THE EFFECT OF HEAT TREATMENT ON CORROSION AND STRESS CORROSION CRACKING OF CARBON STEEL IN AGRO-FLUIDS.

BY

ODESHI AKINDELE GABRIEL

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ABSTRACT

The effect of heat treatment, extraneous ions addition, cathodic and anodic polarisation on corrosion and stress corrosion cracking (SCC) of medium carbon steel in cassava fluid, tomato and pepper juices has been investigated.

The general corrosion performance of the steel in various environment was evaluated by measuring electrochemical potential of steel samples in the environment with respect to Ag/AgCl reference system, and by determining weight loss of some steel samples owing to corrosive action of the environment. In the SCC tests, the steel samples were subjected to conjoint action of stress and corrosion after which, the samples were stressed to failure. The ductility of tested samples gave measure of their SCC susceptibility.

The rate of general corrosion attack of heat treated samples was found to increase as the rate of cooling from austenitising temperature was increased. Quench hardened steel showed minimum susceptibility to corrosion attack when tempered at 300°C.

Results of extraneous ions addition, and polarisation effect have given the mechanistic model of stress corrosion crack propagation. Whereas, mechanism of cracking of quench hardened steel was hydrogen embrittlement in cassava fluid, the same steel cracked due to anodic dissolution in tomato and pepper juices. It was also established that, while steel with martensitic structure

failed due to hydrogen embrittlement in cassava fluid, steel with pearlitic structure failed by anodic dissolution in the same fluid.

The rate of cracking of medium carbon steel in tomato juice was found to increase steadily as applied anodic potential was increased. The steel showed marked susceptibility in cassava fluid and pepper juices when the applied anodic potential was between 12 and 15V.

D E D I C A T I O N

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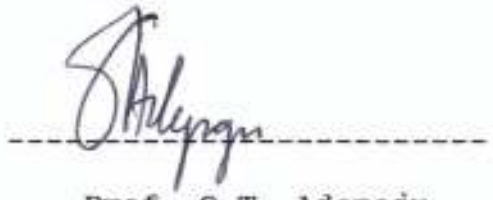
This work is dedicated to the evergreen memory of my late father PRINCE MICHAEL ODESHIKUSIBE ORISATUYI who departed this sinful world on Monday, 10th July 1989. Papa, though you are gone, but your spirit is on.

CERTIFICATION

I certify that this work was carried out by **Mr. ODESHI AKINDELE GABRIEL** 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 a degree.



Prof. O.T. Adepoju

Supervisor.

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Odeshi, A.G.

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CHAPTER ONE

INTRODUCTION

1.1 MEANING AND COST OF CORROSION

The word corrosion is derived from the latin corrodere meaning to gnaw away. It refers to degradation of a material and loss of its properties as a result of reaction or interaction with its environment.

All categories of engineering materials are liable to corrosion attack. The severity of attack however, appears more pronounced in metallic materials. Reason for this is not far - fetched: most metals occur naturally in combined form and the process of metal extraction and refining involves utilization of considerable amount of energy. Metals are thus characterized by high free energy value and are thermodynamically unstable until they revert back to their natural (combined) form. Consequently, metals readily react with their environment to achieve a state of thermodynamic equilibrium.

Virtually all metals and alloys are susceptible to corrosion attack and all environment are corrosive to some degree. However, the extent of corrosion damage depends on so many inter-related variables. A metal for example, may react with a particular environment under certain conditions to form

an impervious surface layer which stops further corrosion attack. The same metal may react with the same environment under different condition to produce a porous reaction product. Attack in this case, will proceed progressively until the metal eventually fails.

The presence of tensile stress, whether residual or applied, has been found to increase the extent of corrosion damage. The accelerated corrosion attack as a result of conjoint action of tensile stress and corrosion is called stress corrosion cracking (SCC). SCC is characterized by initiation and propagation of fine cracks which may act as stress raisers and cause material failure at a stress level much lower than the design stress. A study in the USA as reported by Barnejee (1985) has shown that SCC accounts for about 1/4 of total material failures (mechanical and corrosion).

The condition for SCC is highly specific requiring not only specific metal-environment combination, but also certain level of stress, composition, structural morphology of the metal and quite narrow range of pH and electrode potential of the environment. Thus different corrosion reports are often obtained from seemingly similar metal -- environment combinations.

There has been report of failure due to stress corrosion cracking of non-metallic materials. Schneider and Nagele

(1993) reported that stress corrosion led to a significant decline in flexural strength of loaded cement mortals compared to unloaded ones in Ammonium sulphate solution. The disastrous effect this trend could have on safety and reliability of bridges leaves much to be desired.

The cost of corrosion on global economy is quite enormous. Apart from its drastic contribution to depletion of world mineral resources, huge financial loss and material wastage are incured annually in combating and preventing corrosion. Fontana and Grene (1967) stated that the cost of floods,hurricanes, tornadoes, fires, lightening and earthquake are less than costs of corrosion. Raja Gopalan (1987) put the total cost of corrosion in India as RS 4,000 crores annually, and avoidable cost as RS 1,800 crores. Barnejee (1985) put the direct cost of corrosion in USA (1975) and Britain (1982) at an annual estimate of 70 billion dollars and 14 million pounds respectively. Marinho and Sampaio (1981) reported that the mean annual corrosion cost in light services de ELectricidade, an electric power utility in Rio de Janeiro and Sao Paulo, was about $1,488,805, at least.

The impact of corrosion on Nigerian economy is by no means less. Although adequate record of corrosion costs is yet to be established in Nigeria, the effect is felt in all facet of national economy. This ranges from rusting of domestic items to corrosion of agricultural and industrial equipment.

An awful sum of money is expended in the oil sector to combat corrosion of pipe lines and oil rigs. When pipe lines eventually corrode and oil spillage occurs, the consequence on the ecological build up of the affected area and agrarian economy of the affected community are enormous and disastrous.

1.2 OBJECTIVE AND SCOPE OF THIS STUDY

The fundamental objective of any corrosion study is to minimize the menace of corrosion and its attendant consequence on national economy. Corrosion is spontaneous and inevitable. As Adepoju (1989) emphatically put it; "From the dust cometh the metal and unto the dust shall it return". Corrosion can not be completely eliminated but can be minimized to a tolerable limit by suitable material-environment design. Research efforts are geared towards investigating those variables influencing corrosion with the ultimate intention of prolonging the useful life of valuable metals before they begin the inevitable sojourn back to the mother earth.

The fact that large numbers of variables are involved in corrosion makes the process extremely difficult to analyze. The rather complex nature of corrosion makes it unjustifiable to generalize corrosion report. Fruits and other agricultural products are known to contain common organic acid or solvents. Though there has been corrosion reports on some of these

organic solvents, it is unsafe to extend such reports to corrosion evaluation in agro-fluids. The condition under which the acids are present in agro-fluids may be different from that of the acids used in the laboratory. It is therefore pertinent to investigate the corrosive action of these organic acids as they are found in raw agricultural products.

This project is aimed at evaluating corrosion and stress corrosion cracking of carbon steel in cassava fluid as well as tomatoes and pepper juices and determining the correlation betweeen its microstructural formation and corrosion susceptibility in the environments under study. Effect of anodic/cathodic polarization and introduction of extraneous ions will be considered to determine mechanistic aspect of SCC of carbon steel in the media. Optimum combination of metal-environment variables will also be determined for excellent corrosion performance.

1.3 JUSTIFICATION FOR THE STUDY

Nigeria in the recent times, has embarked on aggresive agricultural policies aimed at boosting food production. Local processing of agricultural products are encouraged and intensified to enhance their storage and make them available for consumption all year round. The high cost of importation and ever increasing demand has necessitated the need for local

fabrication of some food processing equipment which hitherto had been wholly imported for domestic use.

Plain carbon steel, being the cheapest and most readily available metal is commonly used in fabrication of food processing machines in Nigeria. Carbon steel is prone to corrosion attack, even in aerated water, how much more raw agricultural products which are known to contain some aggressive ions. These ions may attack the steel components of food processing machines, resulting in their untimely failure in service. Deliberate efforts are therefore required to enhance the service life of these components if their continuous production (locally) and usage is to be sustained.

In terms of material selection for excellent corrosion performance, stainless steel would have provided a better alternative to carbon steel, but for the prohibitive cost and apparent scarcity of stainless steel in the country. This study is expected to serve as the authors contribution to the effort to preserve the service life of locally produced food processing machines and equipment . If the service life of such machines can be enhanced, the need for application of rather expensive stainless steel will be eliminated. Consequently, the machines can be produced at affordable price for the common man.

CHAPTER TWO

LITERATURE REVIEW

Based on the characteristic nature of its attack, corrosion may be classified as general or localized corrosion. General corrosion describes the attack that is evenly distributed over the entire surface of the metal. Localized corrosion is centered on very small area and is the most destructive and insidious form of corrosion. The type of attack on a particular material will depend on its structural morphology and the precise environmental condition prevailing.

2.1 REVIEW OF CORROSION MECHANISMS

A corrosion process may be classified as chemical or electrochemical corrosion depending on the premise of the mechanism of corrosion reaction. While chemical corrosion is governed by the kinetics of heterogeneous chemical reaction, electrochemical corrosion is subjected to the principles of electrochemical kinetics.

Chemical corrosion processes are typical of high temperature metal/gas reactions and chemical dissolution of metal in non-conducting organic liquids. Corrosion of metals in electrolyte is a typical example of electrochemical corrosion and it occurs with possible generation of galvanic current between two parts of the corroding metal.

2.1.1 HIGH TEMPERATURE METAL/GAS REACTIONS

Metal oxides (sulphides or chlorides) are thermodynamically more stable than uncombined metal. In the presence of dry air, metal readily reacts, chemically, with gaseous oxygen (hydrogen sulphide or halogens) even at room temperature. Equation of the chemical reaction occurring for gaseous oxidation can be represented thus

$$M + \tfrac{1}{2}O_2 \longrightarrow MO \quad \ldots\ldots\ldots (1)$$

For iron-oxygen reaction at elevated temperature, layers of the potentially stable oxide: FeO, Fe_3O_4 and Fe_2O_3 are formed in sequence as shown in figure 1. Equation of reactions are given as follows:

$$Fe + \tfrac{1}{2}O_2 \longrightarrow FeO \quad \ldots\ldots\ldots\ldots (2)$$

$$3FeO + \tfrac{1}{2}O_2 \longrightarrow Fe_3O_4 \quad \ldots\ldots\ldots\ldots (3)$$

$$2Fe_3O_4 + \tfrac{1}{2}O_2 \longrightarrow 3Fe_2O_3 \quad \ldots\ldots\ldots\ldots (4)$$

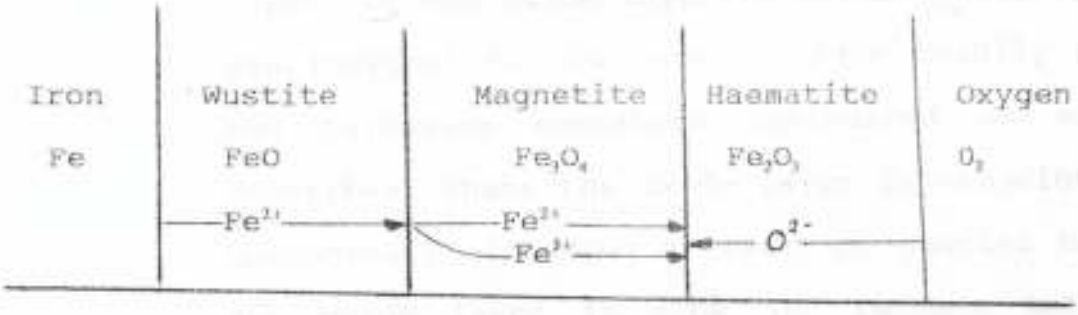


Fig 1. Oxide growth mechanism on iron

The mechanism of oxidation reaction is comprised of three major steps:

i) Adsorption: This is the initial stage of the reaction. Oxygen molecules are accumulated on the surface of the metal, dissociated and ionized at reactive sites. The oxygen ions will react with ionised metal atoms (m') at these sites to form random nucleation of oxide nuclei (Mo).

ii) Oxide nucleation: After formation of metal oxide nuclei, the oxidation proceeds through growth of individual nuclei until the whole surface is covered with oxides.

iii) Oxide growth: Once the initial thin oxide layer is formed, the subsequent mechanism of oxidation is dependent on the protective nature of the oxide layer. If the oxide layer is porous, diffusion of gas (oxygen) to the metal surface readily occurs and oxidation continues unhindered as earlier described. Where the oxide layer is tenacious and non-porous, diffusion of reacting species through the oxide layer is slow and becomes the rate controlling step in preference to the rate of chemical reaction. The mechanism of subsequent oxidation in the latter case is best described by

Wagner's theory of oxidation.

Wagner's theory of oxidation

This is based on the asumption that the oxide layer is protective, i.e. non porous. According to this theory, oxidation by gaseous oxidation is an electrochemical process with the growing film simulated into an electrolytic cell. In this cell, metal/oxide interface acts as the anode and oxide/gas interface acts as the cathode.

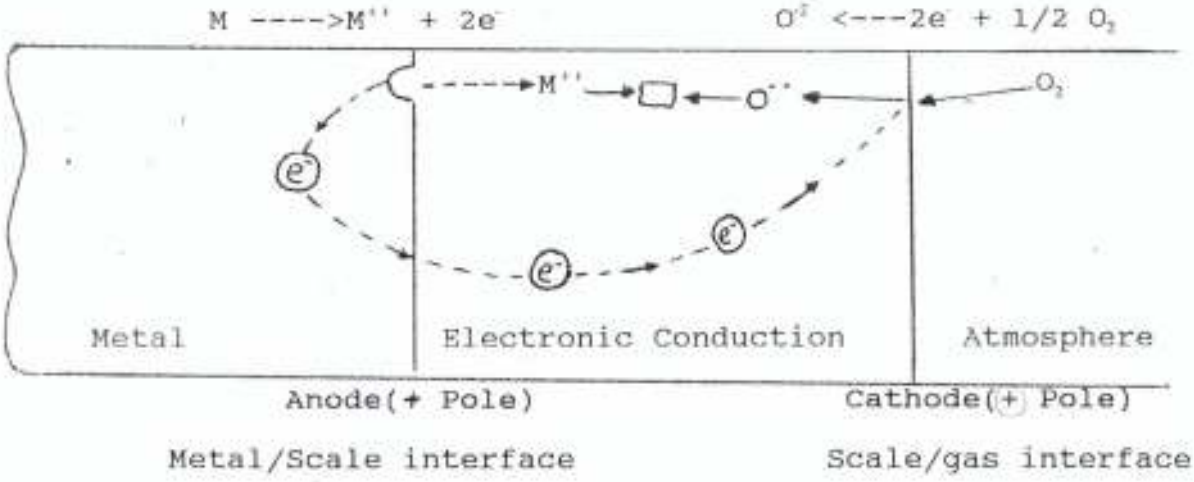


Figure 2: Electrochemical mechanism of gaseous oxidation.

Figure 2 shows schematic illustration of electrochemical process during gaseous oxidation. Oxygen reduction occurs at the oxide/gas interface. Oxidation of the metal occurs at the metal/oxide interface with both the anions and cations

migrating through the oxide layer.

Based on this theory, subsequent metal - gas reaction can be taken to consist of two partial process viz:

$M \rightarrow M^{2+} + 2e^-$ ..... (5) at metal/oxide interface

$\frac{1}{2}O_2 + 2e^- \rightarrow O^{-2}$ ..... (6) at oxide/gas interface

$M + \frac{1}{2}O_2 \rightarrow MO$ overall reaction.

The metal - oxygen reaction which gives the oxide may take place at the metal/oxide interface or oxide/gas interface or at the two interfaces simultaneously. For reaction occuring at the metal/oxide interface, oxygen ions migrate by diffusion through the oxide film to react at the interface and electron migrate to the oxide/gas interface. Gaseous oxidation of Aluminium follows this reaction mechanism.

For reaction occuring at the oxide/gas interface, metal cations migrate (alongside with electrons to maintain electrical neutrality) to the oxide/gas interface to react with oxygen anion at the interface. Examples of metal following this mechanism include Cu, Zn and Ni.

2.1.2 ELECTROCHEMICAL CORROSION IN AQUEOUS SOLUTION.

Corrosion of metals in conducting aqueous solution is essentially an elecrochemical phenomenon. The underlying principle is the generation of anodic and cathodic parts resulting in dissolution (oxidation) of the metal at the

anodic part and reduction of a non-metallic species at the cathodic part.

This type of corrosion differs from the electrochemical dependent gaseous oxidation earlier described in the sense that oxidation of the metal, reduction of the oxidising specie and formation of corrosive product for gaseous oxidation, occur at one and the same place. In aqueous corrosion, oxidation of the metal, reduction of a specie in the solution, and formation of corrosion product occur at different places. Thus the solid corrosion product formed at a distance from the point of attack can not stifle the action. On this basis, aqueous corrosion is often more dangerous than direct gaseous oxidation.

Taking the corrosion of iron in a conducting solution as a case study, the anodic reaction is given by

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \ldots\ldots\ldots\ldots\ldots (7)$$

Electrons generated at the anode are consumed in the cathodic reaction which may be oxygen reduction or hydrogen evolution depending on the nature of the electrolyte. In well aerated solution, oxygen reduction occurs as follows:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad \ldots\ldots (8)$$ for acidic solution

$$O_2 + 2H_2 + 4e^- \longrightarrow 4OH^- \quad \ldots\ldots\ldots (9)$$ for neutral solution

For electrochemical corrosion in de-aerated solution or in acid, the cathodic reaction is hydrogen evolution as

represented by equation 10

$2H^{+} + 2e^{-} \longrightarrow H_2$ ..... (10)

Metal ion reduction or metal deposition can also occur at the cathode, especially when two dissimilar metals are coupled together. The more active metal behaves as the anode and corrodes preferentially to the other one which is protected. The driving force for the corrosion reactions is the electrochemical potential difference between the two metals. 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.

Electrochemical cells can be generated on a metal surface due to presence of heterogeneities such as impurities, chemical segregation, oxides, multiple phase or localised stresses in the structure of the metal. The potential difference between the heterogeneities and the matrix offers the driving force for corrosion reactions. Other source of corrosion current include variation in concentration of reacting species in the solution.

2.1.3 CORROSION IN ORGANIC SOLVENTS

Heitz (1974) has classified corrosium reaction occuring in organic solvents into:

1. Electrochemical reactions which follow a similar mechanism to those in aqueous solution
2. Chemical reaction which involves direct charge transfer between metal atom in metal lattice and the oxidising species.

For electrochemical reaction, the partial anodic reaction results in formation of solvated metal cation M^{2+} solv, a charged or uncharged metal complex MZ^{-} or a solid compound MX_2 where X is an organic acid, halogen etc.

The cathodic partial reaction could be any of the following:

i. Reduction of a solvated proton to H_2 gas

H^{+} solv + e^{-} ---> $\frac{1}{2}H_2$

ii. Reduction of acidic hydrogen of a proton donor

HA + e ---> $\frac{1}{2}$ H_2 + A^{-}

Where A- is a carboxyclic anion, alcoholate ion, etc

iii. Reduction of an oxidising gas Y

Yz + Zme ---> ZY^{m}

Where Y can be O_2, Cl_2, F_2 etc.

iv. Reduction of oxidising ions such as Fe^{3+} Cu^{2+} etc.

The general equation for non-electrochemical dissolution of metal in organic solvent as presented by shrier (1974) can be written as

$$M + 2C_x H_y X_z \rightarrow MX_z + C_{2x} H_{2y} X_{2x-1}$$

where x is a halogen and M is a divalent metal.

2.1.4 POLARISATION, OVERPOTENTIAL AND PASSIVITY.

In most electrochemical corrosion processes, a decrease in the driving force (electrode potential difference) for corrosion reactions at the electrodes is observed with time. This effect is known as electrode POLARISATION: When an electrode is polarised as a result of reaction sequence at the electrode - electrolyte interface, in which case the speed of reaction is controlled by the slowest of the electrode reactions, the type of polarisation is refered to as ACTIVATION POLARISATION. A CONCENTRATION POLARIZATION occurs if the rate of electrochemical reaction is controlled by diffusion in the electrolyte.

The magnitude of the difference between standard electrode potential and the actual value when current flows is termed OVERPOTENTIAL. Yadav (1990) described hydrogen overpotential as the magnitude of polarisation during hydrogen evolution. He attributed the change in overpotential from metal to metal to the difference in their catalytic effect on the rate of combination of hydrogen atoms. Metals such as Pt and Ni which have low values of over potential are good catalysts and those of high values of over potential are poor

catalysts.

PASSIVITY is used to describe the tendency of a metal to form an adherent, protective oxide layer that is stable in the electrolyte. Further corrosion attack is hindered and the metal is rendered inactive. Passivity, however, is a condition obtainable only under specific conditions of pH and electrode potential for a particular metal - environment combination.

2.2 STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) is a conjoint action of corrosion and mechanical destruction. This results in initiation and propagation of fine cracks in the susceptible metal while the metal or alloy is virtually unattacked over most of its surface. SCC will cause brittle failure of materials including those which even conform with the normal ductility standard.

The destructive effects of corrosion and mechanical force are not additive; each component complement one another. The disastrous consequence of SCC however, has shown to be greater than when either of tensile stress or corrosion are acting separately. Ford (1982) stated that stress corrosion cracks may propagate in wide range of velocity ranging from 10^{-4} mmS^{-1} to 10^{1} mmS^{-1}. In this case, time to failure is a matter of minutes under severe conditions of stress and enviroment or of

years when conditions are less severe.

Thompson's (1961) experiment showed that whereas cold rolled bent strip of 70/30 brass fractured in 20 minutes after admission of ammonium hydroxide, 70/30 cupro Nickel remained unaffected after exposure to the same enviroment with the same period of exposure.

2.2.1 CRACK INITIATION AND PROPAGATION

Stress corrosion cracks usually begin to form after an initial incubation period, corresponding to a period of gradual formation of primary corrosion - mechanical cracks on a metal surface by localization of corrosion process and of the tensile stress. Once the crack has been initiated, it propagates initially at more or less a constant rate. As propagation progresses, the cross-section area of the material diminishes and the applied stress increases, as a result. Consequently, the rate or crack propagation will increase rapidly until failure occur as shown in figure 3.

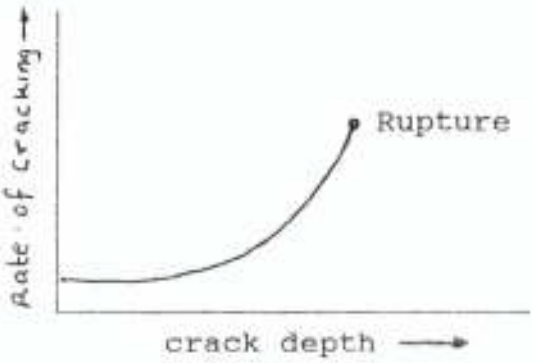


Figure 3: Rate of cracking as a function of crack depth

Total time of failure (t_f) is comprised of incubation time (t_i) and the period of crack propagation: (t_p)

$$t_f = t_i + t_p$$

Pedrazzoli and Spiedel (1992) have shown that crack propagation rate was related to the yield strength of high strength steel exposed to water, as does the threshold intensity factor. The crack velocity was however found to be significantly influenced by sulphur and carbon contents of quenched and tempered steels and by microstructure.

Polarisation has a significant effect upon total time of failure (t_f). Anodic polarization will usually shorten t_i, while cathodic polarization will lengthen t_i and failure may be prevented altogether by cathodic protection. If hydrogen is the endangered species t_i is shortened by both anodic and cathodic polarization, but this will not be true if the surface adsorption of hydrogen is rate controlling step when no change in t_i may occur. The findings of Balasubramaniam and Duquette (1992) as well as Meltis (1992) are in line with this proposition.

2.2.2 CRACK MORPHOLOGY

Stress corrosion cracks give the appearance of a brittle fracture with the mode of failure ranging from being predominantly intergranular to being predominantly

transgranular. Transition from one mode to another is commonly observed in many alloys depending on the stress level, the corrosive medium, heat treatment condition and other variables.

Adepoju (1976) reported that SCC of Ti 155 alloy in methanol/HCl solution occur as an intergranular dissolution process at low value of applied stress or strain rate, while it occurs at higher values by a dual process of transgranular cleavage and low energy ductile tearing. Wu et al (1991) discovered that intergranular cracks in α - brass exposed to various environment are associated with low stresses or stress intensity factor, with transition to transgranular cracking if stress increases and reversion to intergranular if stress decreases again.

Barnejee (1985) wrote that SCC failures of austenitic stainless steel in hot chloride solution occur transgranular, whereas the steel undergoes intergranular SCC in hot caustic solution. Priest et al (1955) reported that annealed specimens of a magnessium base alloy in salt - chromate solution, having small grain size cracked intergranularly, while transgranular cracking was observed in specimens larger than ASTM no 7 regardless of heat treatment condition of the test piece.

Stress corrosion cracks generally proceeds perpendicularly to the applied stress. Depending on metal environment combination and associated variables, crack

morphology can vary from a single crack to crack with extreme branching.

A. INTERGRANULAR STRESS CORROSION CRACKS

Intergranular crack proceeds along grain boundaries. Grain boundaries are normally high energy regions and form path of enhanced reactivity throughout the susceptible metal. In the presence of a suitable environment, grain boundary atoms behave anodically and dissolve preferentially to those in parent matrix. In the absence of stress and impurity segregation, the unstable grain edges dissolve until grain boundary has assumed an equilibrium configuration (Fig. 4).

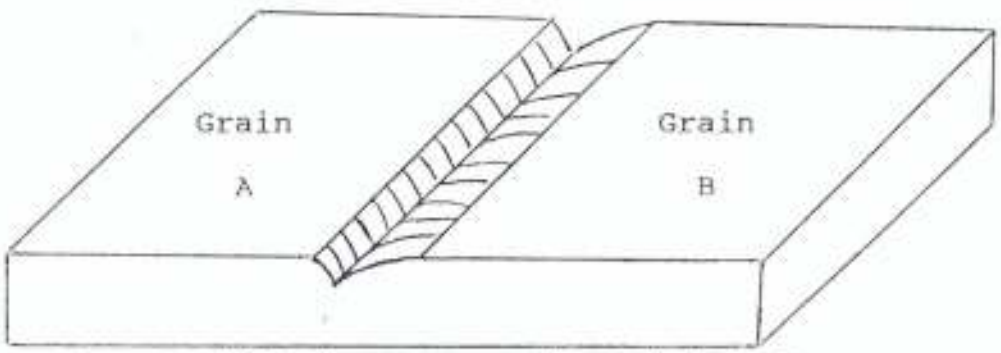


Figure 4: Equilibrium groove at grain boundary (After Robertson and Bakish: cited by Barnejee (1985))

Where there is presence of segregation, chemical activity will not stop until all the boundaries have been eaten away and the metal falls apart. Application of tensile stress across a

chemically active grain boundary will intensify its corrosion attack. Two reasons can be adduced for this trend

i. The yawning - of the penetrated region will facilitate ingress of fresh electrolyte thus reducing concentration polarization at the corrosion front.

ii. Stress is concentrated at the corrosion front because cracking constituting penetrating region behaves as a notch, thereby leading to enhancement of chemical activity at the grain boundary.

B. TRANSGRANULAR STRESS CORROSION CRACKS

Transgranular cracks occur without apparent preference for grain boundaries. It appears to be limited to alloys rather than pure metals, and even alloys having close pack lattices.

Uhlig and white (1960) demonstrated that martensitic type 18 - 8 stainless steels resisted cracking in $MgCl_2$ solution, whereas the austenitic type cracked in the same solution regardless of the austenitic stabilizing agent. This points to the fact that the lattice type is the important factor in transgranular corrosion of stainless steel rather than the chromium or Nickel content.

Electron microscopic studies of copper base alloy as reported by Barnejee (1985) revealed that transgranular cracking occurs when the solute concentration is high such that dislocations move one behind the other in groups on well defined planes. The planes provide coarse slip steps which provide the reactive site. Under the action of applied stress, dislocations move to the surface forming slip steps that fracture the protective film and expose metal surface to corrosive environment. Enrichment of aggresive ions are favoured in the slip step regions thereby promoting localised corrosion attack. The continued motion of dislocation on the slip plane prevents resulting corrosion tunnels from becoming inactive.

Priest et al (1955) found that transgranular cracking of the magnesium base alloy did not always propagate in the direction normal to the applied stress. Instead the direction of cracking was found to be along the slip (0001) plane of the hcp lattice.

2.2.3 VARIABLES INFLUENCING SCC

Not all metal-environment combinations are susceptible to SCC. Stainless steels for example, crack in chloride enviroment but not in ammonia solution, whereas brass cracks in ammonia containing environment and not in chlorides.

The susceptibility of a metal-environment to SCC is dependent on the specific condition of stress, enviroment, alloy composition and microstructure.

STRESS FACTORS

The essential feature of SCC is simultaneous presence of both tensile stress and corrosion. The source of the stress may be externally applied load or internal stresses locked up in the material. The accelerating effect of stress on both intergranular and transgranular cracking has been adequately discussed in section 2.2.2.

Wei and Hao (1987) who concluded that tensile stress not only enhances the tendency for metallic corrosion but accelerates it, also emphasised that the effect of tensile stress accelerating anodic dissolution of metal should be attributed to decrease in the activation energy. The study of the duo indicated that the accelerating effect of tensile stress on different systems is different.

Hoar and Hines (1956) have shown that SCC susceptibility of austenitic stainless steels in $MgCl_2$ solution increased as the applied stress increased. Reed and Paxton (1962) reported that single crystals of stainless steel did not crack unless the applied stress was above a certain yield point.

