

**THE EFFECT OF SURFACE FINISH
ON THE EFFICIENCY OF INHIBITORS
FOR STEELS CORRODING IN 3% NaCl**

BY

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ABSTRACT

Investigations were carried out to study the effects of surface finish on the efficiency of inhibitors for Steels Corroding in 3 % NaCl. This study was carried out owing to its importance in the drive towards curtailing the menace of corrosion in industries where varieties of steels are used for production structures, particularly when these structures are installed offshore. In the course of the study, different grades of steel samples were polished with emery papers of various grades and then subjected to corrosion study by total immersion technique and electrochemical methods, the corrosion media used was 3% NaCl solution containing 0.2% of sodium nitrite, sodium nitrate, sodium benzoate or sodium dichromate as inhibitors. The most prominent conclusions drawn from the results were that the inhibition efficiency of the inhibitors generally rose with surface roughness, but fell at a certain critical surface roughness where higher concentration of the inhibitor in use was required and that corrosion of carbon steels in 3% NaCl increased with increase in the carbon content of the steel.

DEDICATION

This project/thesis is dedicated to the memory of the following beloved ones: Mr D.O. Ebuzome, Prof. D.T. Adepoju and Mrs P.K. Fasae, all of whom left this sinful world at very active ages.

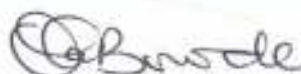
May their humble Souls rest in Peace. Amen.

CERTIFICATION

I hereby certify that this work was carried out by :

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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.



DR. J.O. BORODE

SUPERVISOR

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Okpala A.N

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CHAPTER ONE

1.0 INTRODUCTION

According to Uhlig (1971), until recently Corrosion of Materials and other surface related phenomenon have only been given little attention by metallurgist in spite of the fact that durability of machines and structures is controlled by surface related phenomenon. Prominent among the surface phenomenon is Corrosion.

In nature, most metals are found as Oxides or Sulfides and energy in the form of heat or electricity is required to convert ore into the form in which the metals are commonly used. As a result, metal products always have a higher energy level than the ore from which they are produced, and the laws of nature demand that the metal relinquish a portion of this energy by reverting to some compounds closer to that of its origin. Stanier (1962), therefore defined Corrosion as the destructive alteration of a metal by chemical or electrochemical reaction with its environment.

One of the most prolific corroding media is the sea water (3-3.5% NaCl). Since it is a well known fact that surface preparation as well as inhibitors such as nitrites, nitrates, chromates and benzoates affects the corrosion of metals, this project set out to investigate the Effect of Surface Roughness on the efficiency of these Inhibitors for Steel Corroding in 3% NaCl.

1.1 Objective and Scope of Study

This study was undertaken owing to its importance in the industrial application of different varieties of steels. The main objective of this work is to determine the effect of varying degree of roughness of the surface of steels on the Inhibition Efficiency of Corrosion Inhibitors for Steel Corroding in 3% NaCl. In addition, the determination of the order of effectiveness (or Inhibition Efficiency) of the inhibitors used for this study as well as the effect of carbon content of steels on its corrosion were aimed at.

The corrosion inhibitors used were limited to sodium benzoate, sodium nitrite, sodium dichromate and sodium nitrate. This is due to their easy availability and the fact that more indept study of each inhibitor is enhanced compared to using many inhibitors. The surface roughness variation was limited to polishing with four emery grades (0,1,2 and 3) to also allow for indept study.

Dil pipe carrying petroleum product and other oil product installation made of steel are mostly off shore, therefore are exposed to sea water (3% NaCl). The corroding media used is mainly 3% NaCl, just to simulate sea water conditions.

The corrosion study was conducted using the total immersion testing. This is due to the easy availability of apparatus required and the satisfactory reproducibility obtained by results from this technique.

1.2 Justification for Study

In Nigeria, the main stQy of our economy is Petroleum which is produced by the oil industries. The various stages of production by oil industries involves the use of metals particularly steel, and these steels are susceptible to corrosion. This has in the past

manifested as oil spillages which constitute great loss to the economy. According to Ifeadi and Nwankwo (1987), oil spill incidents due to corrosion involved 18.4% of the total spill incidents in the country from the year 1976 to 1986. They also stated that for this same period, a total of 2005 oil spill incidents were recorded by oil companies in Nigeria, while the estimated total quantity of oil spilled was 2,038,711 barrels. Bajah et al (1982), stated that in 1980, an offshore oil rig exploded and within two weeks the equivalent of 280,000 barrels of oil spilt into the sea. Apart from the actual cost incurred due to oil loss, the negative effect of spill incidents in the marine biological communities is adverse, eliminating all forms of life including fish, which is the major source of livelihood for people in the affected areas.

In order to prevent these losses, the metals used in this region, particularly in sea water ($\approx 3\%$ NaCl), among various other forms of protection, are protected by the use of inhibitors. Therefore, a study of the effect of the surface roughness (of carbon steel) on the efficiency of inhibitors for steel corroding in 3% NaCl is justified at this particular time.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 CORROSION OF IRON AND STEEL

Corrosion of iron or steel, as Shreir (1976) puts it, is essentially the conversion of iron into a hydrated form of iron oxide i.e. rust. The driving force of the reaction is the tendency of iron to combine with oxygen.

