conveniently divided into the initiation phase during which a stress raiser is formed, and a second phase of crack propagation leading to failure.

2.7 MECHANISM OF STRESS CORROSION CRACKING

Many mechanism have been proposed for the propagation of cracks in environment sensitive cracking. Scully (1966) suggested that the important feature in a stress corrosion crack propagation process is the time in which a sequence of events occur, e.g the rate of slip step emergence or the rate of repassivation. Ford (1984) said that three main mechanisms are generally applicable and they will be described here. They are:

(a) Pre-existing active paths

(b) Strain generated active paths

(c) Adsorption related mechanisms.

2.7.1 PRE EXISTING ACTIVE PATHS MECHANISMS

In this mechanism, propagation is believed to occur preferentially along grain boundary regions. Grain boundaries may be anodically polarised for a variety of metallurgical reasons, such as the segregation or denudation of alloying elements. It is quite possible that dislocation pile up can produce the same effect, although this may be less likely where SCC occurs at low stress levels, in which case the role of tensile stress may simply be to keep the crack open, and to allow electrolyte access to the crack tip region. This mechanism predominate where SCC is governed by electrochemical or metallurgical considerations.

The existence of an active path in unstressed mild steel has been shown by its destruction in boiling nitrate solution when anodic currents are applied.

Diog and Edington (1974) stated that similar confirmatory evidence correlating metallurgical structure in the grain boundaries with cracking propensity has been produced for aluminium/copper and aluminium/magnesium alloys with appropriate heat treatments. The mode of cracking is intergranular.

2.7.2 *STRAIN* GENERATED ACTIVE PATHS MECHANISM

In contrast to the cases of cracking which are dominated by the influence of corrosion, Parkins (1976) said that there are many examples e.g. Fe-Cr-Ni steels in chloride solutions in which strain is the controlling influence. Such instances have led to the development of the strain-generated active path mechanism. The cracking is transgranular and the fracture surfaces show signs of slip steps.

The strain-generated active path is based upon the idea of a strain-induced rupture. The propagation rate is governed by three criteria:

1. Rate of film rupture: This is determined by the applied strain rate, or in the case of static loading, by the creep rate.

2. Solution renewal and removal rate at the crack tip: this diffusion controlled process is also governed by the accessibility of the crack tip to the aggressive species.

3. Passivation rate: This is a vital consideration, for if repassivation is very slow, excessive metal dissolution can occur at both the crack tip and sides. The crack widens considerably and blunts, and the usual result is that the crack growth is arrested. Thus; in poorly passivating alloys, general corrosion rather than cracking is to be expected. Conversely, very rapid repassivation leads to slow propagation rates; it is at moderate repassivation rates that the greatest damage is caused. This concepts suggests that the conditions which are most likely to result in cracking are those close to active/passive conditions, found from a potentiodynamic polarization curve.

2.7.3. ADSORPTION RELATED MECHANISM

Uhlig (1974) stated that the specificity of environments that promote SCC has sometimes been adduced in support of a crack tip adsorption model, but Parkins (1975) said that such observations do not appear to discount a dissolution mechanism.

Adsorption related mechanism propose that active species in the electrolyte degrade the mechanical integrity of the crack tip region, thus facilitating fracture of bonds at energies much lower than would be expected. In one mechanism, the aggressive ion which is specific for the case in question is thought to reduce the bond strength between metal atoms at the crack tip by an adsorption process which results in the formation of metal -species bonds. The energy used in binding the aggressor to the metal atoms reduces the metal-metal bond energy allowing mechanical separation to occur more easily.

A second adsorption- related mechanisms is based upon the formation of hydrogen atoms by the reduction of hydrogen ions within the crack. The hydrogen atoms are absorbed by the metal and are thought to cause weakening, or embrittlement, of the metal-metal bonds just beneath the surface of the crack tip.

2.8 FACTORS AFFECTING STRESS CORROSION CRACKING

Having looked at the mechanisms of SCC, it becomes obvious that there are some factors necessary for SCC to occur. These factors are:

(i) Stress factors.

(ii) Environmental factors

(iii) Metallurgical factors

2.8.1 STRESS FACTORS

Increasing the stress decreases the time before cracking occur. There is some conjecture concerning the minimum stress required to prevent cracking. For each alloy-environment combination there is probably an effective minimum, or threshold stress. This threshold value must be used with considerable caution since environmental conditions may change during operation.

The criteria for the stresses are simply that they be tensile and of sufficient magnitude. These stresses may be due to any source: applied, residual, thermal or welding. Fontana (1986) reported that numerous cases of SCC have been observed in which there is no externally applied stress, as-welded steels contain residual stresses near the yield point.

2.8.2 ENVIRONMENTAL FACTORS

At present there appears to be no general pattern to the environments that cause SCC of various alloys.

The presence of oxidizers often has a pronounced influence on cracking tendencies. Fontana (1986) observed that the presence of dissolved oxygen or other oxidizing species is critical to the cracking of austenitic stainless steels in chloride solutions, and if the oxygen is removed, cracking will not occur.

As in the case with most chemical reactions, SCC is accelerated by increasing temperature. In some systems, such as magnesium alloys, cracking occurs readily at room temperature. In other systems, boiling temperatures are required.

2.8.3 METALLURGICAL FACTORS

The susceptibility to SCC is affected by the average chemical composition, preferential orientation of grains, composition and distribution of precipitates, dislocation interactions, and progress of the phase transformation. These factors further interact with the environmental composition and stress to affect time to cracking, but these are secondary considerations.

In the past it has been a common generalization that pure metals do not crack. This has been challenged by observation by Push et al (1966) that cracking occur in 99.999% pure copper exposed in ammoniacal solutions containing $Cu(NH_3)_5$ complex ions. While generally the use of

pure metals is often an available avenue for preventing cracking, it should be pursued only with caution.

High-strength aluminium alloys exhibit a much greater susceptibility to SCC in directions transverse to the rolling direction than in those parallel to the longitudinal direction. This effect is due to the distribution of precipitates which result from rolling.

2.9. EFFECT OF pH ON CORROSION

Uhlig (1971) said that strong acids e.g. HCl, H_2SO_4 the diffusion barrier oxide film on the surface of iron is dissolved below pH 4. Uhlig (1971) reported that weaker acids e.g. acetic acid, dissolution of oxides occur at higher pH, hence the corrosion rate of iron increases accompanied by hydrogen evolution at pH 5 or 6. This difference is explained by the higher total acidity or neutralising capacity of a partially dissociated acid compared with a totally dissociated acid at a given pH.

In other words, at a given pH there is more available H^+ to react with and dissolve the barrier oxide film using a strong acid compared to a weak acid.

Uhlig (1975) reported that the increased corrosion rate of iron or steel as pH decreases is not caused alone by increased hydrogen evolution; in fact, greater accessibility of oxygen to the metal surface oxide favours oxygen depolarization which is often the more important reason.

2.10. EFFECT OF HEAT TREATMENT ON CORROSION

Heat treatment of metals are carried out to obtain structural changes. The structural parameter of importance in corrosion studies is the grain size.

In a study of corrosion of medium carbon steels in lime and cassava environments, Odeshi (1994) observed that the general corrosion rate of

heat treated samples increased with increasing cooling rate from the austentising temperature.

Angellini and Zucchi (1987) observed that pitting potentials for Cr-Co alloy samples heat treated between 750 to 1100^{0}C move towards negative values, indicating a decrease in the corrosion resistance with respect to as cast specimens. They observed that selective corrosion occurs at the grain boundaries between dendritic and interdendritic regions formed during solidification and that water quenching increases the susceptibility to localised corrosion with respect to slowly cooling samples.

Shreir (1979) stated that many alloys are subjected to drastic changes in their response to the effects of corrosive media when they have undergone certain heat treatments. Hahin (1982) and Nelson et al (1976) stated that the effects of the corrosive media on alloy takes the form of concentration of corrosion in particular regions or along certain paths, such as in the vicinity of grain boundaries where phases formed by heat treatment are most likely to be concentrated.

Zucchi and Angellini (1982) observed that although heat treatments may be generally beneficial to corrosion resistance of mild steel in acid solutions, differences are possible depending upon subsequent processing treatments, and response to corrosion resistance inducing heat treatments may be affected by prior metal processing history, for example, cold working prior to heat treatment.

The corrosion process in oxidising and non-oxidising acids may increase the probability of formation, retention and break down of passive films in different microstructures of metals.

Okoroafor (1987) reported that for mild steel immersed in 20% tetraoxosulphate VI acid, corrosion attack was highest for quenched samples, lowest for the normalised samples and intermediate for the as-received and annealed samples.

Razik et al (1989) also reported that for a steel coil manufactured to ASTM A615 grade 60 standard immersed in 2M tetraoxosulphate VI acid, annealing the samples below 750^{0}C showed better corrosion resistance than the as-received ones due to stress relieving and spheriodising of the cementite lamellae.

Alagbe (1990) reported that the order of susceptibility increases as follows:

annealing -----> normalising -----> oil quenching -----> water quenching when mild steel was immersed in agro fluids.

2.11 EFFECT OF ADDITIONS OF EXTRANEOUS IONS ON CORROSION

Where cracking occurs at the free corrosion potential, additions to the environment may cause the potential to move outside the cracking range and so prevent failure, and in a situation where the potential is within the cracking range, additions may influence cracking by their effect upon the passivation or dissolution reactions or both. Additions may also affect rates of both the anodic and cathodic reactions.

2.12 CORROSION AND STRESS CORROSION TEST METHODS

Stress corrosion cracking is a complex phenomenon. The testing for material susceptibility to it requires a considerable understanding of all the factors involved. Parkins (1976) said that methods currently available are numerous; only a few methods will be discussed here.

1. Slow strain rate test : methods developed by Parkins (1976) have involved the slow straining of smooth specimens at a constant, predetermined rate. Tensile test specimen are subjected to different constant strain rates while immersed in a test electrolyte and, after failure, the percentage reduction in area of cross section is determined. The method is useful because it always produces a fracture surface which can

be examined by traditional fractograph, also the time involved for the text is usually quite short, its major shortcoming is that it is largely qualitative.

2. Linear polarization: here a graph of over voltage is plotted against applied anodic and cathodic current. The slope of a linear polarization curve E/ i_{app} is controlled mainly by the corrosion current, i_{corr}.

One of the advantages of this method is that it permits rapid corrosion rate measurements and can be used to monitor corrosion rate in various process streams.

3. Weight loss measurements: this involve measuring the rate of corrosion in terms of weight loss of a specimen immersed in water or exposed to atmosphere for a period of time. Corrosion rate can be expressed in terms of micrometers per year (μm/yr) and millimeter per year (mm/yr); the former for low corrosion rates and the latter for rapid rates.

2.13 METHODS OF PREVENTION

Corrosion and stress corrosion cracking may be reduced or prevented by application of one or more of the following methods.

1. Lowering the stress below the threshold value if one exists. This may be done by annealing in the case of residual stresses, thickening the section, or reducing the load. Plain carbon steels may be stress-relief annealed at 1100 to 1200^0 F.

2. Eliminating the critical environmental species by, for example degasification, demineralization, or distillation.

3. Changing the alloy is one possible recourse if neither the environment nor stress can be changed. For example carbon steel is used in preference to stainless steel where SCC is a problem.

4. Applying cathodic protection to the structure with an external power supply or consumable anodes.

5. Adding inhibitors to the system if feasible. Phosphate and other organic and inorganic inhibitors can be successfully used to reduce SCC effects in mildly corrosive mediums.

6. Coatings are sometimes used, and they depend on keeping the environment away from the metal, for example, coating vessels and pipes that are covered with insulation.

7. Shot peening produces residual compressive stresses in the surface of the metal. Woelful and Mulhall (1982) show very substantial improvement in resistance to stress corrosion as a result of peening with glass beads.

2.14. COMPOSITION OF WOOD PULP

The natural cellulose fibre of plant predominate as raw materials in wood pulp. Others are lignin and hemicellulose. Most wood pulp is made from the coniferous woods, such as spruce and pine, but for various practical and economic reasons, the hard woods, are now being increasingly utilized.

Purified cellulose has the composition: carbon 44.4%, hydrogen 6.2%, oxygen 49.4%. It is represented by the formula $(C_6H_{10}O_5)_n$.

On hydrohysis by acids it yields glucose $C_6H_{12}O_6$.

$$(C_6H_{10}O_5)_n + nH_2O \text{ ---> } nC_6H_{12}O_6 \quad \text{..... (16)}$$

Each $C_6H_{10}O_5$ unit in cellulose contains three hydroxyl groups (0H-) capable of esterification whereas the glucose molecule contains four hydroxyl groups.

Like cellulose, the hemicelluloses are polymeric materials consisting of long chains of sugar residues. They are fairly readily hydrolysed by acids to their constituent sugars.

Lignin is also a polymeric material but it is resistant to hydrolysis by acids.

2.15 PULPING PROCESS

There are three (3) main types of pulping process, and they are chemical pulping, mechanical pulping and chemico-mechanical pulping.

The raw materials for the preparation of pulp for ultimate conversion into paper are:

1. Fibrous raw materials:- these are wood, waste paper, rags, straw.
2. Non-fibrous raw materials:- these are sulphur, sodium hydroxide (NaoH), sodium trioxocarbonate IV (Na_2CO_3), lime, chlorine, clay and alum.

To convert wood into pulp by any method used for pulp making, it is first necessary to remove the bark, and in case of chemical pulp, reduce the debarked wood into small chips of fairly uniform size.

The methods, however differ depending on the quality and relative size of wood being pulped and the kind and quality of pulp being produced by the paper mill.

The debarked wood, without any further preliminary treatment is ready for reduction to mechanical pulp. To make it ready for treatment by any of the chemical pulp making process, the chips must be further reduced.

The chemical pulp liquor is carried out by the sulphate, soda (caustic) or sulphite processes. Cooking of the wood chips is done in a digester.

In the sulphite process, the raw materials are sulphur (or source of sulphur as iron pyrites), lime or limestone and water.

To prepare pulp liquor by the soda process, Na_2CO_3 , lime and water are the principal raw materials used.

The raw materials used in the production of sulphate cooking liquor are sodium sulphate, lime and water. In the preparation of this liquor, use is made of the cooking liquor from previous pulping operations.

The liquor is concentrated by evaporation following the pulp washing operation.

The reactions in the sulphate process are:

$Na_2SO_4 + 2C \text{ ---> } Na_2S + 2CO_2$ ..... (17)

$Na_2CO_3 + Ca(OH)_2 \text{ -- -> } 2NaOH + CaCO_3$ ..... (18)

The $CaCO_3$ sludge is calcined to get CaO for re-use. The filtrate (white liquor), is used for cooking the cellulose fibres to produce pulp.

Black liquor is the name given to liquors recovered from the digesters, up to the point of their incineration in the recovery plant.

Green liquor is the name given to liquor made by dissolving the recovered chemicals in water weak liquor preparatory to causticizing.

White liquor is the name given to liquor made by causticizing green liquor, white liquor is used in the digester and can be called pulping chemical.

After the cooking operations are completed, the contents from the digesters are discharged under pressure into specially designed tanks which permit the rapid removal of steam either to the atmosphere or to a condenser.

The following operations are then conducted:

(i) Washing the chemical pulp

(ii) Screening of the pulp

(iii) Dewatering or thickening

(iv) Bleaching of the pulp by sodium hypochloride or chloride

(v) Brightening the colour of the pulp.

2.16 PULPING OPERATION

An integrated paper mill represents a large cross section of industrial processes.

The most common method for converting wood to fibres for paper making is the kraft pulping process. Both batch and continous digesters

cook the wood chips in a caustic or sulphide liquor. The batch digester is a welded, thick wall, carbon steel pressure that is fully stress relieved. However SCC of the weldments in the top of the digester has been revealed recently by Fontana (1986).

Indirect heating of the digester liquor is accomplished in vertical, shell-tube type heat exchangers called liquor heaters.

After the kraft cook, the softened chips and spent liquor are discharged under pressure to the blow tank. Pipelines called blow lines, for transport to the blow tank, are commonly mild steel in the straight portions. The chip or liquor slurry impacts target plates in the blow tank, thereby breaking the chips into pulp. This action causes severe erosion corrosion of the low alloy steel target plates.

After separation and washing, the pulp is transported to the bleachery or paper mill while the dilute, washed out liquor is sent to recovery for the generation of cooking chemicals.

The recovery boiler is the heart of the kraft chemical recovery cycle. The black liquor is burnt to produce heat for steam and subsequent power generation. A green liquor is obtained from black liquor and finally white liquor which is called the cooking chemicals is obtained from the green liquor.

In other chemical pulping methods, the process systems are similar to kraft, but the construction materials are stainless steels unlike kraft which is low carbon steel.

2.17 CORROSION OF STEEL DURING WOOD PULP PRODUCTION

Pulping of wood takes place in a digester made of carbon steel. Swartz et al (1982) stated that the type of corrosion that takes place in a digester can be divided into two namely primary corrosion and secondary corrosion.

Primary corrosion can be defined as that which occurs in the form of broad attack over the exposed surface of a digester. It results from the interaction of wood, steel and liquor during pulp production. Corrosiveness of the liquor increases with the concentration of sodium sulphide, sodium hydroxide and sodium thiosuplhate which are present during sulphide pulping process. They (1982) stated that in certain cases, appreciable quantities of sodium chloride, sodium sulphate

and sodium carbonate may affect the corrosiveness of the cooking liquor and similarly the concentration of sulphite may have an appreciable effect.

They (1982) said that the corrosiveness of white liquor to steel increases with the content of sodium thiosulphate and polysulphite, but there is some evidence that passivation occurs above certain values.

Secondary corrosion may be defined as primarily due to mechanical effects, being influenced by scale, fabrication methods digester design and operating conditions. Severe corrosion occurs when digester walls are intermittently washed by liquor in intimate contact with air and when liquor is directed against a wall by uneven chip distribution.

They stated that the average current corrosion rate for carbon steel digesters is about 30 mil/year and in critical areas it may vary from 40 to 80 mils/year. The corrosion rates for inconel or stainless lined or clad digesters are about 10% of the above digesters.

The electrochemistry of the dissolution of steel in wood pulp can be explained as this; some of the long chains of the sugar molecules of the wood cellulose are combined with the acetic acid in the form of esters. These groups can react with water to release free acetic acid, thus:

$$\underset{\text{ester}}{CH_3COOR} + \underset{\text{water}}{H_2O} \longleftrightarrow ROH + \underset{\text{acid}}{CH_3COOH} \quad \ldots\ldots\ldots (19)$$

The equlibrum for the reaction always means that the moisture in wood is slightly acidic

Acetic dissolution goes like this,

CH_3COOH -----> $CH_3COO^- + H^+$ ..... (20)

Iron dissolve thus,

Fe -------> $Fe^{2+} + 2e^-$ ..... (21)

The overall reaction is

$Fe + CH_3COOH$ -----> $CH_3COOFe + H^+$.....(22)

soluble complex

CHAPTER THREE
MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 MATERIALS

Hot rolled plain carbon steel, collected from Osogbo Steel Rolling mill was used for the study. The chemical analysis as carried out on a spectrometer is given below.

Table 1: Chemical composition of carbon steel studied.

C	Si	S	P	Mn	Fe
0.21	0.18	0.04	0.04	0.04	Balance

The white liquor and the wood pulp were collected from Nigerian Paper Mill Jebba. The white liquor contains sodium hydroxide, sodium sulphide and sodium trioxocarbonate IV. The wood pulp is made from pine wood which is a long fibre softwood. The age of the wood is about 9 years.

3.2 PREPARATION OF TEST SAMPLES.

The samples used for weight loss test were 8mm in diameter and 20mm long as shown in figure 2.

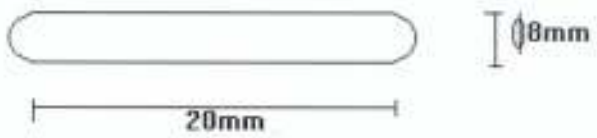

Figure 2: Test piece for weight loss test

The samples for stress corrosion cracking studies were machined to tensile specimens of gauge length 27mm and gauge diameter 5mm as shown in figure 3.

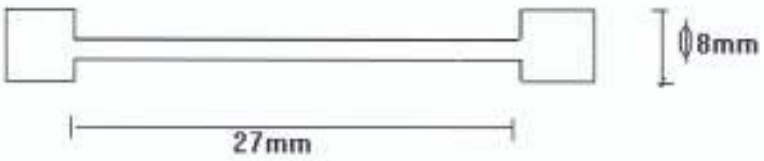

Figure 3: SCC test piece

All corrosion test pieces were ground on 240mm grade emery paper to remove all adhering oxide films and make the surface smooth. Surface grinding of weight loss test samples were done to remove cutting marks, this was done under running water to avoid alteration of surface structure of samples as a result of heating.

All samples were cleaned in alcohol to remove any adherent grease. The specimen were then dried and kept in a desiccator.

For the heat treated specimens, excessive oxide layers were removed by immersion in 10% dilute HCl followed by rinsing in water and alcohol in quick succession.

3.3 HEAT TREATMENT OPERATION.

The samples were solution treated at about 900oC in a Muffle type laboratory furnace. In annealing, furnace cooling of the test pieces was done, for normalising, air cooling was done while water quenching was done for quenching process. For the annealing and normalising operations, soaking time was 10 minutes for both weight loss test and SCC test specimens. Tempering was carried out at 350oC. Soaking time was about 1hour.

3.4 CORROSION AND STRESS CORROSION ENVIRONMENTS

The environments under investigation are wood pulp and white liquor (also called pulping or cooking chemical). The wood pulp is in a dry form and it is usually mixed with distilled water when to be used. The white liquor is in liquid form.

All investigations were carried out at room temperature, under normal atmospheric pressure and prevailing relative humidity. All tests were performed under stagnant conditions.

3.5 EXPERIMENTAL TECHNIQUES.

3.5.1 WEIGHT LOSS TEST.

The mass and surface area of all the specimens used for this study were measured before suspension in various solution. The percentage of the additions ($SnCl_2$ and $HgCl_2$) in the main environments were 3% weight. The set up is as shown in Fig 4.