Uhlig and White's (1960) study on SCC of austenitic

stainless steel in boiling $MgCl_2$ solution showed that a correlation existed between temperature of stressing and time to failure. The correlation showed that bending temperature of annealed samples of the steel, beyond room temperaure, has no effect on cracking time, but for specimens stressed (bent) below 0°c, cracking times became increasingly longer as the temperature was lowered. Similar specimens bent at room temperature and then refridgerated in liquid nitrogen showed normal cracking times.

ENVIRONMENTAL FACTORS

There seem to be no general pattern to the environment which can cause SCC of various metals and alloys. Environmental condition for SCC is highly specific, requiring not only presence of certain specific ions (specific ions effect), but also very narrow range of pH and electrode potential. Several authors have published specific ions causing SSC of many engineering metals and alloys. The presence of these specific ions however, may not cause any significnat damage if not present in the correct proportion. Radeker and Grafen (1956) for instance observed that whilst a little dissolved oxygen apparently promotes cracking, a high concentration prevents failure.

Ishiara et all (1951) observed that SCC susceptibility of

type 304 stainless steel in high temperature water is enhanced by contamination with dissolved oxygen. Increasing oxygen concentration up to 8 ppm enhanced intergranular cracking in the steel and cracks occurred within 30 hours in 8 ppm oxygenated water. The fracture time in 16 ppm oxygenated water increased to about ten times that in 8 ppm oxygen. Further addition of oxygen to 32 ppm raised the susceptibility to intergranular SCC approximately to the same level as that in 8 ppm oxygen water, Weir (1950) reported that dilute solution of NaOH at elevated temperatures is much less effective in causing caustic cracking of steels than those of high concentration.

Lunde and Nyborg (1987) submitted that contamination with air was the primary cause of SCC of certain Carbon-Manganese steels and Nickel steels in ammonia. Pure ammonia was reported not to cause SSC of these steels. Addition of minimum of 0.1 wt % water to the ammonia was found to inhibit cracking in the liquid phase.

Panthania and River (1981) have also shown that addition of oxygen to H_2S saturated water increases the aggressiveness of the environment to cracking of stainless steels and Nickel alloys.

Reviewing recent research efforts on SCC, Parkins (1992) stated that crack growth by dissolution like any localized corrosion problem requires some critical balance between

active and passive behaviours. To retain the geometry of a crack extending by dissolution in the tip region, it is required that reactions at the tip proceed at a considerable faster rate than any dissolution process occuring at all other exposed surfaces of the metal including the cracking sides. The inactivity that develops at the crack side will usually be due to formation of a passive film. This together with the requirement that the metal must be active when the film is not present implies that cracking will be potential dependent again with some pH dependence because of the influence of that quantity upon the potential at which various reactions are possible. The potency of an environment in promoting SCC will depend on pH and potential for such cracking. Hence the influence of oxygen ions on SCC susceptibility.

Alloys such as Aluminium, Titanium or stainless steel which readily form protective film will require agressive ions such as halide to promote SCC. On the contrary, for inherently low corrosion resistance metal such as carbon steel or Mg base alloys, the presence of partially passivating environment is required. Barnejee (1985) stated that carbon steels can be made to fail in solution of anodic inhibitors such as OH^- and carbonates, while cracking of magnessium base alloy is achievable with an approximate mixture of $CrO4^{2-}$ and Cl^- ion but not with either of these species alone.

The physical state of the environment is also important. Ishihara et all (1981) reported that crack initiation of type 304 stainless steel in high temperature water is remarkably influenced by water temperature. The cyclic heating and cooling of the water was observed to cause susbstantial rapid failure of the alloy. Scully (1975) emphasized that hexagonal α - alloys based upon Ti - Al and Ti - O alloys failed by transgranular cleavage in aqueous solution of NaCl at room temperature. At higher temperatures (above 250°c) however, failure was by both transgranular and intergranular mode.

METALLURGICAL FACTORS

The susceptibility of an alloy to SCC is affected by the average chemical composition, size and orientation of the grains and precipitate, and microstructure.

It is widely believed that SCC is predominantly found in alloys, while pure metals appear to be immuned. However, SCC has been reported in pure metals. Pugh et al. (1968) reported intergranular cracking of 99.999% Cu in ammoniacal solution. Elis and Scully (1968) observed intergranular cracking of high purity iron, while Perryman (1951) also reported SCC of high purity magnesium in 0.5KHF solution. Such crackings have been attributed to presence of grain boundary impurities.

For a given alloy, variation in small alloying additions may have a pronounced effect on SCC susceptibility. Thompson

(1961) reported that the susceptibility of brass in ammoniacal solution increases with zinc content. The trend is depicted in Fig. 5, which also show the effect of a third element on the susceptibility of the binary alloy.

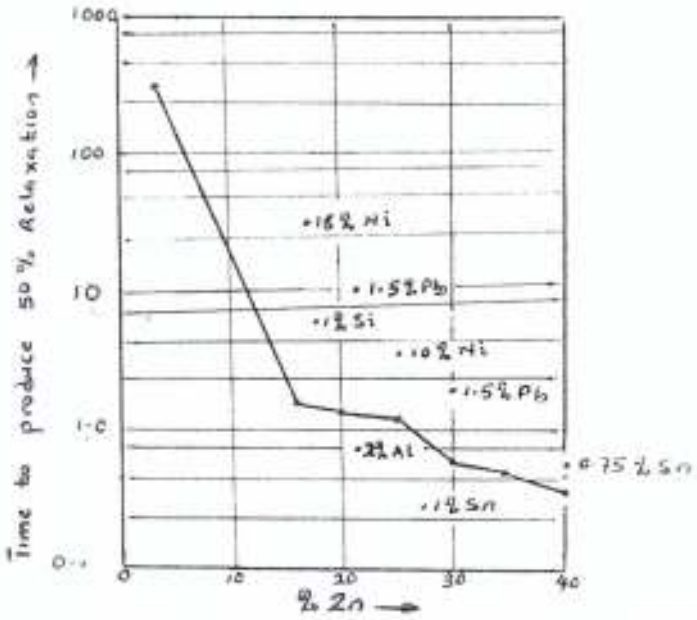


Fig 5: Stress corrosion cracking of brasses and brasses containing a third element in moist ammoniacal solution (Thompson 1961)

Sieradzki et al. (1987) have shown that there exist, a good correlation between SCC and dealloying of Cu - Zn and Cu - Al alloys in ammoniacal - cuprous ion solution. He reported that cracking of these alloys will not occur unless the solute achieves a value at which dealloying occurs. Haden and Perryman (1950) observed that production of magnessium improverished surface caused an improvement on the resistance to SCC of Al.7% Mg Alloys.

Uhlig and White's (1960) experiment on SCC of stainless steel in boiling 42% $MgCl_2$ solution showed that 18-8 austenitic type containing 0.015% carbon or 0.01% nitrogen or less did not crack within maximum time of test (200 - 260hrs). Commercial types containing about 0.08% carbon and 0.04% nitrogen on the other hand cracked within 0.2 to 1.4hr. The test also showed that stable austenitic 20% Cr and 20% Ni are similarly resistant if nitrogen content is sufficiently low (about 0.002%). Carbon contrary to its effect in 18 - 8, confers resistance to cracking.

Large grains contain greater number of imperfections, which on pilling up along suitable barrier favour adsorption of damaging ions at the barrier surface. Susceptibility is therefore expected to diminish as the grain size is reduced. In addition to grain size, grain orientation is also important. Adepoju (1976) submitted that maximum susceptibility of cold rolled Titanium alloy is obtainable in the short transverse direction. The highly elongated pan-cake shape grain structure in the transverse section ensures that an easy path for crack propagation is readily available.

Hovland and veritas (1981) submitted that SCC was strongly related to hardness level of steel. Susceptibility was reported to increase with increasing hardness. Panthania and River (1981) have shown that cold work had a detrimental

effect on the stress corrosion cracking resistance of stainless steels in water saturated with Hydrogen sulphide, while Grover and pavila (1987) reported that the risk of SCC susceptibility of carbon steel in anhydrous ammonia solution increased with strength of the steel. By implication, any metallurgical process variable such as heat treatment or cold work which increases hardness and strength enhances the risk of stress corrosion cracking.

Microstructural morphology have been established to have considerable influence on SCC. Smialowski et al (1951) reported that the form and distribution of cementite phase in a steel is related to the rate of cracking in 40% aqueous solution of NH_4NO_3. It was observed by Baldy and Bowden (1955) that steel became susceptible to SCC when martensite began to show continuity in microstructure. Sheppard and Parson (1987) stressed that Al - Li alloys containing less than 0.44% Cu were not susceptible to SCC. In the alloys that failed, susceptibility was found to increase as aging treatment was extended from the underaged to the peak aged temper.

There also exists a correlation between SCC susceptibility and precipitate morphology. Haden and Perryman (1950) reported that susceptibility of Al - 7% Mg alloy in NaCl solution was related to continuity of grain boundary precipitate. Susceptibility was discovered to be maximum when

precipitate was apparently quite continous. Poole (1974) emphasised that trace impurities in α - iron generally have little effect on SCC, but a pronounced increase in hydrogen uptake results if precipitation of a second phase (Carbides, oxides) occurs.

2.2.4 STRESS CORROSION CRACKING MECHANISM

The mechanistic aspect of SCC is not well understood, at least to the extent that no single mechanism has been found applicable to all metal - environment systems. The rather complex interplay of metal, interface and environment properties does not help in mechanistic understanding of SCC either. A number of mechanisms have however, been proposed for SCC. The essential features of these mechanisms, which are briefly reviewed here will provide a solid foundation for a clear understanding of the mechanistic aspect of stress corrosion cracking.

DISSOLUTION MECHANISM

This mechanism is based on the existence of path of enhanced reactivity in the matrix of the susceptible metal or alloy. Continuing localized dissolution of the metal along the active path is the fundamental process of crack growth.

The pre-existing active path may be provided by the grain

boundaries, and applies primarily to intergranular stress corrosion cracking (IGSCC) of ductile alloys in aqueous environment. The inherently higher activity of disordered grain boundary atoms or more importantly, presence of chemically active grain boundary precipitates or impurities renders the grain boundary chemically more active than the parent matrix. This induces intergranular anodic dissolution that is sustained by the presence of an appropriate stress as described in section 2.2.2. A.

The studies of Abe and Kaneko (1992) as well as Burstein and Woodward (1983) have proved the existence of a correlation between segregation of phosphorous to grain boundaries and intergranular cracking of stainless steels and inconels. Abe and Kaneko (1992) attributed IGSCC of stainless steel to precipitation of Ni - P compound at the grain boundaries. Presence of segregated substance at the grain boundaries does not however, indicate tendency toward IGSCC even when there is propensity for intergranular cracking. Wang et al 's (1992) stress corrosion tests showed that IN718 Nickel base superalloy and Ticolloy are susceptible to a mixture of intergranular and transgranualar cracking in aerated NaCl, whereas, when the solution was deaerated only transgranular cracking was found.

Where enhanced chemically active paths are non existent or in-operative, an alternative active path may be provided by

slip steps on high density dislocation planes (as discussed in section 2.2.2.B). Under the action of applied tensile stress, the slip steps move to the surface causing fracture of protective oxide layer. Anodic dissolution of exposed metal surface will occur and this will continue until protective film reforms. Further dissolution is stiffled until the film is broken again by another slip step. The anodic dissolution continues progressively along the slip plane resulting ultimately, in transgranular cracking of the susceptible metal.

The height of the slip step formed at a surface must be greater than the thicknes of the protective film if bare metal is to be exposed. This implies that deformation associated with coarse (high) slip step is likely to be more effective in promoting SCC than when fine step is operative. Parkins (1974) have emphasised that low stacking fault energy or presence of short range order in alloy make cross-slipping difficult, thereby, enhancing planar dislocation and hence promote formation of high or coarse slip steps.

A correlation between transgranular and stacking fault energy has been proposed by Swann (1963), giving credence to the argument that variation of susceptibility to transgranular cracking with alloy composition may be attributed to the latter's attendant effect on stacking fault. This however, is without prejudice to significant effect of alloying element on

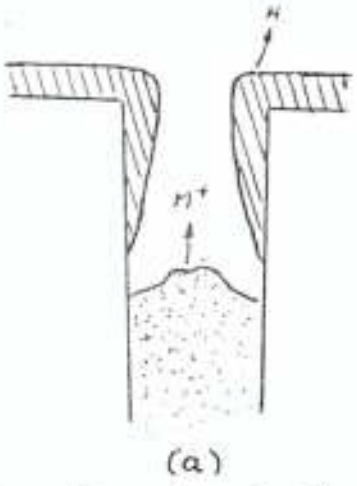
electrochemical parameters.

FILM INDUCED CLEAVAGE MECHANISM

This mechanism was originally proposed by Edeleanu and Forty (1960) who observed that the cracking of α - brass single crystals in ammoniacal solution occured discontinuously, with short bursts of extremely rapid cracking followed by relatively long rest periods.

Film induced cleavage is characterised by rupture of protective film by mechanical action and subsequent oxidation of the exposed metal surface. This is followed by a period of crack arrest which remain in place until rupture of passive film occurs again by plastic deformation. Alternate deformation with rupture and fresh oxidation occurs progressively in this manner leading to discontinous crack propagation in the susceptible metal.

The concept of plastic deformation with rupture of oxide layer at the crack tip was explained by Parkins (1992). He explained that dissolution of the crack tip increases the mobility of near-crack-tip dislocations, this localized enhancement of plasticity leading to the formation of dislocation pile ups at barriers such as Lomer - Cottrell locks. A brittle fracture by mcirocleavage and/or microshearing is then possible, promoted by conditions of restricted slip, although resultant stress relaxation can induce crack arrest.



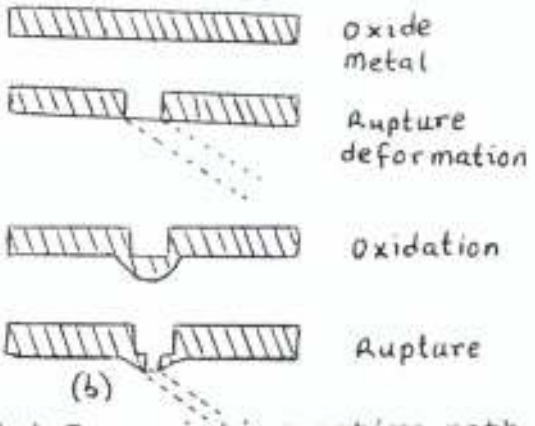


Fig. 6 Dissolution mechanism (a) Pre existing active path (b) strain generated active path

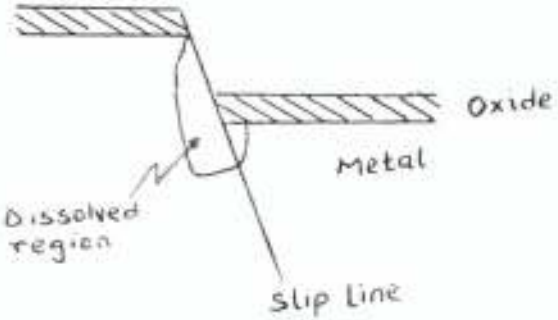


Fig. 7 Film induced cleavage

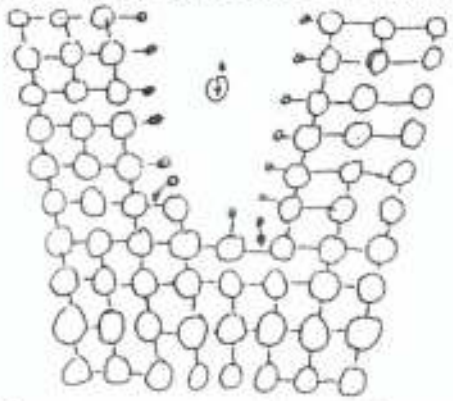


Fig. 8 Stress Sorption theory

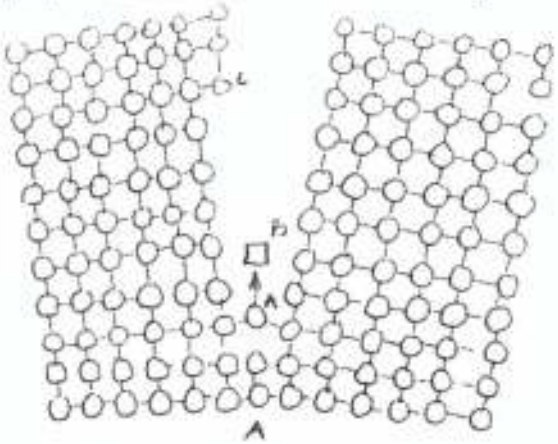


Fig. 9 Surface Mobility mechanism

STRESS - SORPTION THEORY

This mechanism has been proposed to describe subcritical crack propagation which rely primarily on the decrease in mechanical integrity at the crack tip due to adsorption of specific species from the environment followed by absorption into the underlying matrix. A number of models have been put forward to explain crack propagation based on this theory.

Surface energy reduction model, as reviewed by Ford (1982), relies on surface chemisorption of an environmental specie on the crack tip which reduces the surface energy term in the equilibrium Griffth relationship.

$$\sigma_c = \sqrt{\frac{2E\gamma_s}{\pi c}}$$

σc is the fracture stress necessary to cause spread of an elliptical crack length 2c. E is the young modulus and γs is the surface energy term. Obviously, any process which reduces the surface energy term, γs, will reduce stress required for brittle fracture.

Decohesion model has also been argued for subcritical crack propagation based on the stress sorption theory. The characteristic feature of this model is that the adsorbed species weaken cohesive bonds between surface metal ions. The

binding energy between the surface atoms is lowered to such an extent that crack propagation can occur at low stresses and with little plastic deformation.

The difference in mechanism of atom-atom ruputre between the surface energy and decohesion models has been argued to be insignificant by Oriani (1972). Ford (1982) has however written that the main conceptual difference is that, in the surface energy model, rupture occurs at the top surface, whereas, in the decohesion model, subcritical crack *propagation relies on the diffusion* of the agressive atoms to some point beneath the surface where rupture occurs. The latter is specific to hydrogen because of high mobility of hydrogen atoms.

Diffuse species can also react to form stable but brittle phase at the crack tip thereby promoting subcritical crack propagation. Scully and Powell (1970) affirmed that the stress corrosion of α - titanium alloys constitute an example of slow-strain rate hydrogen embrittlement with nucleation of hydride on an operative slip plane leading to cleavage as the important step in this process.

SURFACE MOBILITY MECHANISM

This provides the latest attempt to explain all instances of environment - sensitive cracking. It was proposed by Galvele (1992) and extensively reviewed by Parkins (1992).

Based on this mechanism, an atom at a crack tip is envisaged to be transported by surface diffusion from its highly stressed location at the crack tip to a new site at less stressed cracked sides thereby, advancing the crack by one atom spacing for such movement as illustrated in Fig. 9 Crack propagation rate for such a mechanism may be modelled to produce

$$C_v = \frac{D_s}{L\{\exp[(\sigma\Omega^3 - \alpha E_b)/kT] - 1\}}$$

where

Ds = coefficient of surface self - diffusion of metal

L = The diffusion path length

a = Atomic diameter

σ = maximum stress at crack tip

Eb = hydrogen-vacancy binding energy

α = relative degree of saturation with hydrogen of a vacancy at the tip of crack

k = Boltzman constant

T = Absolute temprature.

Parkins (1992) reiterated that the coefficient of surface self diffusion will dominate crack growth rate and the role of environment is to change that diffusivity. The specificity of metal - environment condition for SCC was accounted for, by Galvele (1992) through the explanation that cracking will only occur in those potential regions where oxide film is partly

unstable and where active-passive or pitting - passive transition occurs.

Surface mobility has been subjected to several criticism. For instance there were Newman and Procter (1990) who noted that many of the correlations that Galvele cited to support surface mobility mechanism would work equally well if his criterion was surface energy reduction rather than increase in surface diffusivity. Parkins (1992) opined that surface mobility may be more feasible in relation to metal-induced fracture than to other forms of environment - sensitive cracking.

HYDROGEN EMBRITTLEMENT

Hydrogen embrittlement is caused by adsorption of atomic hydrogen into the susceptible metal. The chemically adsorbed hydrogen aids crack initiation and propagation by reducing the surface energy term in the Griftth equation and hence reduce the stress required for brittle fracture. Adsorption of atomic hydrogen into a metal may also lower the maximum cohesive force against separation of metal atoms or lock up dislocation and make plastic flow more difficult.

Ordinarily, the presence of atomic hydrogen in steels are not always harmful though the steel will alsways lose its ductitlity. The presence of tensile stress (residual or applied) above a critical value will cause initiation and

propagation of cracks as a result of either reduction of cohesive strength, or blocking of dislocaion in the hydrogen enriched zone or both. The higher the hydrogen content, the lower the critical stress. Figure 10 exemplify a typical failure curve for hydrogenated high tensile steel.

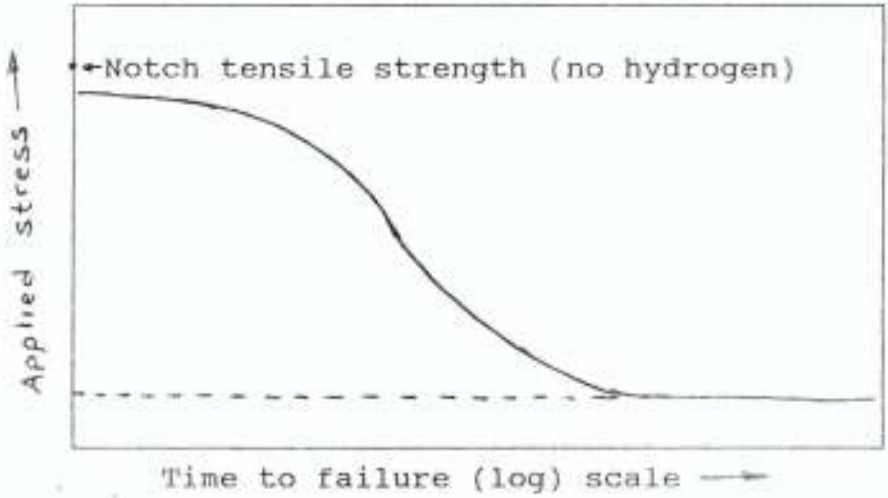


Fig 10: Typical delayed failure for hydrogenated high tensile steel.

Poole (1974) stated that steel composition has a marked influence on the extent of trapping and hence hydrogen adsorption, while the submission of Barnejee (1985) indicated that carbon steels are especially susceptible to hydrogen cracking when heat treated to form martensite, but are less if structure is pearlitic. Austenitic steels in which hydrogen is more soluble than ferrite and diffusion rate is lower have also been reported immuned under most conditions of exposure.

Parkins (1992) pointed it out that some metals such as Nb, Ta, Ti, V and Zr form stable, brittle hydrides and exposure to a source of hydrogen can lead to formation of hydride phases in the crack-tip stress field, where the strain field and the volume change associated with hydride formation interact to promote crack propagation.

2.3 ELECTROCHEMICAL AND STRESS CORROSION REVIEW OF CARBON STEEL.

ELECTROCHEMICAL CORROSION

Carbon steel is a very reactive metal, although it has the tendency to enjoy immunity or passivity under certain conditions of pH and electrode potential. The corrosion susceptibility of carbon steel is influenced greatly by certain features of composition, microstructure, corrosive medium, surface condition among others.

Ross (1977) explained that exposure of iron or steel to powerful oxidizing acids induces passivity by formation of an adherent and protective film of oxide. Mild steel was also reported by Sundaran et al (1987) to act as active-passive metal in hot carbonate solution. The addition of vanadium pentoxide slightly increased the passive region of the steel in carbonate solution. The study however showed that at temperature above 90°c, vanadium pentoxide did not have any

effect on passivity of mild steel.

The effect of various alloying element on corrosion of steel in O.1N H_2SO_4 has been discussed by cleary (1967) Phosphoruous and carbon are detrimetal to corrosion resistance; copper is mildly beneficial and silicon slightly harmful; sulphur, chromium and Nickel are found to have no effect. Takamura et al (1969) observed that the effect of phosphorous on corrosion of carbon steel in 1% H_2SO_4 was suppressed by the presence of copper and sulphur.

It was argued by Ross (1977) that carbon or cementite acts as efficient discharge points for hydrogen. Their presence in the surface of steel exposed to acidic conditions encourages the corrosion of adjacent ferrite grains. In line with this argument, Razik et al (1989) reported that air cooling of austenitised steel increased the corrosion tendency of carbon steel and attributed this to large interfacial area offered by cathodic cementite lamellae with the adjoining anodic ferrite plates.

A reaction kinetic study of corrosion of iron in acids by Haseeb et al (1989) showed that corrosion rate increased exponentially with acid concentrations. Temperature was also reported to remarkably influence the corrosion rate of carbon steel in the acid solution under study. Haseed wrote the reaction rate (r) over all range of concentration (c) and

temperatures (T) studied as follows:

For H_2SO_4 $r = 6.792 \times 10^{9} \times C^{1.86} \times \exp^{(-6667/T)}$

For HCl $r = 6.054 \times 10^{13} \times C^{1.5} \times \exp^{(-9523/T)}$

For H_3PO_4 $r = 6.6.3468\ 10^{10} \times C^{1.02} \times \exp^{(-7500/T)}$

Sharma et al (1987) on studying the effect of introduction of sodium sulphate to organic media, discovered that addition of sulphate ions to organic medium increased the corrosion of steel in the medium. Suitable corrosion allowance therefore need to be provided for, when designing for where there is possible contamination. Although the presence of chloride ions in natural water increases electrical conductivity and can therefore be expected to increase corrosion rate of mild steel, studies by Odeshi (1987) and Shih et al have shown that dissolved oxygen play a prominent role over any other factor.

Several research efforts to date have shown that surface condition of mild steel can influence significantly its corrosion rate in a number of environments. Wu et al (1987) reported that case hardening of spring steel which produces fine martensite under compresssive state with higher hardness improves its corrosion resistance. Millet et al (1987) observed that nitrided steel parts in acidified NaCl solution exhibited very poor corrosion resistance whatever the substrate and the type of heat treatment. Centre et al (1987)

in another study reported that silconized mild steel have an outstanding corrosion resistance in sulphuric acid.

STRESS CORROSION OF CARBON STEEL

The incidence of SCC of steel has continued to increase with passage of time. This is attributable to rather pertinent attempt on the part of designer to avoid general corrosion or increasing demand for extensive use of high strength steels to meet design specifications. It has been widely reported that susceptibility of steel to SCC increases with the strength of the steel. Grover and Pavila (1987) favoured this argument and emphasised that the risk of SCC of steel in ammonia solutions increases with stength of the steel.

Carbon content has been shown to control susceptibility of steel to SCC in most enviroment. Long and Uhlig (1974) reported that its susceptibility in nitrates goes through a minimum as carbon is reduced to very low levels (Fig. 11). while Parkins (1967) was of the opinion that electrochemical effect of carbon is the predominant factor, Long and Uhlig (1974) regarded the effect of carbon on mechanical properties as the means by which the element is important in SCC.

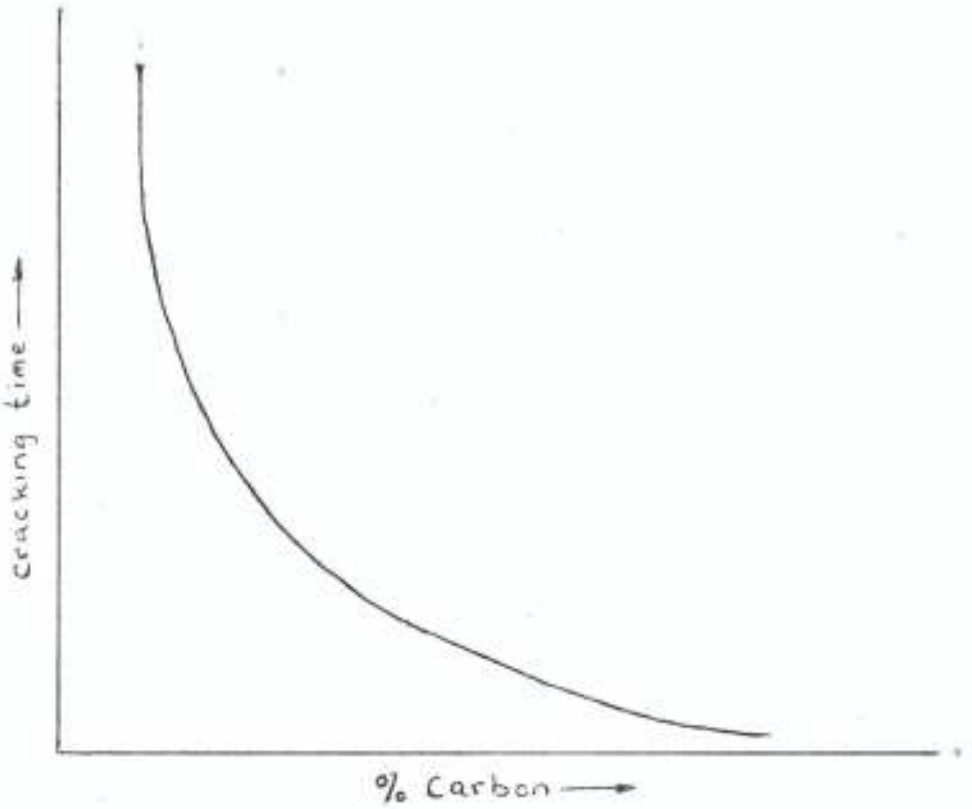


Fig 11: Effect of carbon content on very - low - carbon steels quenched from 92°c on cracking in calcium nitrate - ammonium solution (after long and Uhlig (1974)).