It has long been known that iron is not visibly corroded in the absence of either water or oxygen. The overall reaction in their presence may be written as:



When the supply of oxygen is restricted, the corrosion product may contain ferrous ions.

The overall reaction can be broken down into two reactions, one producing electrons and the other consuming them as shown in the equations in the next page.



the overall reaction is therefore:



In the presence of oxygen, the ferrous hydroxide will be converted into rust in the reaction,



Evans (1960), has established that the conversion of iron to rust is accompanied by a flow of electrons in the metal from anodic to the cathodic region and by the movement of ions in solution. This was buttressed by the fact that the spatial separation of the anodic cathodic zones on the surface of metal under laboratory conditions, was so complete that the current flowing was equivalent to the corrosion rate. In order to inhibit corrosion, it is necessary to stop the flow of current. This can be achieved by suppressing either the cathodic or the anodic reaction or by inserting a high resistance in the electrolytic path of the corrosion current.

The corrosion of iron and steels takes place in three major types of environment; atmospheric fumes and vapour, by fluids and by soils. However, since this project is based on steels corroding in a solution, we shall consider only the corrosion of steels by fluids.

2.1.1 Corrosion of Steels by Fluids

Corrosion by fluid is of primary importance to the process industry and as Staniar (1962) put it, is second only to atmospheric corrosion in total wastage of metals. This type of corrosion is almost entirely electrochemical, since all metals in contact with an electrically conducting fluid have a tendency (known as the "solution potential") to go into solution in the form of ions. When this occurs another metal or hydrogen must be displaced from solution.

Typical of corrosion of metals by fluids is that of steels. When steel is immersed in an aqueous solution, iron enters the solution by displacing hydrogen, as illustrated by figure 1 below.

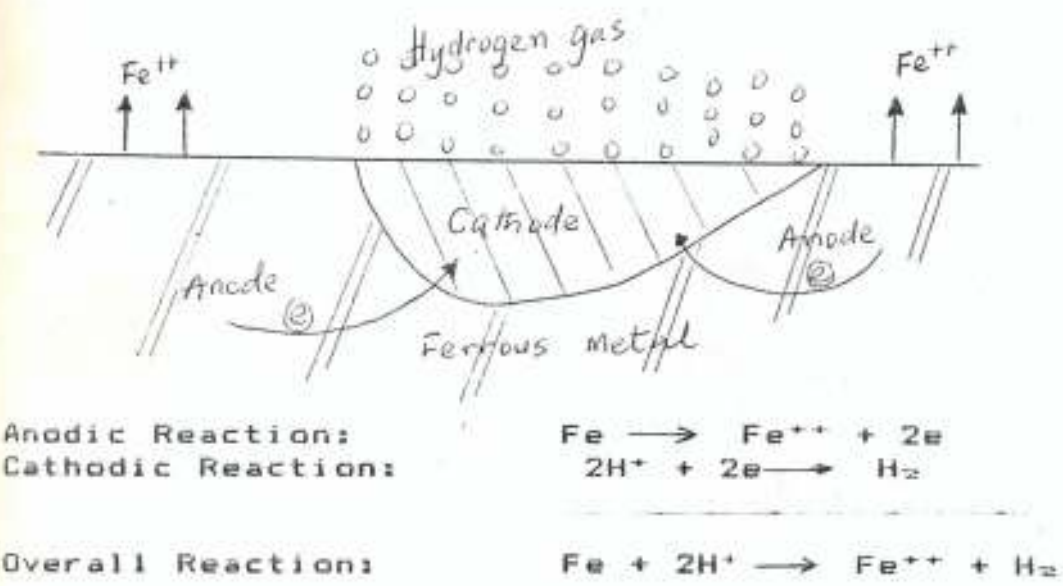


Fig. 1: Corrosion of Steel by Fluids.

The surface where iron enters the solution is known as the "anode" and the area where hydrogen is displaced from the solution is known as the "cathode". Bockris ~~et al~~ (1965), concluded from permeation experiment that in acidic as well as in alkaline solution, hydrogen evolution on iron occurred according to a coupled discharge - recombination - mechanism. As long as there are hydrogen ions in the solution, the corrosion process will continue. However, as corrosion proceeds, the hydrogen formed at the cathode is not immediately evolved and a gaseous layer is formed over the surface of the metal. This layer of hydrogen gas interferes with the flow of electrons by preventing the electron required to produce more nascent hydrogen. This reduction in the flow of electrons slows the corrosion process and is called "polarization" and the metal is said to be polarized.

2.1.2 Factors affecting the Rate of Corrosion of Steels by Fluids

It is a generally known fact that the majority of corrosion reactions are very slow. However, certain factors serves as catalyst, increasing the rate of corrosion where as other serves to retard the corrosion process, either by slowing the rate of surface film growth or by improving on the passivity of the surface

film in the corroding media. Some of the more common factors are hydrogen-ion concentration, temperature and velocity of fluids.

2.1.2.1 Hydrogen Ion Concentration:

Anything that interferes with the removal of hydrogen from solution will slow down the corrosion process, while anything that aids in the removal of hydrogen from solution will speed up the corrosion process.