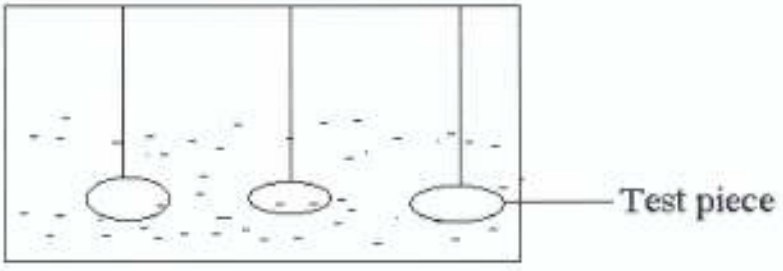

Figure 4: Schematic view of the set up for weight loss test

Immersed samples were removed at various time interval held under a stream of running water and brushed with a wire brush to remove adherent corrosion products, rinsed in alcohol and dried under ceiling fan.

The specimens were then weighed to obtain the loss in weight as a result of corrosion in the environments under study. The corrosion rate was measured in weight loss per unit surface area of the specimen.

3.5.2 PRE - EXPOSURE TEST.

The set up for this study is as shown in fig 5.

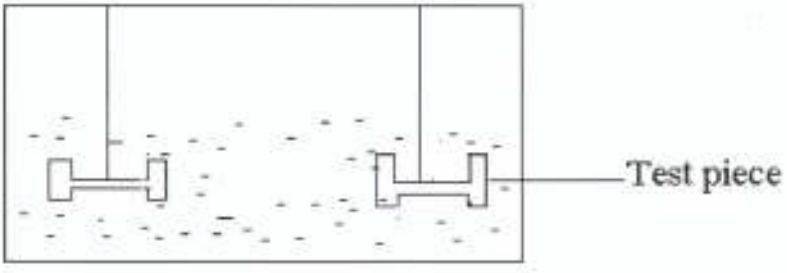

Figure 5: Schematic view of the set up for SCC test

Immersed test samples were removed at various time interval and fractured to test for their tensile properties. Fracturing was done with the aid of a tensometer. Percentage elongation to fracture (% E_f) was obtained for each sample.

3.5.3 pH AND POTENTIAL MEASUREMENT

CRISON micro pH 200 microprocessor controlled pH meter was used to monitor and measure the pH variation of the prepared corrosive media solutions under investigation with time. The same equipment was also used to measure the electrochemical potential of various structure under study in the solution with respect to Ag/AgCl reference system. The pH measurements gave variation of hydrogen ion concentration of the solutions with time as a result of decomposition in the corrosive solution.

With the electrochemical potential measurement, it was possible to monitor and ascertain the tendency of various structures under study to corrode in the corrosive solution.

CHAPTER FOUR
RESULTS

4.1 EXPERIMENTAL OBSERVATIONS.

During experimentation, small bubbles of gases were observed to evolve from the solution after about 3-5 hours of exposure of the steel samples to wood pulp and white liquor.

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

The quantity of evolved gas was very small for both wood pulp and white liquor. The liquor gas evolution stopped after about 5 hours. The rate of corrosion attack was higher in the case of wood pulp than in white liquor. Generally for both white liquor and wood pulp, the corrosion rate decreases with the exposure time. The implications of this is that the decrease in corrosion rate with time is more of passivity rather than retarding layer effect of the reaction product on the steel samples.

4.2 EFFECT OF EXTRANEOUS ION ADDITION

Studies were carried out to determine the effect of extraneous ion on the corrosion of carbon steel in white liquor and wood pulp. Appropriate solution of Sn^{++} and Hg^{++} were added to in known quantity to the white liquor and wood pulp followed by immersion of steel samples. The corrosion rate was measured by weight loss. The results obtained are given in figures 6 to 15.

4.3 EFFECT OF HEAT TREATMENT

Studies were carried out to determine the effect of heat treatment on the corrosion of carbon steels in wood pulp and white liquor. The heat treatment techniques used are annealing, normalising, quenching and tempering. The heat treated samples were subsequently immersed in white liquor and wood pulp where their corrosion rate was monitored by weight loss. The results obtained are presented in figures 16 to 21.

4.4 STRESS CORROSION CRACKING.

Studies were carried out to determine the effect of heat treatment on the stress corrosion cracking of carbon steel in white liquor and wood pulp. The ductility of the samples used were measured after the exposure time of 30 days in each medium. The ductile properties measured were used to assess the stress corrosion susceptibility of the samples under study. The results obtained are given in figures 22 to 37.

4.5 pH AND ELECTROCHEMICAL POTENTIAL MEASUREMENT

Studies were carried out to measure the variation of electrochemical potential difference of carbon steels immersed in white liquor and wood pulp with and without addition of Sn^{++} and Hg^{++}. The pH of each medium was measured and the potential difference noted. The results obtained are given in figures 38 to 41.

CHAPTER FIVE
DISCUSSION OF RESULTS

5.1 WEIGHT LOSS

5.1.1 EFFECT OF EXTRANEOUS ION.

The additions of extraneous ions are known (Odeshi 1994) to influence the corrosion of steels by way of passivation and dissolution reactions. Studies were carried out to ascertain the effect of addition of extraneous ions such as Hg^{++} and Sn^{++} in the corrosion of low carbon steel in the wood pulp and white liquor. Results obtained are plotted in figures 6 to 15. From these figures, it can be seen that both Hg^{++} and Sn^{++} addition increases the corrosion rate of the carbon steel in wood pulp and white liquor. The corrosion rate was found to be higher following the addition of Hg^{++} ion than that of Sn^{++} ion. Thus, it can be stated that the additions promote dissolution of steel samples in the media under investigation, thus Hg^{++} addition promotes dissolution more than Sn^{++} addition.

5.1.2 EFFECT OF HEAT TREATMENT

Parkins (1971) has observed that the susceptibility to corrosion varies with heat treatment. The manner by which the heat treatment affects corrosion is of relative importance especially the resulting microstructure obtained during the heat treatment. Figures 16 to 21 show the results obtained and the order in which corrosion susceptibility increases is found to be annealing → normalising → as received → tempering → quenching. Comparison of the results indicates that it is in good agreement with the findings of Okoroafor (1987) and Alagbe (1990) who both concluded that corrosion rate was higher for quenched samples in various media studied.

The high rate of corrosion of quenched samples is attributed to the presence of high quenching stress or strain concentrations. The low rate

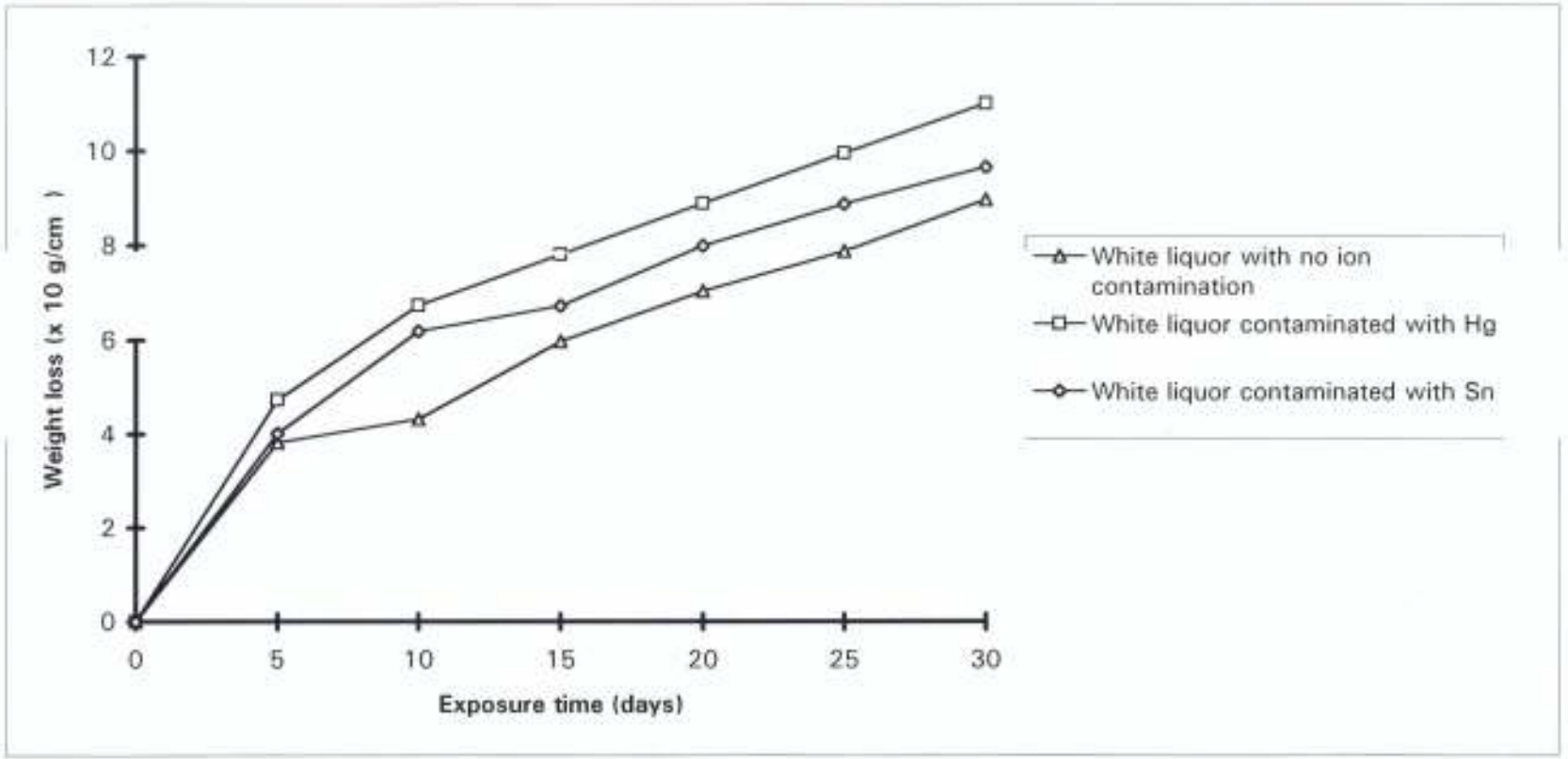

Figure 6: Effect of extraneous ions addition on corrosion of as received carbon steel in white liquor

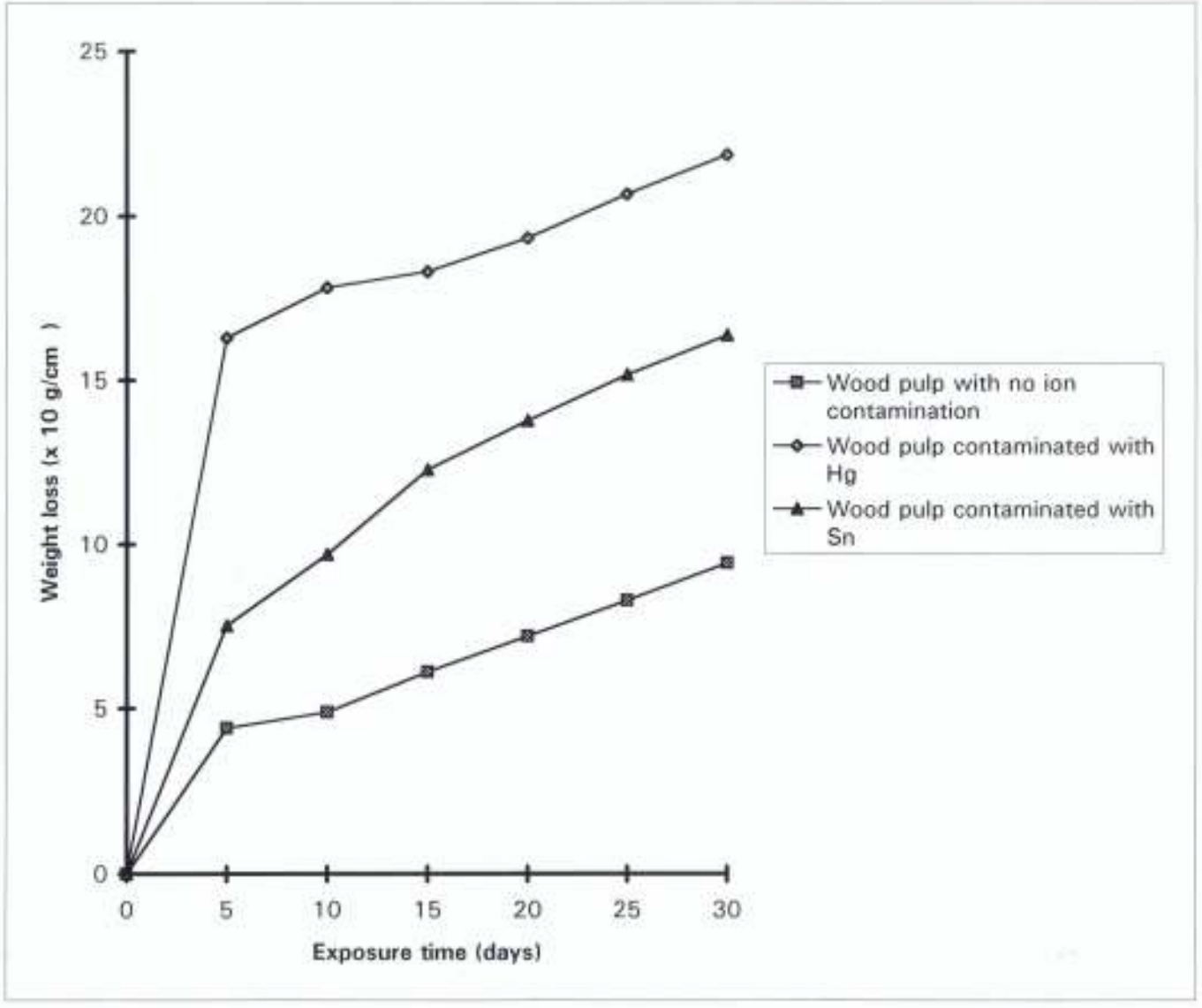

Figure 7: Effect of extraneous ions addition on corrosion of as received carbon steel in wood pulp

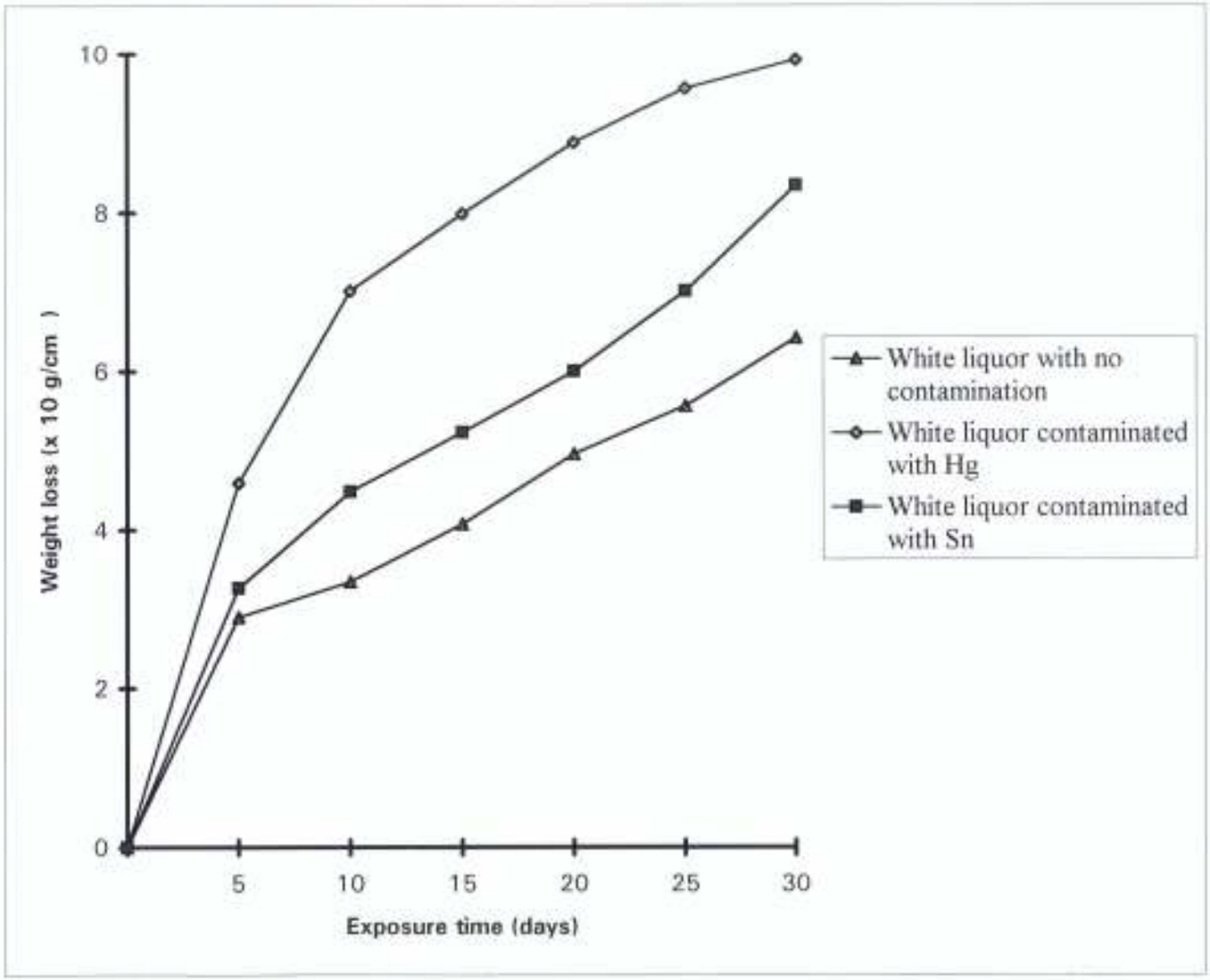

Figure 8: Effect of extraneous ions addition on corrosion of annealed carbon steel in white liquor

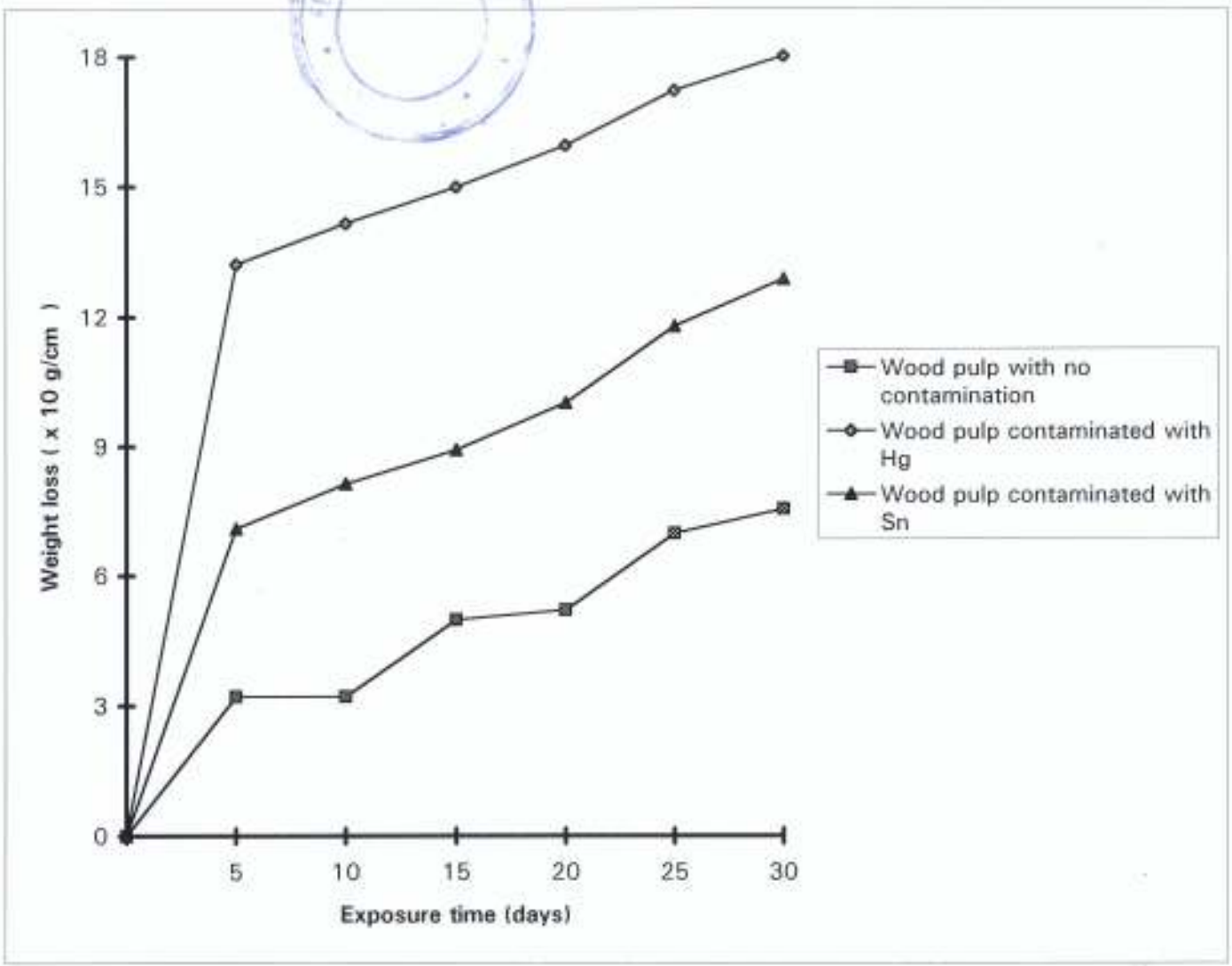

Figure 9: Effect of extraneous ions addition on corrosion of annealed carbon steel in wood pulp