The distribution of carbon in the matrix is also important. Humphries and Parkins (1969) as well as Smialowski et al (1951) favour this proposition. Parkins and Green (1968) observed that ferrite (near those region rich in carbon) is preferentially attacked in nitrate enviroments. Parkins

(1974a) reported that similar effect is observed in other cracking enviroment, except in caustic solution where preferential attack may be upon the cementite.

Increase in cooling rate from austenite has severally been reported to result in increase in cracking susceptibility. Parkins (1974) appear to agree with this assertion, however, with a reservation that such a trend is relative. The effect of tempering temperature has been extensively studied but there are variations in trend exhibited by various steel- evironment combination.

Houdrement et al (1940) reported that tempering of 0.26%c steel above 300°c increase the cracking resistance in boiling $CaNo_3$ - NH_4NO_3 solution. The benefit of tempering temperature was observed to be maximum at tempering temperature of 600°c or above. Cracking studies of 0.06%c in the same solution by Uhlig and Sava (1963) shows that full benefit of tempering is obtained from 250°c with return to marked susceptibility at 700°c. Long and Lockginton (1967) showed that low carbon steel containing 1% Mn exhibited increased susceptibity initially when tempering temperature was increased above 200°c and that increasing resistance begin to be obseved when the tempering temperature exceeds about 500°c.

Waber et al (1946) profered an arguement for the assumption that nitrogen is the direct cause of SCC of mild

steel. High carbon content was reported to have a retarding effect on precipitation of iron nitride.

Parkins (1974a) wrote that cracking of mild steel is commonly associated with anodic inhibitors such as nitrates and hydroxides. These ions impart necessary oxidising potential required to render steel susceptible to cracking. There has been reports of SCC of steel in $(NH4)_2CO_3$ containing solutions, Parkins and Usher (1959) however, argued that presence of H_2S and HCN is necessary to promote cracking.

Schroeder et al (1937) and Radeker and Graffen (1956) submitted that cracking of steels in strong alkalis could not be reproduced unless the solution is contaminated with oxidising salts or oxygen itself. Radeker and Grafen went further to state that whilst a little dissolved oxygen obviously promote cracking a high concentration prevents failure.

Stress corrosion cracking of high strength steel has been reported in wide range of environment. It has generally been accepted that most cases of SCC of high strength steel are due to hydrogen cracking. Whilst Shelock and Sheir (1974) claimed that phosphate coating of steel with bath containing free acids and certain agent reduces the amount of hydrogen absorption into steel, Poole (1974) opined that steel composition has a marked influence on the extent of trapping

and hence on hydrogen absorption.

2.4 ELECROCHEMICAL DISSOLUTION OF STEEL IN AGRO-FLUIDS UNDER STUDY

Cassava contains cyanogenic glucosides, linamarin and lotaustrain which are hydrolysed after tissue damage, by the endogenous enzyme, linamarase to the corresponding cyanohydrins and further to hydrogen cyanide, HCN (Conn, 1969). The hydrogen cyanide on ionisation will produce H^+ and CN^- :

$$HCN \longrightarrow H^+ + CN^-$$

At the anode, oxidation of ion occurs according to the reaction:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At the cathode, reduction of H^+ in the solution occurs:

$$2H^+ + 2e^- \longrightarrow H_2$$

The overall reaction thus becomes

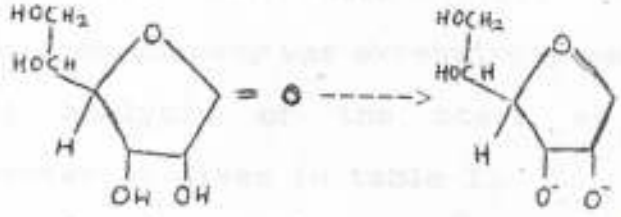
$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow \quad \ldots\ldots\ldots\ldots\ldots (16)$$

Tomato fruits contains organic acids which are mainly ascorbic acid (Vitamin C) and benzoic acid. These acids, though weak, can ionise to form H^+ ions which are utilised in the cathode reaction. The ionisation reaction of these acids are presented as follows.

Benzoic acid

+ H' ..... (17)

Ascorbic acid



..... (18)

The principal cathode reaction is oxygen reduction as represented by equation 8 with the overall reaction being:

$2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$ ..... (19)

Pepper is consists of essentially protein which ionises as follows

..... (20)

where R is any alkyl radical.

The H' ion produced from the ionisation reaction is consumed in the cathode reaction which is also oxygen reduction.

CHAPTER THREE

MATERIALS & METHODS

3.1 MATERIALS

Hot rolled medium carbon steel, collected from Oshogbo Steel Rolling Company was extensively used for the study. The chemical analysis of the steel as carried out on a spectrometer is given in table 1.

C	Si	S	P	Mn	Ni	Cr	Cu_2	Fe
0.3575	0.2483	0.0211	0.0543	1.0759	0.0172	0.0173	0.0029	98.197

Table 1. Chemical compostion of carbon steel studied.

3.2 PREPARATION OF SAMPLES FOR CORROSION STUDIES

The samples used for general corrosion studies were machined to cylindrical rods: 20 mm diameter and 40 mm long as shown in figure 12.

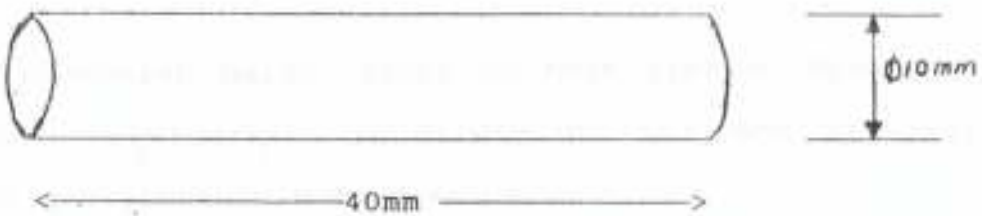


Figure 12: Test piece for general corrosion (weight loss) tests and electrochemical potential measurement.

The samples for stress corrosion cracking studies were machined to tensile specimens of average gauge length 2.80cm and gauge diameter 0.50cm Fig. 13 depicts SCC test piece as used in the investigation.

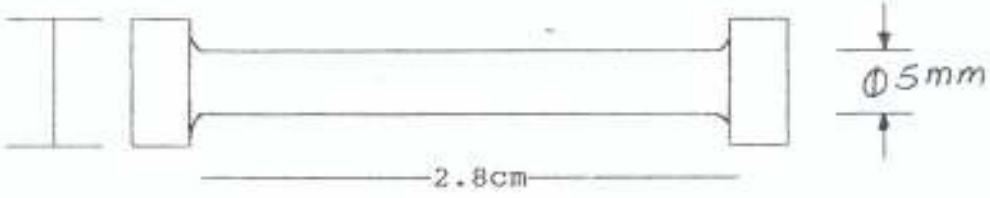


Figure 13: stress corrosion cracking test piece.

All corrosion test pieces were ground on 240mm grade emery paper to standardise the surface profile. Surface grinding of specimens was done under running water to avoid heating which may alter surface structure of the specimens. This was followed by cleaning in alcohol to remove any adherent grease and stop corrosive action of water. Cleaned specimens were then dried and kept in a dessicator ready for use.

Excessive oxide layers on heat treated specimens were removed by immersion in dilute HCl followed by rinsing in water and alcohol in succession.

3.3 HEAT TREATMENT OF CORROSION SPECIMENS

All heat treated samples were solution treated at 900°c. Soaking time was 10 minutes for SCC test specimens and 30 minutes for general corrosion test pieces. The subsequent cooling to room temperature was achieved in a number of ways to obtain desired structures. Soaking time at various tempering temperature was 1 hr.

3.4.0 CORROSION AND STRESS CORROSION ENVIRONMENTS

The environments under study are cassava fluid, tomatoes and pepper juices. Fresh cassava tubers were procured, grated and the fluid manually squeezed out and stored at a temperature of 10°c. Fresh tomatoes and pepper fruits were ground and small quantity of distilled water added to obtain .the tomatoes and pepper juices respectively. Any juice not meant for immediate use was stored in the refrigerator at 10°c to prevent fermentation and decomposition of the extracted solutions. Solutions taken out of refrigerator for corrosion studies were allowed to reach room temperatures before use.

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

i.e. the samples were stable and firmly held on the stand.

3.5 EXPERIMENTAL METHODS

3.5.1 pH AND ELECTROCHEMICAL POTENTIAL MEASUREMENT

CRISON micropH 200 microcompressor controlled pH meter was used to monitor and measure the pH variation of the prepared corrosive solutions under investigation with time. The same equipment was also used to measure the electrochemical potential of various structure under study in the solutions with respect to Ag/Agcl reference system. The pH measurement gave the variation of hydrogen or hydroxide ion concentration of the solutions with time as a result of biological process of fermentation or decomposition occurring in the organic fluids. With the electrochemical potential measurement, it was possible to monitor and ascertain the tendency of various structures under study to corrode in the organic fluids.

3.5.2. STRESS CORROSION TESTS

In the stress corrosion tests, the tensile samples, after being subjected to simultaneous action of tensile stress (residual or applied) and corrosive action, and then suitable heat treatment where applicable, were stressed to fracture on a tensiometer. The percentage elongation to fracture (% Ef),

percenta reduction in area (% R.A.) and fracture time were deduced and recorded.

3.5.2.1 DETERMINATION OF EXTRANEOUS IONS EFFECT

This test was carried out to deliberately alter the polarisation of electrochemical corrosion reactions on carbon steel in the agro fluids, so as to enhance the chance of predicting the mechanism of crack propagation. Mercury and tin have different hydrogen overpotential values and are expected to have differing polarisation effect on hydrogen evolution reactions. Contamination of an electrolyte with Hg^{++} and Sn^{++} ions will therefore produce differing effects on crack propagation rate if the mechanism of cracking is hydrogen embrittlement, rather than anodic dissolution at the crack tip.

In this study, the agro-fluids were contaminated separately with prepared solutions of $HgCl_2$ and $SnCl_2$ which on ionisation would introduce Hg^{++} and Sn^{++} ions into the fluids. $SnCl_2$ solution was prepared by putting 10gm of $SnCl_2$ crystals in a 100ml standard flask and adding distilled water up to the mark to produce a concentration of 10% by weight. 7.5% by weight concentration of $HgCl_2$ solution was prepared in a similar manner. Contamination of the fluids under study were made by adding 10% by volume of prepared $SnCl_2$ or

$Hgcl_2$ solution into separate flask containing the fluids. Samples to be tested were divided into three sets, a set was exposed to fluid with no extraneous ion contamination, another to fluid contaminated with $Hgcl_2$ (Hg^{++}) and the remaining set with fluid contaminated with $Sncl_2$ (Sn^{++}).

EXTRANEOUS IONS EFFECT ON AS RECEIVED SAMPLES

The As Received samples are hot rolled steels with little or no internal stresses that can facilitate initiation and propagation of stress corrosion cracks. SCC evaluation of these samples was done by passing tensile specimen of the steel through rubber tubings containing the prepared solutions. The set up (Figure 14) was fixed into the tensometer while a tensile load of 7KN was applied.

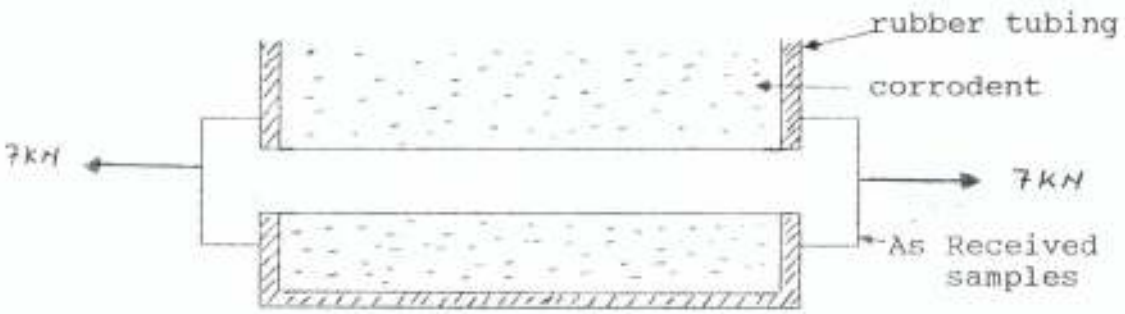


Figure 14: Schematic view of section through SCC test set up for As Received samples.

EXTRANEOUS ION EFFECT ON QUENCH HARDENED STEEL

Samples to be tested were water quenched from austenitised temperature of 900°c to lock up internal stresses that will be responsible for initiation and propagation of stress corrosion cracks in the matrix. The quenched samples were suspended firmly in the prepared solutions, withdrawn at various time interval and tested for tensile properties. Prior to the tensile test, withdrawn samples were tempered at 650°C for one hour to relieve the internal stresses.

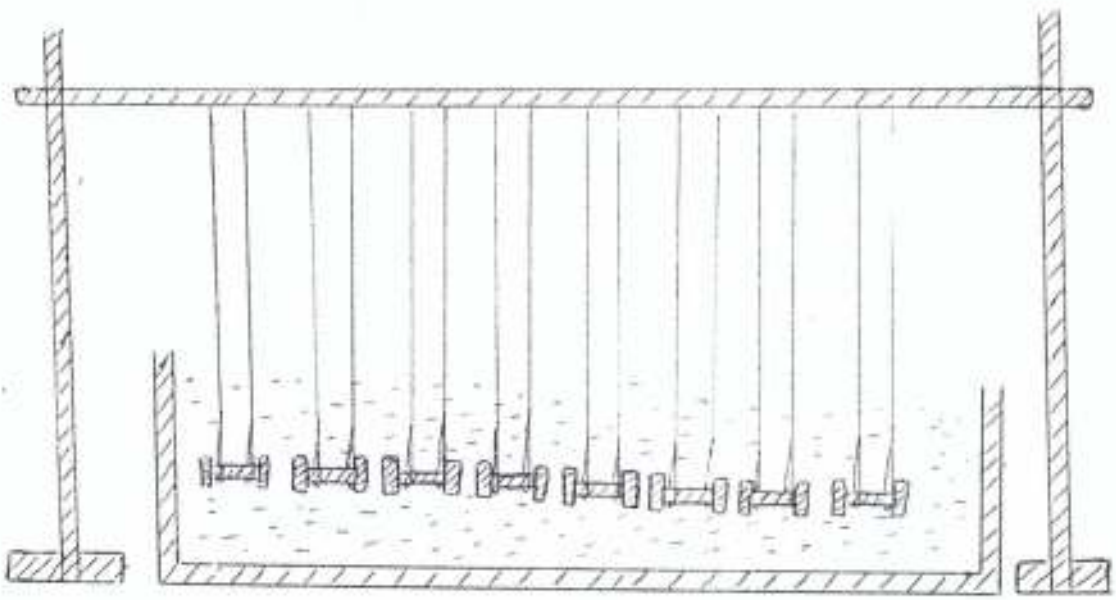


Figure 15 Schematic view of section through the SCC test set up of Quenched sample

3.5.2.2 TEST TO DETERMINE THE EFFECT OF CATHODIC AND ANODIC POLARISATION

CATHODIC POLARIZATION

The negative terminal of a rectifier was connected to oil quenched tensile specimens while positive terminal was connected to chromium plated steel rod (counter electrode). The two electrode were immersed into fresh agro fluids and d.c. voltage values of 5v, 10v, 15v, 20 and 25v were applied. In this set up (Figure 16) the steel sample acted as the cathode and is expected to be protected from electrochemical corrosion as a result of continous supply of electron to it. The counter electrode would act as the anode and corrode preferentially to the carbon steel sample. Exposure time was 30 minutes. The quench hardening imparted the internal stresses required for stress corrosion crack initiation and propagation of the test piece in the fluids. At the expiration of the exposure test, the samples were tempered at 350°c for one hour to relieve the internal stresses before stressing them to failure.

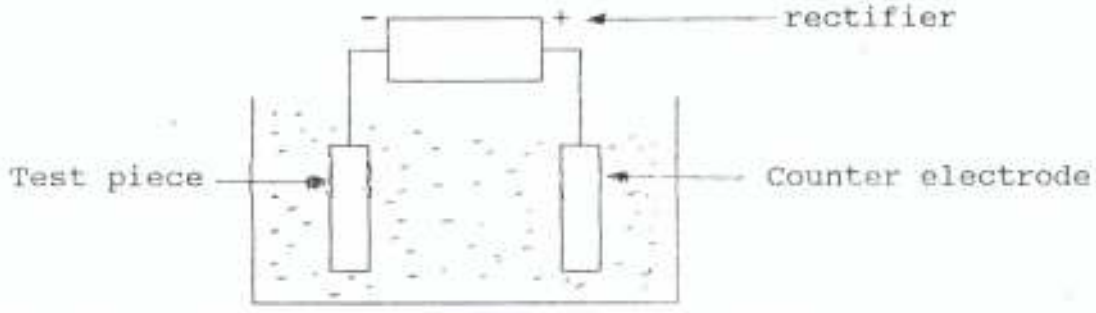


Figure 16: Set up for cathodic polarization

ANODIC POLARISATION

The procedure was the same as that of cathodic polarisation except that the test piece was made the anode in the circuit by connecting it to the positive terminal of the rectifier while the counter electrode was connected to the negative terminal.

3.5.3 TEST TO DERTERMINE WEIGHT LOSS

This test was performed to evaluate the variation of general corrosion rate of the steel with various parameters being investigated. Parameters studied included, heat treatment structure, extraneous ion addition, tempering temperature among others.

The mass and surface area of the test piece for this particular study were measured before suspension in various solution. The set up is as shown in Fig. 17

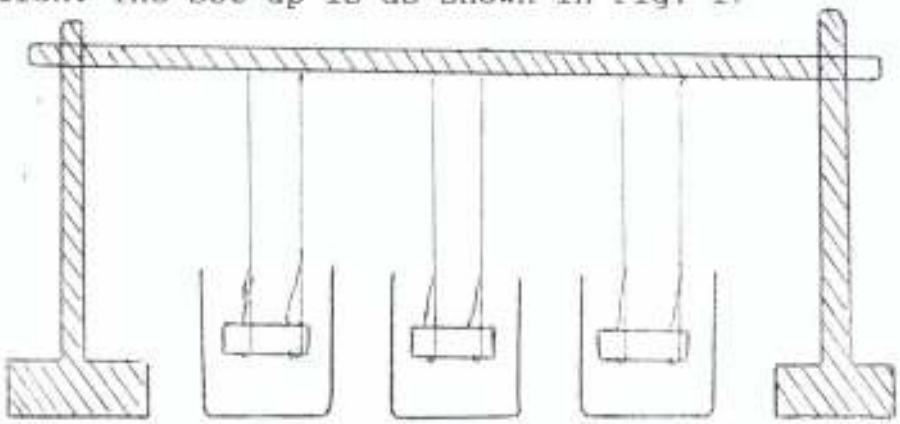


Fig. 17 Schematic view of the set up for weight loss

Immersed samples were withdrawn at various time interval, cleaned thoroughly with wire brush under running water to remove adherent corrosion products, rinsed in alcohol and dried under ceiling fan. Rinsing in alcohol was to hinder corrosive action of water used in cleaning and also facilitate the drying process. The samples were then weighed to determine the loss in weight as a result of corrosive action of the solutions. The corrosion was estimated in weight loss per unit surface area of the specimen.

CHAPTER FOUR

OBSERVATIONS, RESULTS AND DISCUSSIONS

4.1 OBSERVATIONS

Bubbles of gases were observed to evolve from the solution after about 4 - 6 hours exposure of carbon steel to cassava juice. The magnitude of gas evolved was observed to have a direct correlation with the corrosion rate of various steel samples in the juice. This implies that the principal cathodic reaction in corrosion of carbon steel samples in cassava fluid is hydrogen gas evolution.

The amount of gas observed coming out of tomato and pepper juices was very small. This may be attributed to the fact that hydrogen evolution may not be the principal cathodic reaction. In which case, cathodic reaction may be a combination of hydrogen evolution and oxygen reduction, with oxygen reduction being the principal cathodic reaction.

It was observed that the rate of corrosion attack on all immersed samples was decreasing with exposure time. The trend still remained, even on changing the corrosive medium after the 4th day of exposure. This implies that passivity rather than retarding effect of reaction products, was responsible for decreasing rate of corrosion attack with time.

4.2 RESULTS

4.2.1 PH AND ELECTROCHEMICAL POTENTIAL MEASUREMENT

Figures 18 , 19 and 20 show the pH variation of cassava fluid, tomato and pepper juices with time. Electrochemical potential variations of as received steel samples in these solutions and in solution contaminated with extraneous ions are shown graphically in figures 21, 22 and 23. Figure 24 illustrates the variation of electrochemical potential of various heat treated samples in cassava fluid. All electrochemical potentials were measured with respect to Ag/Agcl reference system.

4.2.2 WEIGHT LOSS TESTS

The effect of heat treatment on weight loss of immersed samples in the environment under study are presented in figures 25, 26 and 27. Results show that in all the three media, water quenched steel samples were the most susceptible to corrosion attack with oil quenched, air cooled, as received and annealed samples following in that order.

martensite was tempered in the temperature range of up to 300°C, corrosion rate decreased with increasing tempering temperature to a minimum value al 300°C. Further increase in tempering temperature beyond 300°c led to an increase in rate of attack. Increasing tempering temperature beyond 600°c led to decrease in rate of attack as tempering temperature was increased.

Figures 31, 32 and 33 give the graphical representation of the effect of extraneous ions of sn'' and Hg'' on corrosion rate of as received steel samples in the corrosive media under investigation.

4.2.3 STRESS CORROSION CRACKING TESTS

The effect of extraneous ion addition on SCC susceptibility of Quenched hardened steel samples in the corrosion media under study is presented in figures 34 - 39. In Cassava fluid, addition of Hg'' ions rendered the steel more susceptible while the presence of sn'' decreased the SCC susceptibility of the steel. Addition of each of Sn'' and Hg'' ions to tomato and pepper juices rendered the steel less susceptible to SCC in these juices.

The effect of extraneous ion addition on SCC susceptibility of As Received samples in cassava fluid is shown in figures 40 and 41. Addition of both Hg'' and Sn'' ions to cassava fluid rendered the As Received samples exposed to this fluid less

susceptible to SCC.

The effect of Cathodic polarisation on SCC of quench hardened steels in three media under study is presented if figures 42-47. Cathodic polarisation was found to reduced the rate of SCC of the steel in tomatoes and pepper juices while application of cathodic protection increased the rate if SCC attack in cassava fluid.

Figures 48 - 53 is a graphical representation of the influence of anodic polarisation on rate of SCC in the fluids under study. In cassava fluid and pepper juice, maximum susceptibility is obtained when the applied voltage is in the range 12 - 15v. Steel samples exposed to tomato juice and subjected to anodic polarisation showed steady increase in rate of cracking as applied voltage was increased.

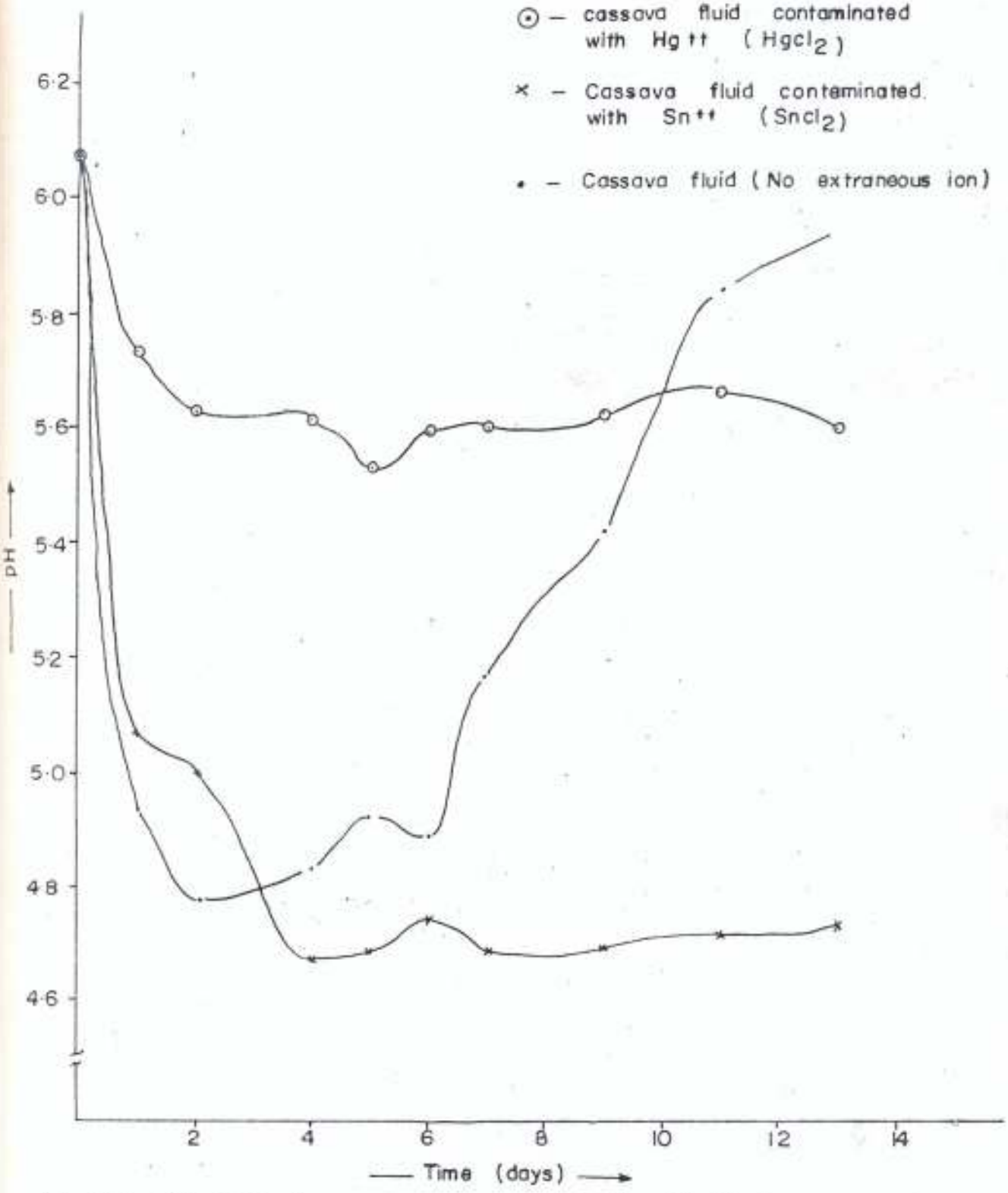


Fig: 18 pH Variation of cassava fluid with time.

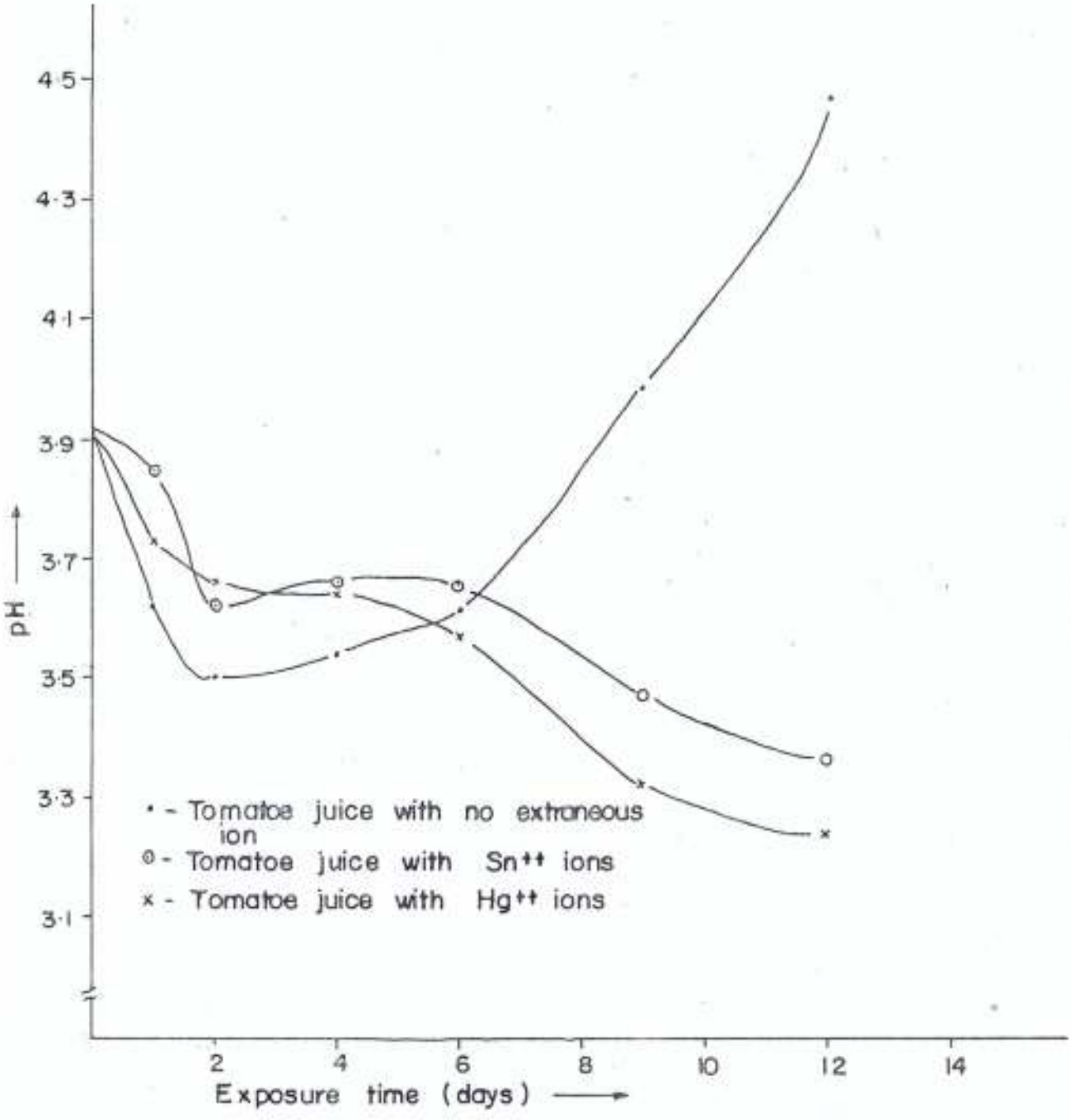


Fig. 19: pH variation of tomatoe juice with time.