The addition of an alkali such as caustic soda, reduces the corrosion of steels by reducing the hydrogen-ion concentration of the solution and thereby decreasing the number of hydrogen ions available for displacement. Conversely, the addition of an acid to a solution accelerates corrosion by increasing the hydrogen-ion concentration. Thus the hydrogen-ion concentration can determine the rate at which corrosion occurs.

2.1.2.2 Temperature

Temperature is a major factor controlling the rate of corrosion by fluids. In general, a rise in temperature increases the rate of corrosion process by increasing the ionization and the mobility of all reacting-fluid phases.

Also temperature may have an important effect upon surface film formation and its solubility. Films forming at one temperature may not form at another, and in general, the solubility of the film increases with increasing temperature.

Local differences in the solution temperature can establish localized galvanic cells and cause serious corrosion in systems where corrosion would be negligible under uniform temperature conditions.

2.1.2.3 Velocity of Fluid

The velocity of corrosive fluid can have an effect upon the corrosion of steel used in construction of pipelines, valves, pumps, heat exchanger and agitated vessels. Fluids moving at high velocity may damage protective surface films and accelerate corrosion in localized areas. In general, the flow of a corroding fluid across the surface of a metal relying upon a passive film for corrosion resistance should be streamline and in the words of Staniar (1962), should not exceed a velocity of 1.8 - 2.4 m/s.

2.1.3 Effect of Surface Condition of Metals on Corrosion

The surface condition of a metal has considerable bearing upon its corrosion resistance. In general, a smooth surface furnishes greater resistance to corrosion than a rough one.

A smooth surface possesses fewer crevices and indentations which might induce concentration - cell corrosion and offers less surface area on which attack may initiate. Also, certain metals, such as aluminum, lead and stainless steel, rely entirely upon the formation of a protective surface film for corrosion resistance. This film is more readily formed and maintained upon a smooth surface than upon a rough surface.

Clean, smooth metal surfaces usually require lower concentration of inhibitors for protection than do rough or dirty surfaces. Relative figures for minimum concentration of benzoate, chromate, and nitrite necessary to inhibit corrosion of mild steel with various types of surface finish, in a recent laboratory study by Brasher and Mercer (1968). The results shows that benzoate effectiveness is particularly susceptible to surface preparation. A particular method of preparing rusted surfaces is that involving the phosphate-delayed-chromate (PDC) technique as accomplished by Ride (1958) and Edward et al (1966). This method involves the treatment of the rusted metal surface with an acid phosphate solution to remove rust prior to the introduction of chromate inhibitor.

The ideal corrosion-testing equipment would be designed to duplicate conditions to which the materials to be tested are exposed to under operating conditions. Such equipment would incorporate features making it possible to determine the effect of temperature, velocity, aeration, turbulence, entrainment, impingement, galvanic couples, plastic deformation, residual and applied stresses and joining and fabrication methods on the corrosion rate. However the cost of such equipment would approximate if not exceed that of a small-size plant. The most commonly used method in the laboratory are the total-immersion test, the alternate-immersion test, the partial-immersion test, and the salt-spray test; the last being employed extensively for protective coatings.

2.2.1 Total-Immersion test

The method of total immersion test consists essentially of immersing prepared and weighed sample in the test solution for a number of periods of usually two or more days duration and determining the weight loss by cleaning and reweighing the sample after each period.

According to Staniar (1962), the corrosion rate of metals and alloys is expressed as weight loss per unit area or as penetration-rate factor. The calculation of the rate, of centimetres penetration per month, is made as follows:

$$R = (720 \times W) / (A \times D \times T)$$

where :

R = Corrosion rate, cm penetration per month

W = Weight loss, grams

A = Area, sq. cm

D = Density, gram /cc

T = Time, hour

The total-immersion test is the most widely used method. Test data obtained by this test method are very valuable, although it is desirable to confirm results by special tests and by semi works or plant exposure (if possible).

Since variation in aeration, temperature and velocity have been found to affect the result from this test, various devices have been used for providing control of these three major factors. Where only moderate test velocities are required, an apparatus in which the specimen are moved in a vertical circular path, all portions of the surface of a specimen moving at the same speed, has been used very successfully.

Statistical analysis of data from tests with this apparatus by wesley (1943), demonstrated satisfactory reproducibility of results.

2.2.2 Alternate-Immersion Test

In this testing procedure, special mechanical equipments is required which permits automatic immersion and withdrawals of the samples from the solution. The test is designed to determine the effect of alternate exposure to the corrodant and to air, such as occurs in many tanks, pipelines, and on roofs. The tests are normally conducted at room temperature or only slightly above. The test period is usually longer than is employed in total-immersion testing. The procedure for preparing test samples and determining the degree of deterioration is the same as that used in the total immersion test.

2.2.3 Partial-Immersion Test

In this test the samples are only partially immersed in the test liquid. The object of this test is to determine the rate of corrosion at the liquid-vapour level. This is important in constant-level tanks and in partially filled pipelines.

2.2.4 Salt-Spray Test

The most common of the spray test is the salt-spray test which was originally developed by Capp (1914) for studying the protective value of metallic coatings on steel under conditions that he hoped would stimulate exposure to a sea-coast atmosphere.