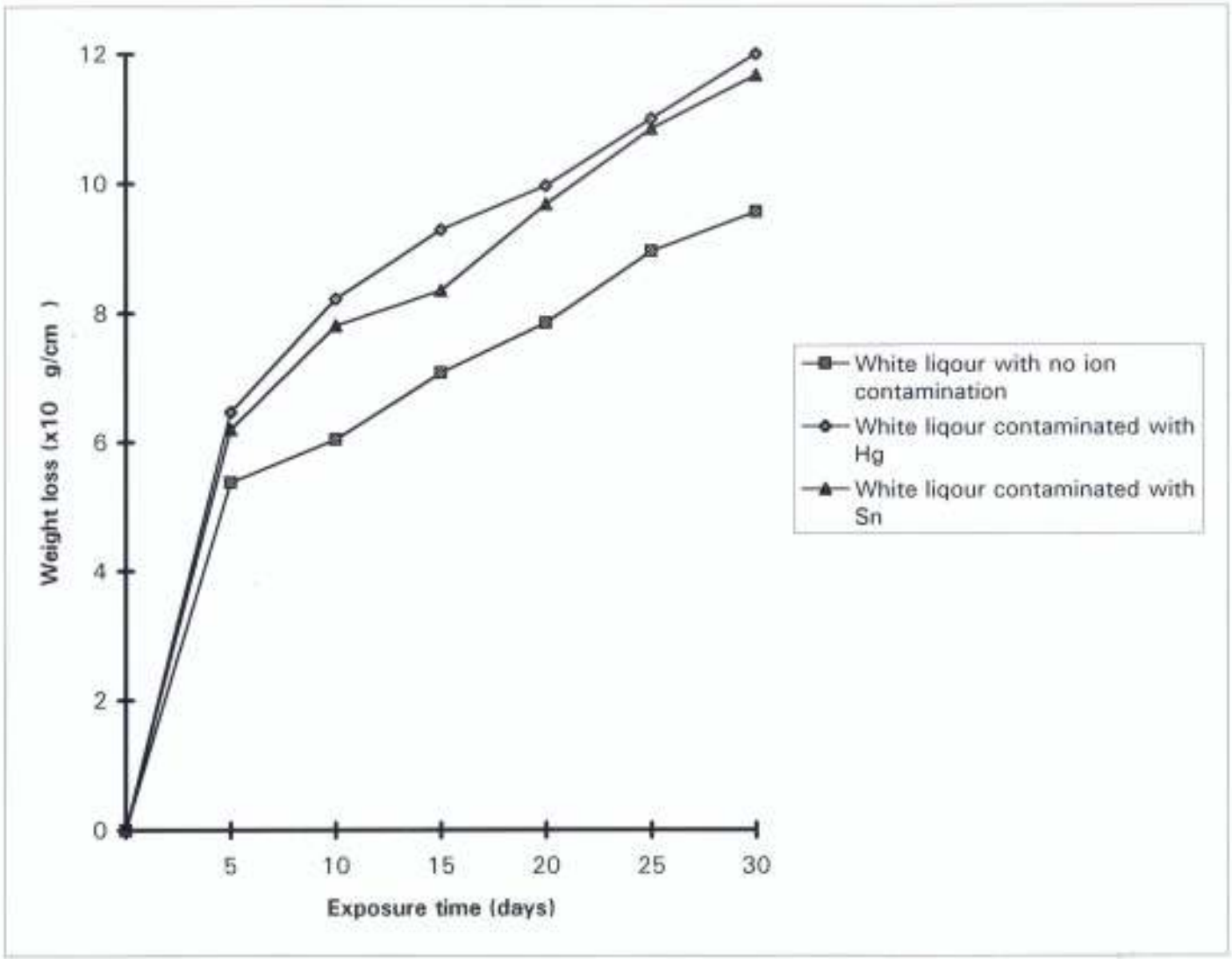

Figure 10: Effect of extraneous ions addition on corrosion of quenched carbon steel in white liquor

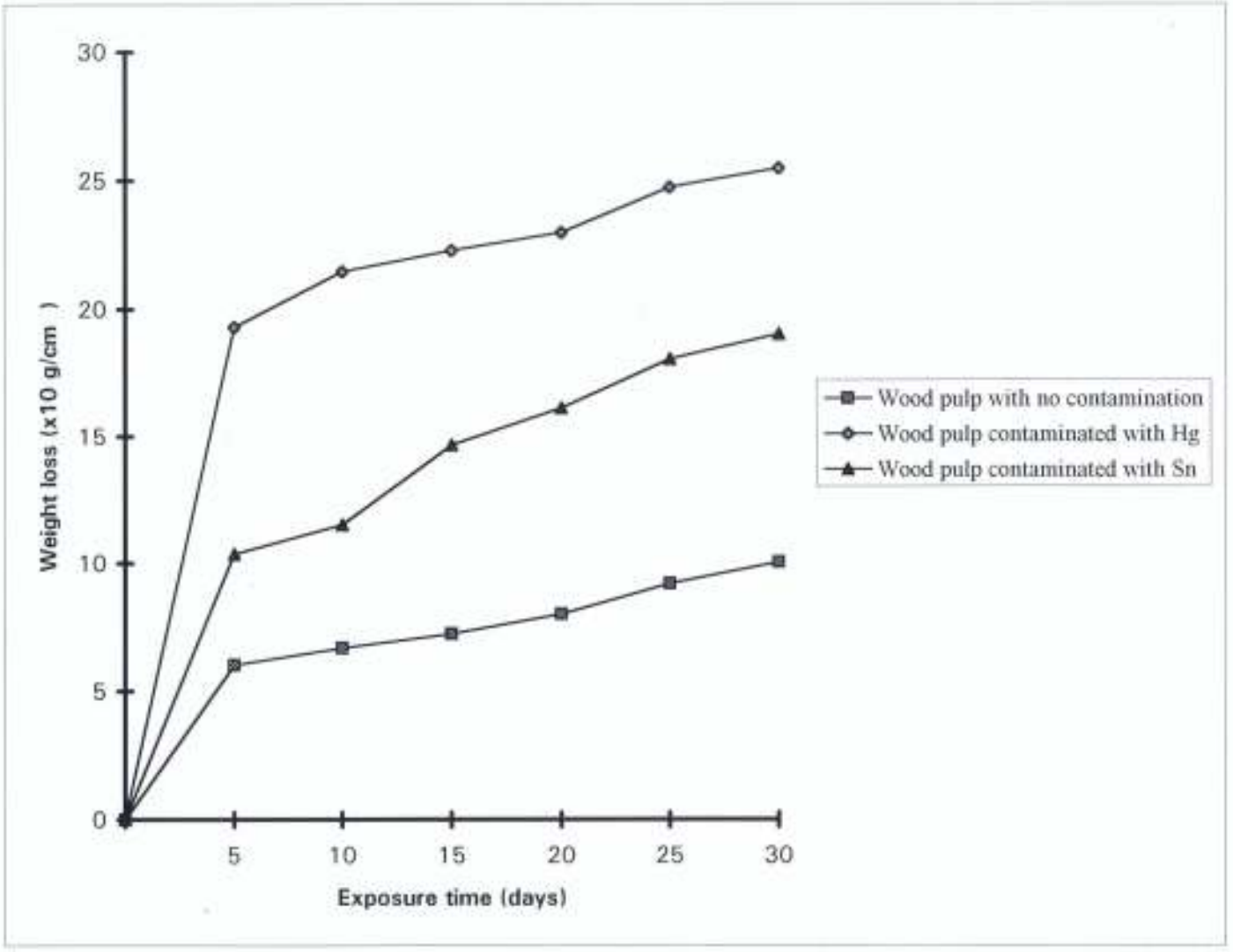

Figure 11: Effect of extraneous ions addition on corrosion of quenched carbon steel in wood pulp

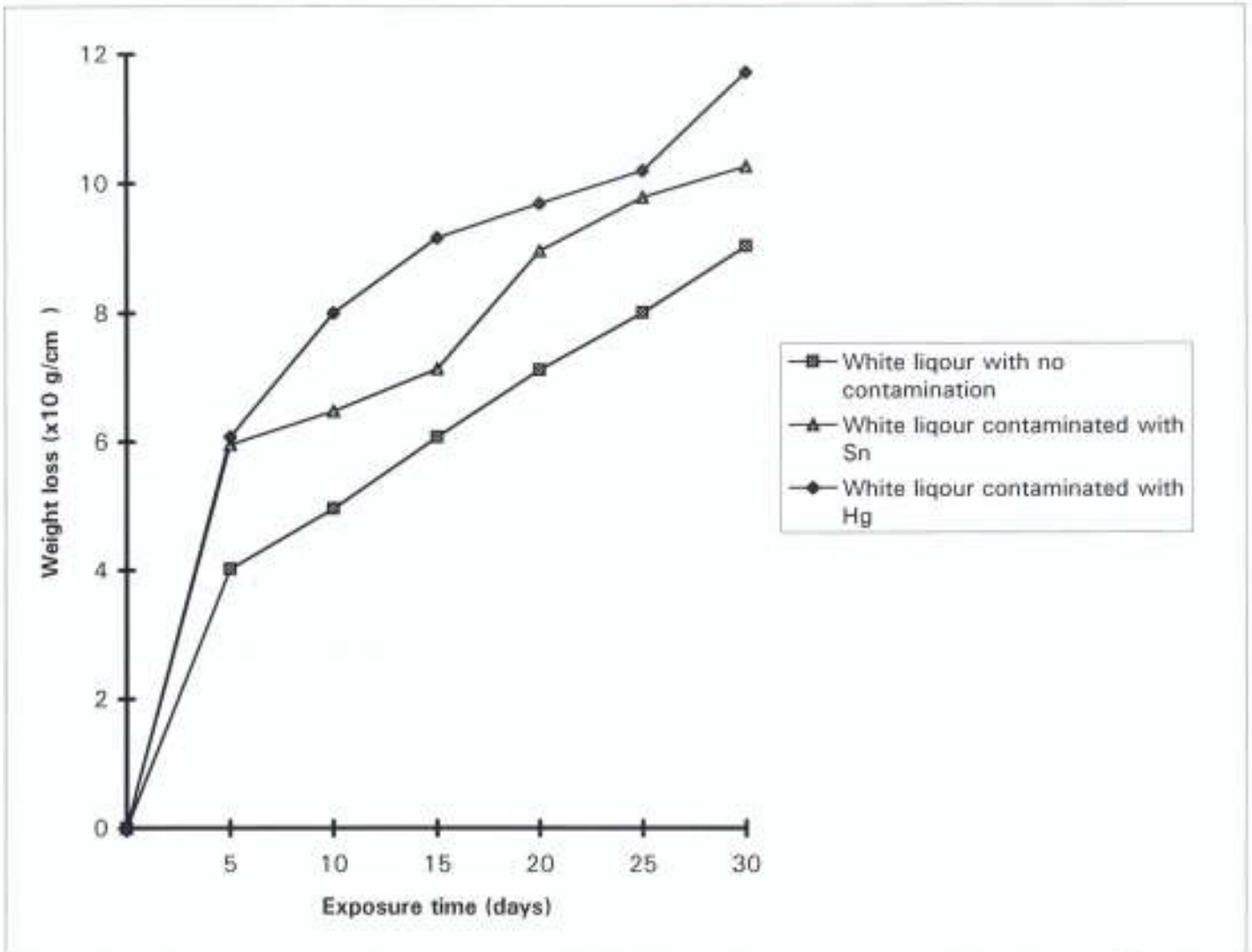

Figure 12: Effect of extraneous ions addition on corrosion of tempered carbon steel in white liquor

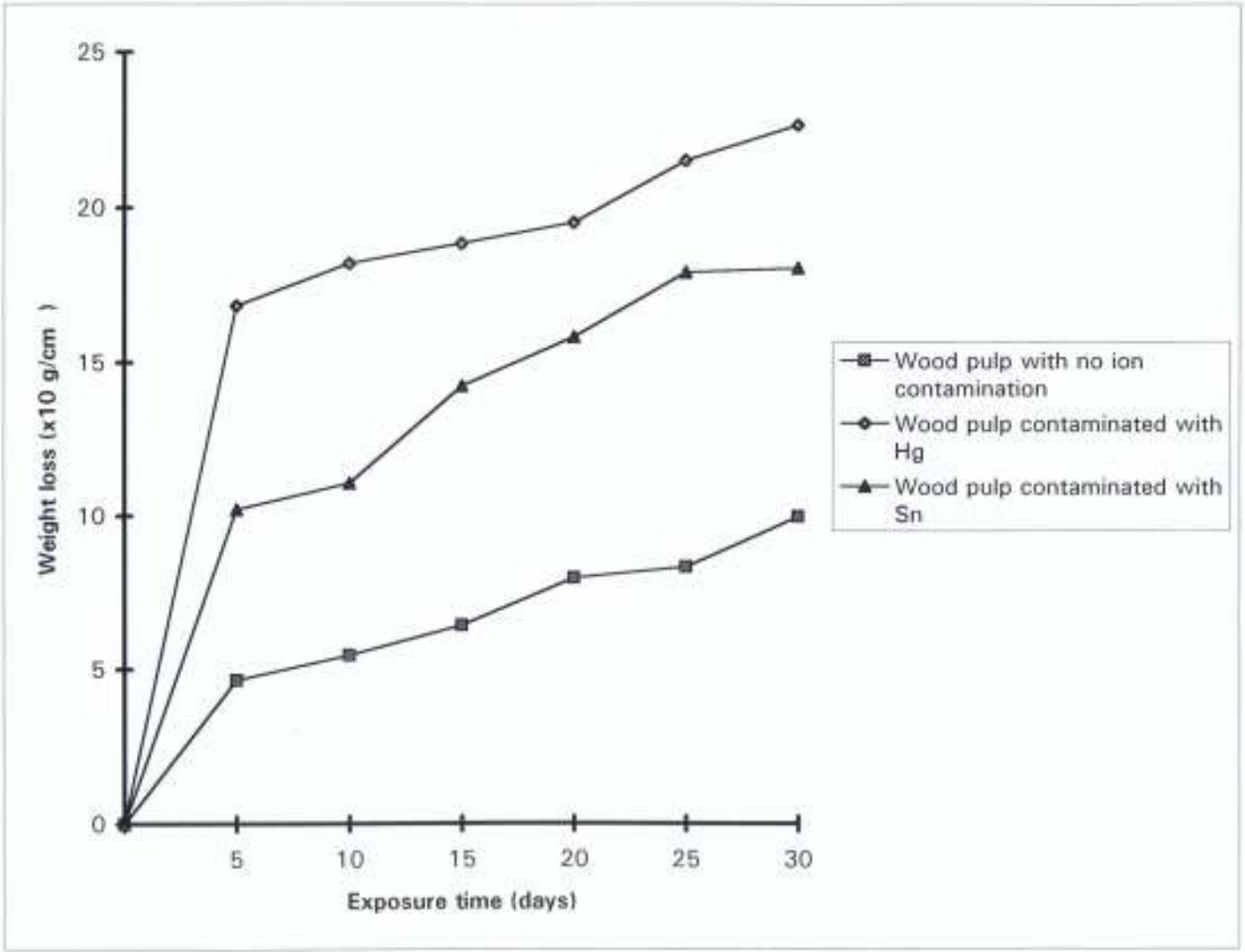

Figure 13: Effect of extraneous ions addition on corrosion of tempered carbon steel in wood pulp

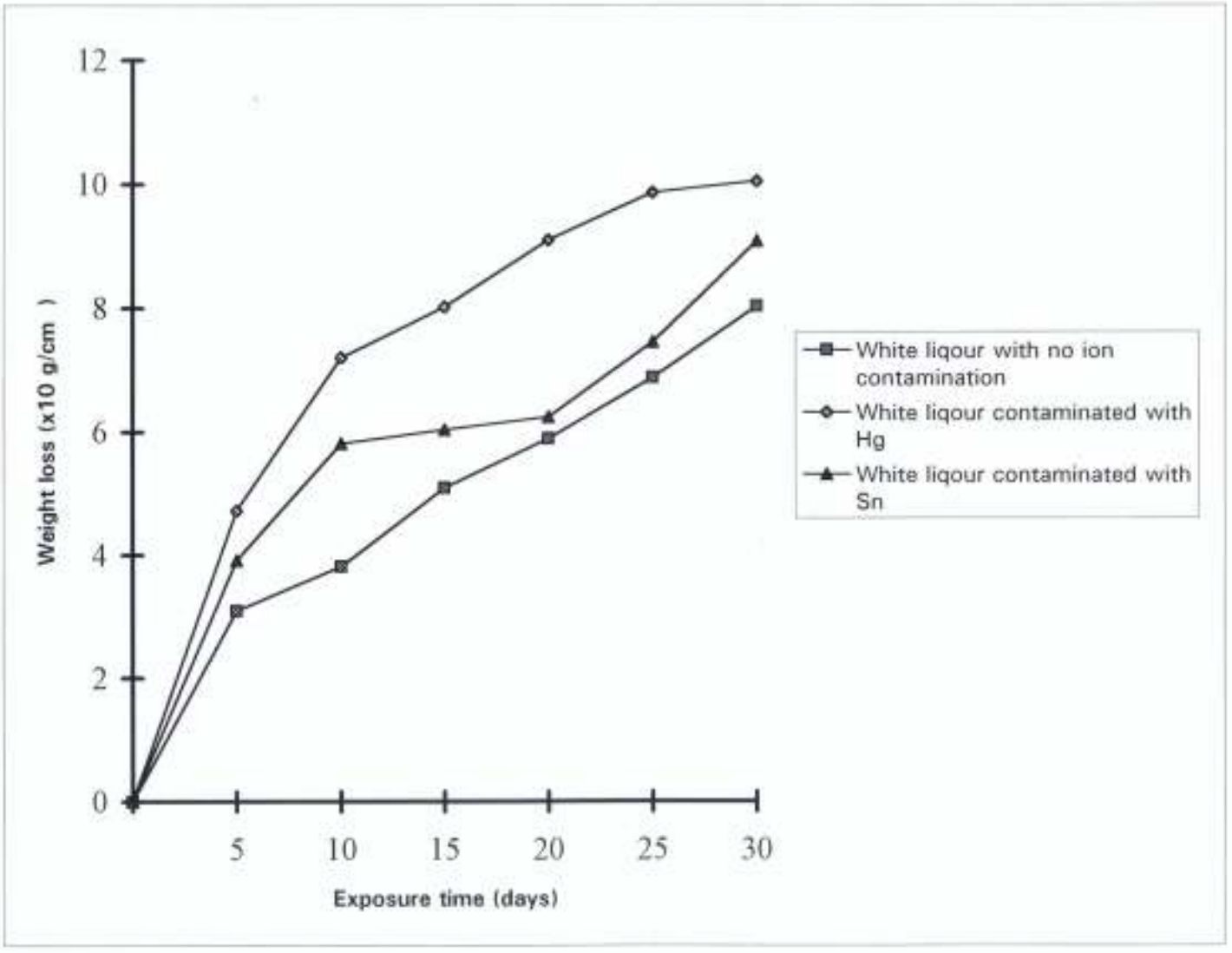

Figure 14: Effect of extraneous ions addition on corrosion of normalised carbon steel in white liquor

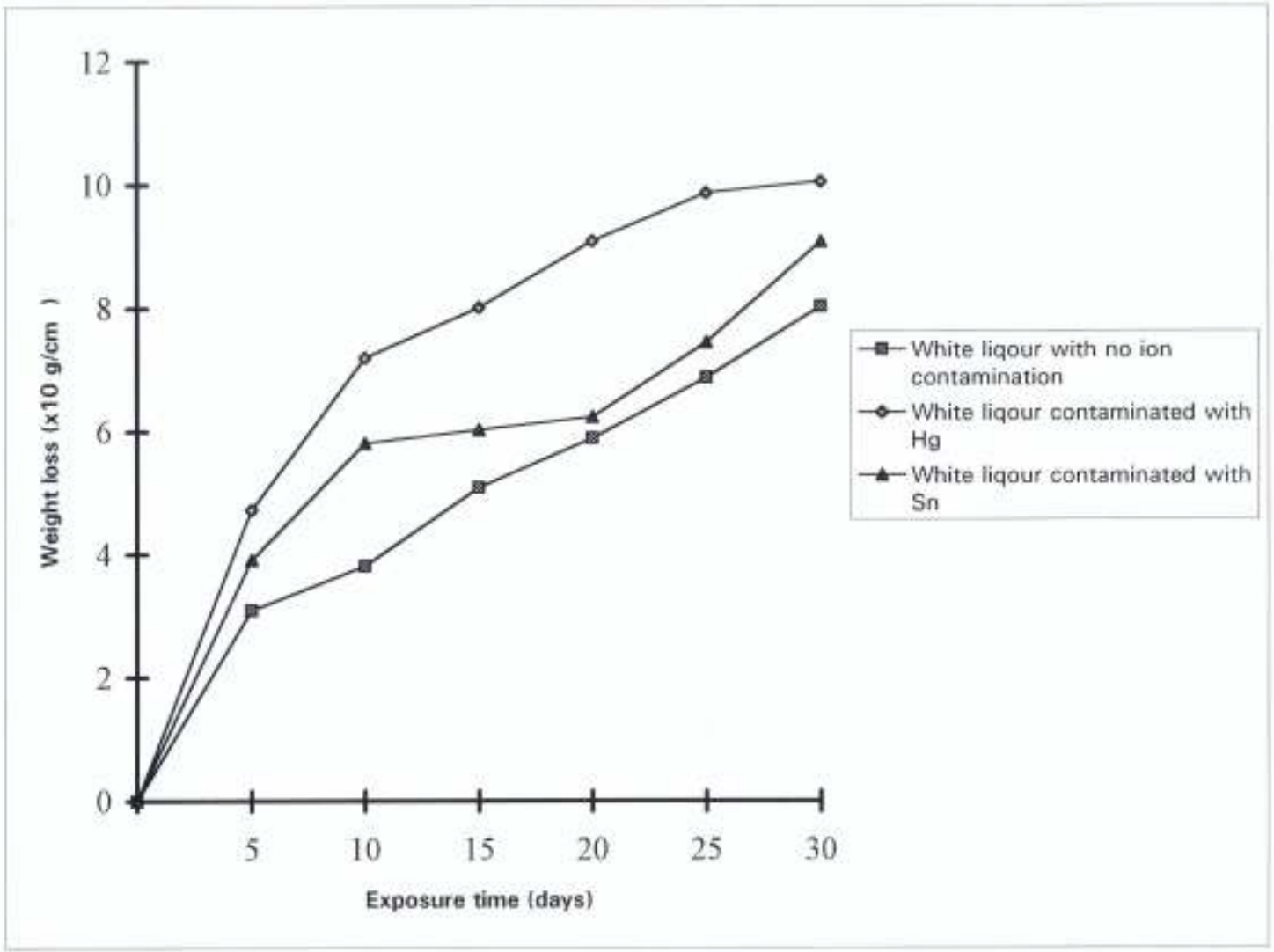

Figure 15: Effect of extraneous ions addition on corrosion of normalised carbon steel in wood pulp