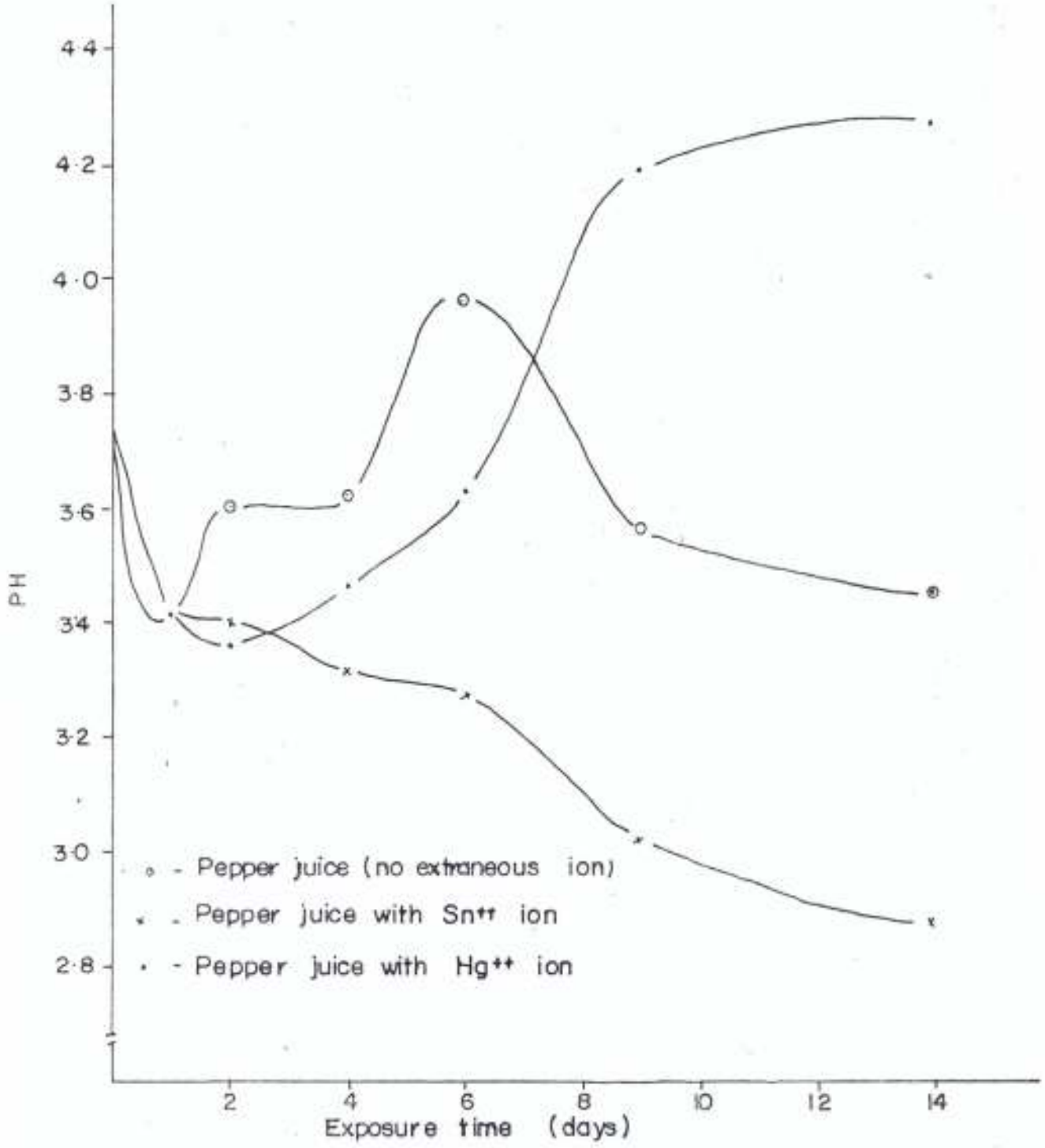


Fig. 20: pH variation of pepper juice with time.

4.3 DISCUSSIONS

4.3.1 pH AND ELECTROCHEMICAL POTENTIAL MEASREMENT

5.2.1 pH VARIATION WITH TIME

pH of cassava fluid, tomato and pepper juices decreased in in the first two days of exposure, after which it started to increase (Figs. 18, 19 and 20). The variation in pH of the juices with time is due to their decomposition owing to bacteria action. The variation observed in the graph for fluids contaminated with extraneous ion may be due to the catalytic (or otherwise) effect of these ions on decomposition reaction by bacteria.

POTENTIAL VARIATION WITH TIME IN CASSAVA FLUID

The electrode potential of the steel samples exposed to uncontaminated cassava fluid and the one contaminated with Sn^{++} ions shifted towards the passive region in the first 24 hrs of exposure (Fig 21). This indicates possible progressive formation of passive film on the metal surface on exposure to the solutions within this period of exposure. However, a downward shift in the direction of active region was observed after 24hrs of exposure signifying possible break up of the passive film. The upward and downward trend in the graph shows that the trend of corrosion attack was characterised by alternating formation and breakage of passive film on the metal surface.

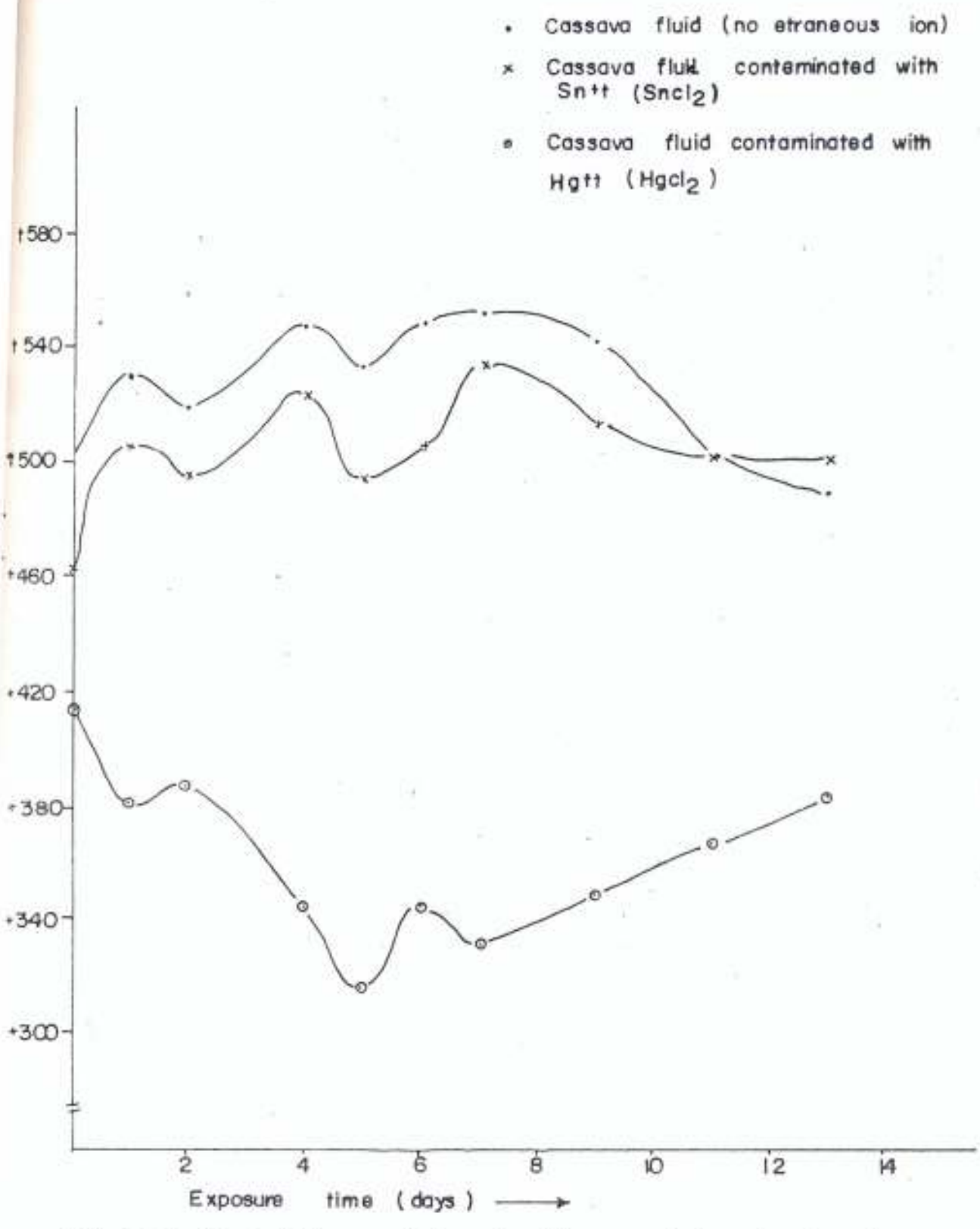


Fig. 21 : Potential variation (with respect to Ag/Agcl reference system) with time in cassava fluid.

Numerous cases are known where voluminous rust product have developed forces strong enough to cause breakage of passive film (Evans, 1981). This, coupled with the effect pH could have on the properties of the passive film may be responsible for alternating breakage and formation of passive layers. The general trend however shows that the electrode potential of the metal moved towards passive region as exposure time was increased.

The presence of Hg^{++} shifted the electrode potential of steel in the active direction. Passive film did not begin to form on the steel surface in those solutions until after 5 - 6 days of exposure. Presence of these ions therefore, in cassava juice will be expected to promote corrosion of steel.

5.2.3 POTENTIAL VARIATION WITH TIME IN TOMATOES JUICE

Addition of Sn^{++} ions to tomato juice shifted the electrode potential of immersed steel samples in the passive direction (Fig. 22) showing possible formation of certain complexes which may either promote passivity or polarise corrosion reaction in some other ways.

Addition of Hg^{++} ions to tomato juice, as in the case of cassava fluid, shifted potential in the active direction, an indication that the presence of these ions in tomato juice will increase its corrosion aggressiveness. The transpassivity observed in uncontaminated tomato juice can be attributed to

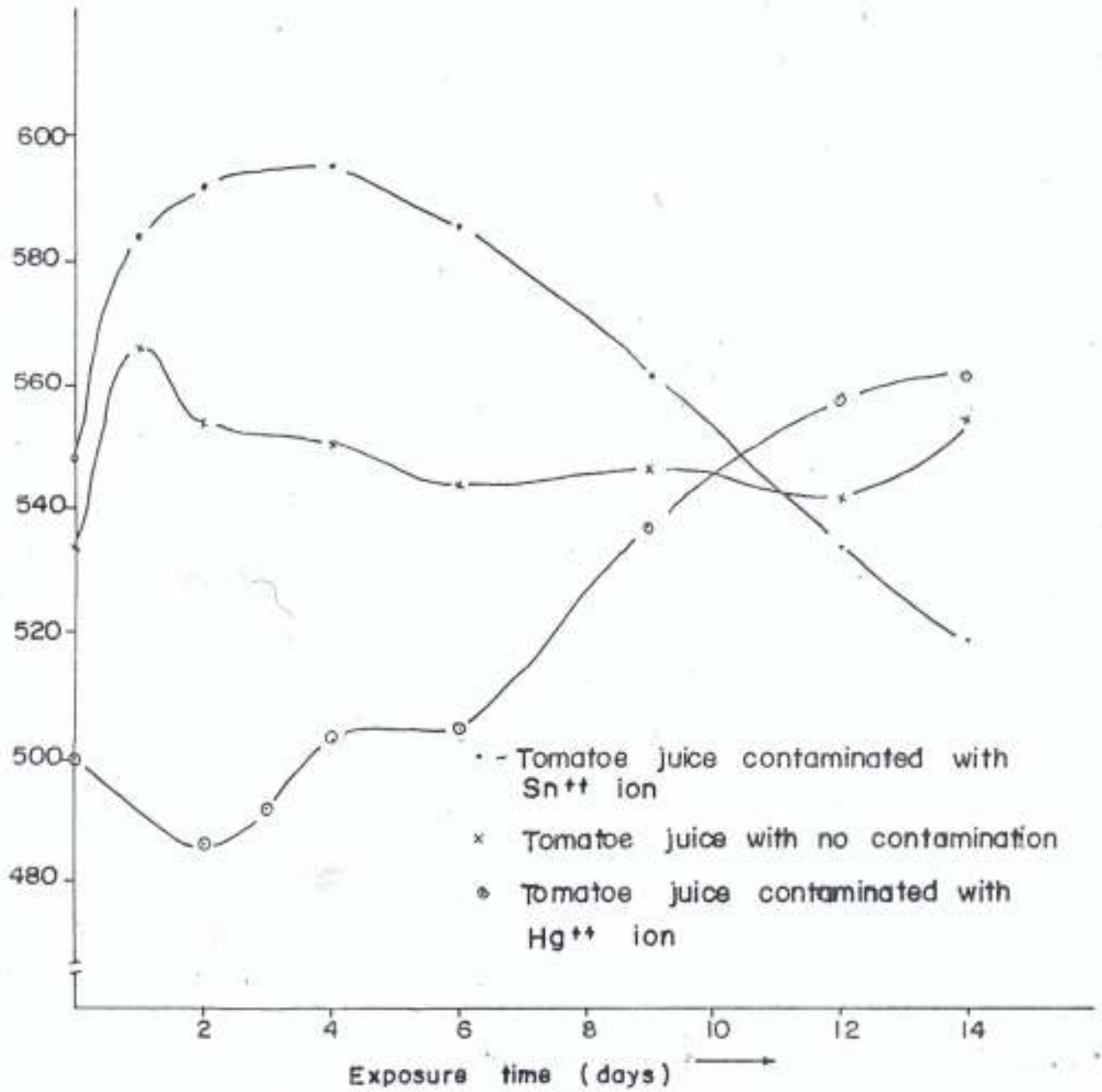


Fig. 22 : Potential variation (with respect to Ag/Agcl reference system) with time in tomatoe juice.

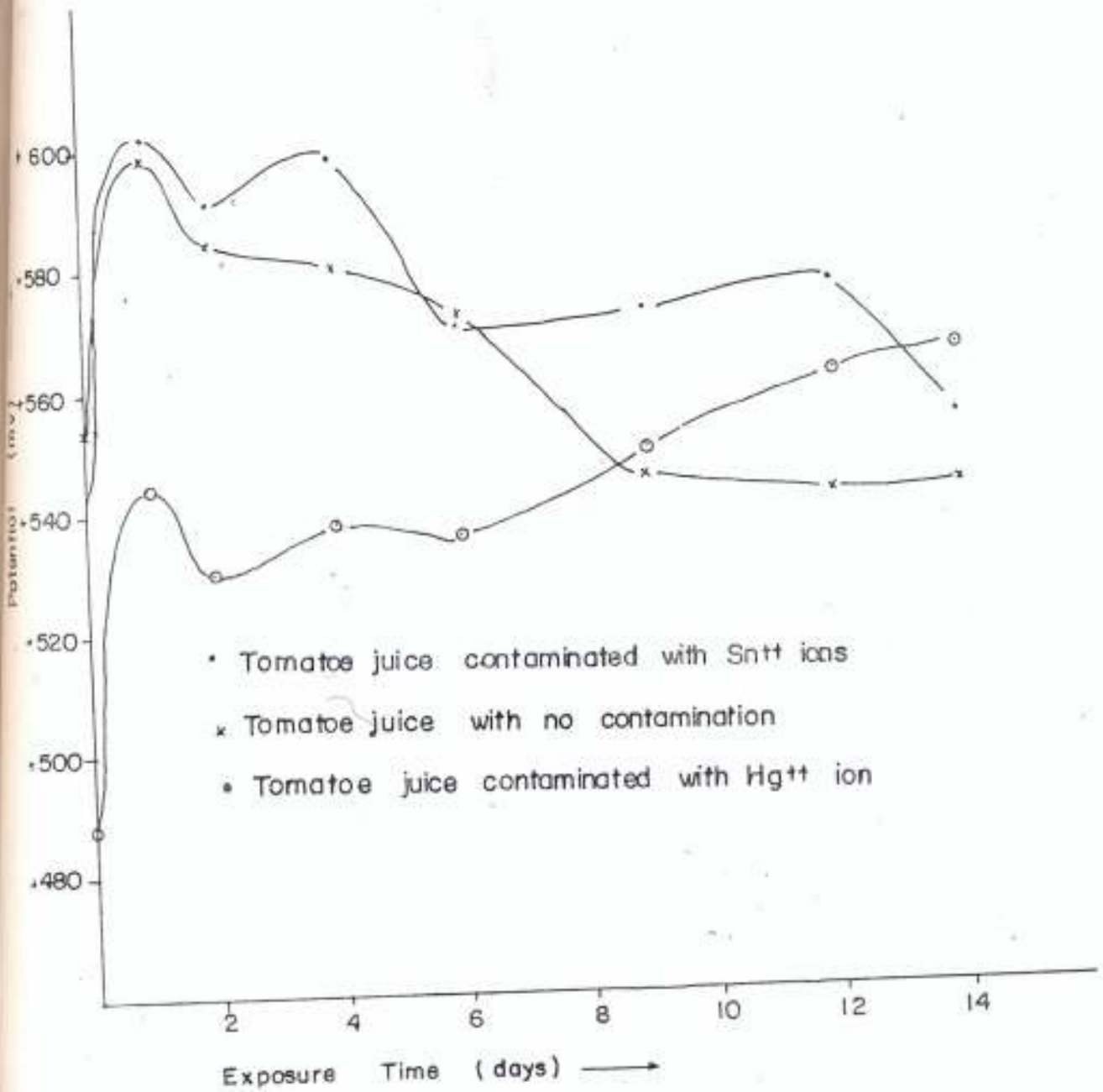


Fig. 23: Potential variation (with respect to Ag/Agcl reference system) with time in pepper juice.

breakdown of passive film.

POTENTIAL VARIATION WITH TIME IN PEPPER JUICE

The trend is similar to those found in tomatoes juice except that pepper juice contaminated with Hg^{++} ions showed formation of passive films within the first 24hrs exposure of steel samples (Fig. 23).

EFFECT OF HEAT TREATMENT ON ELECTRODE POTENTIAL

Electrode potential was found to increase in the passive direction as cooling rates of austenitised steel was decreased (Fig 24). The high activity of Quench hardened steel is attributed to presence of high dislocation density as a result of the drastic quenching. Dislocations increase the number of kink sites on the surface of metal and possibly increase the anodic exchange current density (Procter, 1974). As the cooling rate was reduced the number of kink sites was reduced and consequently activity of the metal was reduced.

The continuous intersection of the curves for various heat treated samples suggests that corrosion of various samples is characterised by alternating formation and breakage of passive films on the surface of the metal.

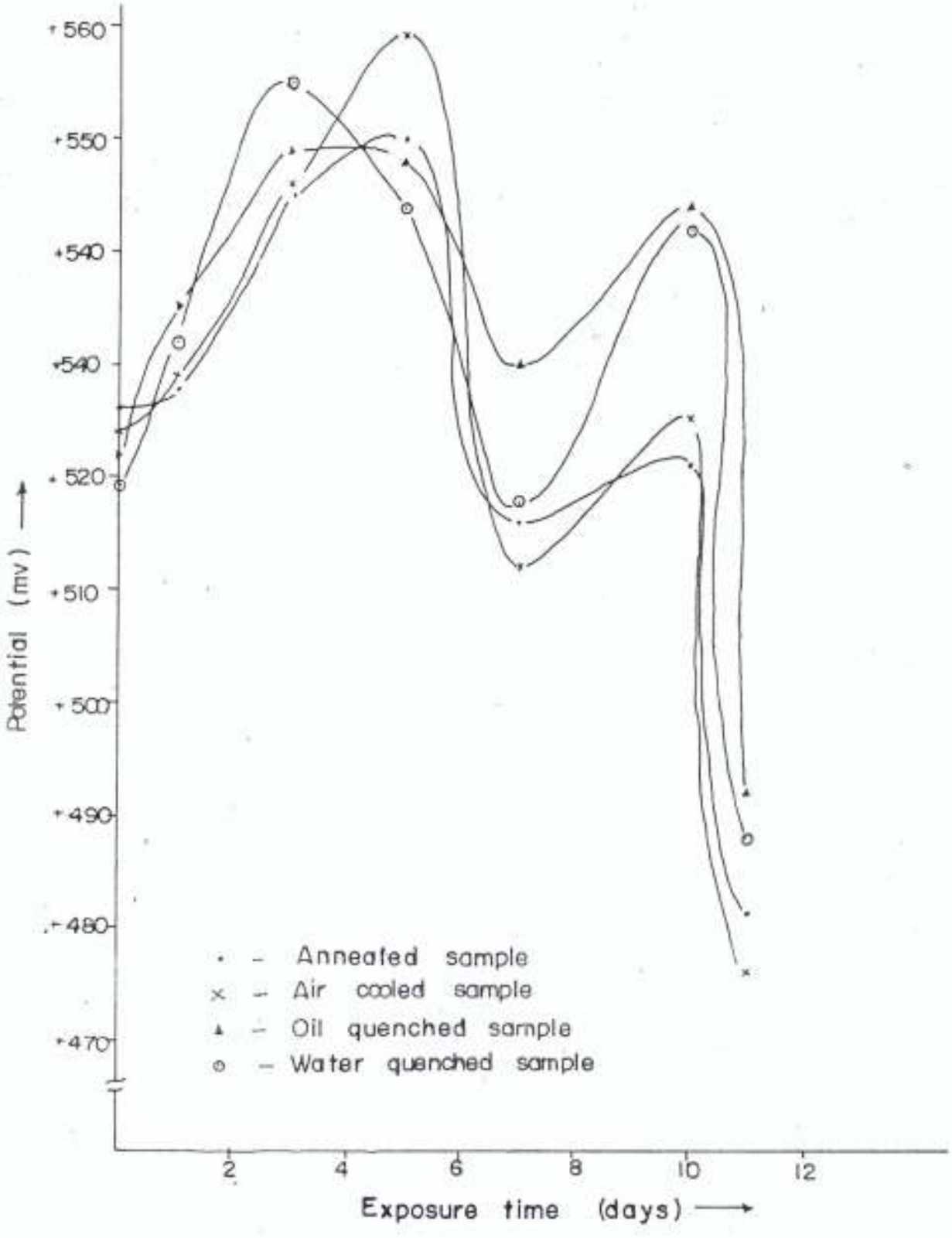


Fig.24: Effect of heat treatment on electrochemical potential of carbon steel in cassava juice.

4.3.2 WEIGHT LOSS

EFFECT OF HEAT TREATMENT

Martensitic formation resulting from rapid quenching of austenite is usually accompanied by an increase in volume which produce residual stresses in the structure of the martensite. This transformation stresses, together with thermal stresses arising from different cooling rates of the surface and interior of steel, will introduce high dislocation density in the martensite plate or lath. These dislocation sites provided sites for preferential attack, and consequently, corrosion rate of as quenched samples were greater than those of other samples (Fig. 25, 26 and 27).

When compared to water quenched samples; residual stresses of oil quenched samples are much less. This explains the lower corrosion rates of oil quenched steel relative to those of water quenched.

The very low rate of attack found in annealed samples is attributed to two reasons. Firstly, the very slow cooling of annealed samples facilitated recovery of virtually all dislocations in the annealed structure and elimination of chemical segregation. Secondly, the rather coarse structure comprising of pro-eutectoid ferrite and pearlite produced by annealing process reduce the very active grain boundary area, thereby lowering rate of attack.

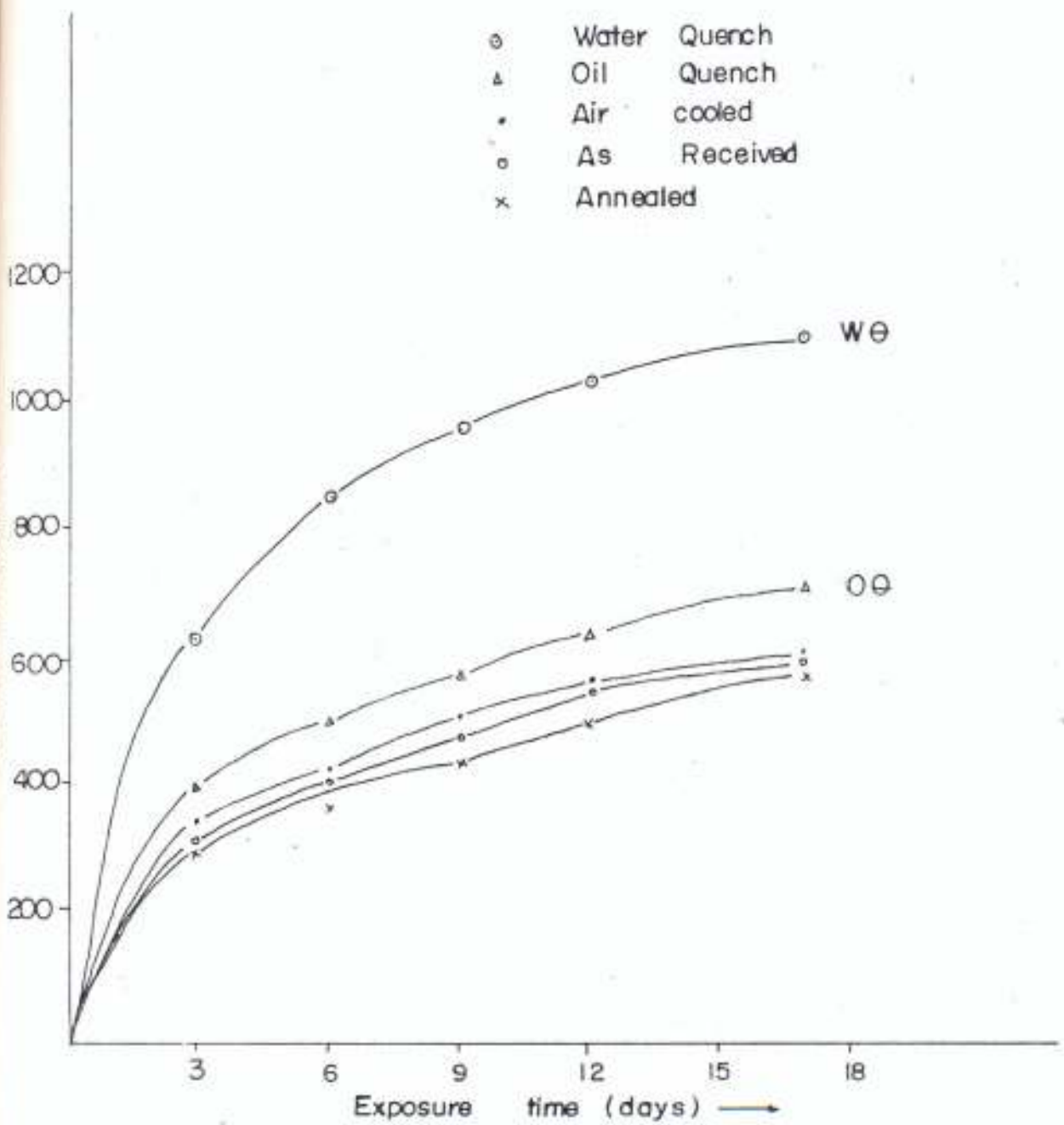


Fig. 25 : Effect of heat treatment on corrosion of carbon steel in cassava fluid.