Phosphate coatings are occasionally tested by continuous salt spray without sealing oil film and are expected to withstand one or two hours spray without showing sign of rust. The value of such a test in cases where sealing is normally undertaken is extremely doubtful.

However, Dix (Jr) and Bowman (1937), ascertained that the best results have been secured when the spray has been interrupted for so many hours each day.

2.3 ELECTROCHEMICAL MEASUREMENT

In view of the electrochemical nature of corrosion, the measurements of electrical properties of the interface of metal/solution, are used extensively in fundamental studies of the mechanism of corrosion, corrosion testing and in monitoring and control in service. The wide spread use of potentiostatic control and the availability of a range of commercial potentiostats have given a tremendous impetus to electrochemical testing, though La Que (1969), has expressed concern

about the proliferation of publications describing electrochemical techniques for corrosion testing, and cautioned regarding the extrapolation of results obtained in the laboratory with a potentiostat to the performance of metal in service.

Important contributions in the use of electrical measurements in testing have been made by numerous workers. prominent among them is Stern and Geary (1957) who have developed the important concept of linear polarization, this in turn led to a rapid electrochemical method for determining corrosion rates, both in laboratory and plants. Pourbaix (1973) and his co-workers on the basis of a purely thermodynamic approach to corrosion have constructed potential-pH diagrams for majority of metal-H₂O systems, and by means of a combined thermodynamic and kinetic approach have developed a method of predicting the conditions under which a metal will corrode uniformly, pit, passive or remain immune.

2.4 PASSIVITY

When a metal is exposed to an environment under conditions such that reaction of the metal with the environment ought to occur with decrease in the thermodynamic free energy of the system, and it (the

metal) remain visibly unchanged for an indefinite period, the metal surface is said to be passive. According to Shreir (1976), Faraday suggested that passivation is caused by an invisible oxide film on the metal surface or by an oxidized state of the surface, that prevents contact between the metal and the solution. The modern form of the oxide film theory due primarily to Evans (1960), has been challenged by proponents of theories of change of the metallic surface involving not film formation but allotropic modifications, electronic modifications or adsorption of ions or molecules. However studies by Muller (1933), has shown quantitative evidence of the presence of a compact solid film on passivated metal surface.

During passivation, the following may be observed :

- (i) The appearance of the metal surface may change if the passivating film is sufficiently thick.
- (ii) The electrode potential of a passive metal is always appreciably more noble than its potential in the active state.
- (iii) Passivity is an anodic phenomenon, and control of corrosion by decreasing cathodic reactivity or by cathodic protection is not passivity.

Prominent among various causes of passivation in metals is the use of oxidizing and non-oxidizing inhibitors. According to Antropov (1977), passivation may be enhanced by the introduction of small amount of special substances called inhibitors into the corrosive medium, thereby depressing its aggressiveness.

2.4.1 Passivating Oxide Film

Various independent techniques have been used to study iron surfaces inhibited in solutions of anions. Studies by Hancock and Mayne (1958) and Brasher (1966) have shown that immersion of iron bearing its air-formed oxide film into solutions of inhibitive anions usually result in a thickening of the oxide layer. However, Mayne and Page (1972) have confirmed by their study, the exception of this at low pH.

Kubaschewski and Brasher (1959) have shown that oxide film growth on iron in inhibitive solutions of anions as well as in air, follows a direct logarithmic law, the rate constant being generally slightly greater in solution than in air. According to Hoar (1956), inhibition of the corrosion of iron by anions results from their effects on this oxide layer.

Potential-pH Diagram for Fe - H₂O System

The Pourbaix plot of thermodynamic data of systems as a function of electrode potential and pH has contributed immensely to the science of corrosion. A recent paper by Pourbaix (1970), exemplifies the usefulness of potentiostatic polarization curves in the experimental plotting of various domains, such as protecting, pitting, general corrosion and passivity, in these diagrams. This phenomenon is well illustrated by simplified version of the Fe-H₂O potential-pH equilibrium diagram (shown in fig 2) after Deltonbe and Pourbaix (1954), in which corrosion proceeds when the activity of Fe²⁺, Fe³⁺ (aq) or FeO₂⁻ (aq) is in excess of 10⁻⁶ g ion/l (0.06 p.p.m. of Fe) whereas passivity is achieved when Fe(OH)₂, Fe₂O₃ or Fe(OH)₃ (i.e rust product) is in equilibrium with the metal ions at activities less than 10⁻⁶ g ion/l. Also immunity is achieved if Fe metal in equilibrium with Fe²⁺ (aq) or FeO₂ H⁺ (aq) at an activity less than 10⁻⁶ g ion/l