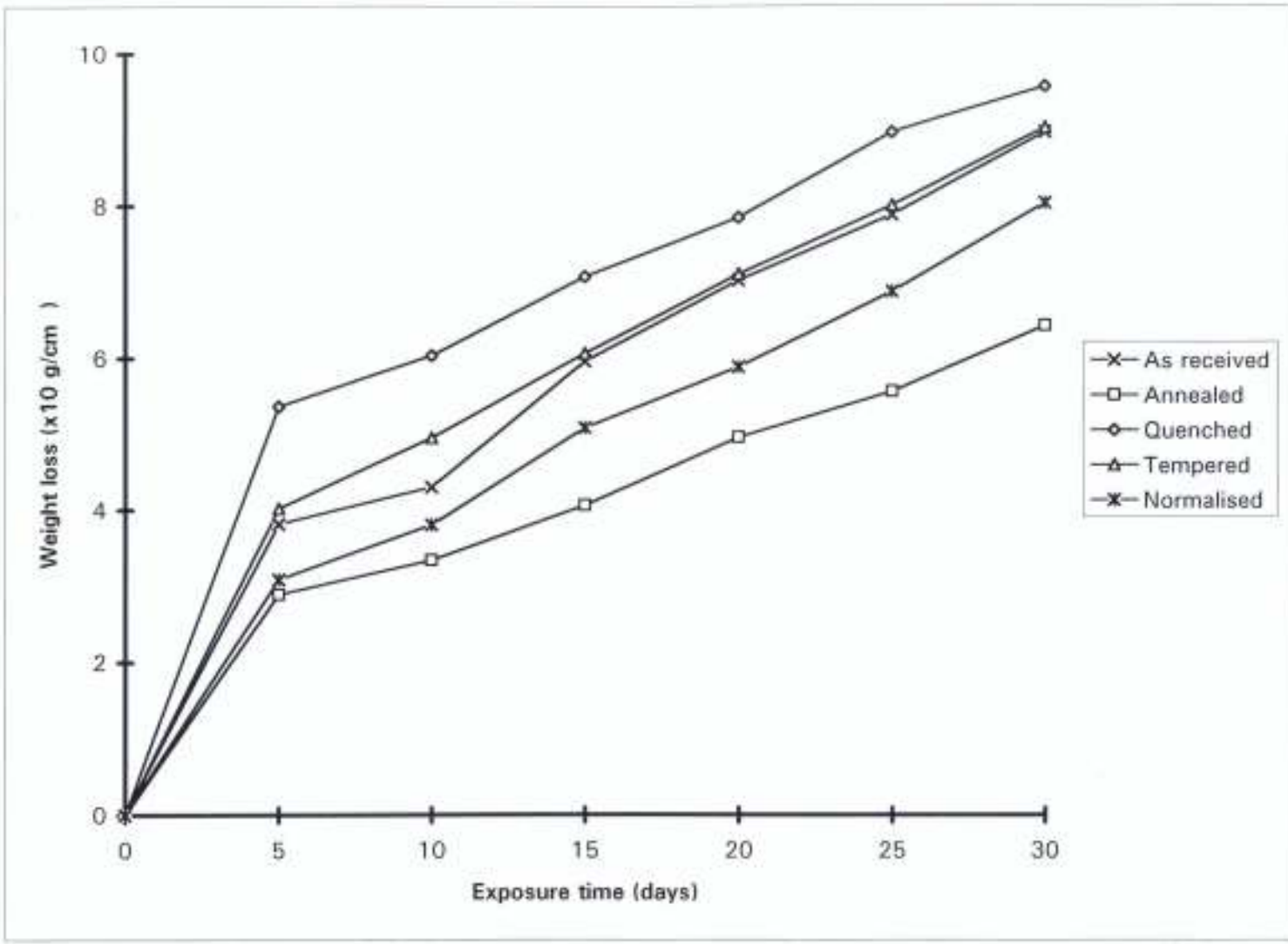

Figure 16: Effect of heat treatment on corrosion of carbon steel in white liquor only

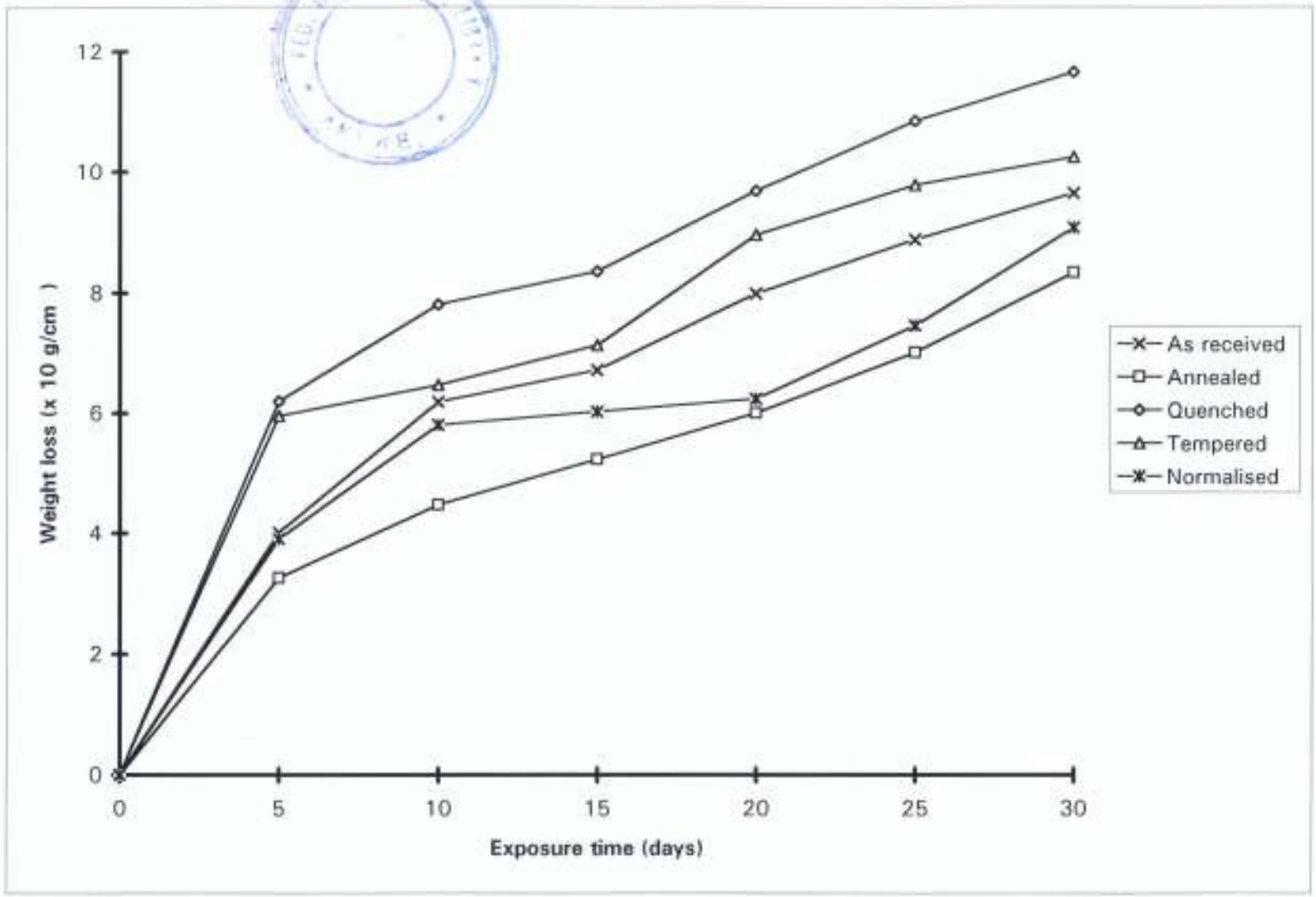

Figure 17: Effect of heat treatment on corrosion of carbon steel in white liquor contaminated with Sn ions

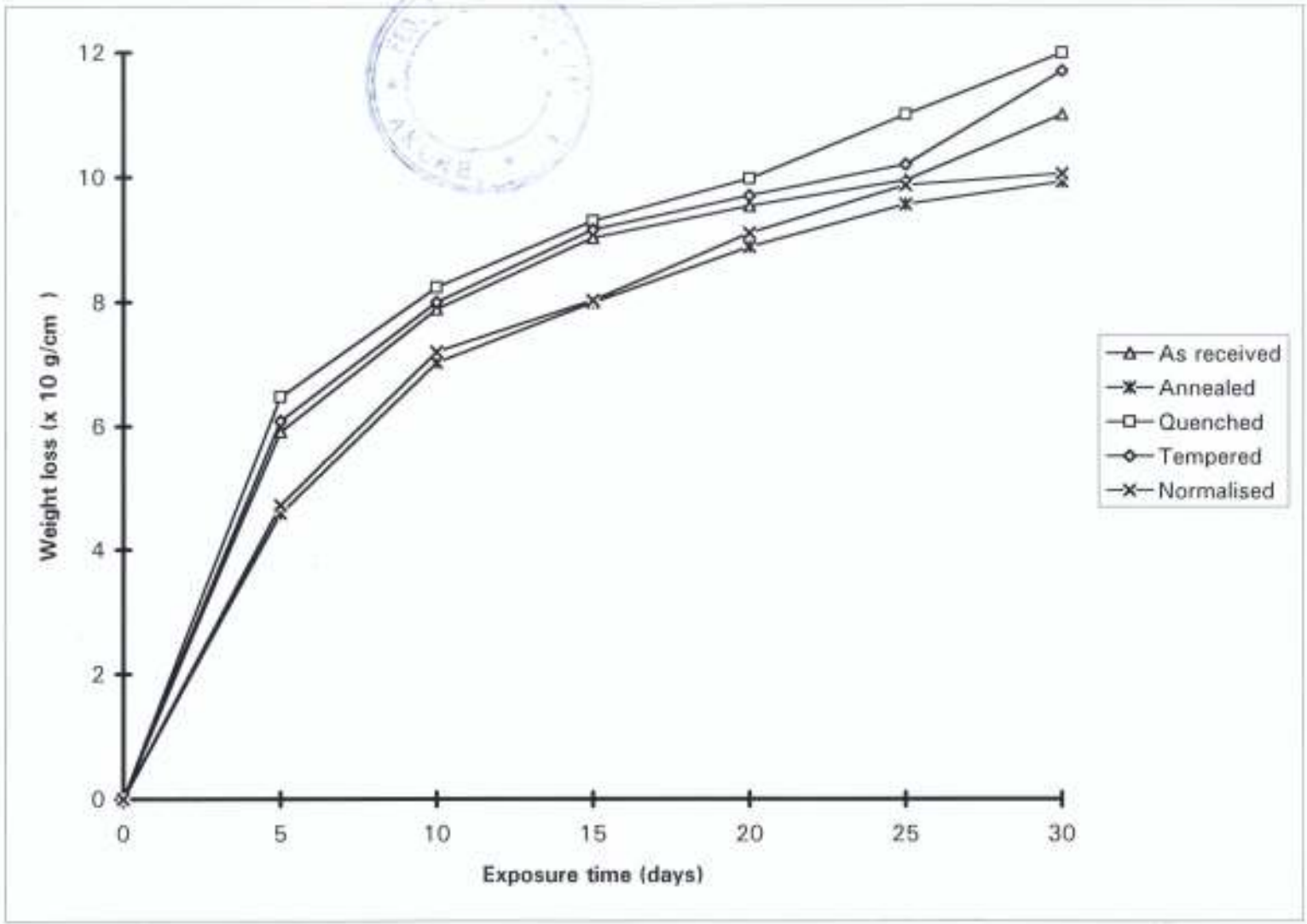

Figure 18: Effect of heat treatment on corrosion of carbon steel in white liquor contaminated with Hg ions

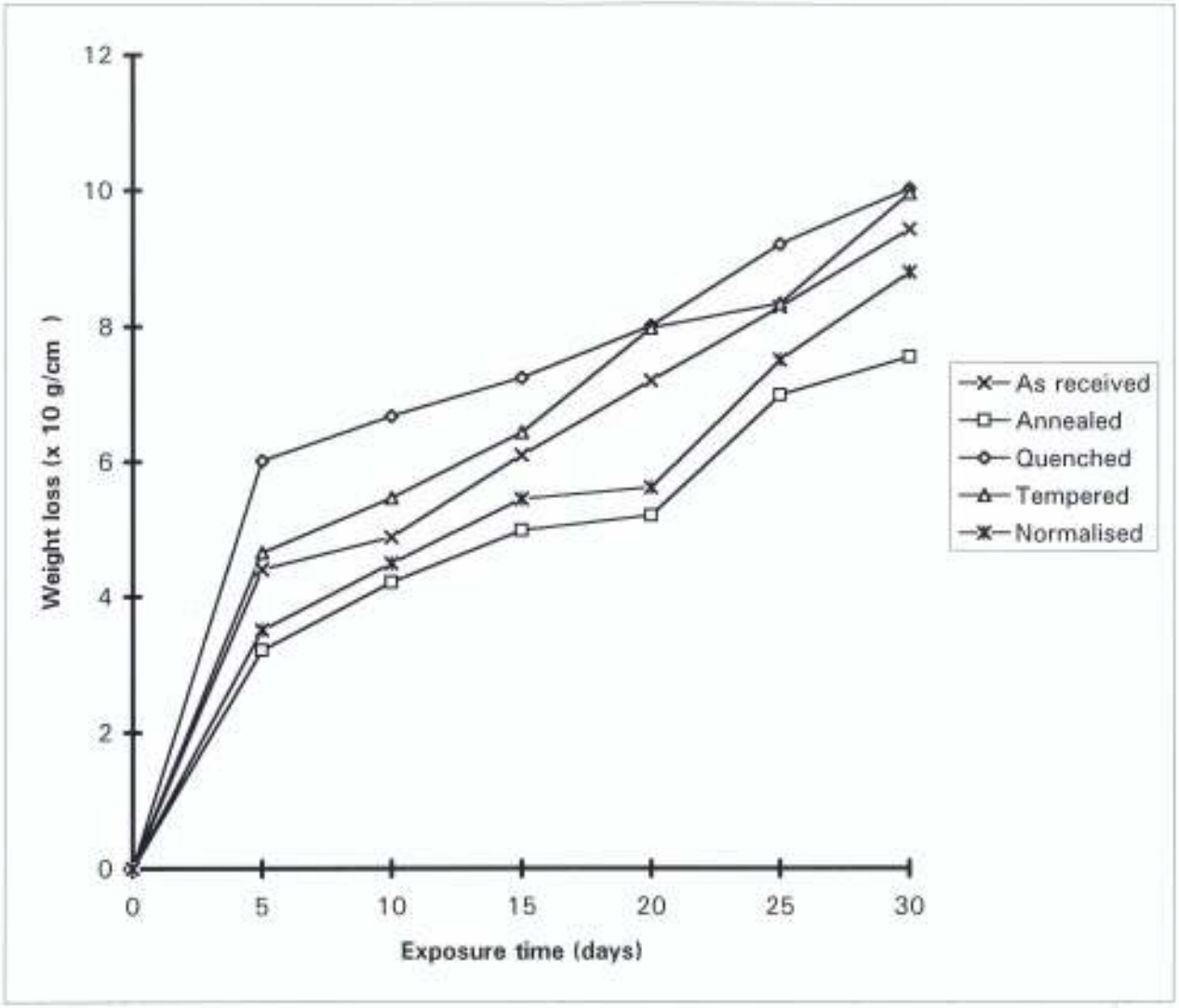

Figure 19: Effect of heat treatment on corrosion of carbon steel in wood pulp only

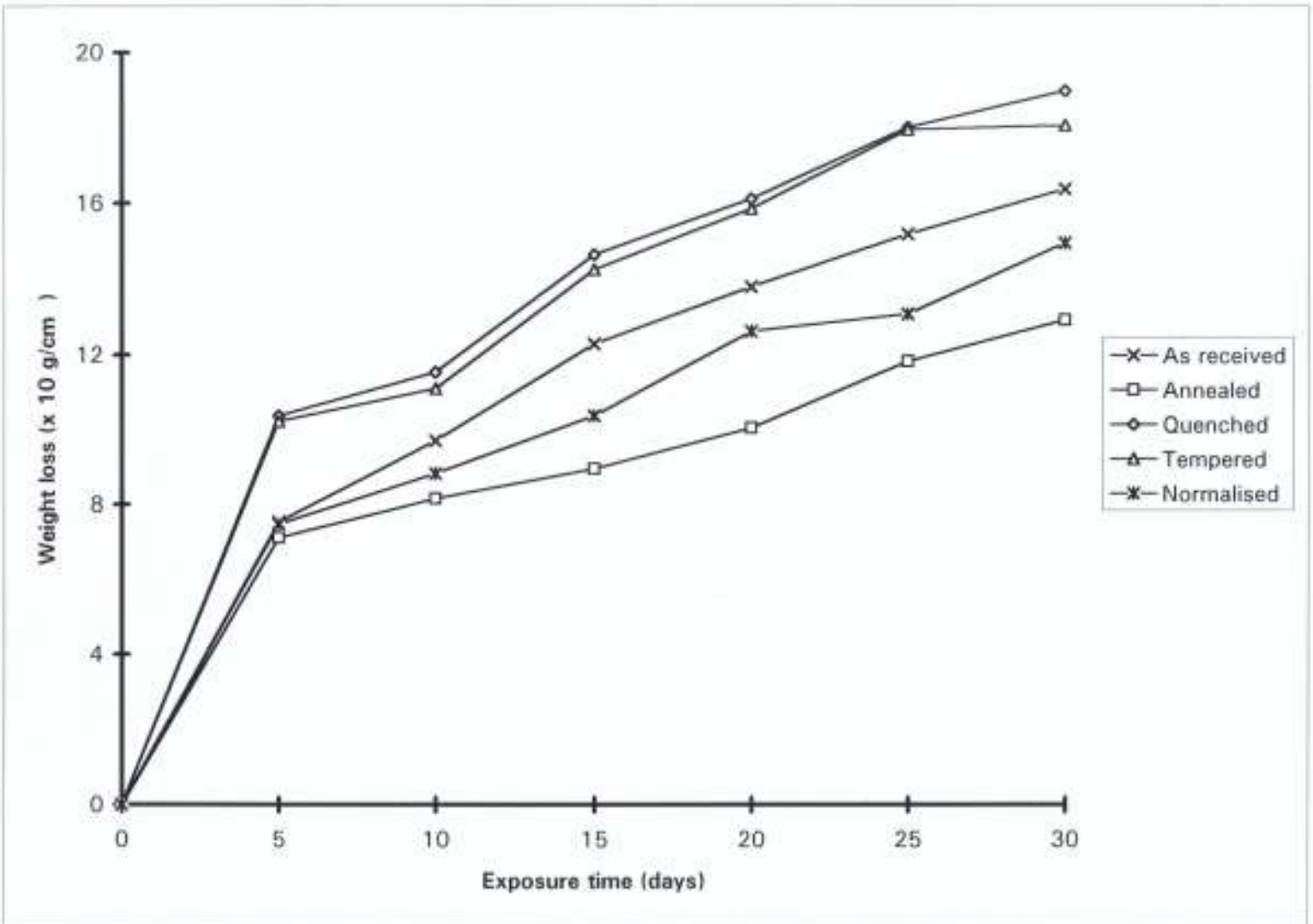

Figure 20: Effect of heat treatment on corrosion of carbon steel in wood pulp contaminated with Sn ions

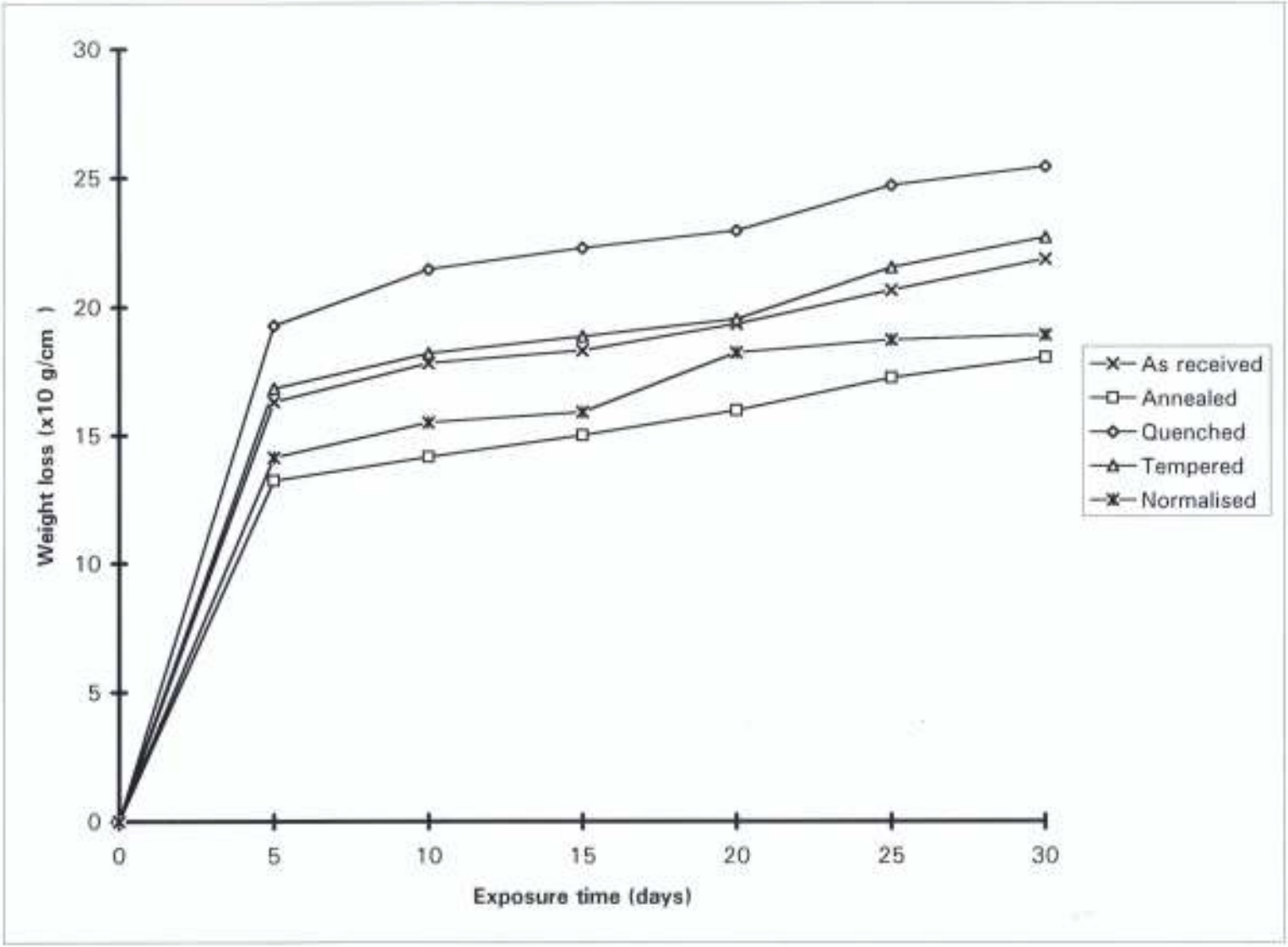

Figure 21: Effect of heat treatment on corrosion of carbon steel in wood pulp contaminated with Hg ions

of attack of the annealed samples is attributed to microconstituents and refinement of structure. The microstructure of the normalised samples which consisted essentially of areas of ferrite and zones of pearlite in normalised samples showed coarse grain features. The observed trend in the tempered steels is due to the fact that the internal stresses set up during quenching has been reduced thus the carbon trapped in the super saturated solution during quenching can be precipitated in a more stable form i.e. iron carbide particles.