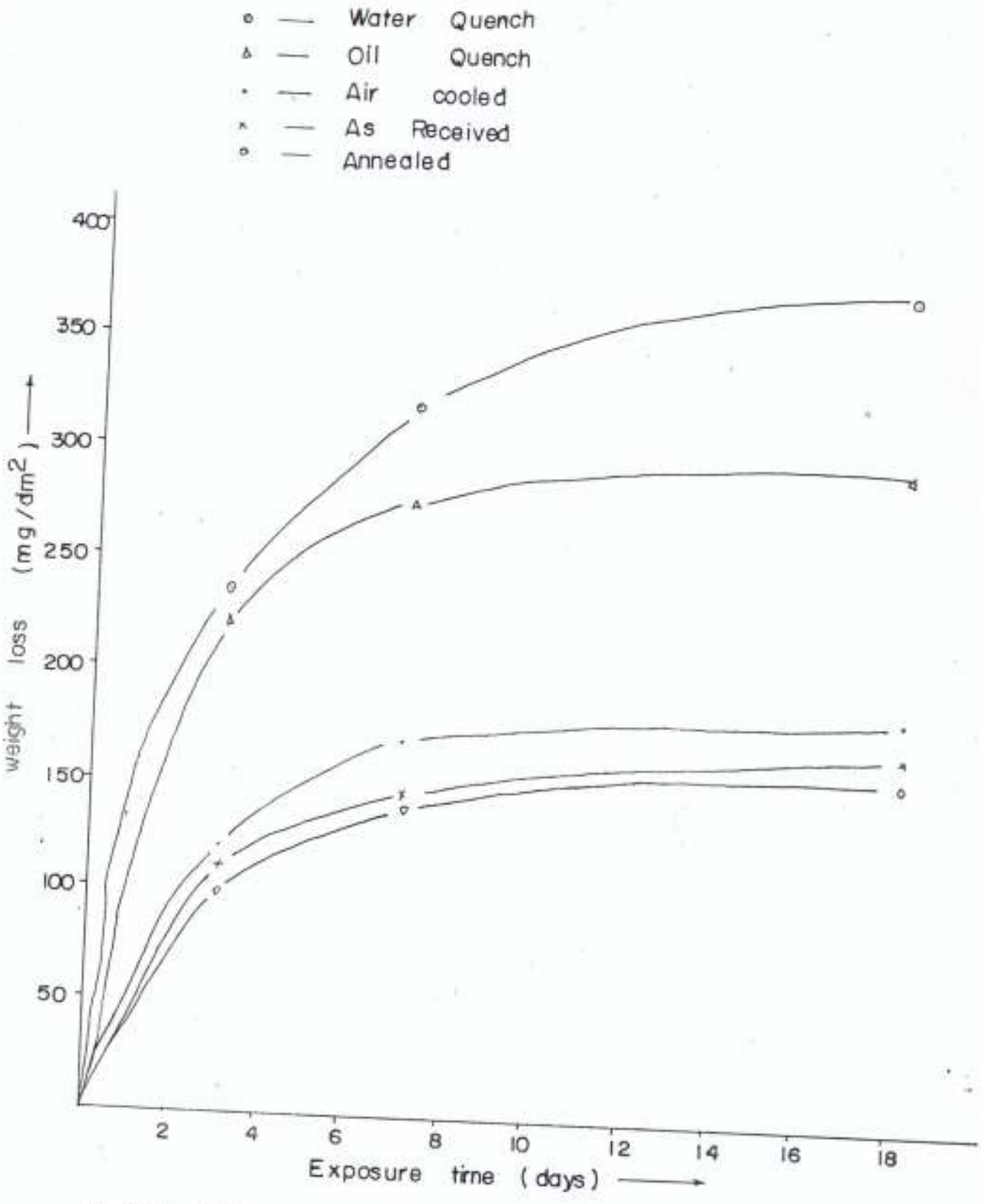


Fig. 26: Effect of heat treatment on corrosion of carbon steel in tomatoe juice.

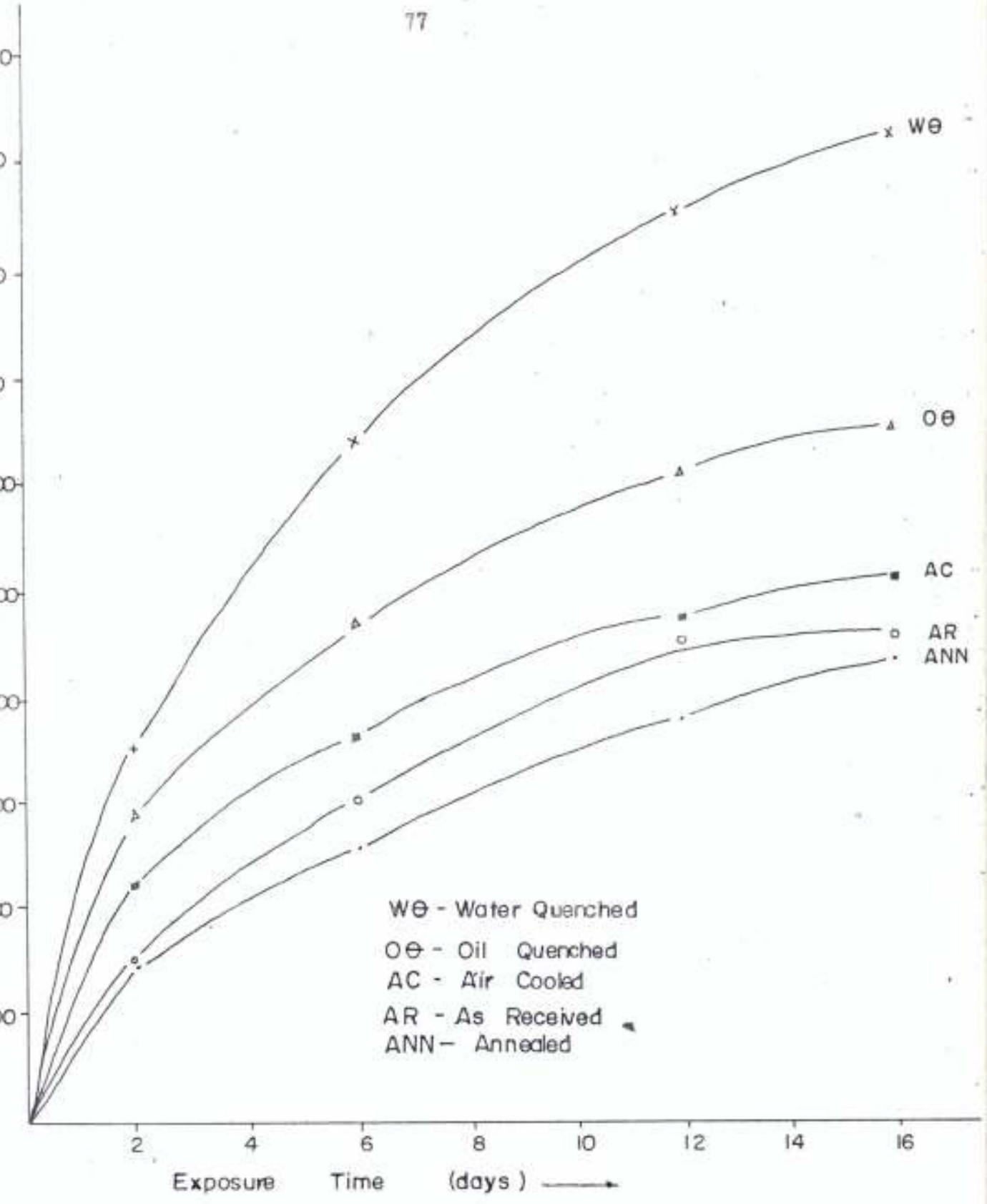


Fig. 27 : Effect of heat treatment on corrosion of steel in pepper.

Normalised steels produced from air cooling of austenite have much lower dislocation density than quenched steels and fine grain structure than annealed steel. Hence the intermediate rate of corrosion attack of normalized steels as shown in Fig. 25, 26 and 27.

EFFECT OF TEMPERING TEMPERATURE

The effect of tempering temperature on corrosion attack of quench hardened steel samples is as presented in figures 28, 29 and 30.

Martensite is a Single - phase, super- saturated solid solution of carbon in interstitial position of a body centered tetragonal lattice of iron. Consequently its rate of corrosion attack is expected to be low. The presence of high dislocation density in as quenched steels explains the highest corrosion rate found in them as shown in the figures.

When the as - quenched martensite was tempered at low temperature range of up to 300°C, the internal stresses were reduced as a result of precipitation of Σ - iron carbide out of the martensite plate. The reduction of the internal stresses is responsible for the reduction in rate of corrosion attack as tempering temperature was increased up to 300°C.

X - ray measurements have shown that lattice coherency of Σ - iron carbide with martensite is likely at early stages of precipitation (Honeycombe, 1987). The coherency of Σ - iron

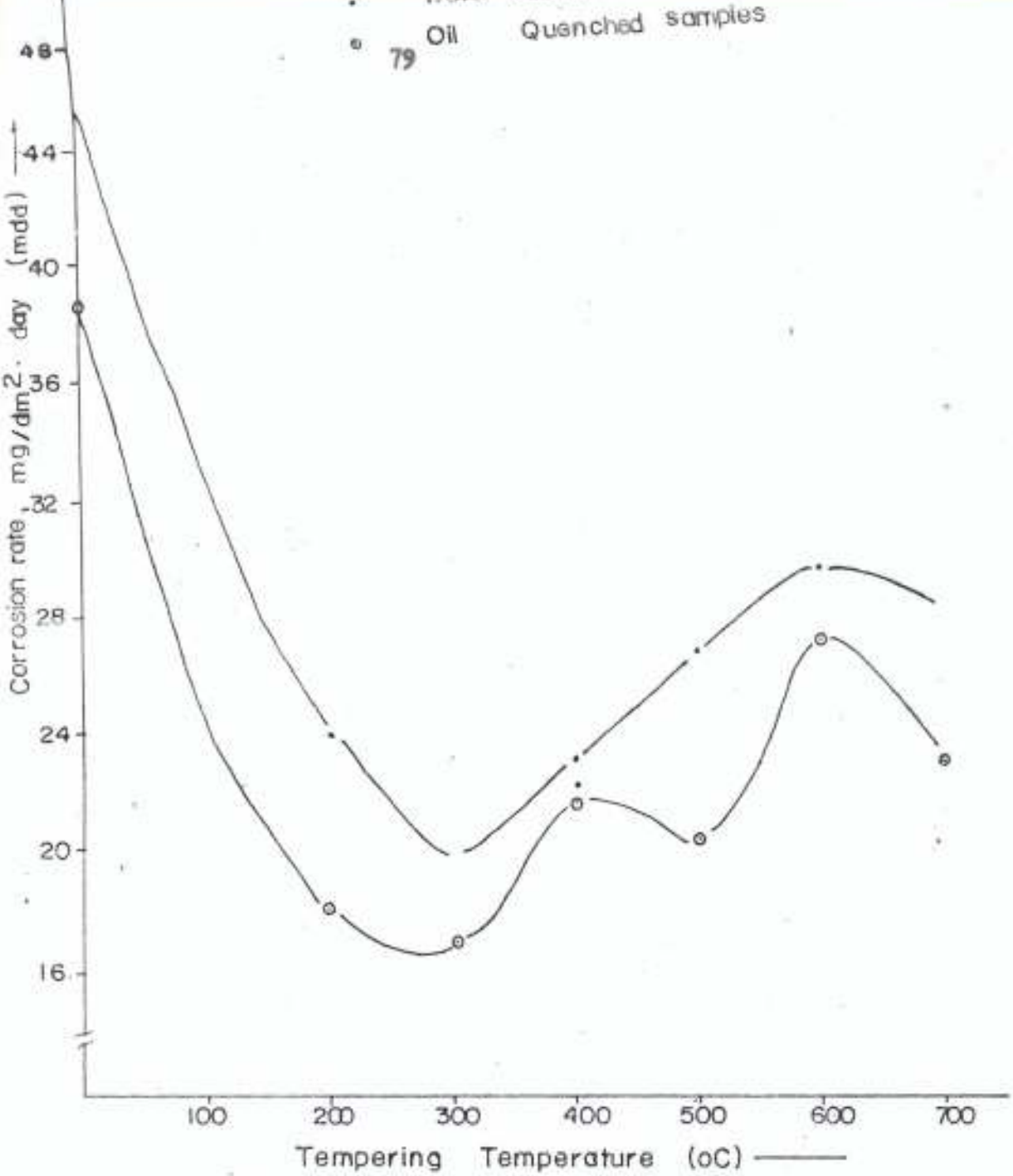


Fig. 28: Effect of Tempering Temperature on corrosion rate of steel in cassava fluid

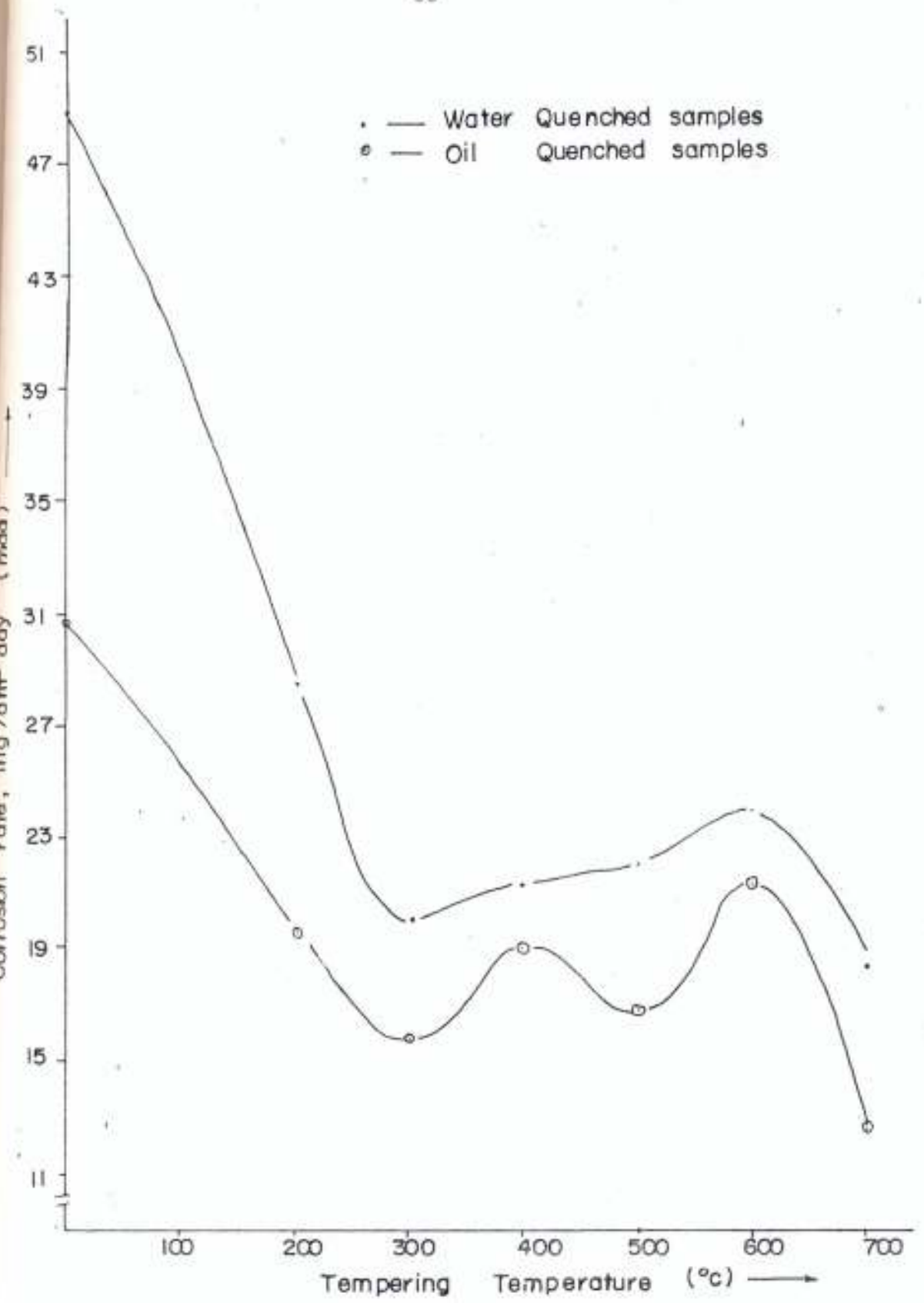


Fig. 29 : Effect of Tempering Temperature on corrosion rate of carbon steel in tomatoe juice.

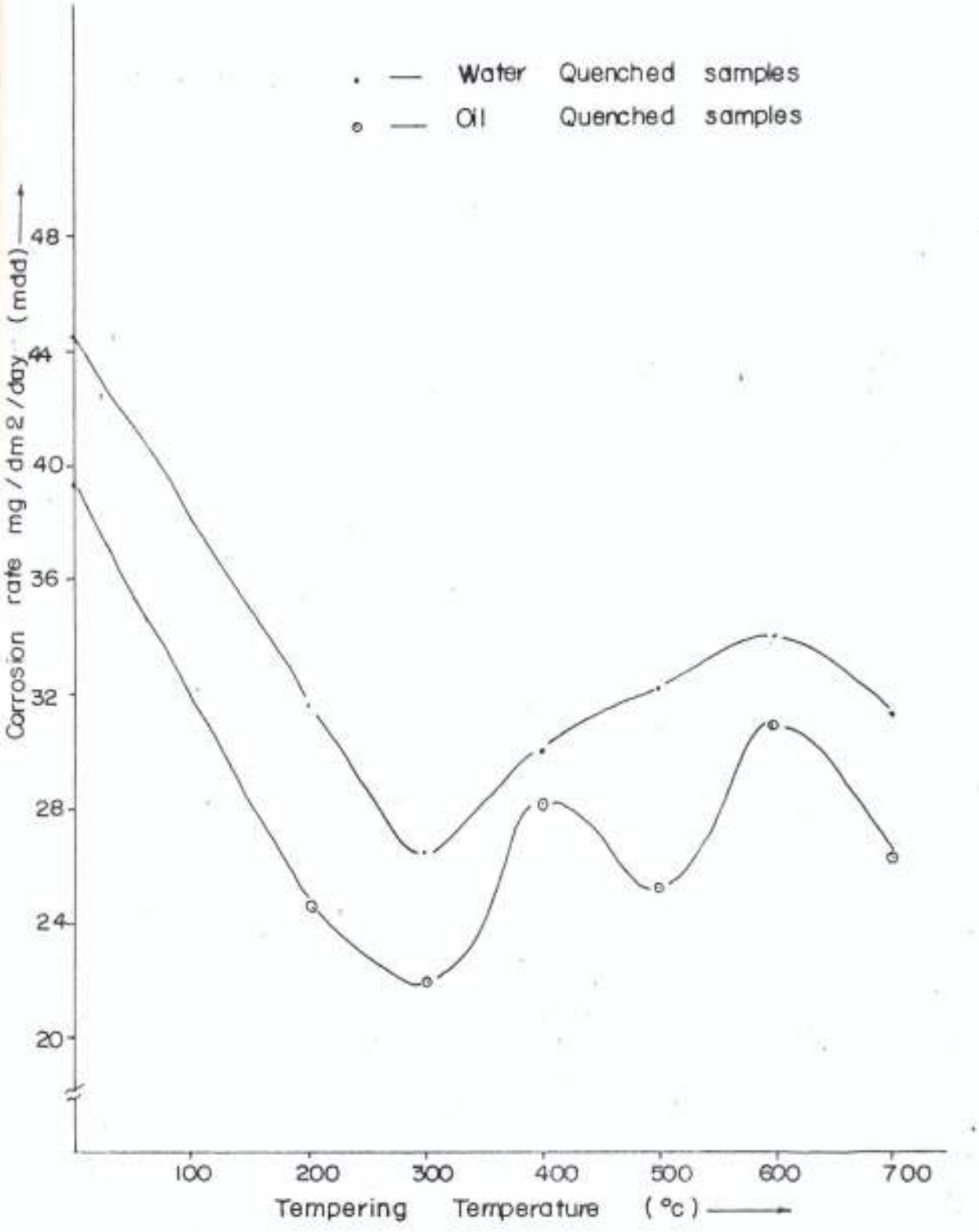


Fig. 30 : Effect of Tempering Temperature on corrosion rate of carbon steel in pepper juice.

carbide lath with the martensite might be responsible for non generation of electrochemical cell between the martensite plate and Σ - carbide lath.

When tempering temperature was increased beyond 300°C, the rather coherent Σ - iron carbide was replaced by cementite. The resulting two - phase structure encouraged setting up of galvanic cells between cementite and martensite. This led to enhanced corrosion attack as tempering temperature was increased beyond 300°C. This is in line with Ross's (1977) submission that since carbon or cementite grains act as efficient discharge points for hydrogen, their presence in the surface of metal encourages the corrosion of adjacent ferrite grains.

Above tempering temperature of 600°C, the cementite underwent a coarsening process and eventually lost their crystallographic morphology, becoming spheroidized. The final structure is an equi-axed array of ferrite grains with coarse spheroidized particles. The coarsening of cementite beyond tempering temperature of 600°C accounts for reduction in the rate of corrosion attack as tempering temperature was increased beyond 600°C.

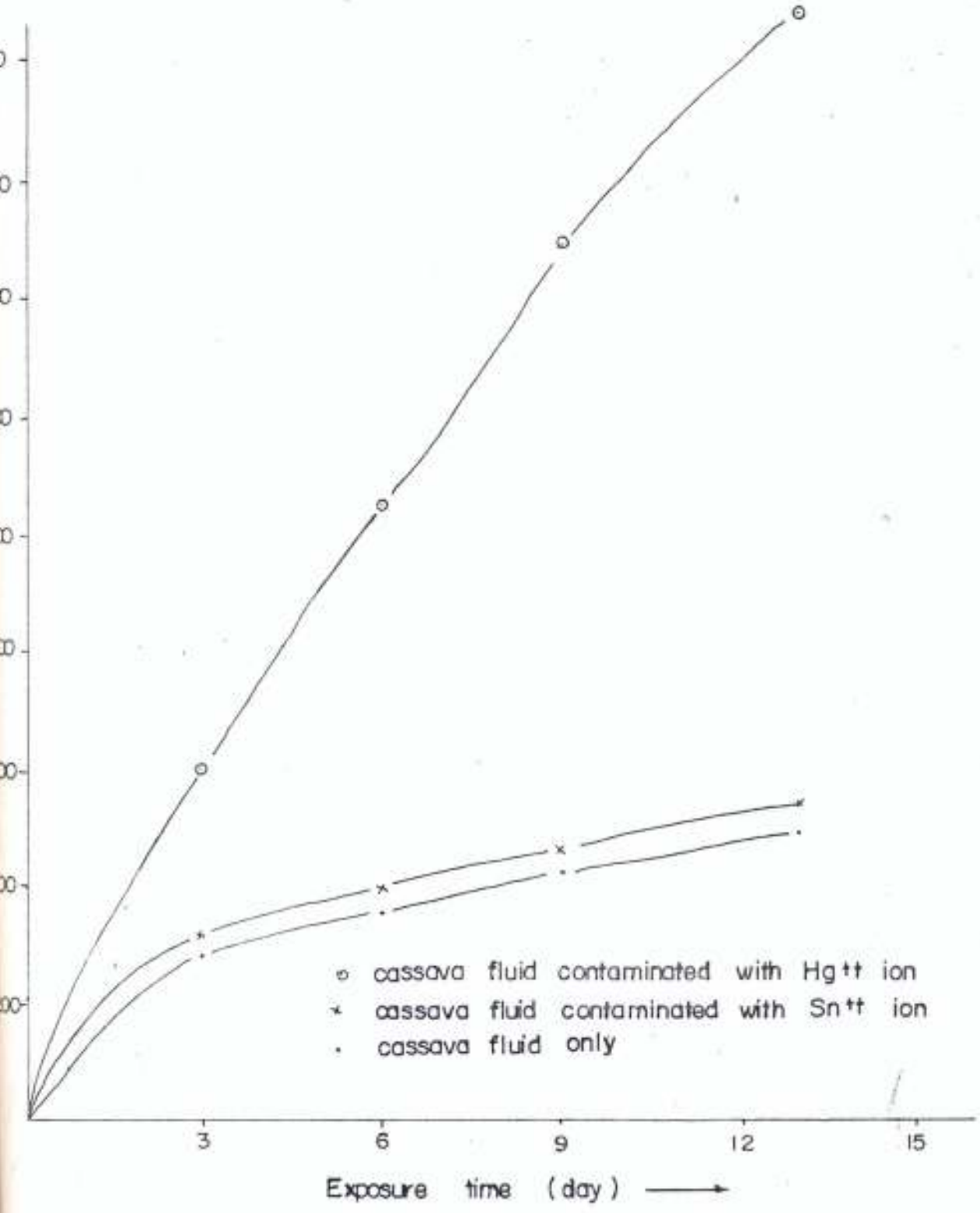
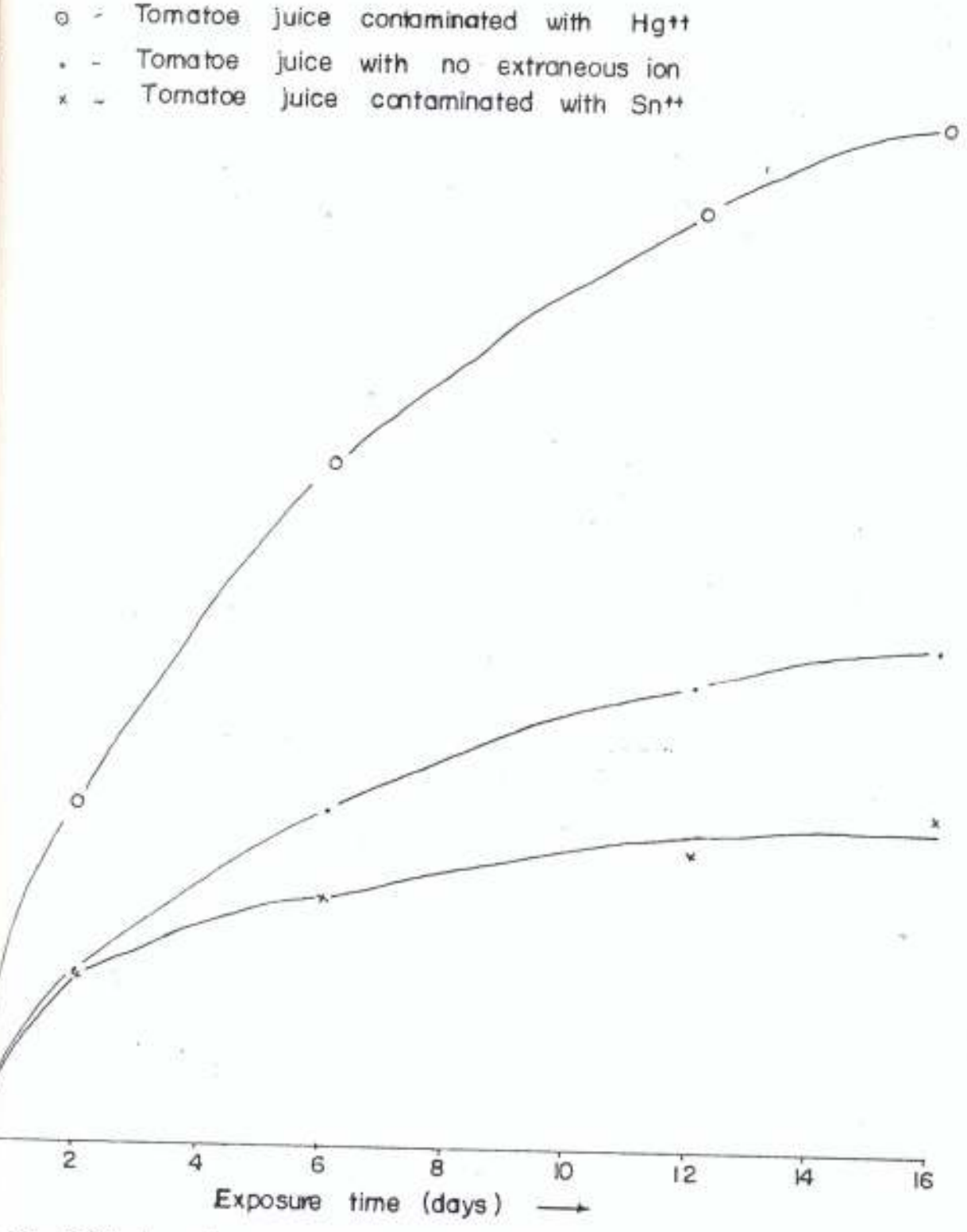


Fig. 31: Effect of extraneous ion addition on corrosion of carbon steel in cassava fluid.



32. Effect of extraneous ion addition on corrosion of carbon steel in Tomatoe juice.

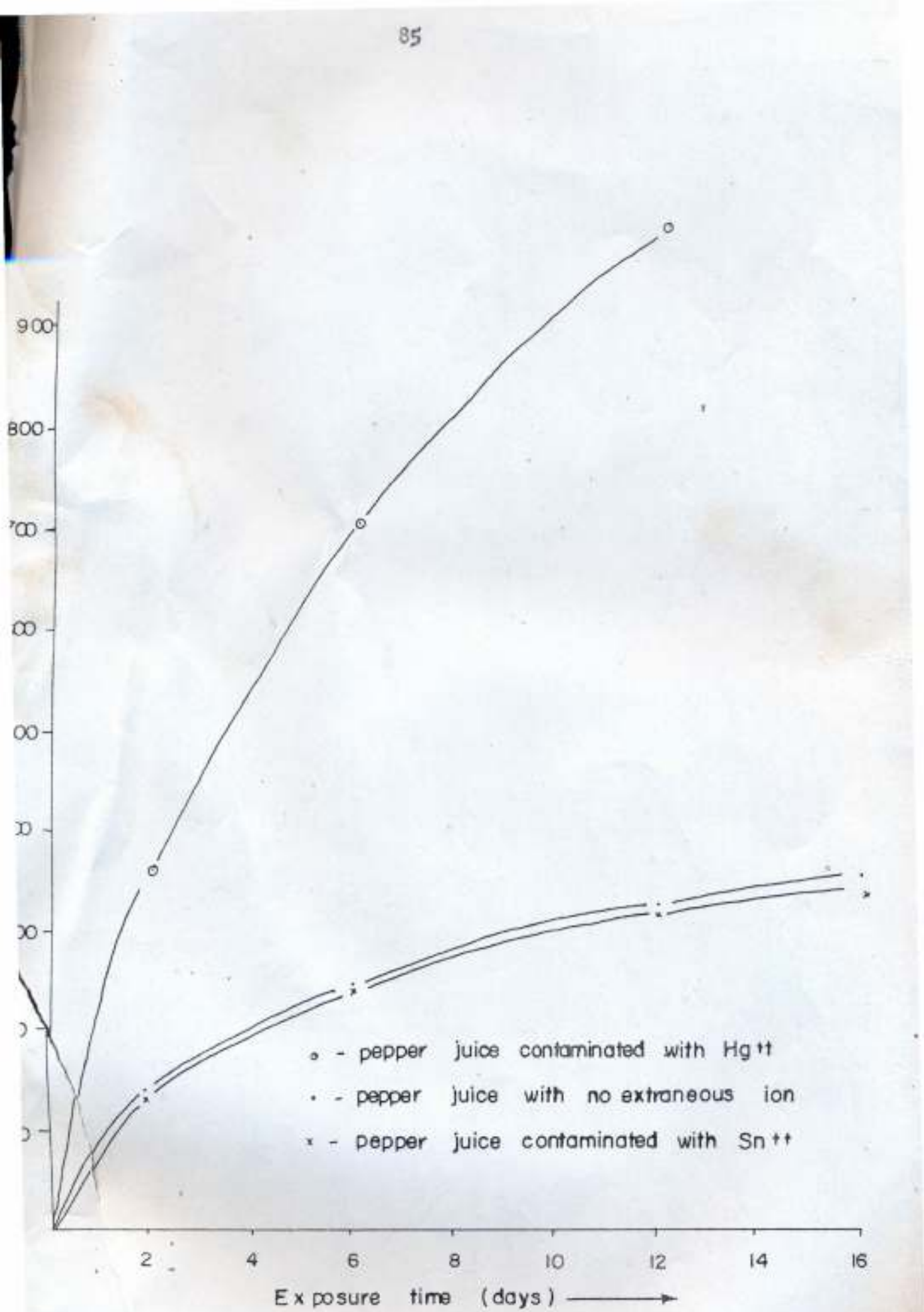


Fig.33. Effect of extraneous ion addition on corrosion of steel in pepper.