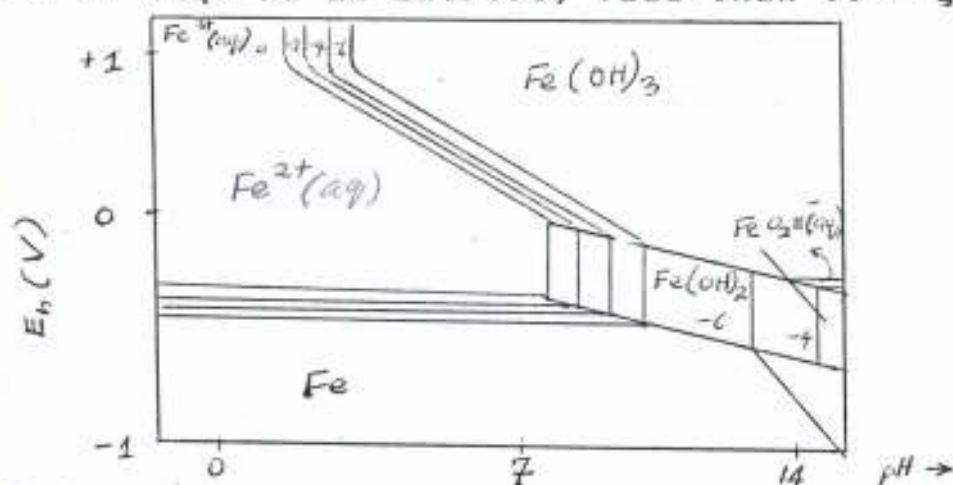


FIG 2: Equilibrium Potential-pH diagram for the Fe-H₂O System showing the zones of stability of Cation, anions and solid hydroxides (after Deltonbe and Pourbaix)

A corrosion inhibitor is a substance added to an environment in small concentrations to reduce the corrosion rate or prevent corrosion entirely. The majority of inhibitor application for aqueous, or partly aqueous systems are concerned with three main types of environment. viz:

- (i) Natural waters, supply waters, industrial cooling water etc, in the near-neutral pH range.
- (ii) Aqueous solutions of acids as used in metal cleaning processes such as pickling for the removal of rust or rolling scale during the production and fabrication of metals, or in the post-service cleaning of metal surface.
- (iii) Primary and secondary production of oil and subsequent refining processes.

2.6.1

Classification of Inhibitors

Various methods of classifying inhibitors into types or group are in existence. However, these classifications are not entirely satisfactory because there is not always general agreement on the allocation of an inhibitor to a particular group. Some of the main classifications used particularly for inhibitors in near-neutral pH aqueous systems are as follows.

2.6.1.1 Anodic or Cathodic Inhibitors

This classification is based on whether the inhibitor causes increased polarization of the anodic reaction (metal dissolution) or of the cathodic reaction i.e. oxygen reduction (in near-neutral solution) or hydrogen discharge (in acidic solution).

2.6.1.2 Oxidizing or Non-Oxidizing Inhibitors

These are characterized by their ability to passivate metal. In general, non-oxidizing inhibitors require the presence of dissolved oxygen in the liquid phase for the maintenance of the passive oxide film, whereas dissolved oxygen is not necessary with oxidizing inhibitors.

2.6.1.3 Organic or Inorganic Inhibitors

This distinction is based on the chemical nature of the inhibitor. However, in their inhibitive action, many compounds that are organic in nature as for example, the sodium salts of carboxylic acids, often have more similarities with inorganic inhibitors.

2.6.1.4 Other Classifications of Inhibitors

According to Antropov (1977), corrosion inhibitors may also be classified as liquid-phase and vapour-phase or volatile, depending on the conditions of their use.

2.6.1.4.1 Liquid-Phase Inhibitors

These are subdivided according to their utilization (in neutral, alkaline, or acidic media). The inhibitors most often used for neutral solutions are inorganic compounds of the anionic type. Their inhibiting effect being associated with either the oxidation of the metal surface (eg nitrites and chromates) or with the formation of a film of a difficulty soluble compound between the metal, and the given anion and possibly, oxygen (eg phosphate). An exception is benzoate, whose inhibiting effect is mainly associated with adsorption phenomena. All corrosion inhibitors used for neutral solutions slow down predominantly the anodic reaction.

In alkaline solutions, only high-molecular-weight compounds possess some inhibitive properties.

Corrosion inhibitors for acidic solutions are almost exclusively organic substances containing nitrogen, sulphur or oxygen - in the form of amino, imino, and trio groups and also as carboxyl and carbonyl. The inhibitive action of organic substances is due to their adsorption at the metal-acid interface which retards cathodic and anodic reactions, thereby reducing the corrosion rate.

2.6.1.4.2 Vapour-Phase Inhibitors

These are used for corrosion protection of machines, apparatus and other metal articles during their service in the air medium, during transportation and storage. These inhibitors are usually sprinkled as solid in container or placed in a muslin bag close to the surface to be protected. As a result of the sufficiently high vapour pressure, volatile inhibitors reach metal-air interface and dissolve in the moisture film covering the metal.

The compounds commonly used as vapour-phase inhibitors are anions of low molecular weight to which corresponding groups (eg NO_2 or CO_2) are added.

2.6.2 Mechanism of Corrosion Inhibition by Inhibitors

It is not often possible to assign a single, general mechanism of action to an inhibitor, because the mechanism may change with the condition of the corroding media. For instance, the corrosion of metals in neutral solutions differs from that in acid solutions in two important respects. In air-saturated solution, the main cathodic reaction in neutral solutions is the reduction of oxygen, in the reaction



whereas in acid solution, it is hydrogen evolution in the reaction



Corroding metal surfaces, therefore, in acid solution are oxide free, whereas in neutral solutions metal surfaces are covered with films of oxides, hydroxides or salts, due to the reduced solubility of these species. Because of these differences, substances which inhibit corrosion in acid solution by adsorption of oxide-free surfaces, do not generally inhibit corrosion in neutral solution.