5.2 STRESS CORROSION CRACKING

5.2.1 EXTRANEOUS IONS ADDITION

According to Odeshi (1994) additions of Hg^{++} ions intensified the rate of cracking of quench hardened steel in cassava fluid while introduction of Sn^{++} ions led to a remarkable reduction in the rate of cracking.

As observed from figures 22 to 31, additions of Hg^{++} and Sn^{++} was found to decrease the percentage elongation to fracture when they were added to wood pulp and white liquor.

To explain the observation in SCC, if the principal cathodic reaction is hydrogen evolution, then the rate controlling step is the formation of hydrogen molecules by combination of hydrogen atoms. Thus any addition of ions to the solution that results in delaying the recombination of hydrogen atoms to form hydrogen molecule will increase the stress corrosion susceptibility of the material. This is known as hydrogen embrittlement.

Since tin has a low hydrogen overpotential, presence of Sn^{++} ions in a solution will increase the formation of hydrogen gas. Thus if hydrogen is the embrittling specie, rate of cracking will be reduced. Based on the same reasoning, because mercury has a high value of hydrogen overpotential, presence of Hg^{++} ions in a solution will reduce formation

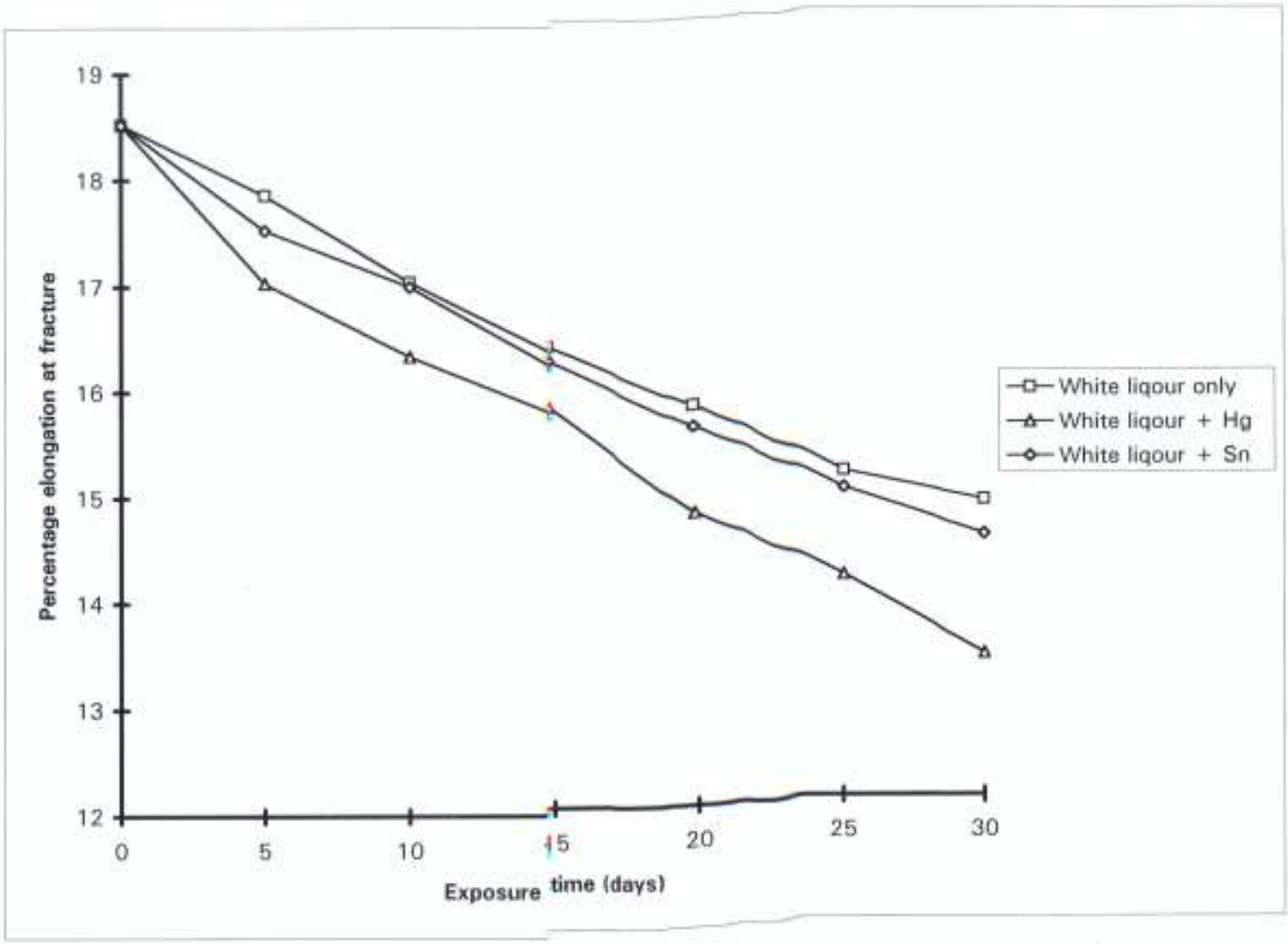

Figure 22: Effect of extraneous ion addition on SCC of normalised carbon steel in white liquor only

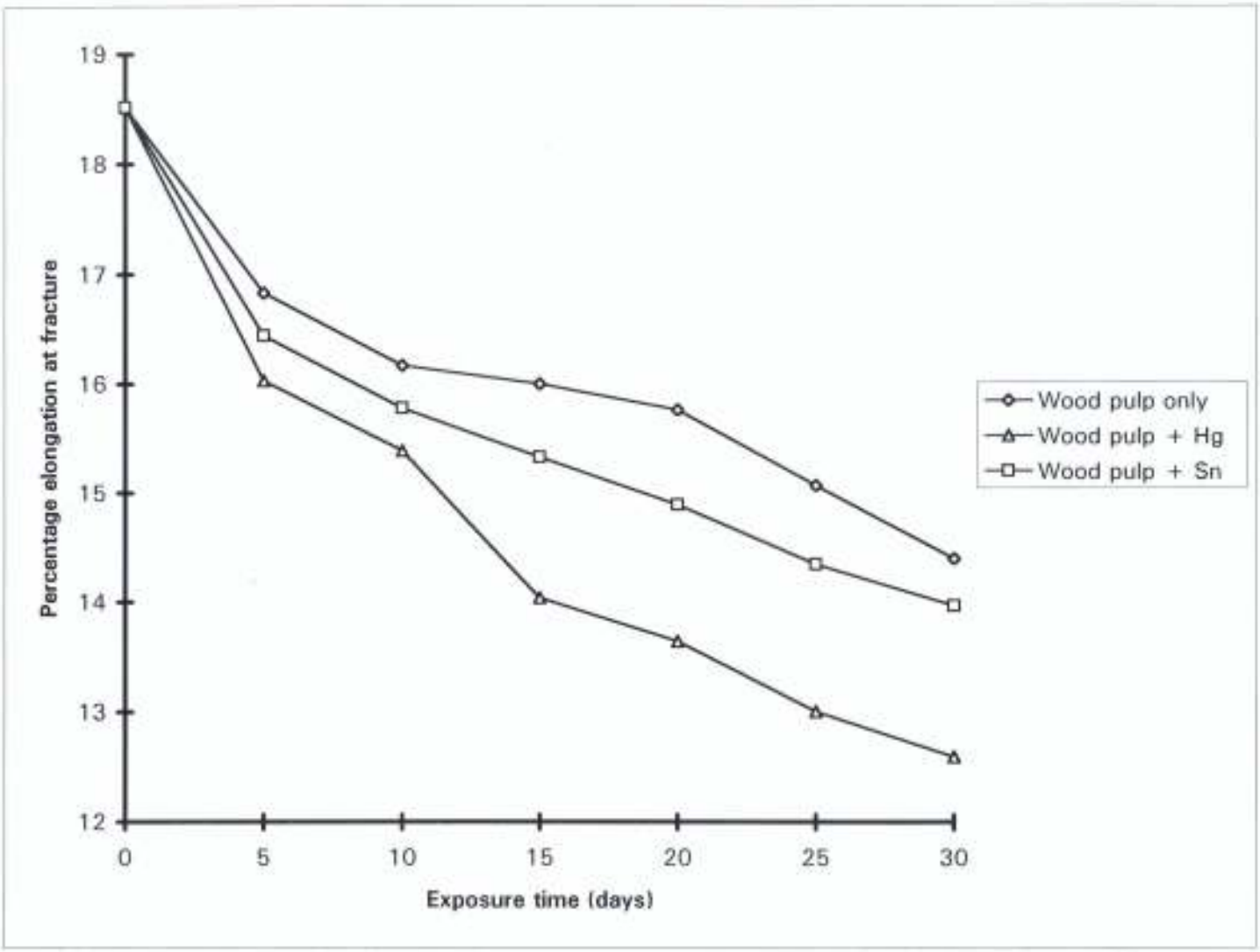

Figure 23: Effect of extraneous ion addition on SCC of normalised carbon steel in wood pulp only

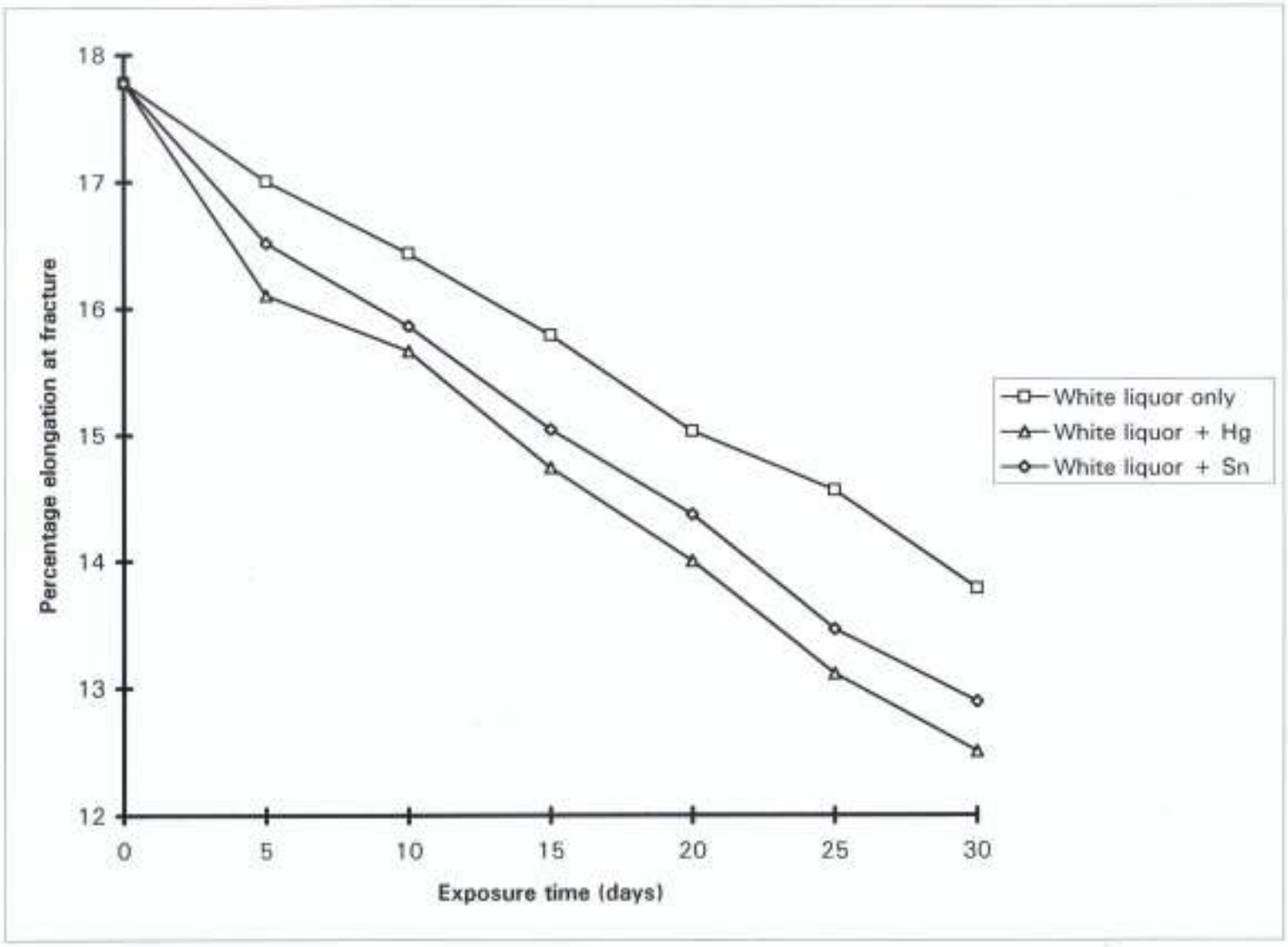

Figure 24: Effect of extraneous ion addition on SCC of as received carbon steel in white liquor only

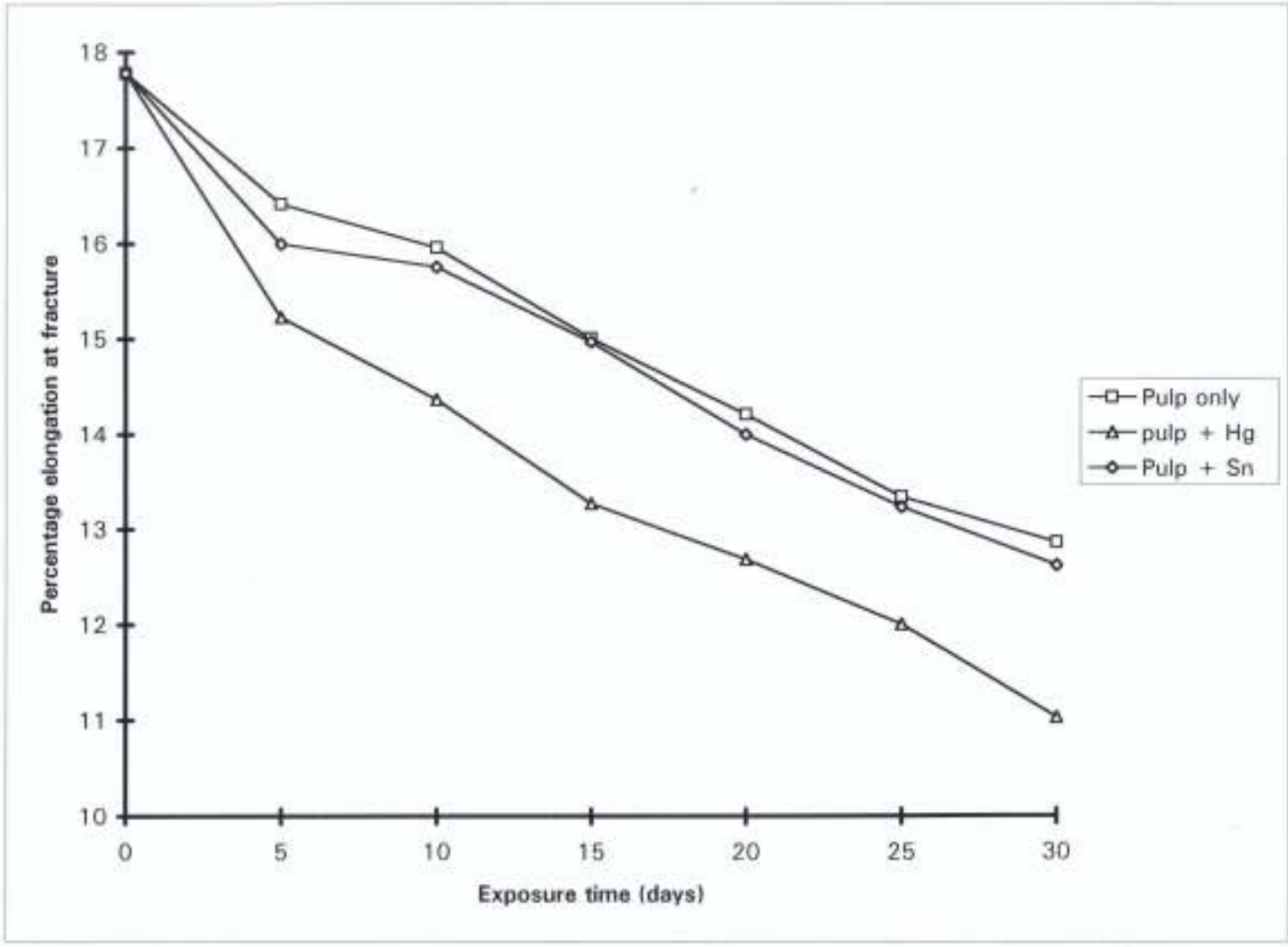

Figure 25: Effect of extraneous ion addition on SCC of as received carbon steel in wood pulp only

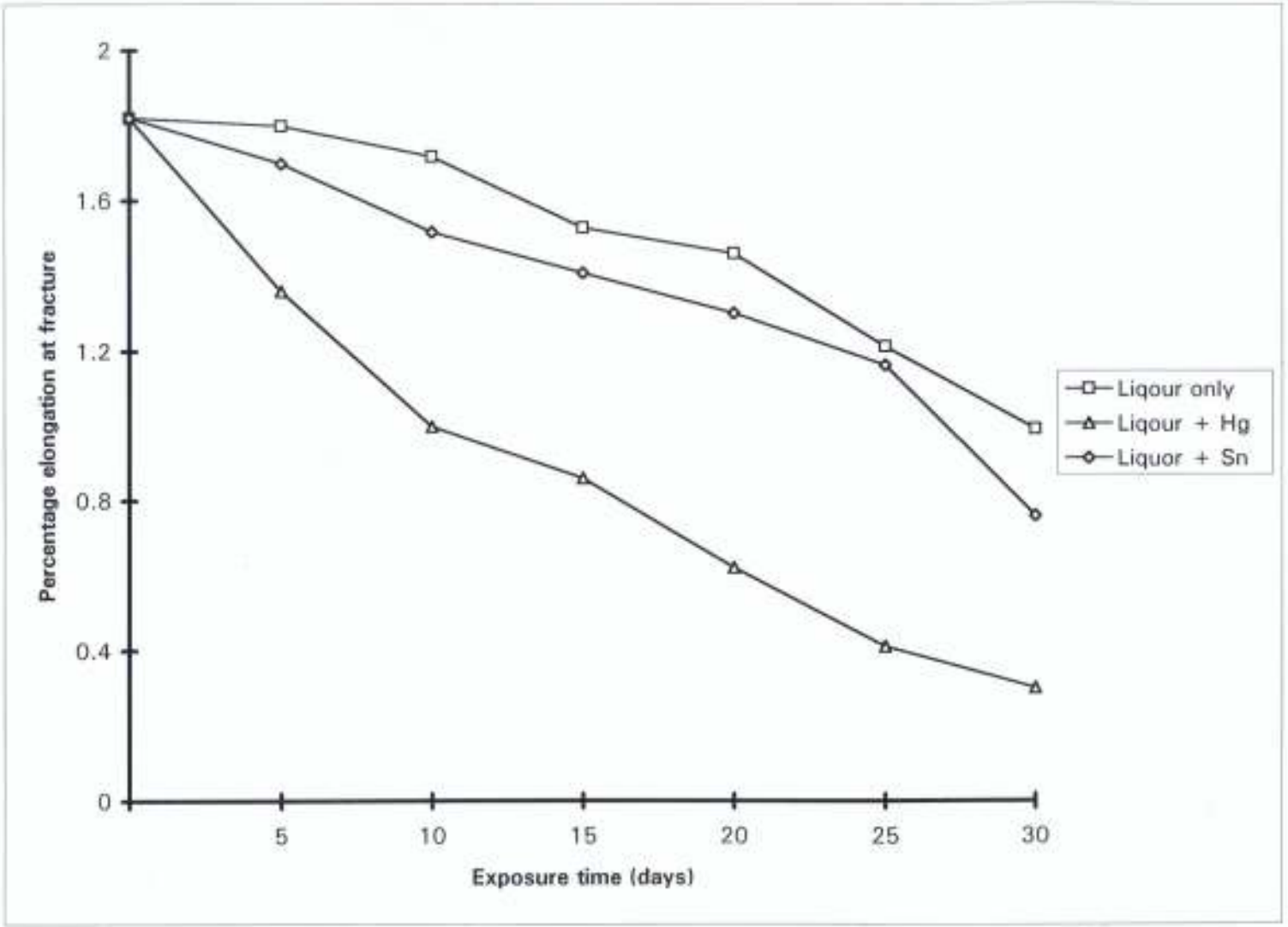

Figure 26: Effect of extraneous ion addition on SCC of quenched carbon steel in white liquor only