EFFECT OF EXTRANEOUS ION

Addition of Hg^{++} ions to the three media under study caused a significant increase in their corrosion aggressiveness to the carbon steel (Fig. 31, 32 and 33). Addition of Sn^{++} ions to cassava fluid also increased its corrosion aggressiveness. Presence of these ions possibly increased the oxidation potential of the respective solutions or hinders passive film formation. Result of electrochemical potential measurement showed that the presence of Hg^{++} ions in the agro- fluids under study increased the electrochemical potential in the active direction.

The presence of Sn^{++} ions in tomato and pepper juices probably enhanced the formation of certain complexes which may facilitate formation of passive layer on the surface of the metal. This result agrees with the one obtained in the electrochemical test in which presence of Sn^{++} ions in tomatoes and pepper juices shifted the electrode potential in the passive direction.

4.3.3 STRESS CORROSION CRACKING

EFFECT OF EXTRANEOUS ION

Where hydrogen evolution is the cathodic reaction in a corrosion process, combination of hydrogen atoms to form hydrogen molecules is the rate determining step. Hg^{++} and Sn^{++} ions are deliberately chosen as extraneous ion additions to the fluids

under study because of the difference in their catalytic activity on the rate of combination of hydrogen atoms.

Tin has a low value of hydrogen overpotential and hence acts as good catalyst to rate of combination of hydrogen atoms. The presence of Sn^{++} ions in a solution will therefore promote rapid formation of hydrogen molecules. In this respect, if hydrogen is the embrittling species, rate of cracking will be reduced since the amount of hydrogen atom available for diffusion into the metal structure is significantly reduced. Mercury on the other hand, has a high value of hydrogen overpotential and Hg^{++} ions are known to delay recombination of hydrogen atoms to form hydrogen molecule (Adepoju, 1977). This implies that more hydrogen is absorbed which can cause hydrogen embrittlement. Thus, if hydrogen is the embrittling specie rate of cracking will be intensified by the presence of Hg^{++} ions in a solution.

Figures 34 and 35 show that addition 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. This suggests that hydrogen is the embrittling specie in the SCC of quench hardened steel in cassava fluid.

Figures 36 - 39 indicate that addition of both Hg^{++} and Sn^{++} ions reduced the rate of cracking of quench hardened steel in tomato and pepper juices. Since the presence of Hg^{++} ions did not

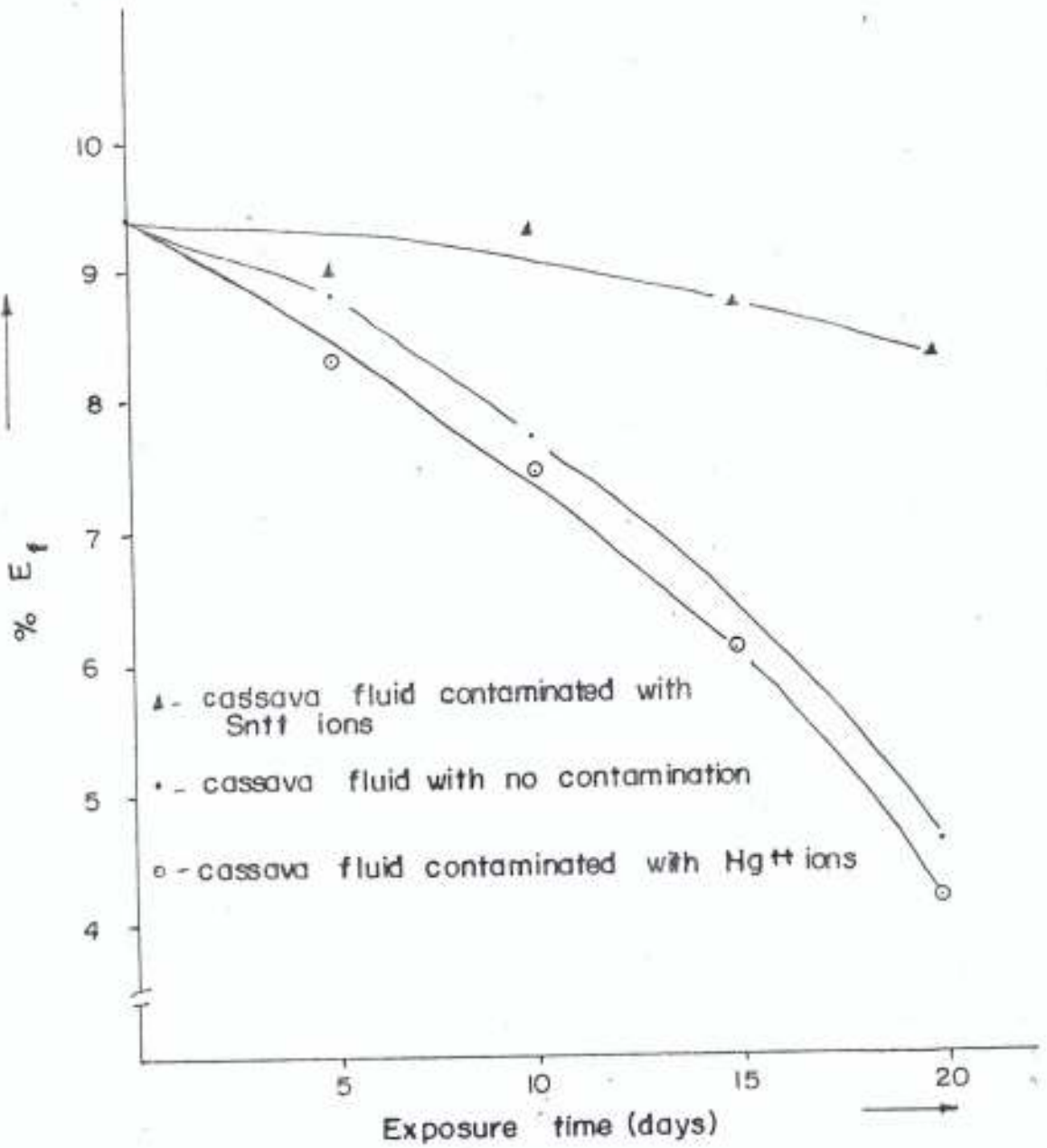


Fig. 34 : Effect of extraneous ion addition on SCC (% E_f) of Quench hardened steel in cassava fluid.

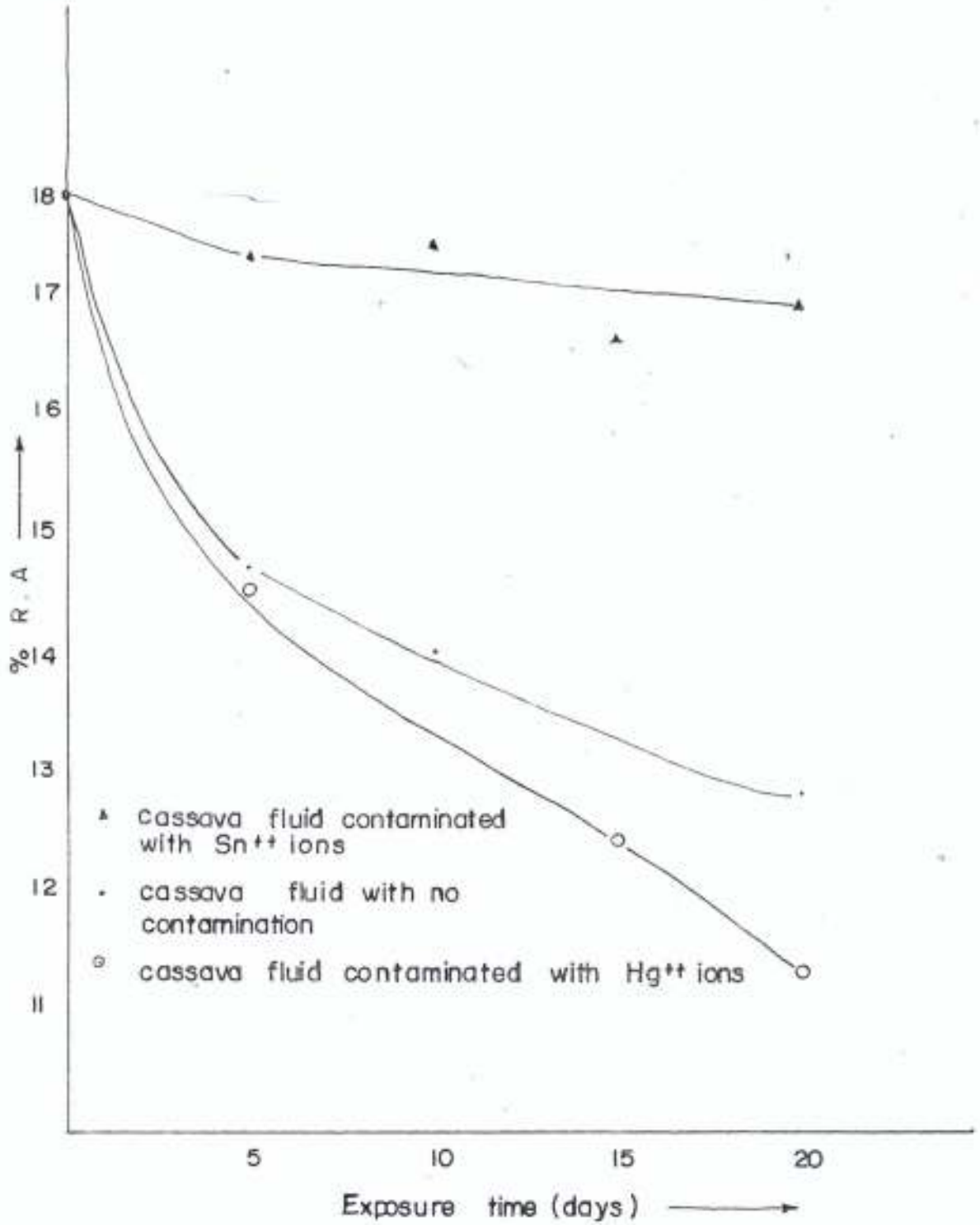


Fig 35 Effect of extraneous ions addition on SCC (% R.A) of Quench hardened steel in cassava fluid.

aggravate the rate of cracking of quench hardened steel in the juices, it is most unlikely that hydrogen is the embrittling specie. The most probable mechanism of cracking is anodic dissolution ahead of crack tip. The retarding effect of Hg'' and Sn'' ions on the rate of cracking of quench hardened steels is accounted for by potential - dependence of stress corrosion cracking. With the addition of Hg'' and Sn'' ions there is no critical balance between active and passive behaviours to enhance rapid propagation of cracks.

The effect of extraneous addition of Hg'' and Sn'' ions on rate of cracking of as received steel samples (Figures 40 and 41) indicates that hydrogen is not the embrittling specie in cracking of as received steel in cassava fluid. Anodic dissolution ahead the crack tip is suggested as the possible mechanism of SCC. Comparing this with the result obtained on cracking of quench hardened steel in cassava fluid, it is obvious that the mechanism of cracking of quenched hardened steel in cassava fluid was hydrogen embrittlement while the cracking mechanism for as received samples was anodic dissolution. This result agrees with the submission of Barnejee (1985) that carbon steels are especially susceptible to hydrogen cracking when heat treated to form martensite, but are less if structure is pearlitic. As received samples was essentially pearlitic while the quench hardened steel had martensitic structure.

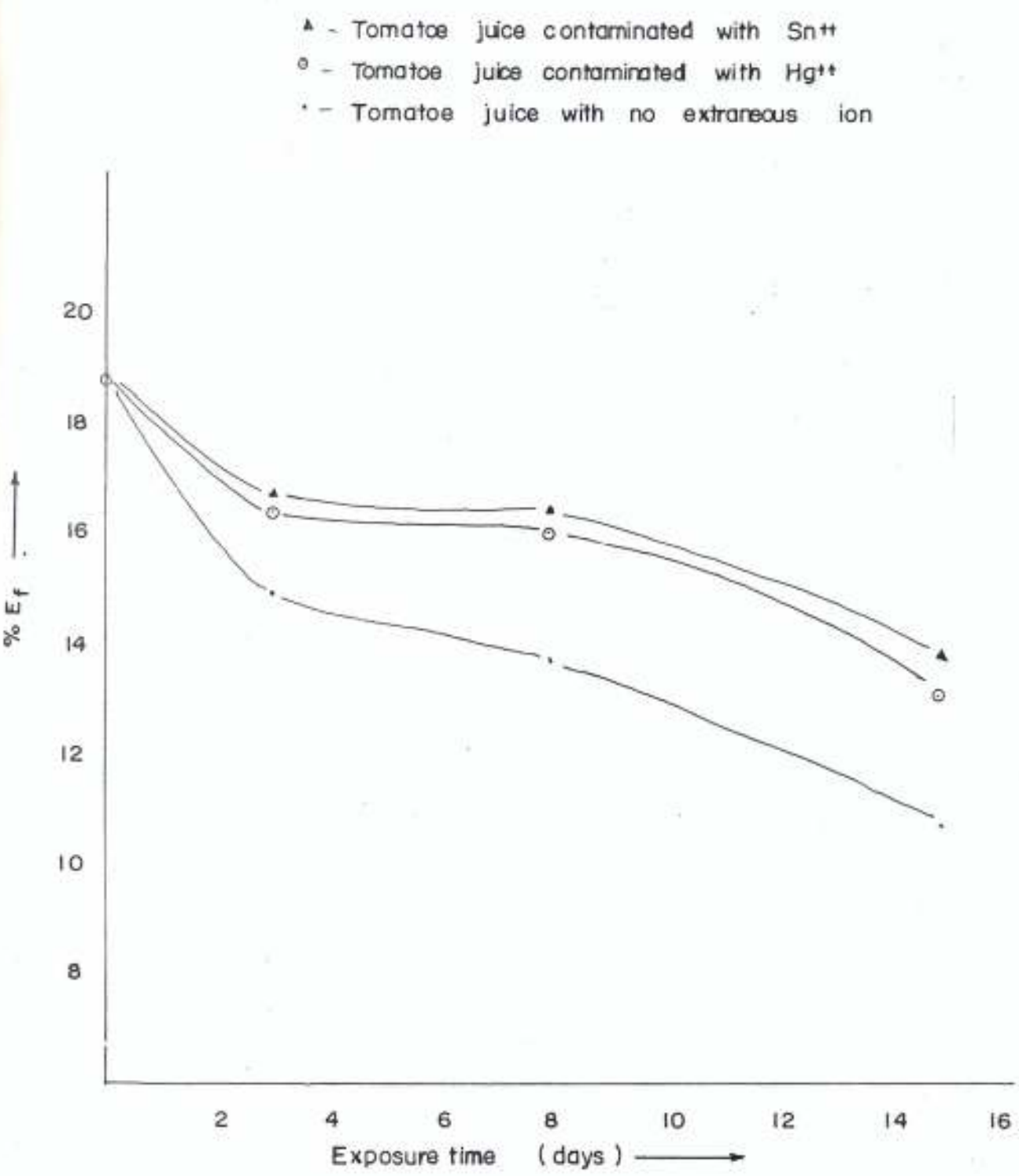


Fig 36: Effect of extraneous ions addition on SCC (% E_f) of Quench hardened steel in tomatoe juice

▲ - Tomatoe juice contaminated with Sn^{++}
⊙ - Tomatoe juice contaminated with Hg^{++}
• - Tomatoe juice with no extraneous ion

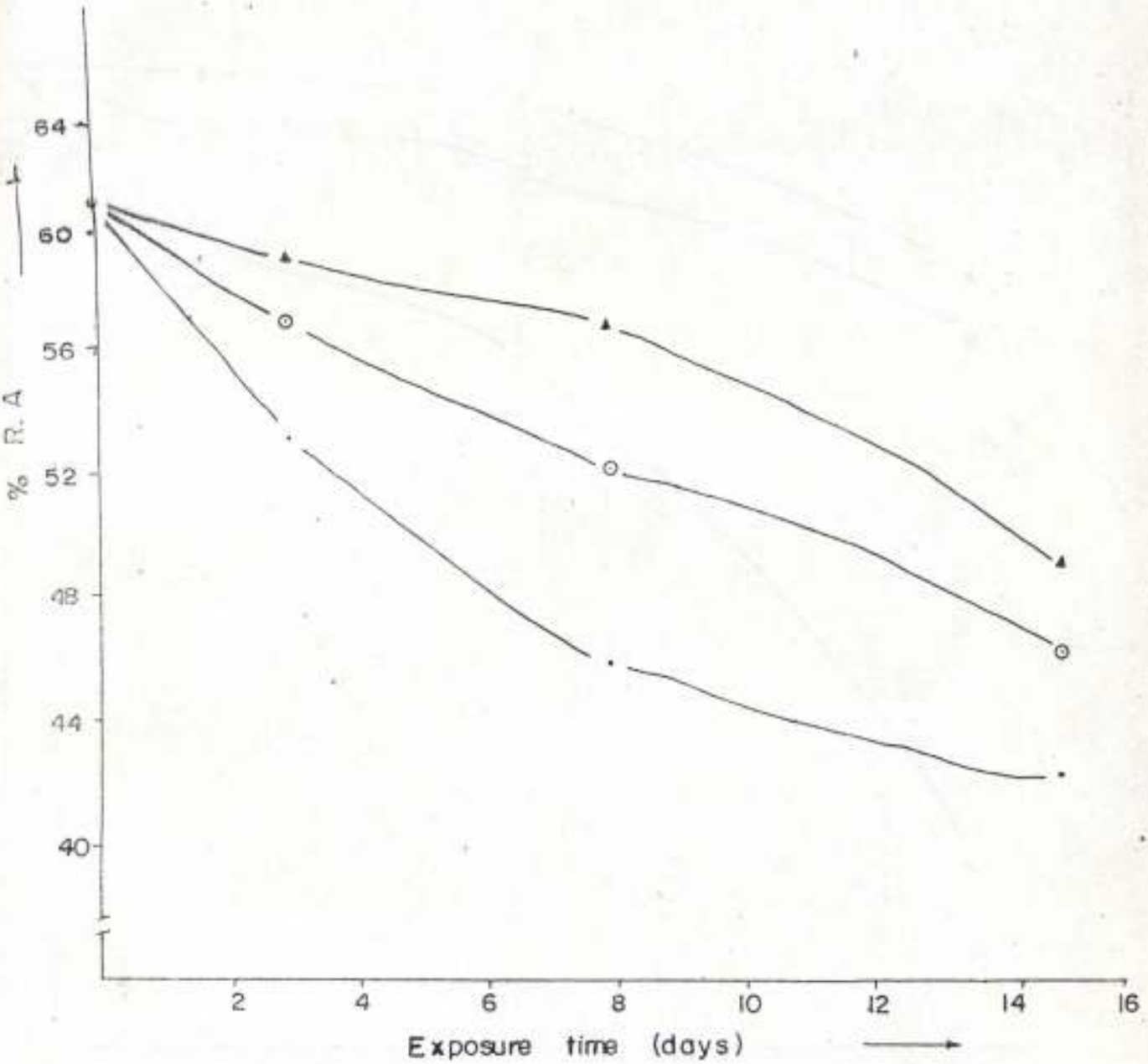


Fig. 37 : Effect of extraneous ions addition on SCC(% R.A) of Quench hardened steel in tomatoe juice

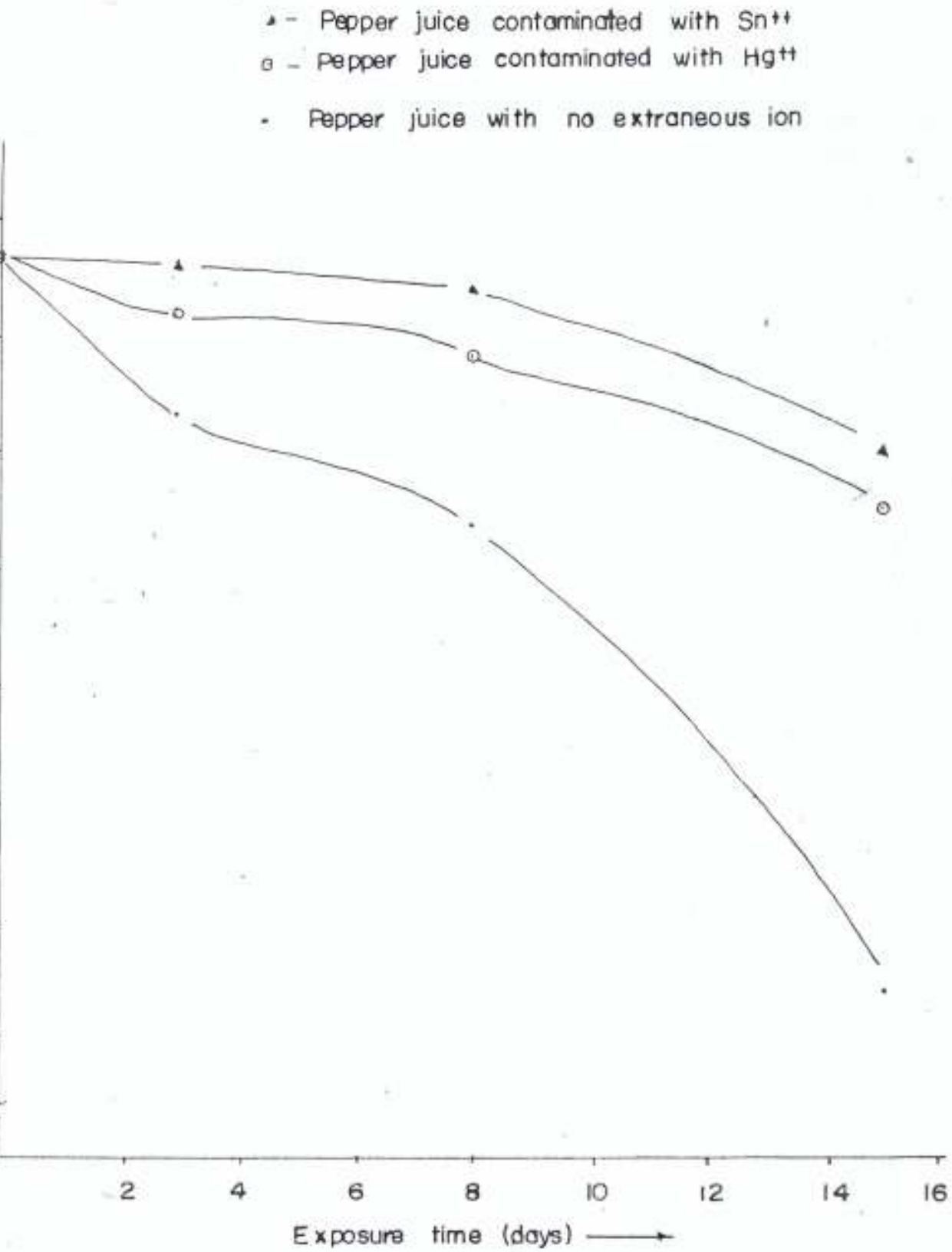


Fig. 38: Effect of extraneous ions addition on SCC (% E_f) of Quench hardened steel in pepper juice

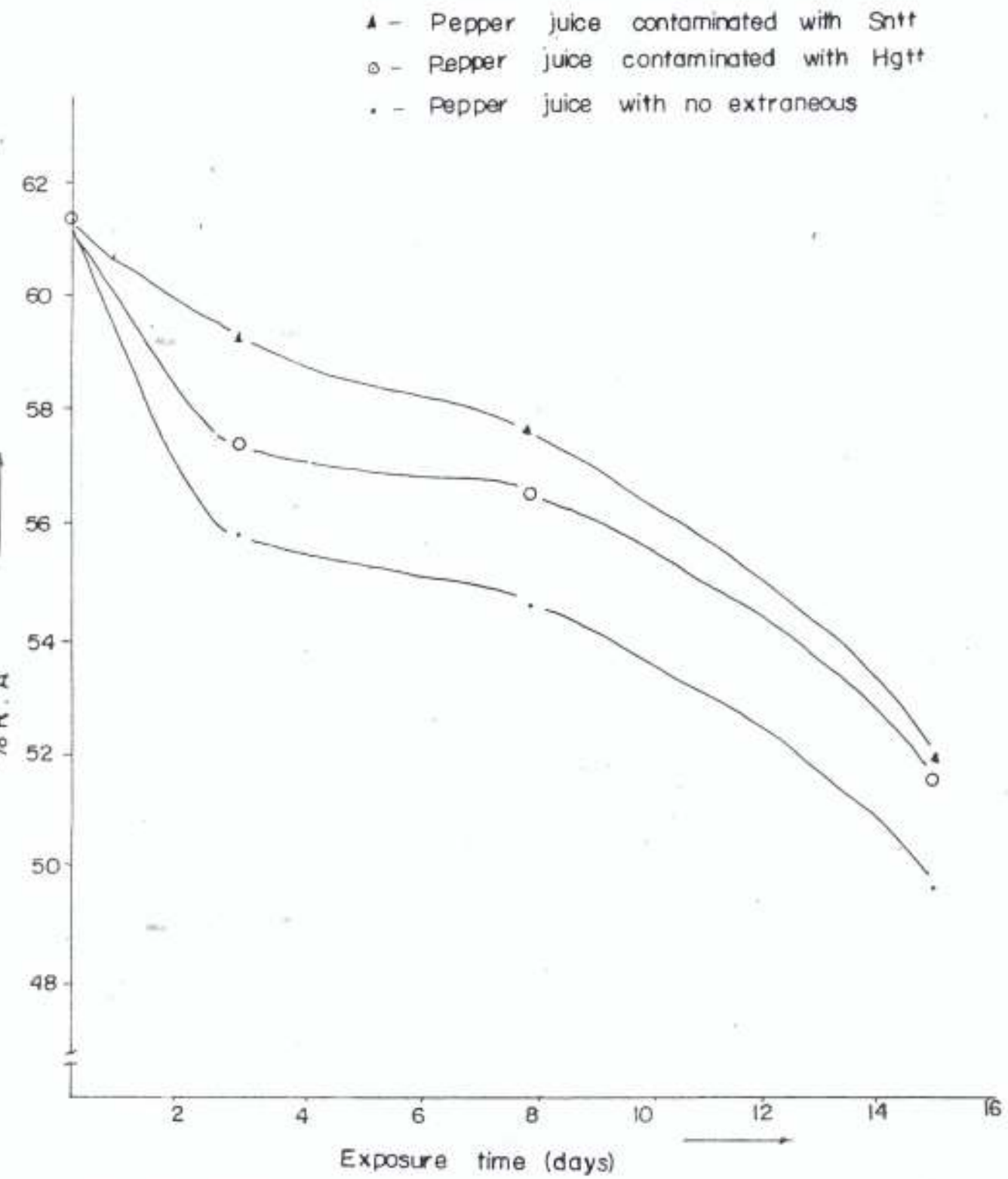


Fig. 39 : Effect of extraneous ions addition on SCC (% R.A) of Quench hardened steel in pepper juice.