2.6.2.1 Mechanism of Corrosion Inhibition in Acid Solution

Putilova et al (1960) and TrabANELLI and Carassiti (1970) stated that the corrosion of metals in aqueous acid solutions can be inhibited by a very wide range of substances. The primary step in the action of these inhibitors being generally adsorption on the metal surface, which is usually oxide-free in acid solution. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical processes of the corrosion.

Epelboin et al (1972), obtained consistent result, using the double layer capacity measurement for determination of inhibitors adsorption on corroding metals. Studies by Zucchini et al (1970), Fujii and Aramaki (1966) show that the efficiency of inhibition can be quantitatively related to the amount of adsorbed inhibitor on metal surface.

2.6.2.2

Mechanism of Corrosion Inhibition in Neutral Solutions

Inhibition in neutral solution is due to compounds which can form or stabilize protective surface films. The inhibitor may form a surface film of an insoluble salt by precipitation or reaction. Inhibitors forming films of this type include salts of metals such as Zn, Mg, Ni, Soluble Calcium Salts and Polyphosphates. Evans (1960), stated that the mechanism of action of inhibitors seems fairly straight forward. The salt films which are often quite thick and may be visible, restrict diffusion, particularly of dissolved oxygen to the metal surface. The salt film being poor electronic surface, and are thus referred to as Cathodic Inhibitors.

Another class of inhibitors is near-neutral solutions acts by stabilizing oxide films on metals to form thin protective passivating films. Such inhibitors are the anions of weak acids, some of the most important in practice being chromate, nitrite, benzoate, silicate, phosphate and borate. The passivating oxide films on metals offer high resistance to the diffusion of metal ions and the anodic reaction of metal dissolution is inhibited, thus these inhibitive anions are referred to as Anodic Inhibitors.

Independent studies by Brasher (1968), Freiman and Kolotyrkin (1969), Gouda (1967), Poling (1970), and others show that the mechanism of action of inhibitive anions on the corrosion of iron, Zinc and aluminum near-neutral solution involves the following important functions.

- (i) Reduction of the dissolution rate of the passivating oxide film.
- (ii) Repairs of the oxide film by promotion of the reformation of oxide.
- (iii) Repairs of the oxide film by plugging pores with insoluble compounds.
- (iv) Prevention of the adsorption of aggressive anions.

2.6.3 Efficiency of Inhibitors

The efficiency of an inhibitor under a given set of condition according to Antropov (1977), is expressed by the relationship:

$$I.E = \frac{A - B}{A} \times 100$$

Where : I.E is the percent inhibition efficiency

A is the corrosion rate in uninhibited medium

B is the corrosion rate in a medium containing a certain concentration of inhibitors.

In general the efficiency increases with an increase in inhibitor concentration. According to Shreir (1976), a typical good inhibitor gives 95% inhibition at a concentration of 0.008% and 90% at 0.004%.

2.6.4 Factors Affecting the Efficiency of Inhibitors

Brasher (1969), affirmed that the corrosion of iron or steel can be inhibited by the anions of most weak acids under suitable conditions. However, other anions particularly those of strong acids, tend to prevent the action of inhibitive anions and stimulate breakdown of the protective oxide film. Examples of such aggressive anions are the halides, sulphates, nitrates etc.

It has been shown that most anions exhibit some inhibitive and some aggressive behaviour towards iron. The balance between the inhibitive and aggressive properties of a specific anion depends on the following factors.

2.6.4.1 Concentration of Anions

According to Pryor and Cohen (1953), inhibition of iron corrosion in distilled water occurs only when the anion concentration exceeds a critical value. At concentrations below the critical value, inhibitive anions may act aggressively and stimulate breakdown of the oxide film. Judging from their critical inhibitive concentrations, Brasher (1969) has classified a number of anions in order of their inhibitive power towards steel. The order of decreasing inhibitive efficiency is: azide, ferricyanide, nitrite, chromate, benzoate, ferrocyanide, phosphate, tellurate, hydroxide, carbonate, chlorate, O-chlorbenzoate, bicarbonate, fluoride, nitrate and formate.

2.6.4.2 pH Value of Corrosive Media

Inhibitive anions are effective in preventing iron corrosion only at pH values more alkaline than a critical pH value. For instance, the approximate critical pH value for the inhibition of iron or steel in about 0.1.M solution of the anion increases in the order: Chromate, 1.0 Brasher et al (1970), azelate, 4.5 Mayne and Ramshaw (1960); nitrite, 5.0-5.5 Legault and Walker (1964); benzoate, 6.0 Davies and Slaiman (1971); phosphate, 7.1 Pryor and Cohen (1951); hydroxide, = 12 Hersch et al (1961). The critical pH value for inhibition depends on the concentration of the inhibitive anion. In azelate and nitrite solutions,

the critical pH for inhibition decreases as the anion concentration increases while in the case of benzoate solution, increasing the benzoate concentration displaces the critical pH to more alkaline values.