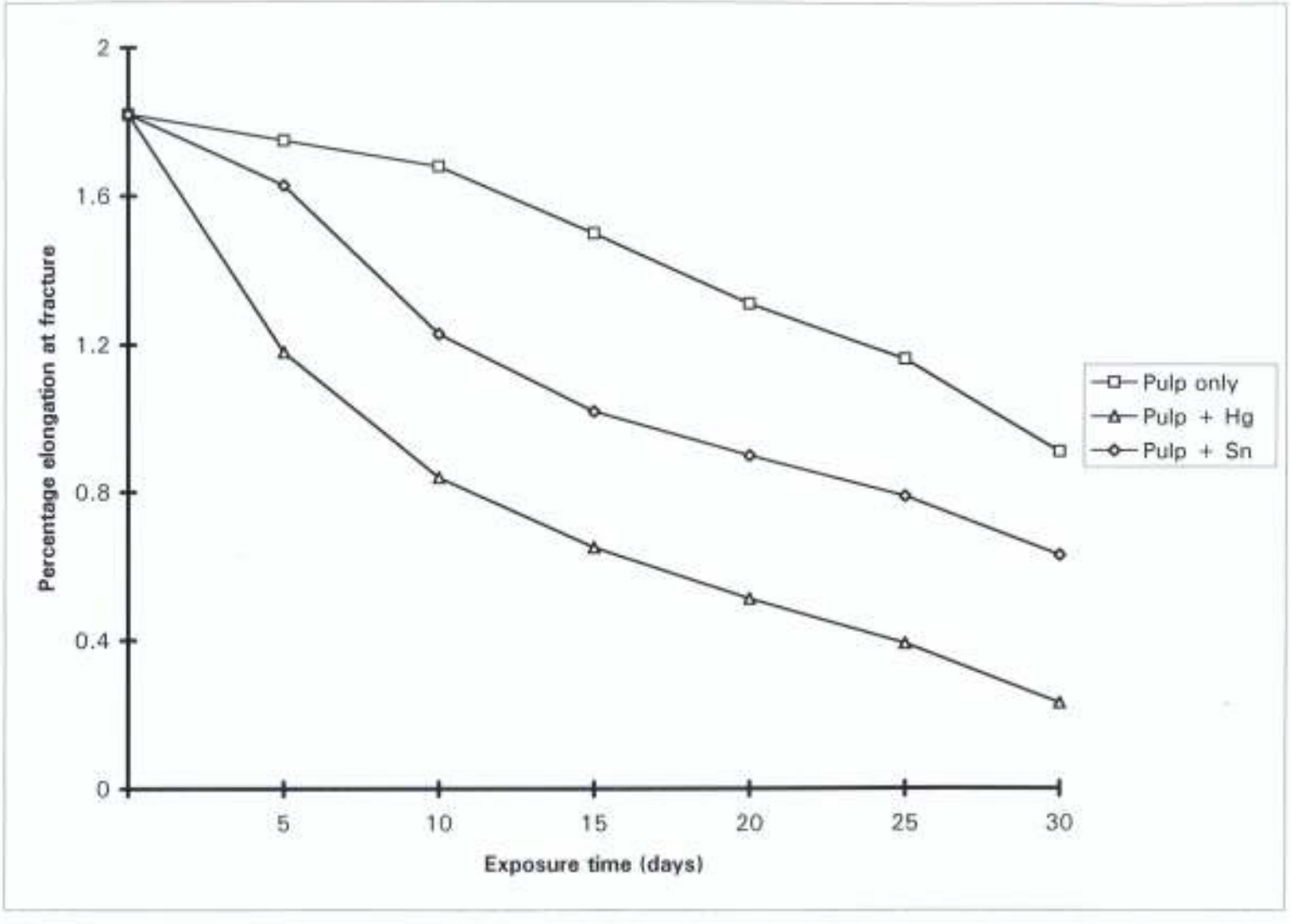

Figure 27: Effect of extraneous ion addition on SCC of quenched carbon steel in wood pulp only

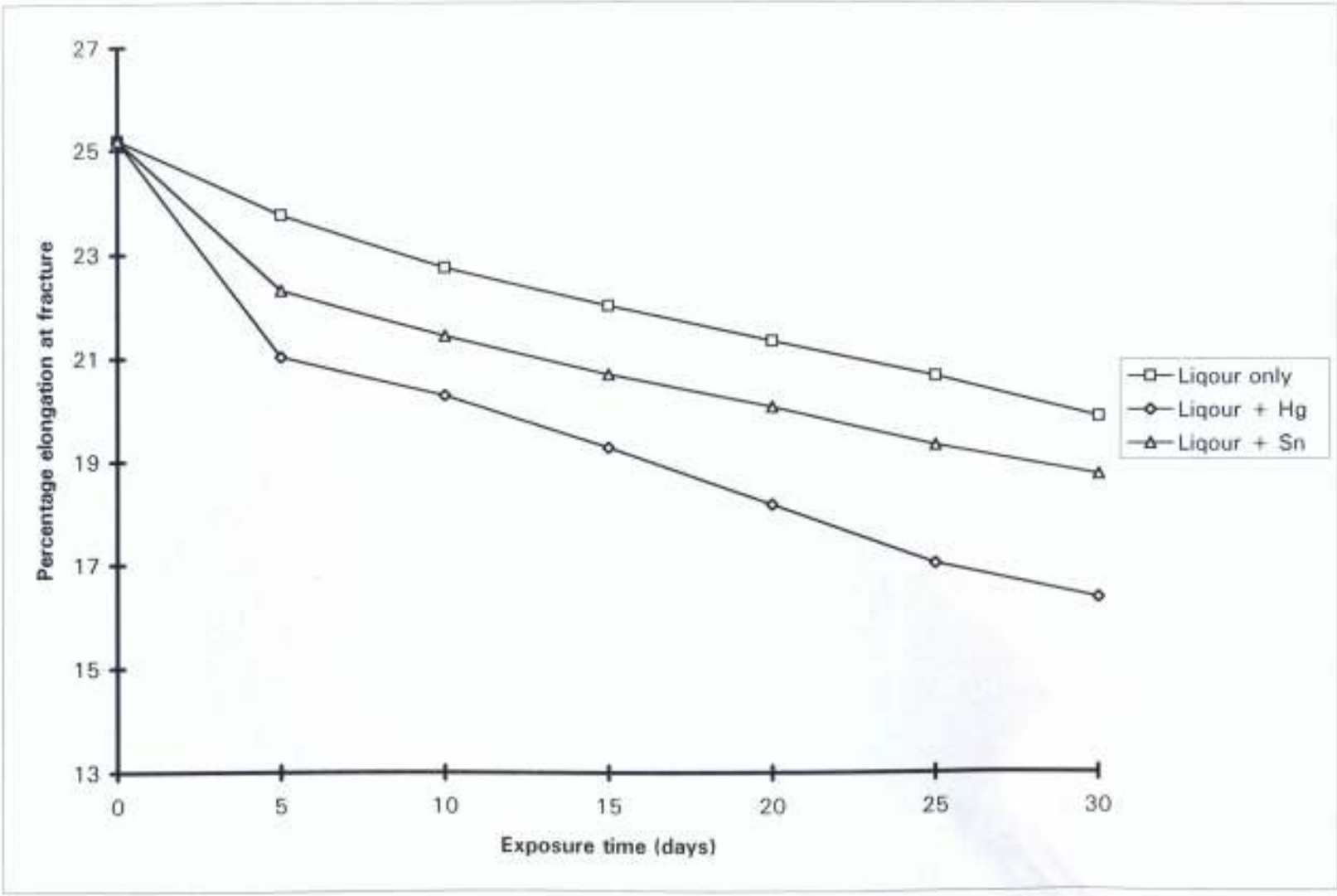

Figure 28. Effect of extraneous ion addition on SCC of annealed carbon steel in white liquor only

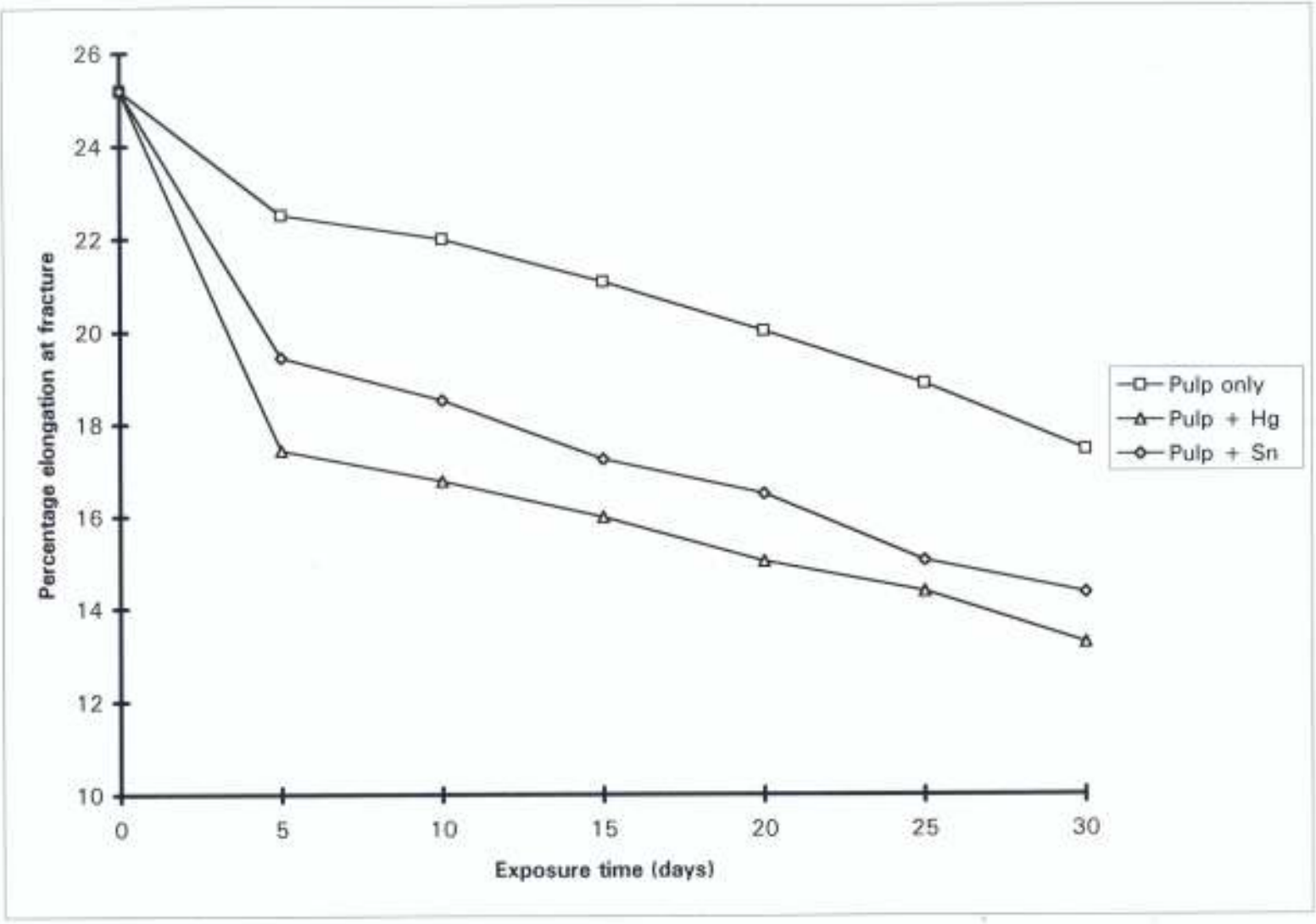

Figure 29: Effect of extraneous ion addition on SCC of annealed carbon steel in wood pulp only

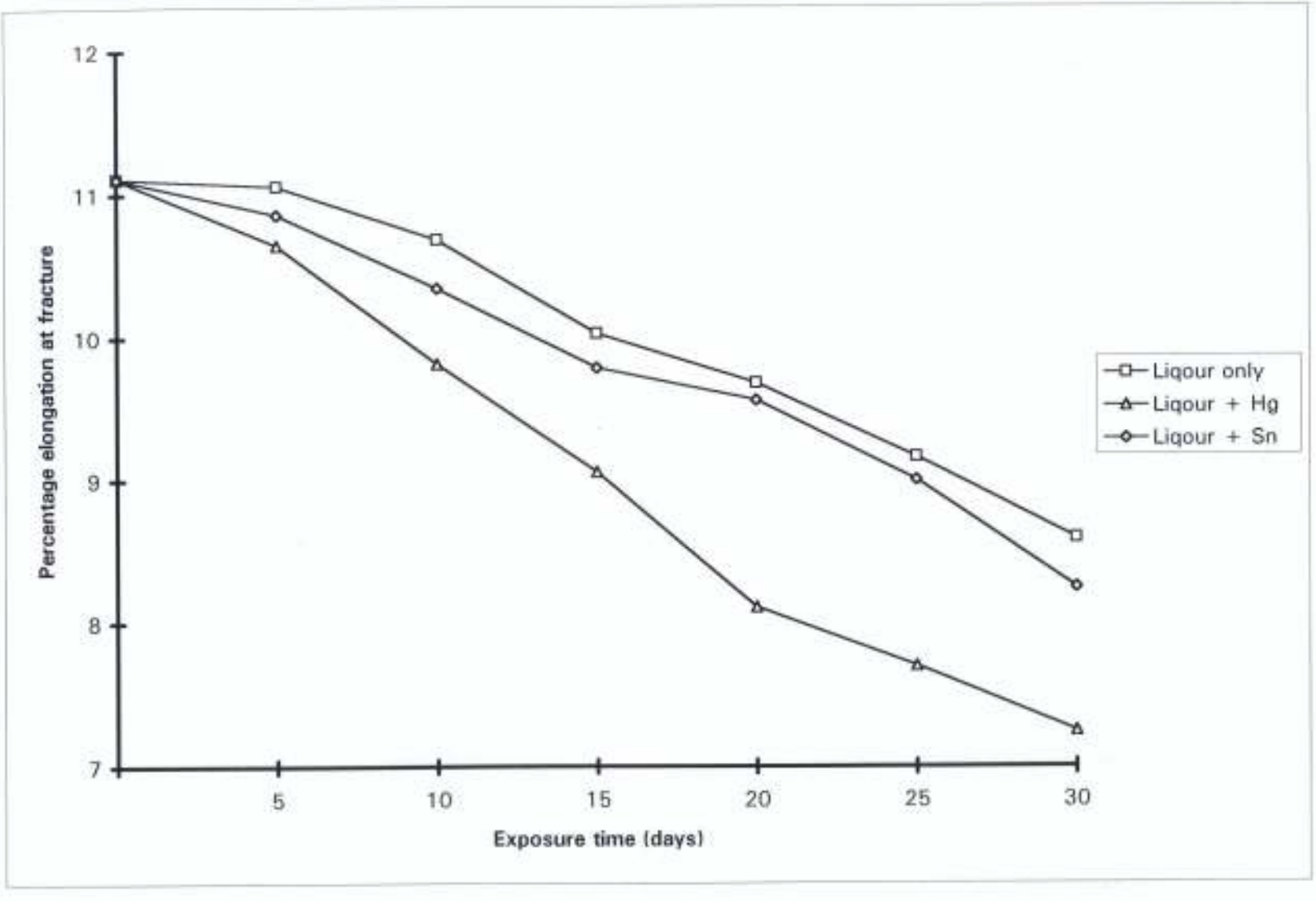

Figure 30: Effect of extraneous ion addition on SCC of tempered carbon steel in white liquor only

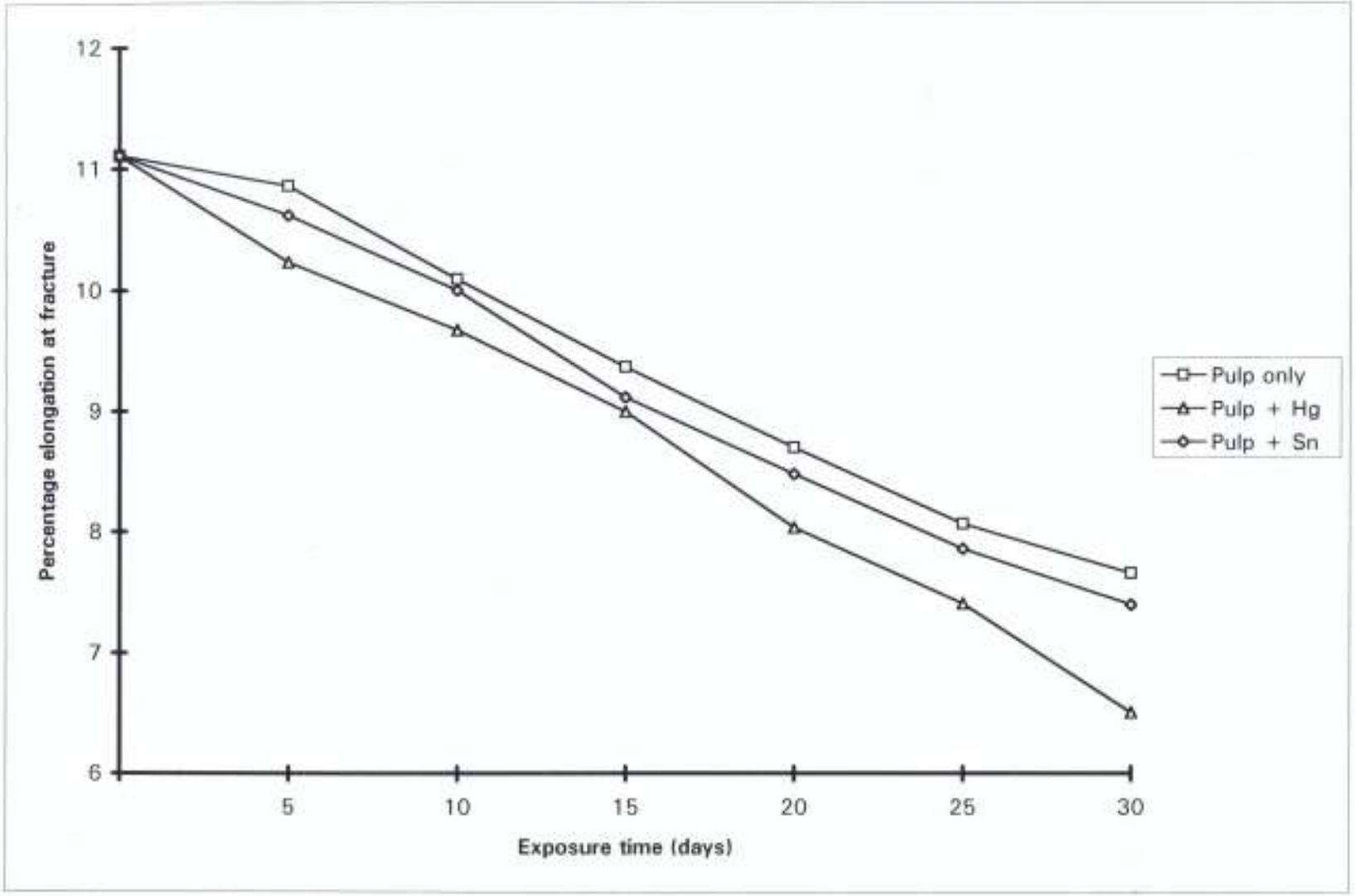

Figure 31: Effect of extraneous ion addition on SCC of tempered carbon steel in wood pulp only

of hydrogen atoms thus increasing rate of loss of ductility provided that hydrogen is the embrittling specie.

Thus it can be concluded that hydrogen is the probable embrittling specie with Hg^{++} ions while anodic dissolution at the crack tip is the probable mechanism with Sn^{++} additions.

5.2.2 EFFECT OF HEAT TREATMENT

The reason for the marked variation (figures 32 to 38) +is due to the different rate of cooling that each samples were subjected to. The finer the grain size of a sample, the higher the ductility of the material.

During the process of annealing and normalising, most of the dislocation sites and chemical segregation or impurities that could serve as sites for preferential attack have been eliminated thus lowering the rate of crack propagation. The dislocation density is higher in normalised steel than in annealed steel thus low ductility value for normalised steel relative to that obtained for annealed steel.

In the quenched steel, high residual tensile stresses were induced after quenching due to the formation of martensitic structure. The martensite present in the samples tends to make them brittle and makes them susceptible to cracking and distortion which favours SCC.

During tempering, the internal stresses set up during quenching has been reduced thus improving the ductility and toughness at the expense of hardness and strength.

5.3 pH AND ELECTROCHEMICAL POTENTIAL MEASUREMENT

5.3.1 POTENTIAL VARIATION WITH TIME IN WHITE LIQUOR

Measurement was taken of the variation of potential with time in white liquor with and without contamination with Sn^{++} and Hg^{++} ions.