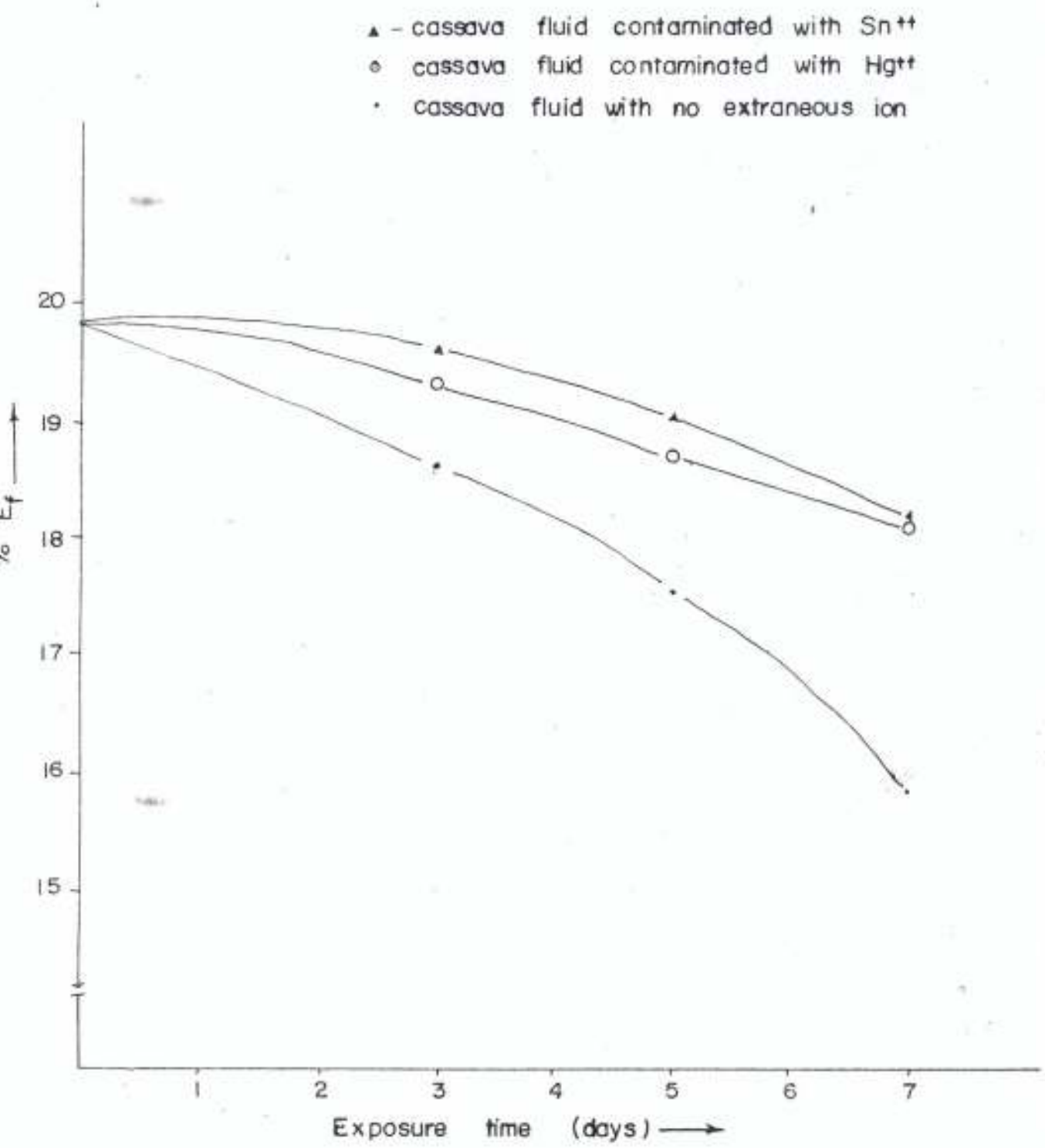


Fig. 40: Effect of extraneous ion addition on SCC ($\%E_f$) of As Received samples in cassava fluid (Applied Load 7000 N)

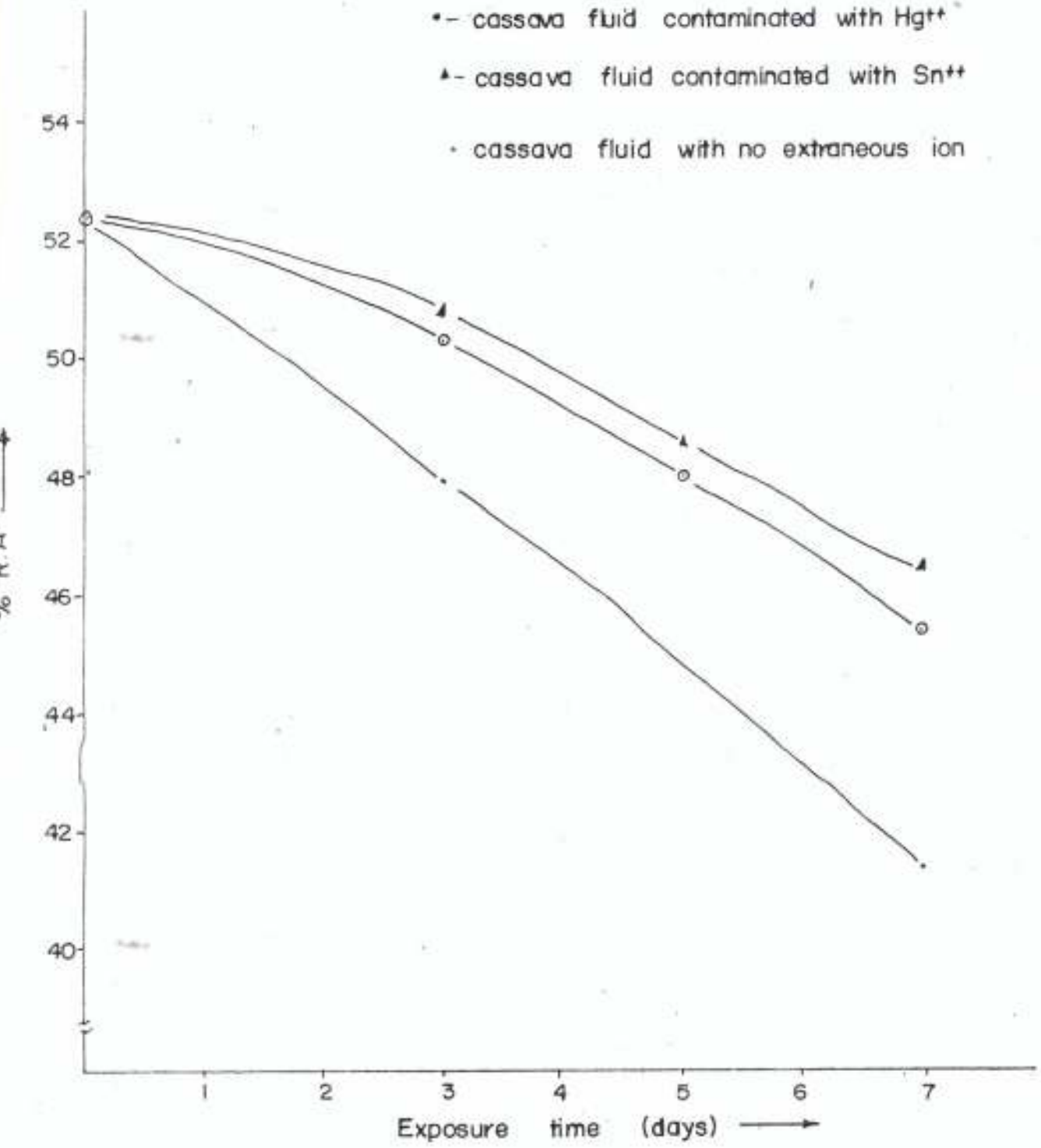


Fig. 41 : Effect of extraneous ion addition on SCC (% R.A) of As Received samples in cassava fluid (Applied Load = 7000 N)

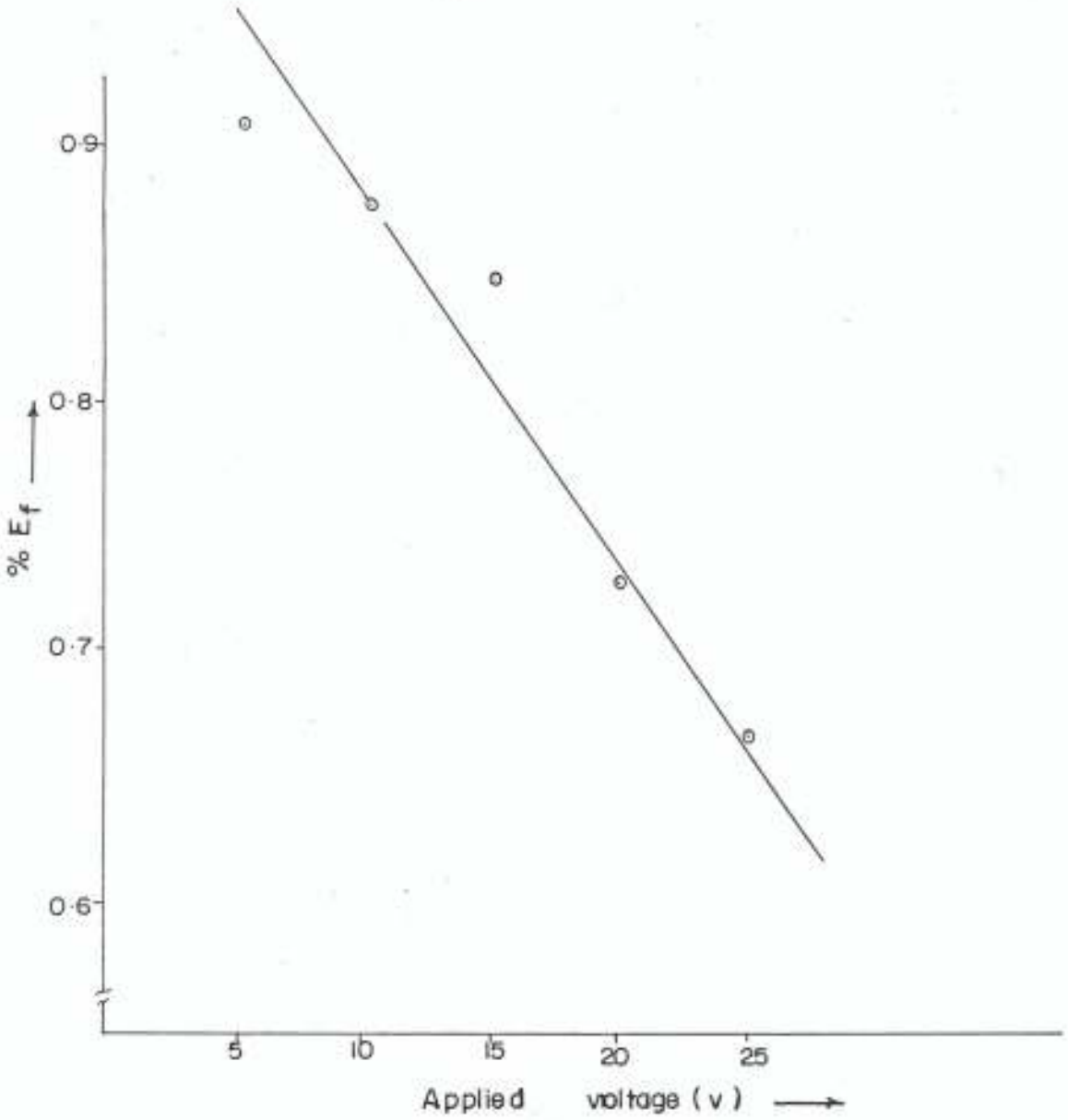


Fig. 42 : Effect of cathodic polarisation on SCC (% E_f) of Quench hardened steel in cassava fluid.

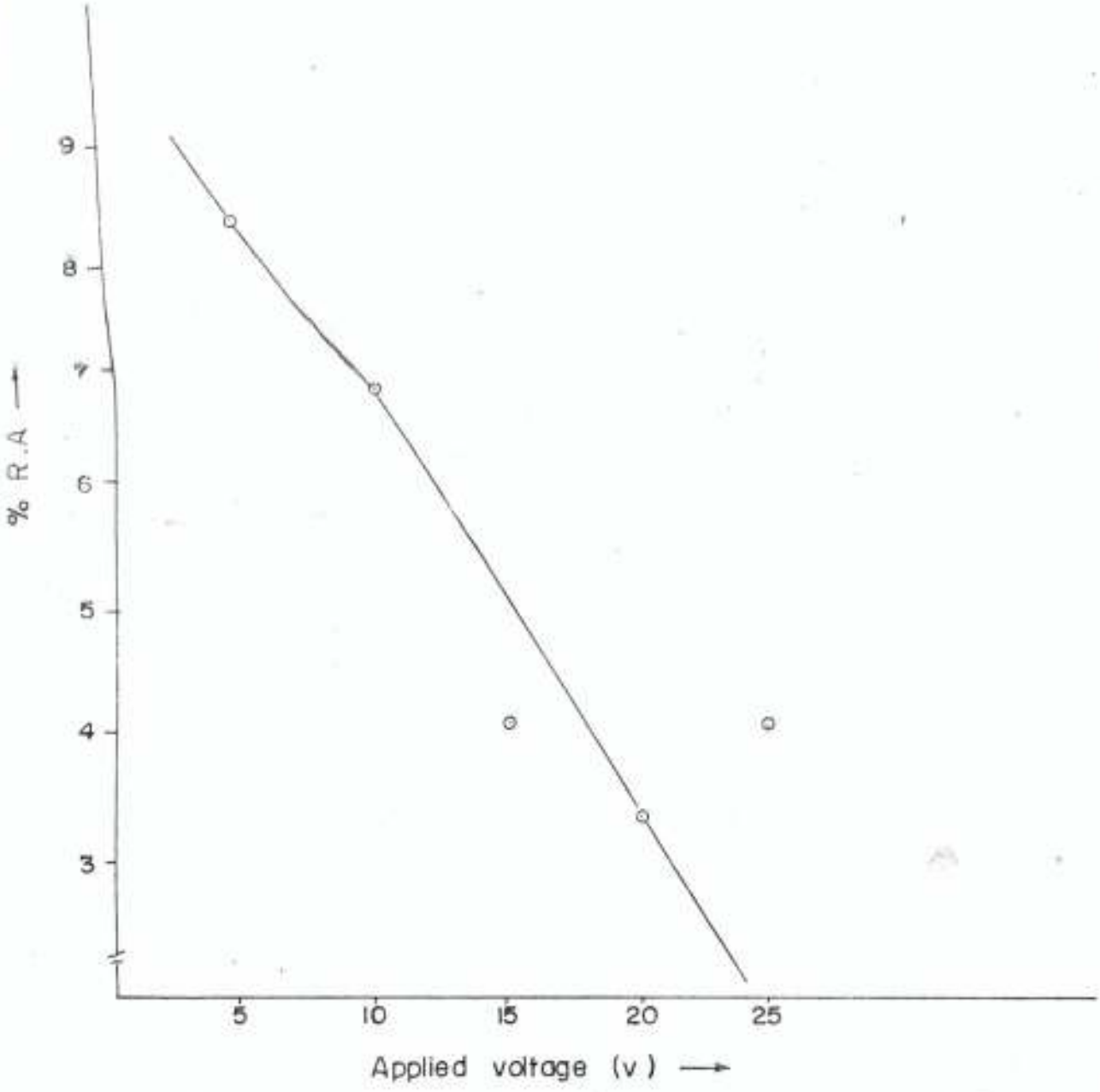


Fig. 43: Effect of cathodic polarisation on SCC (% R.A) of Quench hardened steel in cassava fluid.

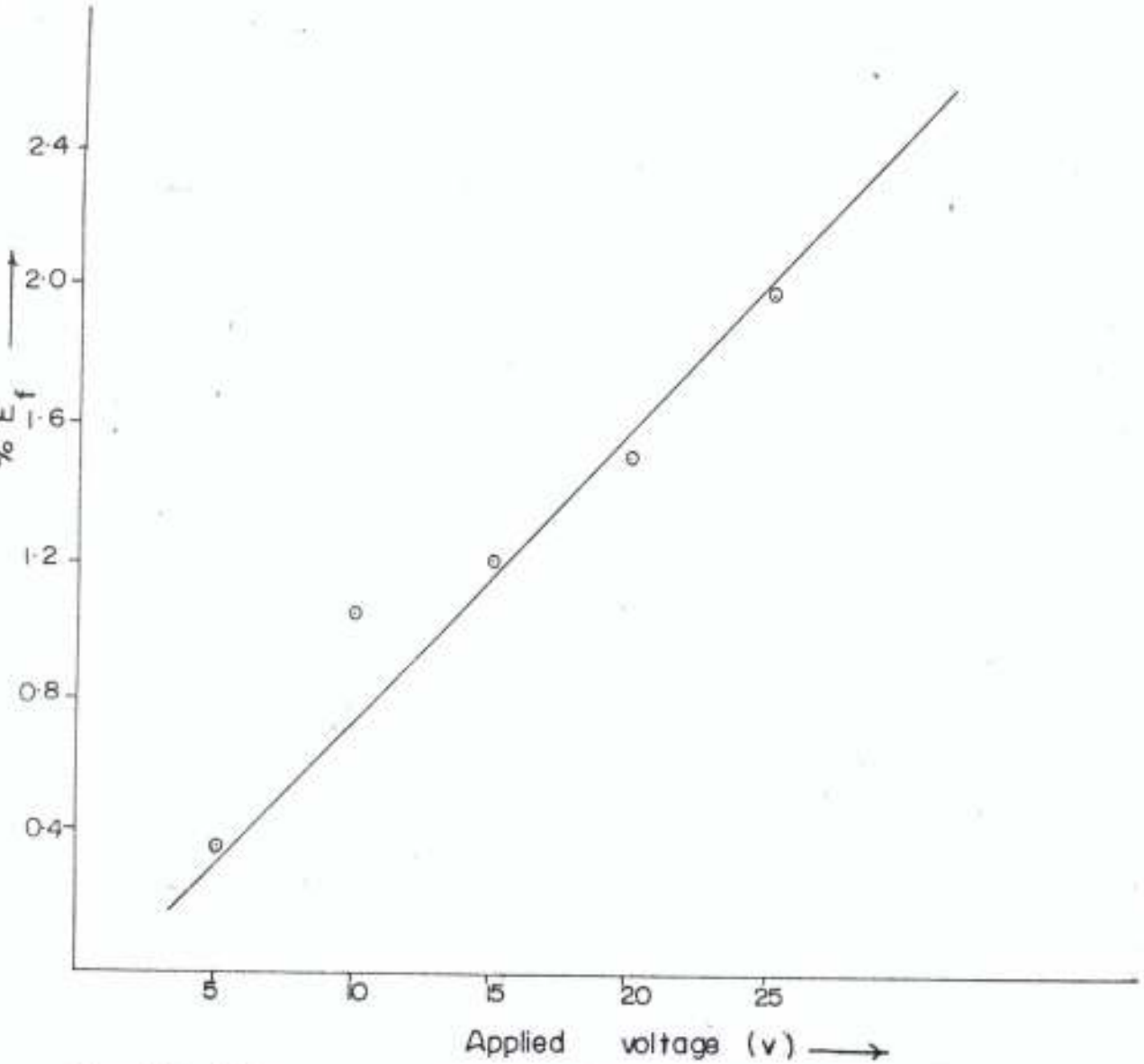


Fig. 44 Effect of cathodic polarisation on SCC (% E_f) of Quench hardened steel in tomatoe juice

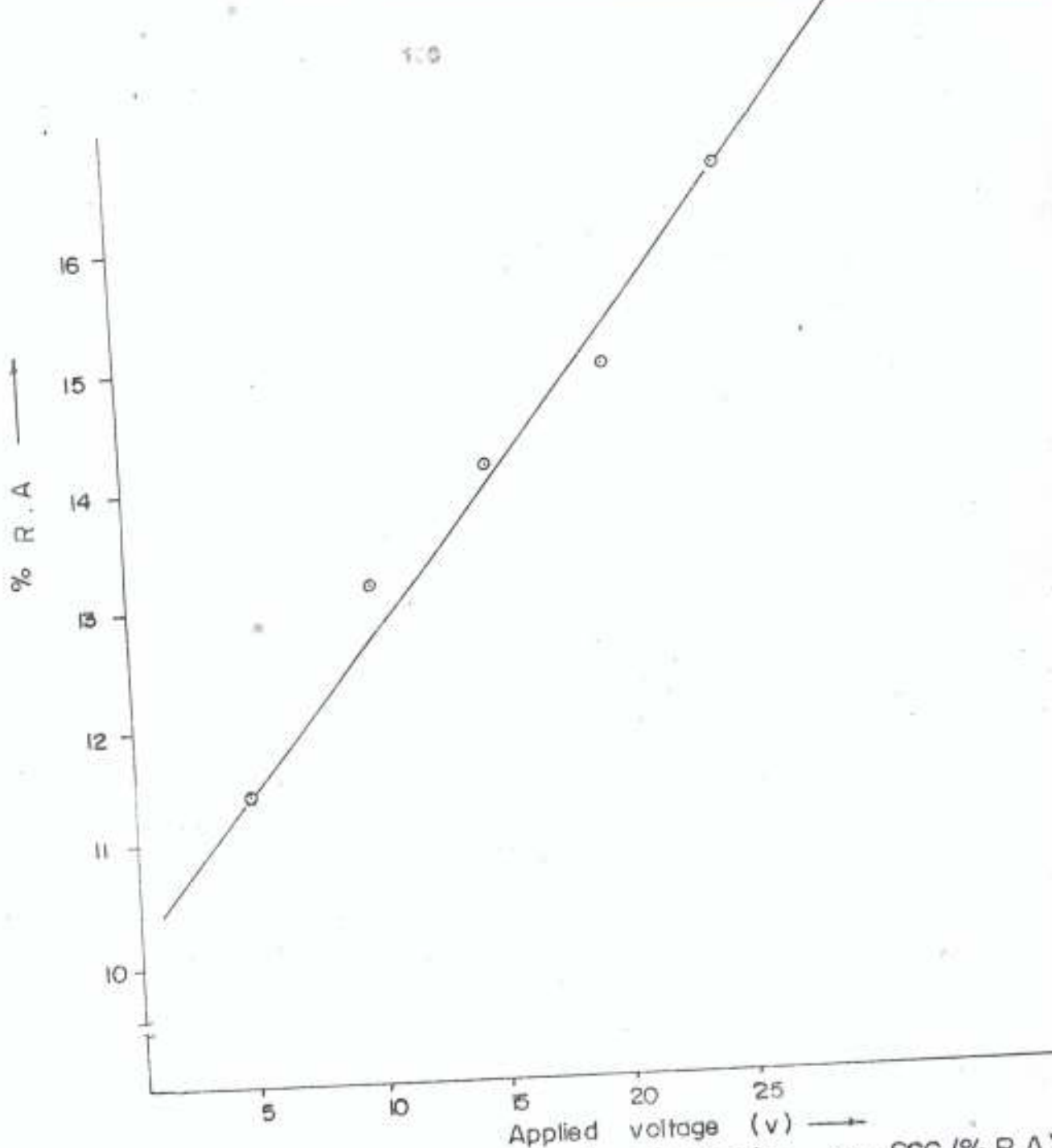


Fig. 45 : Effect of cathodic polarisation on SCC (% R A) of Quench hardened steel in tomatoe juice

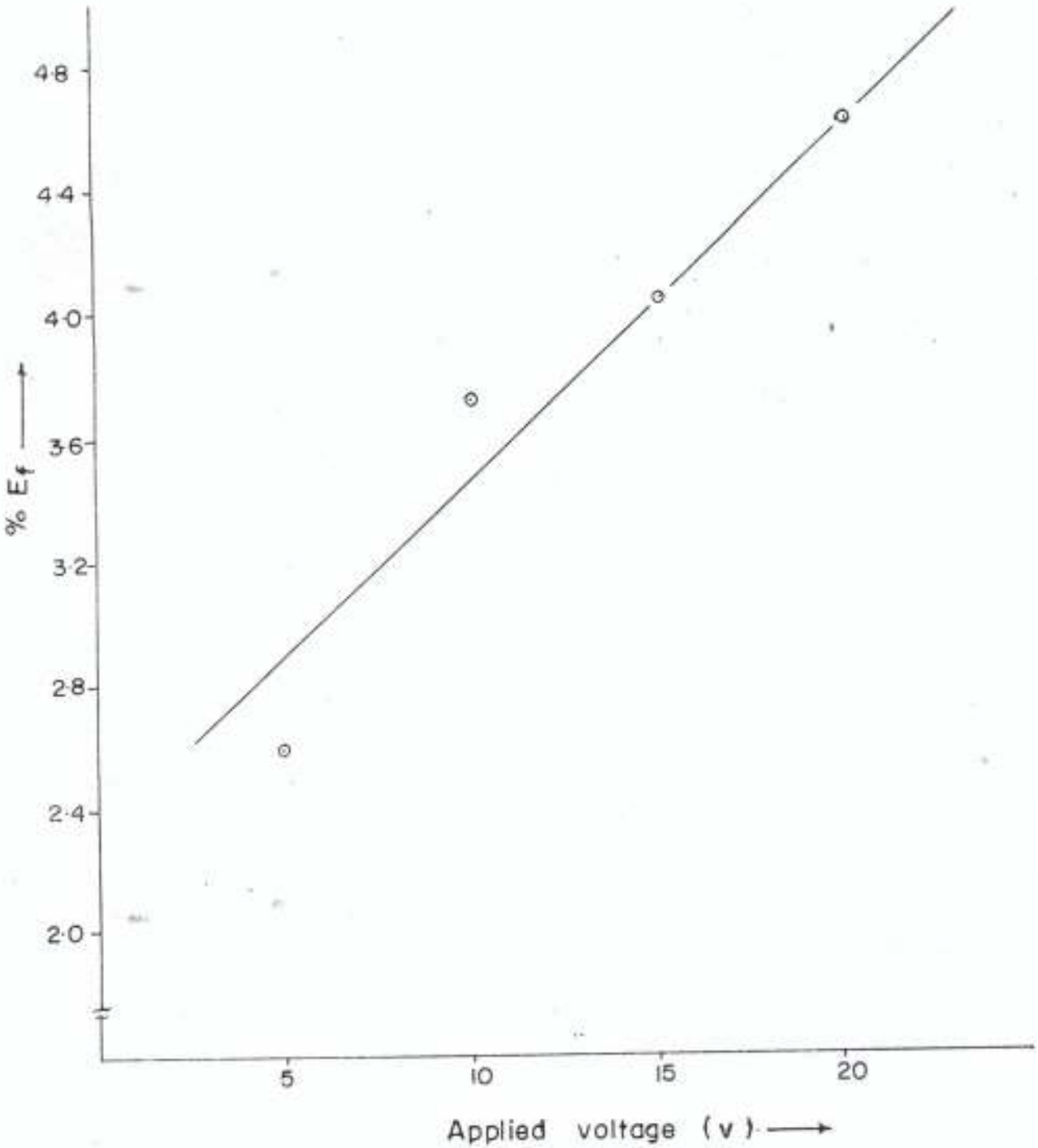


Fig. 46 : Effect of cathodic polarisation on SCC (% E_f) of Quench hardened steel in pepper juice.

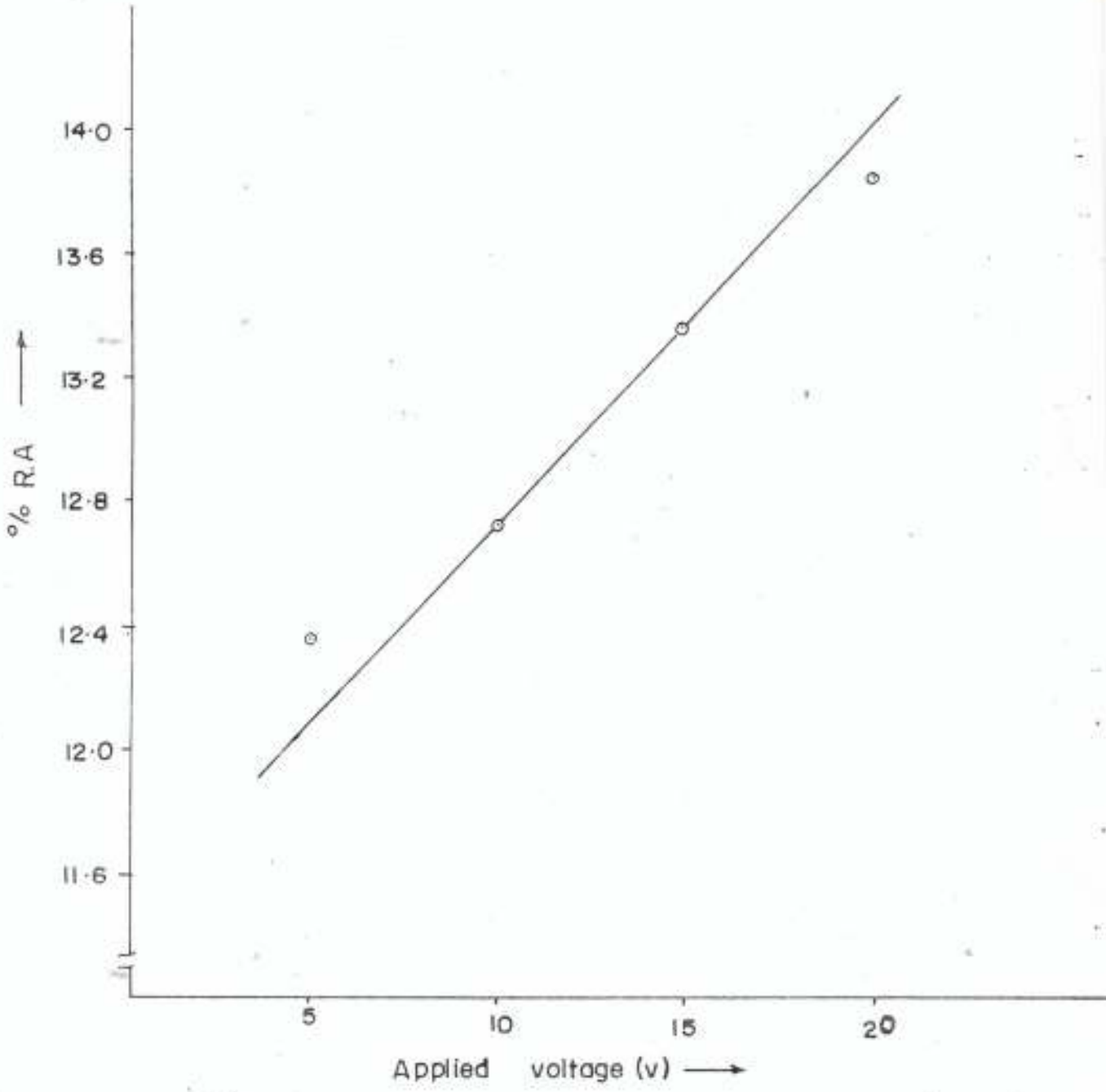


Fig. 47: Effect of cathodic polarisation on SCC(%R.A) of Quench hardened steel in pepper juice.