2.6.4.3 Dissolved Oxygen Concentration and Supply

The inhibition of iron by anions requires a critical minimum degree of oxidizing power in the solution. This is normally supplied by the dissolved oxygen present in air saturated solutions. Gilroy and Mayne (1965) have shown that the critical oxygen concentration for inhibition of iron in 0.1M sodium benzoate (pH 7) is ≈ 0.3 p.p.m., considerably less than the air saturated concentration of ≈ 8 p.p.m. As the oxygen concentration is reduced below this critical value, the rate of breakdown of the passivating oxide film increases.

The critical oxygen concentration for inhibition depends on the nature of the anion. For instance if the inhibitive anion possesses oxidizing properties eg chromate, nitrite, etc then the presence of dissolved oxygen may not be necessary for inhibition.

Addition of an oxidizing agent may improve the efficacy of inhibitive anion eg Mayne and Page (1970), recently showed that the presence of hydrogen peroxide lowers the critical concentration of sodium benzoate and sodium azelate required for the inhibition of steel and also lowers the pH values for inhibition.

2.6.4.4 Aggressive anion concentration

According to Bogatyreva and Balezin (1959), when aggressive anions are present in the solution, the critical concentration of inhibitive anions required for protection of iron are increased. Brasher and Mercer (1968), have shown that the relationship between the maximum concentration of aggressive concentration of inhibitive anion C_{inh} is of the form

$$\log C_{inh} = n \log C_{agg} + K$$

where 'K' is a constant depending on the nature of the inhibitive and aggressive anion; and

'n' is an exponent which is approximately the ratio of the valency of the inhibitive anion to the valency of the aggressive anion.

In general, the more aggressive the anion, the smaller the concentration which can be tolerated by an inhibitive anion. According to Brasher et al (1970), the order of tolerance of aggressive anions is, with certain exceptions, consistent with the order of aggressiveness of these anions as determined from their tendency to induce breakdown of the oxide film on iron in aerated solutions.

2.6.4.5 Nature of the Metal Surface

The critical concentration of an anion required to inhibit the corrosion of iron may increase with increasing surface roughness. Brasher and Mercer (1968), showed that the minimum concentration of benzoate required to protect a grit-blasted steel surface was about 100 times greater than that required on abraded surface.

2.6.4.6 Temperature of Corroding Media

The critical concentrations of anions eg benzoate, chromate and nitrite required for the protection of steel increases as the temperature of the corroding media increases. Studies by Omar (1987), showed that effect of temperature on the percentage inhibition efficiency depends largely on the concentration of inhibitors. He concluded that at lower concentration of inhibitor, the efficiency of the inhibitor decreases with temperature whereas at higher concentration the efficiency of the inhibitor increases with temperature.

CHAPTER THREE

3.0 EXPERIMENTAL MATERIALS AND PROCEDURE

3.1 Experimental Materials

The samples used for the study consists of hot rolled Dead Mild Steel, Mild Steel and Medium Carbon Steel, collected from Oshogbo Steel Rolling Company. The classification of the samples were based on Bailey (1972). The chemical analysis of these samples as carried out on a spectrometer is given in table 1. The mechanical properties of the samples are also given in table 2.

Table 1: Chemical Composition of Carbon Steels Studied .

Sample	c	Si	Mn	P	S	Cu	Cr	Ni	Sn
Dead Mild Steel	0.1453	0.1531	0.5793	0.0587	0.0291	0.2366	0.0961	0.1073	0.0495
Mild Steel	0.1892	0.2377	0.7210	0.0392	0.0319	0.2211	0.0975	0.0988	0.0316
Medium Carbon Steel	0.3575	0.2413	0.9092	0.0432	0.0397	0.2051	0.0872	0.6140	0.0328

Table 2: Mechanical Properties of Carbon Steel Samples studied

Samples	Tensile Strength (N/mm ²)	Upper Yield Point (N/mm ²)	Elongation at rupture (%)
Dead Mild Steel	405	235	26
Mild Steel	510	275	22
Medium Carbon Steel	640	335	16

3.1.1 Preparation of Samples for Corrosion Studies

The samples used for general corrosion studies were machined to cylindrical rods of diameter 6mm and length 30mm as shown in figure 3 below.



Fig 3: Test piece used for corrosion studies.

Each of the Dead mild steel, mild steel and medium carbon steel samples were divided into four groups which were then polished using the "0", "1", "2" and "3" in order to get the required surface roughness of the samples.

The samples were then cleaned in a mixture of water and acetone to remove any adherent grease and dirt. This was followed by cleaning and drying of the samples, which were later placed in a desiccator in readiness for the experiment.

3.1.2 Corrosion Environment

The corroding medium used for this study was 3% Sodium Chloride (NaCl) solution which was prepared by mixing thoroughly in proportion 3 grams of NaCl to 100ml of distilled water.

The inhibitors used included Sodium Nitrate (NaNO_3), Sodium Nitrite (NaNO_2), Sodium Benzoate and Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$). The concentration of the inhibitor used in each case was 0.2%. While the temperature of the corroding medium as recorded from the temperature probe fluctuated between 28°C and 30°C .

3.2 Experimental Procedure

The experimental procedure adopted for this study is the total immersion test method. A sketch of the experimental set up is shown in fig 4 below.