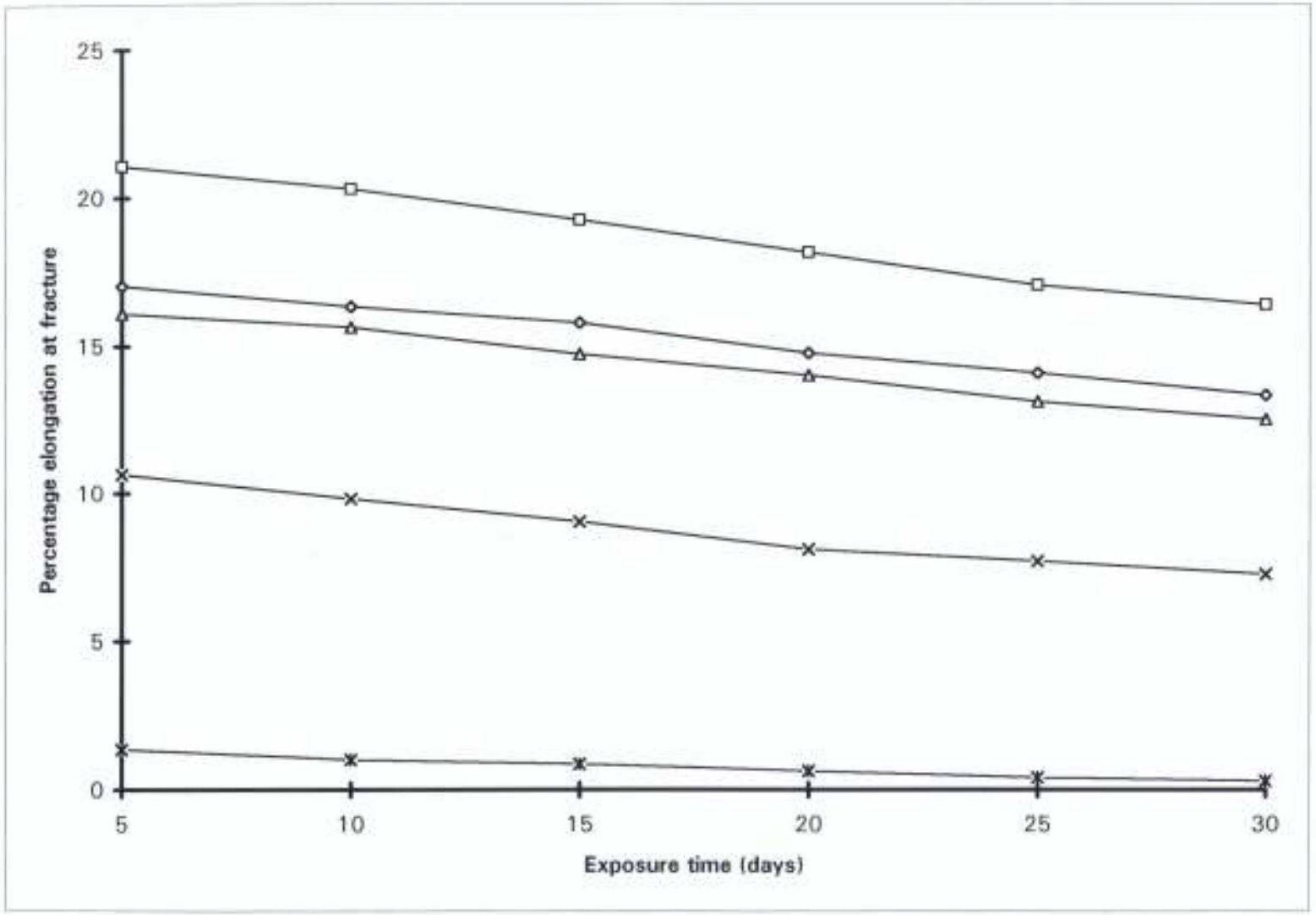

Figure 32: Effect of heat treatment on SCC of carbon steel in white liquor contaminated with Hg ions

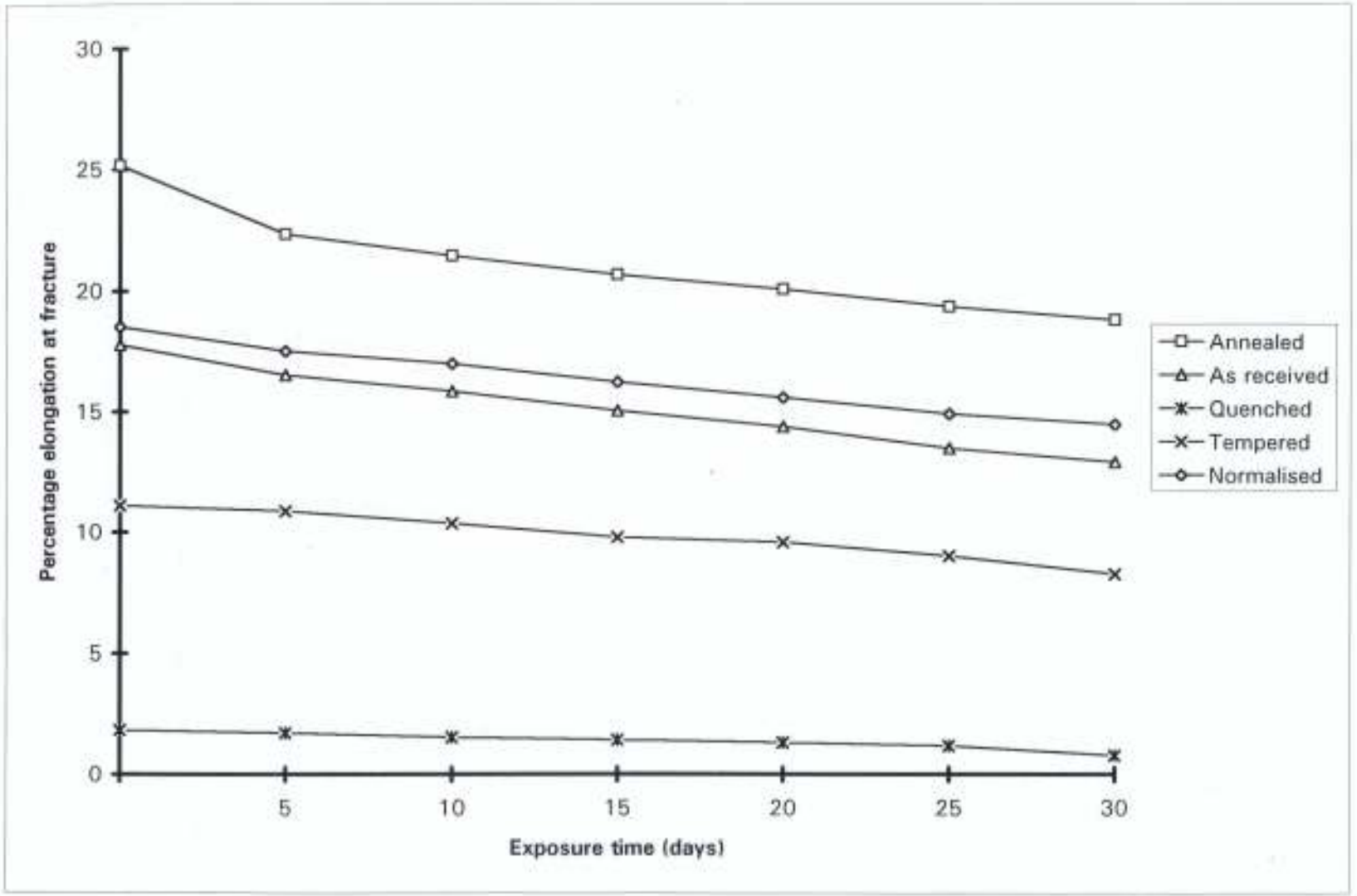

Figure 33: Effect of heat treatment on SCC of carbon steel in white liquor contaminated with Sn ions

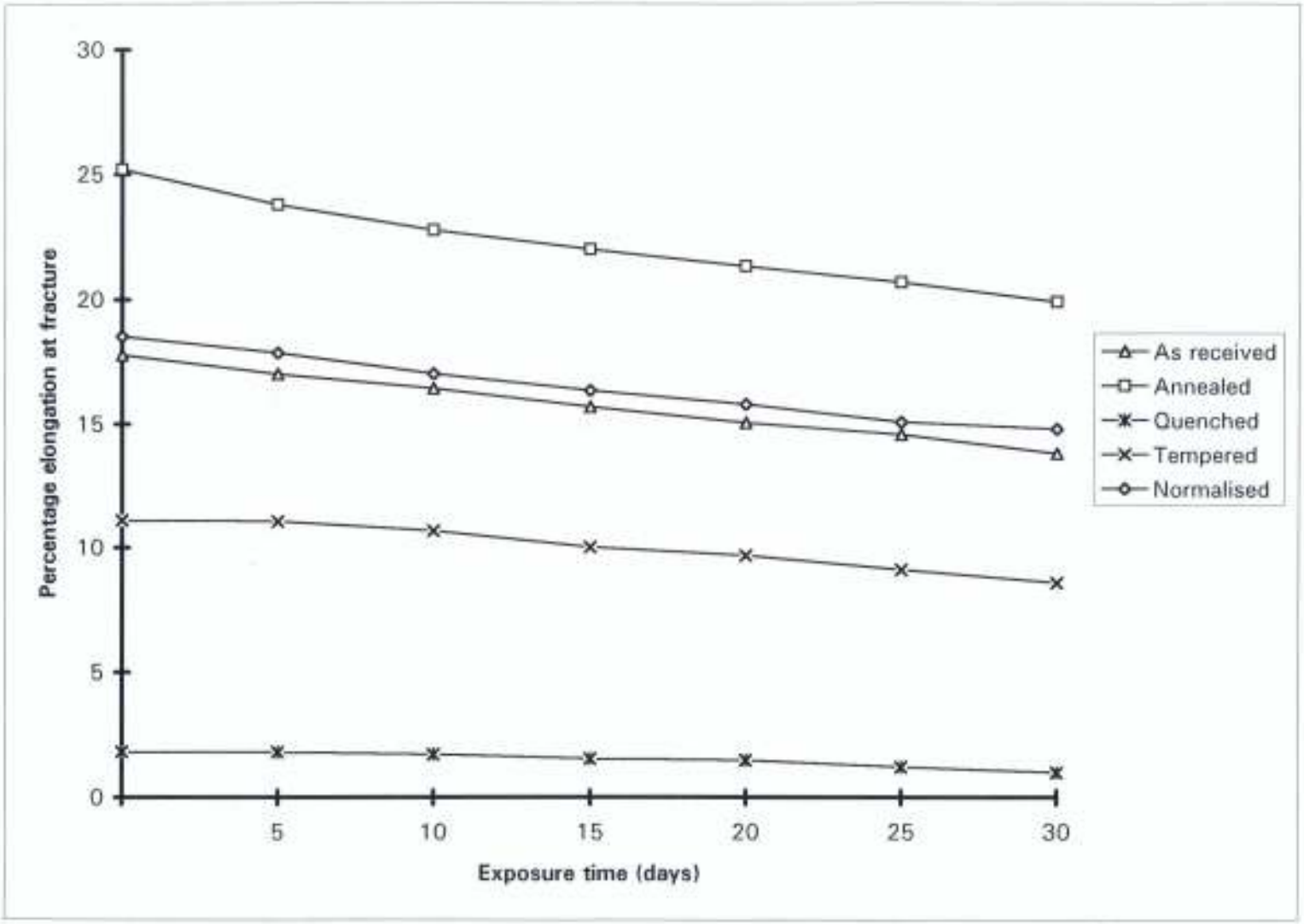

Figure 34: Effect of heat treatment on SCC of carbon steel in white liquor only

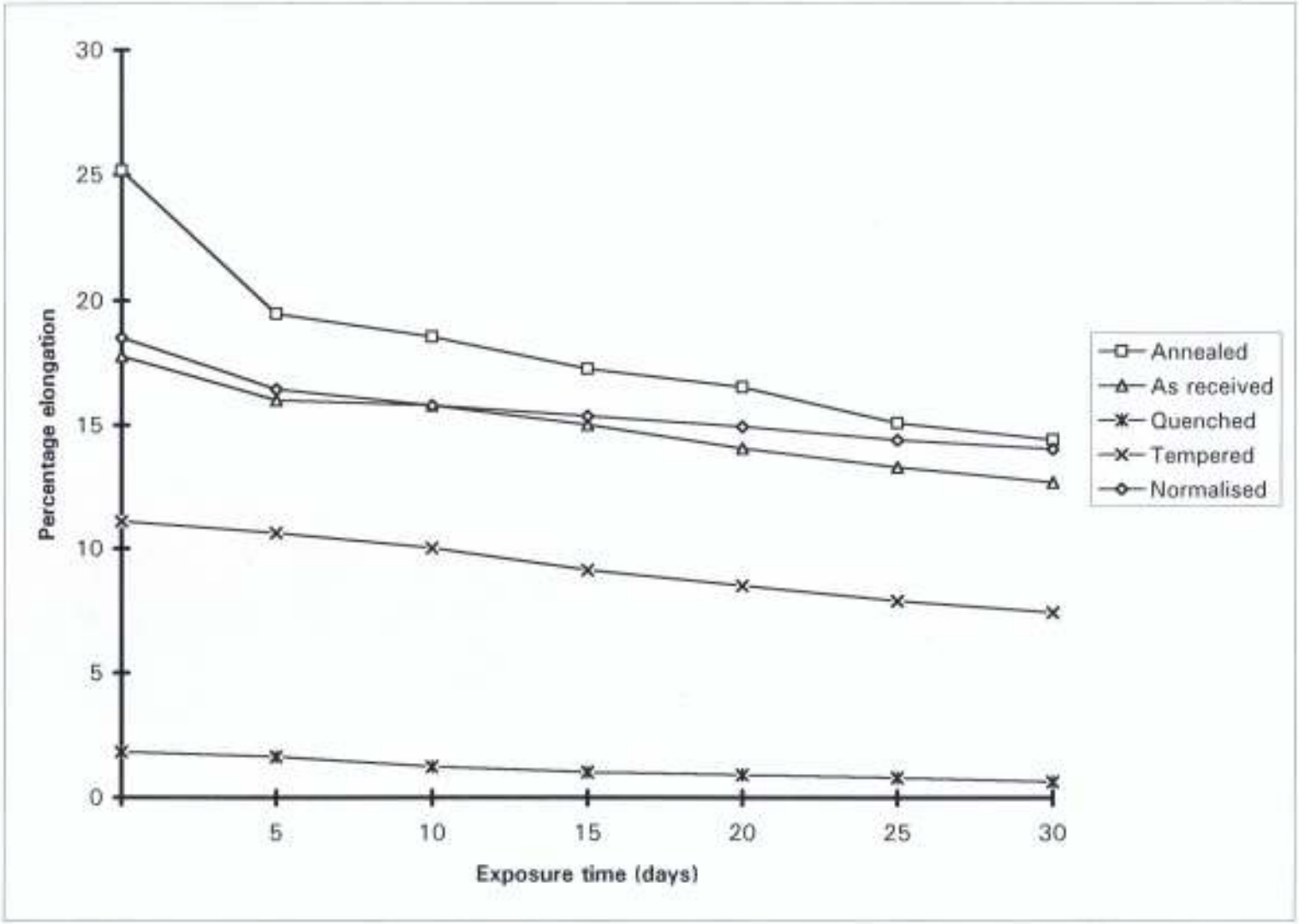

Figure 35: Effect of heat treatment on SCC of carbon steel in wood pulp contaminated with Sn ions

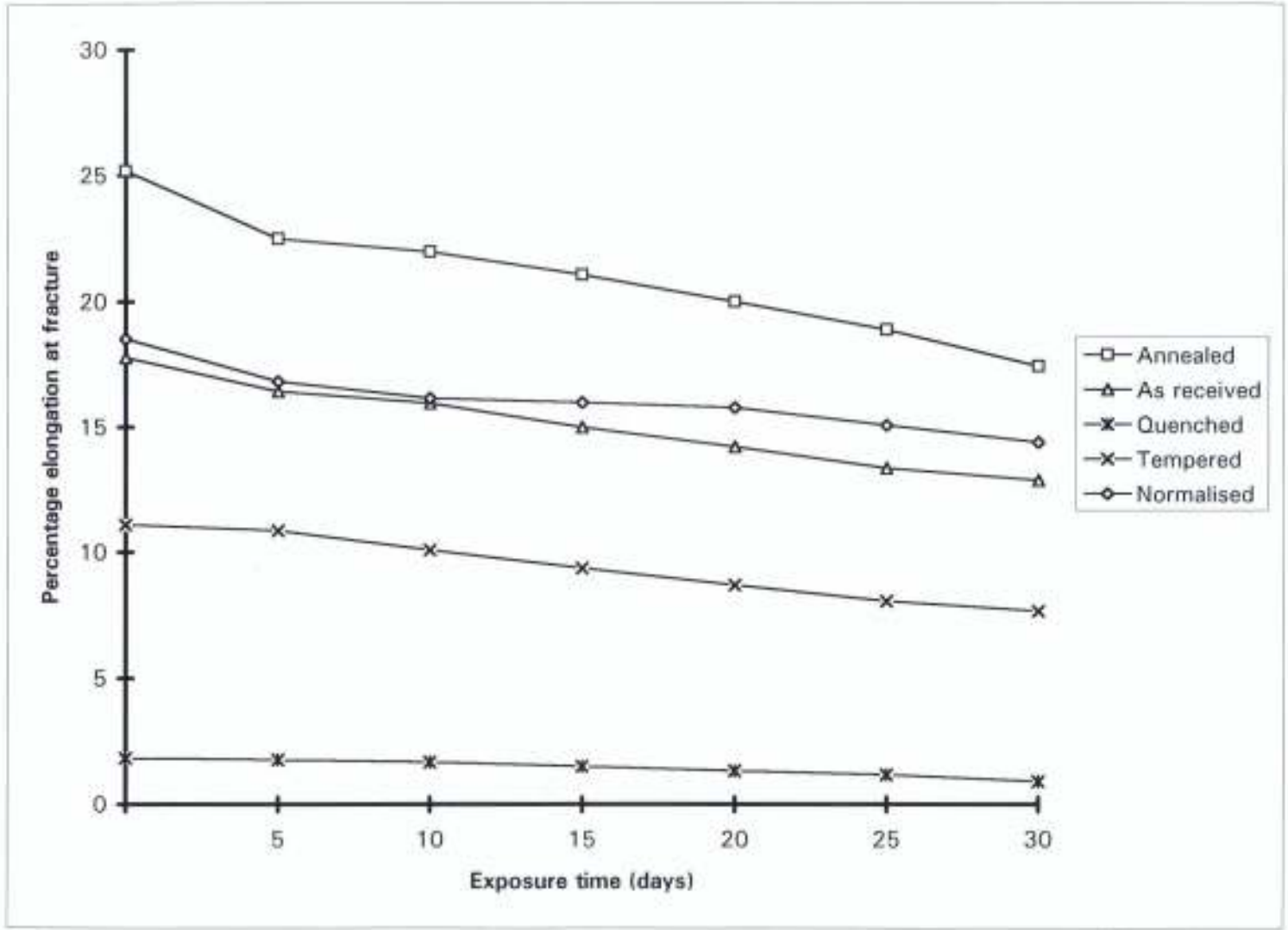

Figure 36: Effect of heat treatment on SCC of carbon steel in wood pulp only

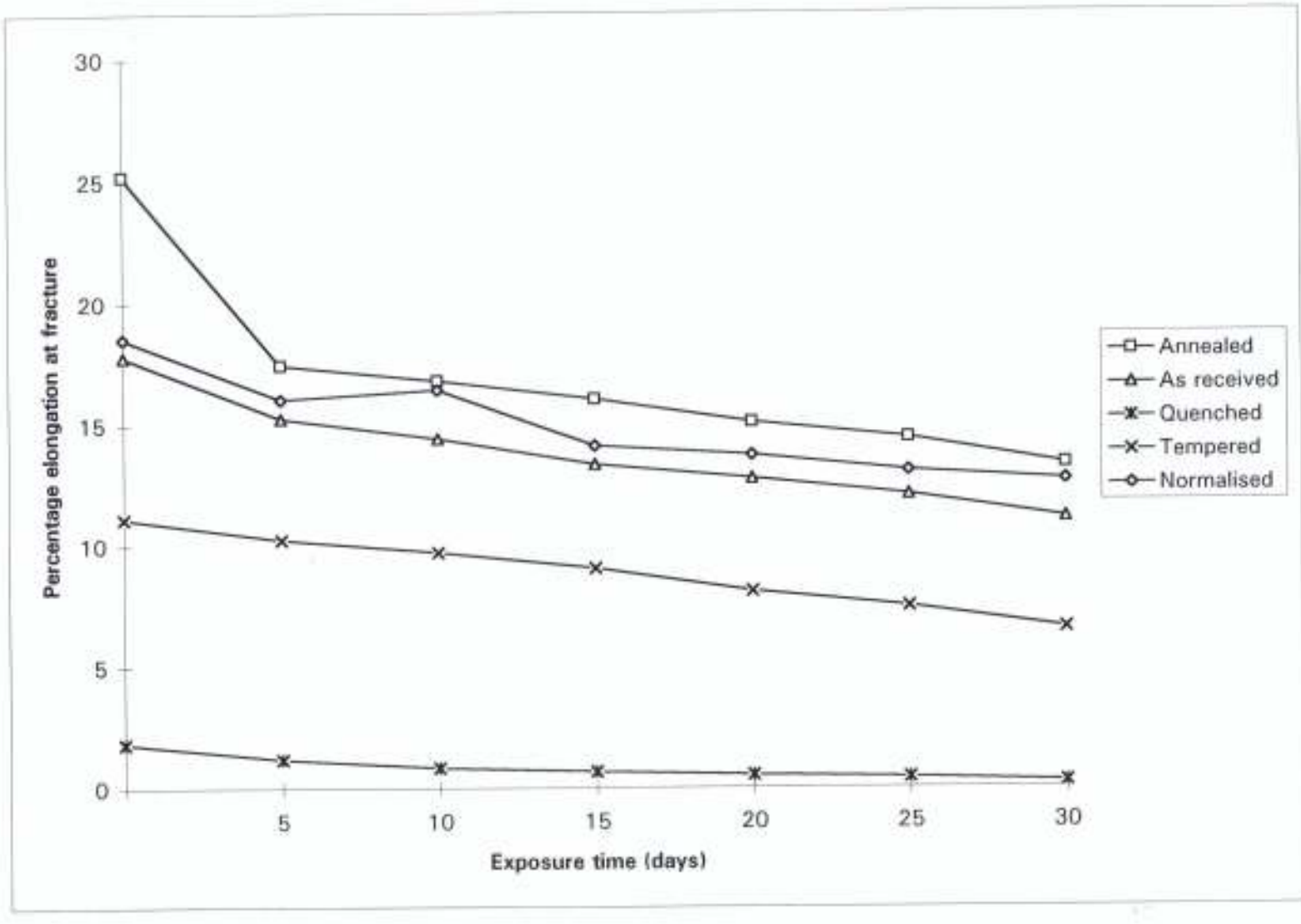

Figure 37: Effect of heat treatment on SCC of carbon steel in wood pulp contaminated with Hg ions