EFFECT OF CATHODIC POLARISATION

The effect of cathodic polarisation on the rate of cracking of quench hardened steels in all the three fluids under study (Figures 42 - 47) corroborates the result obtained in the preceding subsection. Application of cathodic polarization led to an increase in the rate of attack in cassava fluid. This suggests that the mechanism of stress corrosion cracking is hydrogen embrittlement in cassava fluid.

The fact that application of cathodic polarisation on quench hardened steel in tomatoes and pepper juices led to a decrease in the rate of attack is an indication that mechanism of cracking is anodic dissolution rather than hydrogen embrittlement.

EFFECT OF ANODIC POLARISATION

Figures 48 and 49 give the graphical representation of the effect of anodic polarisation on SCC of quench hardened steel in cassava fluid. It has been established that cracking of this steel in cassava fluid is due to hydrogen embrittlement. Application of anodic current will be expected to generate less hydrogen and consequently reduce the rate of cracking. This explains the decrease in rate of cracking experienced when the applied anodic potential was increased from 5v to 10v and from 15v and 25v.

The reduction in ductility (or increase in the rate of cracking) observed when applied anodic potential was increased in

the range of 10v to 15v is attributed to possible change of cracking mechanism from hydrogen embrittlement to anodic dissolution in this applied potential range. The potential range may correspond to region within which, from indication of high anodic activity, soluble corrosion products are formed at the bare metal exposed at the crack tip. When applied potential was increased beyond this potential range, soluble species are possibly no longer formed at the crack tip consequently cracking mechanism returned to being predominantly hydrogen embrittlement. Rate of cracking thus, started to decrease with increase in applied potential beyond 15v. Reversibility of embrittlement in Al-Li-Cu alloy has also been suggested (Balasubramanan and Diquette, 1992).

The effect of anodic polarisation on SCC of quench hardened steel in tomatoes juice is shown in figures 50 and 51. Previous discussions have shown the mechanism of cracking in this case to be anodic dissolution. Applied anodic potential led to an increase in anodic activity and formation of soluble corrosion product at the crack tip. This is responsible for increase in the rate of cracking with applied anodic potential. As applied voltage was increased, there was an increase in anodic activity at the crack tip and the rate of cracking became faster.

Figures 52 and 53 gives the trend of the variation of applied anodic potential on the rate of cracking of quench hardened steels in pepper juice. The mechanism of cracking, as

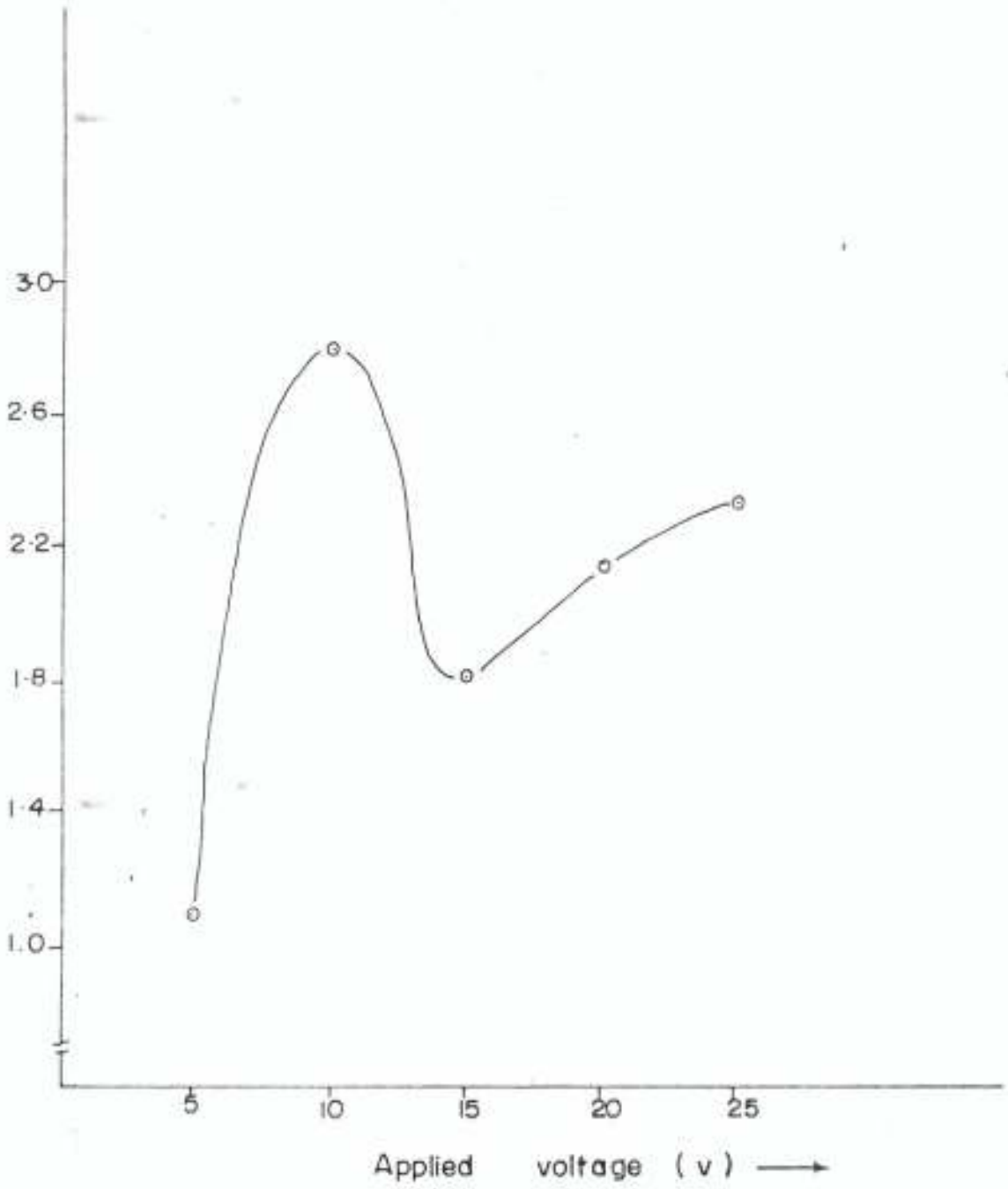


Fig. 48 : Effect of Anodic polarisation on SCC (%E_f) of Quench hardened steel in cassava fluid.

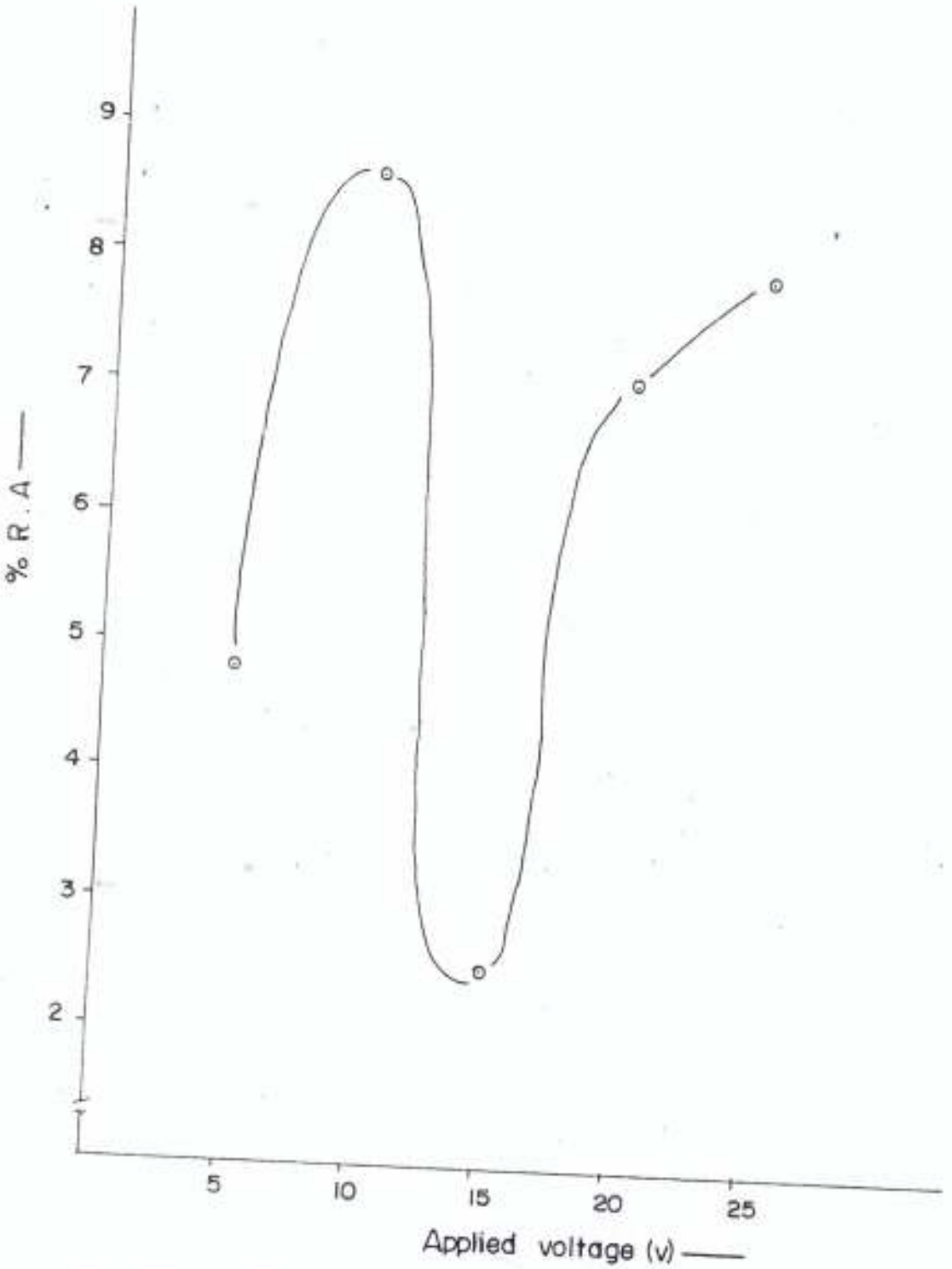


Fig.49: Effect of Anodic polarisation on scc (% R.A) of Quench hardened steel in cassava fluid.

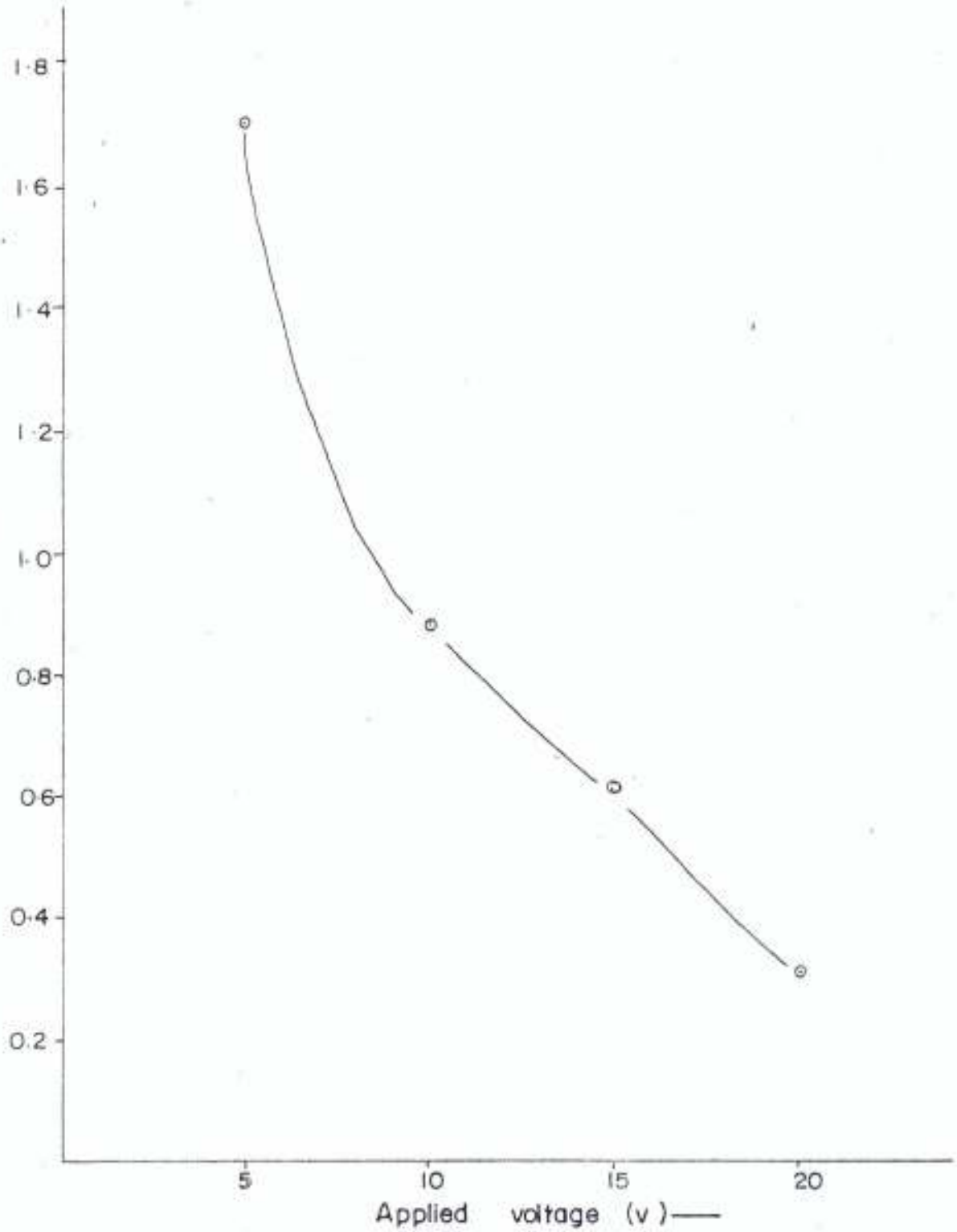


Fig . 50: Effect of Anodic polarisation on SCC (% E_f) of Quench hardened steel in tomatoe juice .

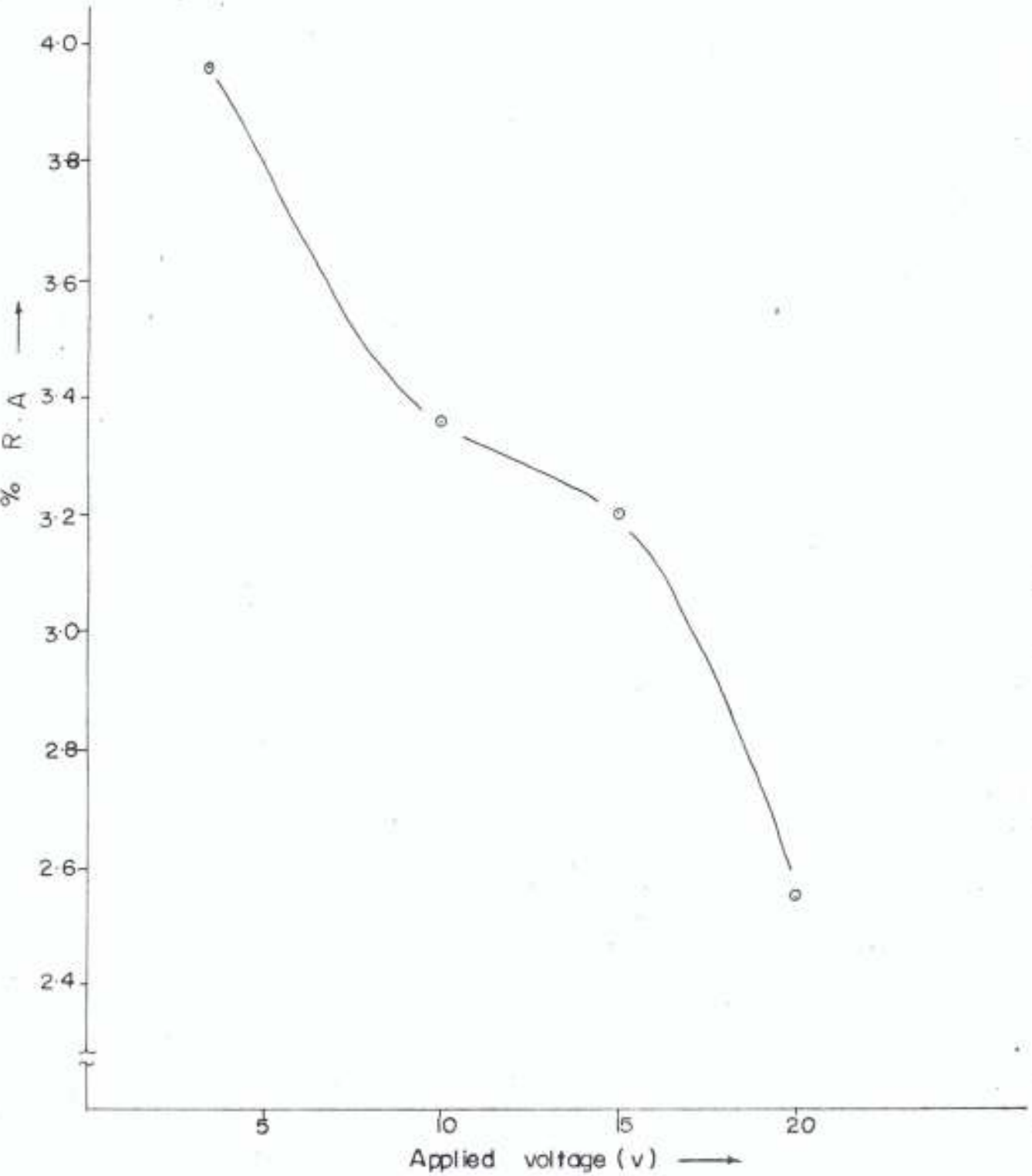


Fig.51: Effect of Anodic polarisation on SCC (% R.A) of Quench hardened steel in tomatoe juice.

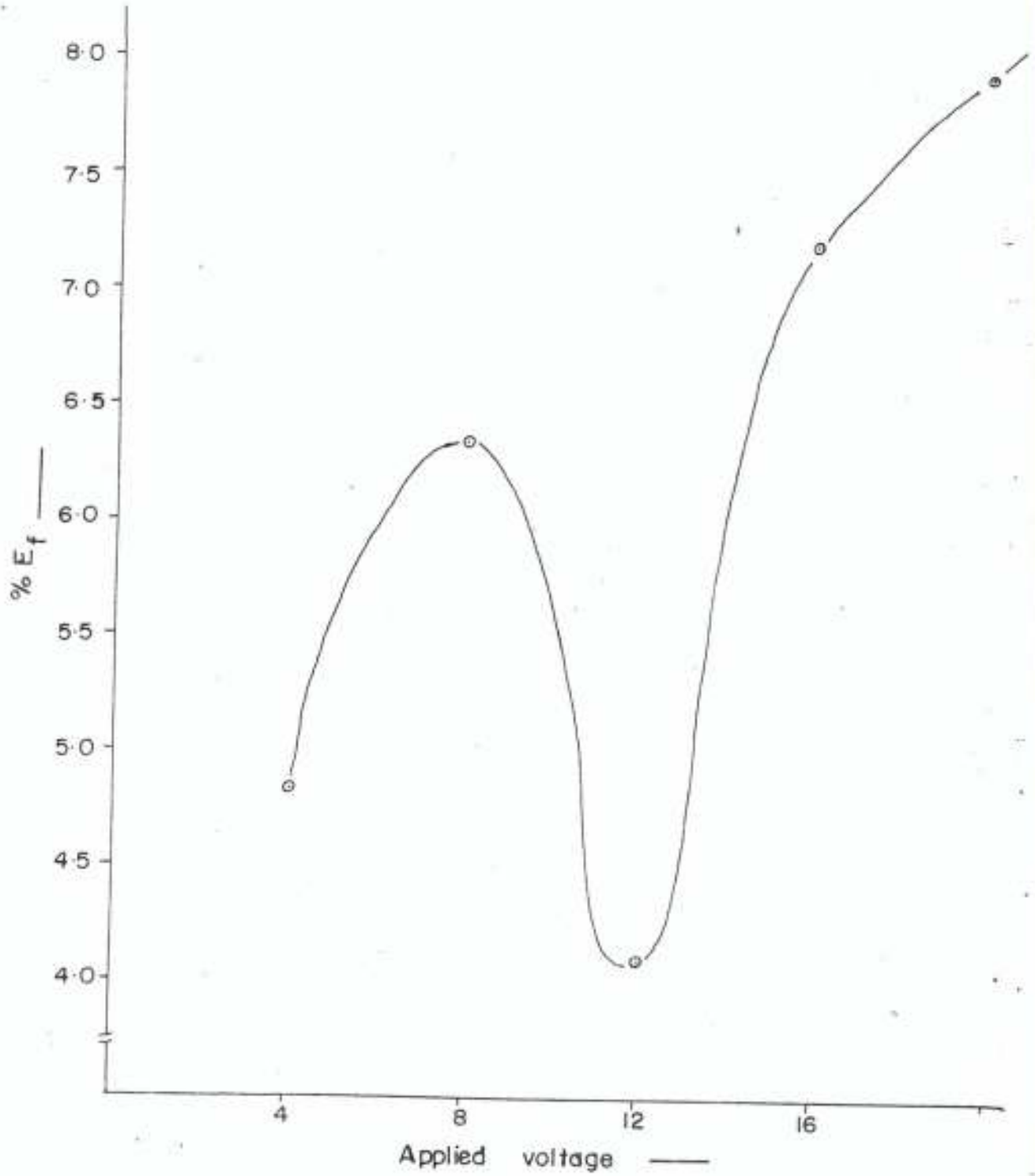


Fig. 52: Effect of Anodic polarisation on SCC (% E_f) of steel in pepper.

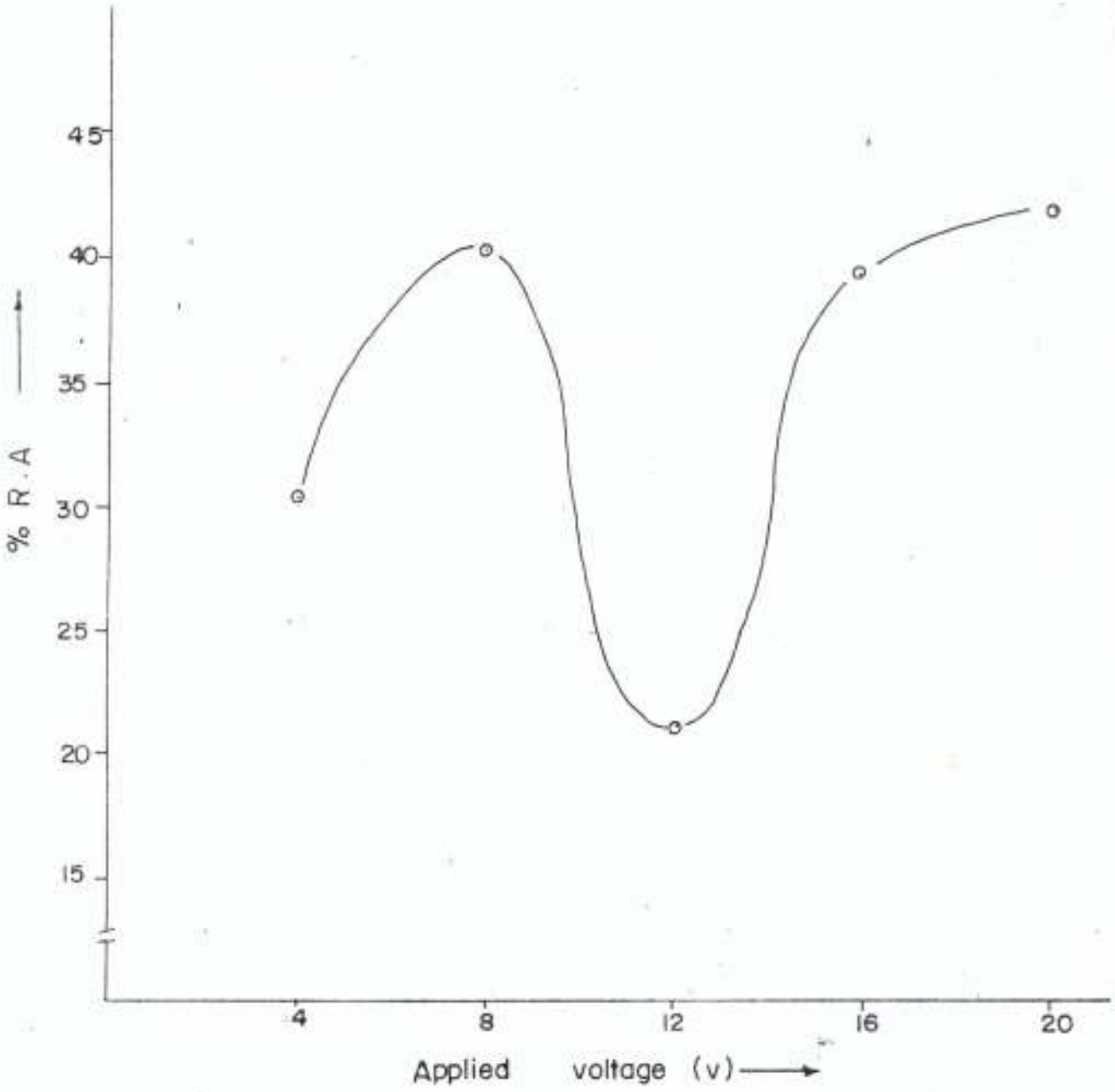


Fig.53: Effect of Anodic polarisation on SCC (% R·A) of steel in pepper.

discussed earlier is anodic dissolution at the crack tip reduction in rate of cracking observed when potential was increased in the range 4 - 8v and 12 - 20v is attributed to reduction in anodic activity at the crack tip. This may perhaps be as a result of decrease solubility of reaction products in the crack tip region. Marked increase in the rate of attack as the applied potential was increased from 8 - 12v is attributed to increased anodic activity and formation of soluble corrosion products as potential was increased in this range. Maximum susceptibility was observed at applied potential of 12v.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

1. Medium carbon steel is susceptible to corrosion and stress corrosion cracking in cassava fluid, tomatoes and pepper juices.
2. Rate of general corrosion attack in these fluids diminishes with exposure time owing to progressive formation of passive film on the metal surface.
3. The presence of Hg^{++} and Sn^{++} ions in cassava fluid increases the corrosion aggressiveness of the fluid to medium carbon steel.
4. Whereas the presence of Hg^{++} ions increases corrosion aggressivess of tomato and pepper juices, Sn^{++} ions presence in these juices will reduce their corrosion aggressiveness to medium carbon steel.
5. Sn^{++} ions, when present in tomato and pepper juices can act as corrosion inhibitor. Tin plating can thus be used to enhance corrosion performance of medium carbon steel in tomato and pepper juices.
6. The faster the cooling rates of heat treated samples from austenitising temperature, the more rapid is the rate of corrosion attack.

7. Quench hardened (martensitic) steel shows minimum susceptibility to corrosion when tempered at 300°C.
8. Hydrogen atom is the endangering species in cracking of quench hardened (martensitic) steel in cassava fluid.
9. Whereas, medium carbon steel with martensitic structure fails due to hydrogen embrittlement in cassava fluid, the mode of cracking in pearlitic type is anodic dissolution at the crack tip in the same medium.
10. The mechanism of stress corrosion cracking in tomato and pepper juices is anodic dissolution at the crack tip.
11. Rate of cracking of medium carbon steel in tomato juice increases steadily as applied anodic potential is increased.
12. Medium carbon steel shows marked suspectibility in tomato juice and cassava fluid when applied anodic potential is between 12 and 15v.
13. The most suitable heat treated condition for optimum corrosion performance of medium carbon steel in agro- fluids is quench hardening and tempering at 300°C.

5.2 RECOMMENDATIONS

Based on the results of research findings, the following recommendations are made for optimum utilisation of medium carbon steel in the fabrication of food processing machines:

1. Tempering of quench hardened steel must be kept at 250°C - 350°C.
2. Tin plating is recommended for medium carbon steel intended for processing of tomato and pepper fruits.
3. Tin plating should be avoided for medium carbon steel intended for processing of cassava tubers.
4. Where steel storage tank is needed for storing tomato or pepper juices, cracking of welded parts can be avoided by application of cathodic protection technique.
5. Cathodic polarisation of steel parts of cassava processing machines must be avoided. On no account must such parts be electrically coupled with a less active metal.

5.3 SUGGESTION FOR FURTHER STUDIES

Although mechanistic model of cracking in the various agro-fluids has been suggested, detailed fractographic studies of stress corrosion cracks, and chemical analysis of corrosion products at the crack tip are necessary for a better

understanding of mechanistic aspect of stress corrosion crack propagation. For example, it is considered necessary to determine whether the anodic dissolution found in tomato and pepper juices are due to pre-existing active path, strain generated active path or film induced cleavage. The appropriate mechanistic model for hydrogen embrittlement of martenistic steel in cassava fluid needs to be established as well. This will enhance a better formulation of appropriate protection techniques for excellent stress corrosion performance of medium carbon steel in each of the fluids under study.

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