The results obtained were plotted in figure 38. It can be seen that the

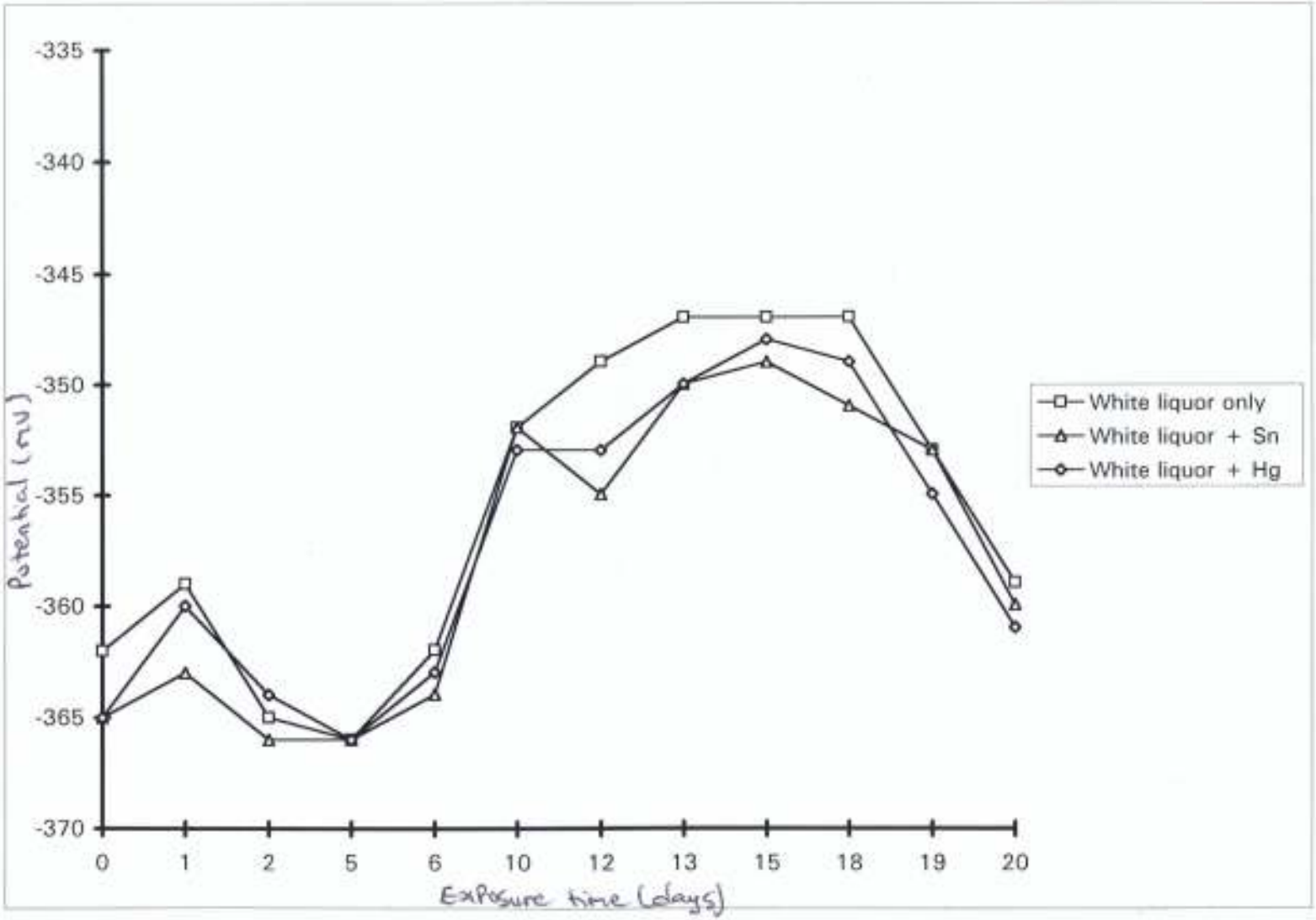

Figure 38: Potential variation with time for white liquor and its additives

electrode potential of both the contaminated and the uncontaminated shifted towards the passive region in the first 24 hours of exposure. This indicates possible progressive formation of passive film on the metal surface on exposure to the solution.

After the first 24 hours, a downward shift in the direction of the active region was noticed signifying possible break up of the passive film. The upward and downward trend in the graph shows that the trend of corrosion was characterised by alternating formation and breakage of passive film on the metal surface.

Evans (1991) observed that voluminous rust products develop forces strong enough to cause breakage of passive film. This, coupled with the effect pH can have on the properties of the passive film may be responsible for alternating breakage and formation of passive layers. The general trend revealed that the electrode potential of the metal moved towards passive region as exposure time increases.

5.3.2 POTENTIAL VARIATION WITH TIME IN WOOD PULP

Measurement was taken of the variation of potential with time in wood pulp with and without contamination with Sn^{++} and Hg^{++} ions. The results obtained were plotted in figure 39. It can be seen that the electrode potential of both the contaminated and the uncontaminated shifted towards the active region from the first 24 hours of exposure till the end of 30 days. This indicates possible progressive dissolution of the low carbon steel thus not giving room for formation of passive film on the metal surface during the exposure time.

5.3.3 pH VARIATION WITH TIME IN WHITE LIQUOR

As shown in figure 40, the pH move towards the acidic region between the first 6 days of exposure, this is followed by alternating value in pH , this can be as a result of decomposition owing to bacteria action.

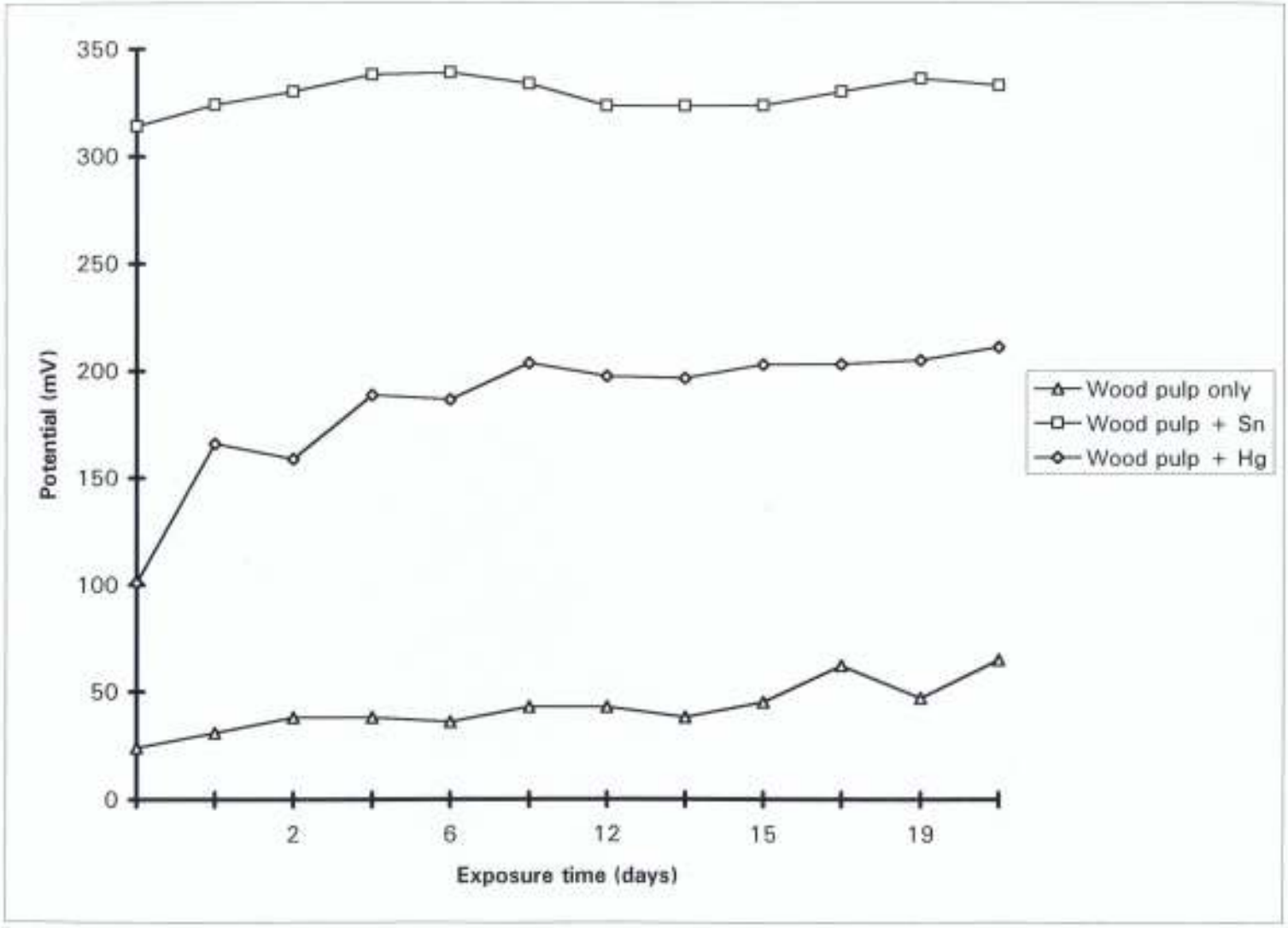

Figure 39: Potential variation with time for wood pulp and its additives

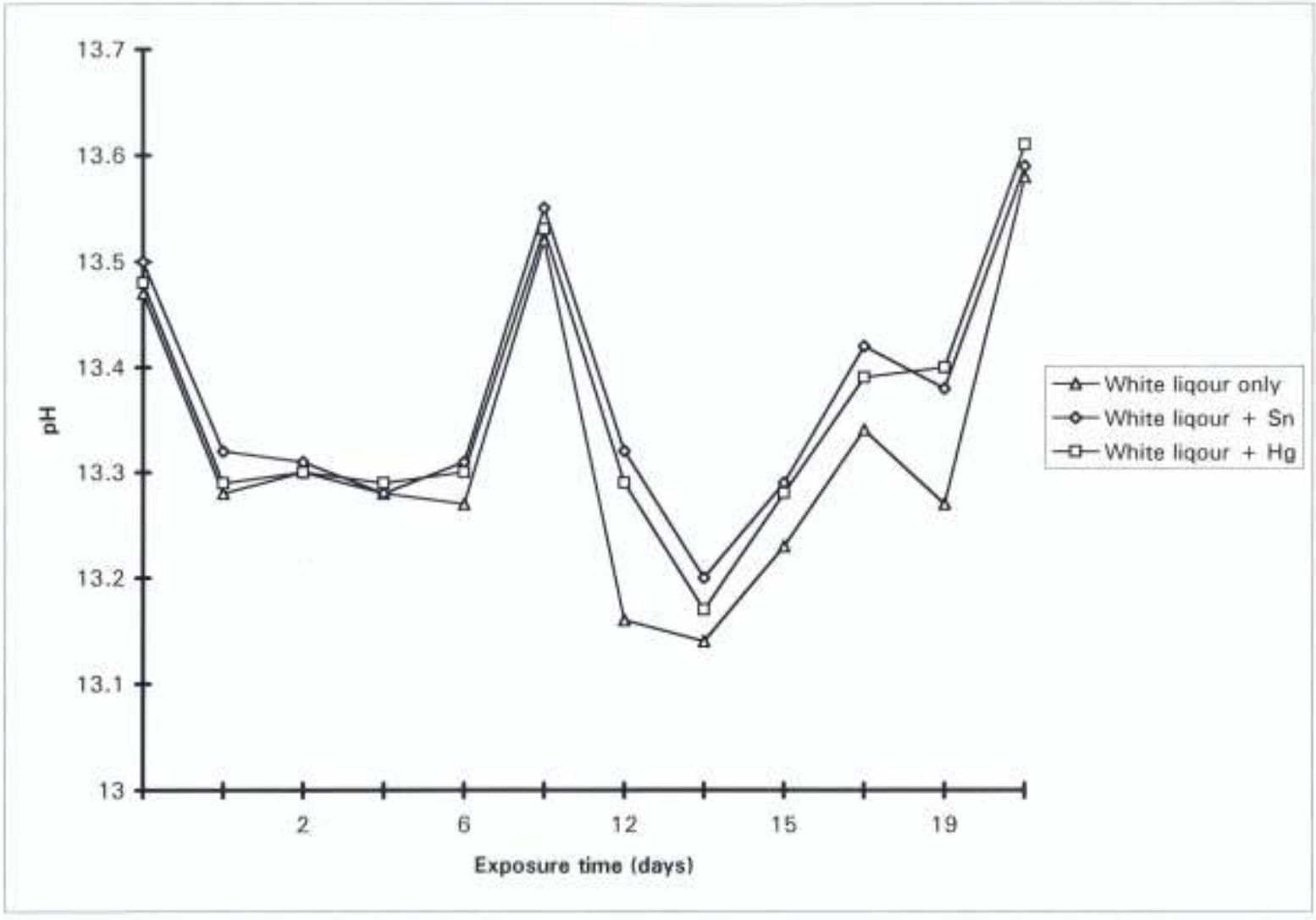

Figure 40: pH variation with time for white liquor and its additives

The extraneous ions effect may be as a result of the catalytic effect of these ions on decomposition reaction by bacteria.

5.3.4 pH VARIATION WITH TIME IN WOOD PULP

As shown in figure 41, the pH for the greater part of the exposure time increases towards the acidic region thus explaining the observed high corrosion rate and loss of ductility in the wood pulp and its additives relative white liquor and its additions.

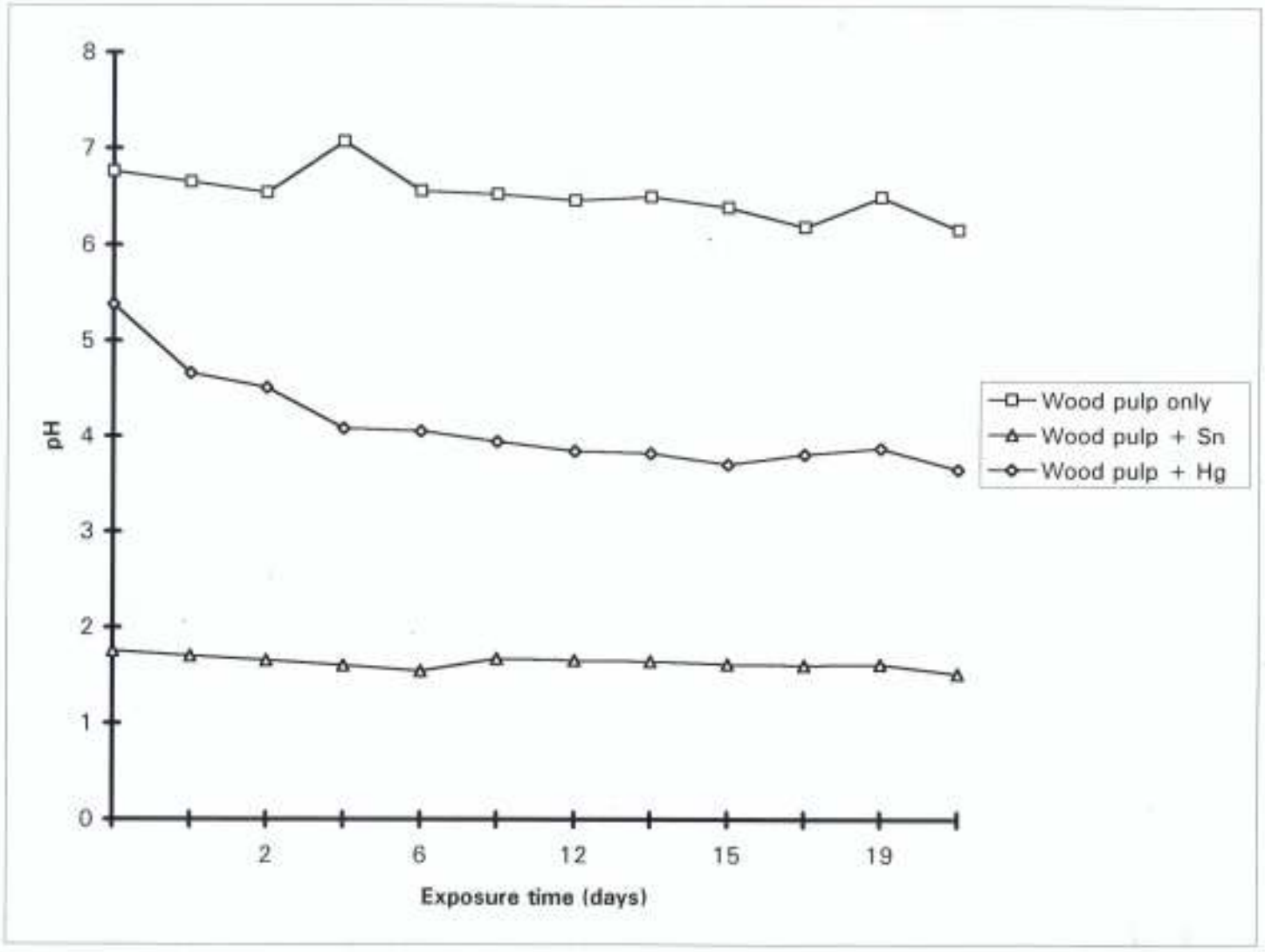

Figure 41: pH variation with time for wood pulp and its additives

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS.

6.1. CONCLUSIONS.

1. Plain carbon steel is susceptible to corrosion and stress corrosion cracking in wood pulp and white liqour.

2. Weight loss per surface area of the metal increases with exposure time.

3. The presence of Hg^{++} and Sn^{++} ions in both wood pulp and white liqour increases the corrosion aggressiveness of the solution to plain carbon steel.

4. The rate of corrosion attack is a function of the cooling rates of heat treated samples from austenitizing temperature, i.e. the slower the cooling rate, the lower the corrosion attack.

5. The mechanism of cracking with Sn^{++} ions addition is anodic dissolution at the crack tip.

6. The mechanism of cracking with Hg^{++} ion addition is hydrogen embrittlement.

7. High corrosion attack and loss of ductility in steel samples is higher in

wood pulp than in white liqour.

6.2 RECOMMENDATIONS.

Based on the result of this work, the following recommendations are made for maximum utilisation of plain carbon steel in the fabrication of paper making machines.

1. A fully annealed plain carbon steel should be used in the fabrication of paper making machines.

2. A fully annealed plain carbon steel should be used in the fabrication of storage tanks for wet wood pulp and white liqour.

3. Tin plating should not be used for plain carbon steel intended for use in a paper mill.

6.3 SUGGESTION FOR FURTHER STUDIES.

1. More detailed fractographic studies of stress corrosion cracks and chemical analysis of corrosion products at the crack tip are necessary for a better understanding of the mechanism of stress corrosion cracking propagation.

2. Establishment of appropriate mechanistic model for hydrogen embrittlement in martensitic steel in wood pulp and white liqour.

3. Studies should be carried out to test the efficiency of some inhibitors in the environment under investigation.

REFERENCES.

1. AGRAWAL A.K., PEDNEKEV S.P. CHAUNG H.E. and STAEHLE R.W.(1979), Journal of electrochemical society, 126 p. 701

2. ALAGBE M., (1990), Stress corrosion cracking of plain carbon steel in agro fluids, B.Eng. thesis, unpublished

3. ANGELLINI E. and ZUCCHI F. (1987), Proceedings of the 10th international congress on metallic corrosion, Oxford and IBH,2, p. 1671

4. DOIG P and EDINGTON J. W. (1974), British corrosion journal 9, p. 88

5. EVANS U.R. (1991), An introduction to metallic corrosion, Edward Arnold publishers

6. FONTANA M. G. (1986), Corrosion engineering McGraw Hill,: p. 6, 109, 173, 360, 434 - 439.

7. FORD F. P. (1984), Current understanding of the mechanisms of stress corrosion and corrosion fatigue, in Dean S. W., Pugh E. N., Ugiansky G. M.(eds), environment sensitive fracture, ASTM - STP 821, p. 32 - 51.

8. HAHIN C. (1982), Corrosion, 38, p. 116

9. HOAR T. P. (Chairman), (1971), Report of the committee on corrosion and protection HMSO.

10. KORBIN G., (1987) Metals handbook, 13, corrosion, 9th edition, ASM international, metals park OH, p. 326

11. LIU R., NARITA N., ALSTETTER C., BIRNBAUM H., and PUGH E.N. (1980), Metallurgical transaction, 11a, p. 1563

12. LONG R. L., UHLIG H.H. and OLSZEWSKI J.S. (1983), Corrosion/83, paper No 141, NACE Houston

13. McREYNOLDS R. F. and VENNETT R. M (1975). Materials performance 14 (1), p. 23.

14. MOLOZINK K.L, BRIANT C.L and McMAHON C.J (1979), Journal corrosion, 35 p. 331

15. NELSON B., HAHIN C., STOSS R. and REUCROFT R. (1976), Corrosion, 32 P. 229

16. ODESHI A.G. (1994), Corrosion and stress corrosion cracking of medium carbon steel in agro fluids, M.Eng. thesis, unpublished

17. OHTANI H., FENG H.C and McMAHON C.J (1979), Journal metallurgical transaction 5, p. 516

18. OKORAFOR O. E. (1987), Corrosion prevention and control p. 133

19. PARKINS R. N. (1976), Mechanisms of stress corrosion cracking, in Shreir L. L. (ed), corrosion (2nd edn; vol. 1). Newness-Buttlerworths, 8, p. 24.

20. PARKINS R. N. The theory of stress corrosion cracking in alloys - NATO (ed. J. C. Scully) Brussels 1971.

21. PARKINS R.N. (1990), Environment induced cracking of metals, NACE, Houston, p. 1

22. PUSH E. N., MONTAGUE W. G. and WESTWOOD A. R. C. (1986), Corrosion science 6 p. 345.

23. RAZIK N.A., ZAYAN M.H., FAYEED A.M. AND B.A. ABD-El-NABEY (1989), Corrosion prevention and control, p. 141

24. RICKER R.E. and JONES R.H (1987), Metals handbook, 13, corrosion, 9th edition, ASM international, metals park OH, p. 145

25. SHREIR L.L (1979), Corrosion, 1, P. 34,52

26. SWARTZ I. N., METTONEN I. M. et al, Alkaline Pulping, in pulp and paper manufacture (1982).

27. TRETHWEY K. R. and CHAMBERLAIN J. (1992), Corrosion for students of science and engineering; Longman Scientific and Technical p. 175.

28. UHLIG H. H. (1971), Corrosion and corrosion control. John Wiley and sons inc, New York.

29. UHLIG H. H. (1974), ref. 7

30. UHLIG H. H. (1975) Corrosion handbook.

31. WILDE B.E (1986), corrosion 42, p. 147

32. WOELFUL M. and MULHALL R. (1982), Glass bead impact testing, Metal progr. p. 57 - 59.

33. ZUCCHI F. and ANGELLINI E. (1982), British corrosion journal, 17, p. 4, 184