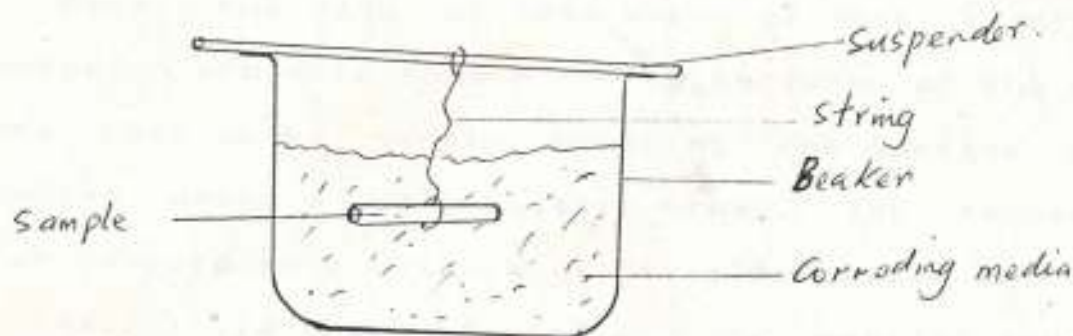


Fig 4: Experimental set up for Total Immersion Test.

200ml of the prepared 3% NaCl solution was poured into different beakers containing 0.2% of the nitrate, nitrite, benzoate and chromate inhibitors respectively. The weight of each sample under investigation was then taken, using an electronic weighing balance.

Dead mild steel samples polished with emery grade 0 were placed in four different beakers, each containing 3% NaCl and one of the four inhibitors mentioned above. The electrochemical potential of the corroding media containing these samples was also noted using the ELE digital temperature/pH/potential meter. This procedure was repeated after every two days interval for twelve days. Dead mild steel samples polished with emery grades 1, 2 and 3 were also immersed in different beakers, each containing 3% NaCl solution and one of the four mentioned inhibitors.

The above procedure was repeated for the mild steel and medium carbon steel samples. The results are presented in graphical form.

3.2.1 Test To Determine Weight Loss

After two days of immersion of each sample, the corrosion products formed on the surface of the samples were removed by gently brushing the surface of the samples, using a soft plastic brush. The samples were then dipped in a mixture of distilled water and acetone to facilitate quick drying of the samples and avoid water-deposited films.

The samples were then weighed using an electronic weighing balance. This procedure was repeated for twelve days. The corrosion was estimated by weight loss per unit surface area of samples. Results of this test were plotted as graphs of variation of weight loss with time of immersion, variation of weight loss with surface roughness and variation of surface roughness of the samples with the Inhibition Efficiency of each of the four inhibitors used (as in figs 5 - 22 and 38 - 40).

3.2.2 Electrochemical Potential Measurement

After two days of immersion of each samples, the electrochemical potential of each of the corroding media was noted, using the ELE digital temperature/ pH/potential meter equipped with a reference platinum electrode. This procedure is repeated after every two days interval for twelve days. Results from this test are shown in figures 23 - 37.

3.2.3 Determination of Inhibition Efficiency

The inhibition efficiency was obtained using datum from the weight loss test by application of the formula suggested by Antropov (1977)

$$I.E. = \frac{A - B}{A} \times 100 \%$$

Where A = Weight loss of sample without the use of
an inhibitor and

B = Weight loss when the inhibitors are used.

For the purpose of this study, the weight loss used
(values of B) was the total weight loss of each of the
samples per surface area in 12 days.

CHAPTER FOUR

4.0 OBSERVATIONS, RESULTS AND DISCUSSIONS

4.1 OBSERVATIONS

Few hours after immersion of all the samples in the various corroding media, bubbles of gases (supposed to be hydrogen gas), were observed to evolve from the samples, at varying degree. Particularly, the evolution of the gas bubbles in samples inhibited with sodium dichromate, and nitrite were very pronounced while the evolution of gas on samples inhibited with sodium benzoate and nitrate was negligible and hardly visible. This is a pointer to the fact that in carbon steel (immersed in 3% NaCl) inhibited by sodium dichromate and nitrite, hydrogen evolution is the predominant cathodic reaction where as, in other solutions oxygen reduction is predominant, although hydrogen evolution to a lesser extent still occurs as an additional cathodic reaction.

It was also observed that the surface roughness of the samples had little effect on the extent of hydrogen gas evolution. After about the sixth day of immersion, the extent of evolution of the gas bubbles was markedly reduced. This coupled with the fact that the observed rate of corrosion was decreasing with time of immersion implied the formation of passive oxide films on the surface of the samples with time. The potential of the samples were observed to be generally fluctuating with immersion time.

4.2 RESULT

4.2.1 Weight Loss Variation With Immersion Time

The variation of weight loss per unit surface area of Dead Mild Steel, Mild Steel and Medium Carbon Steel samples of various surface roughness with immersion time in 3% NaCl, without corrosion inhibitors are presented in figures 5, 6 and 7. Similarly, figures 8 - 10, 11 - 13, 14 - 16 and 17 - 19 shows the variation of weight loss per unit surface area of Dead Mild Steel, Mild Steel and Medium Carbon Steel of various surface roughness with immersion time in 3% NaCl using Sodium Nitrate, Nitrite, Chromate and Benzoate respectively as inhibitors.

4.2.2

Weight Loss Variation With Surface Roughness

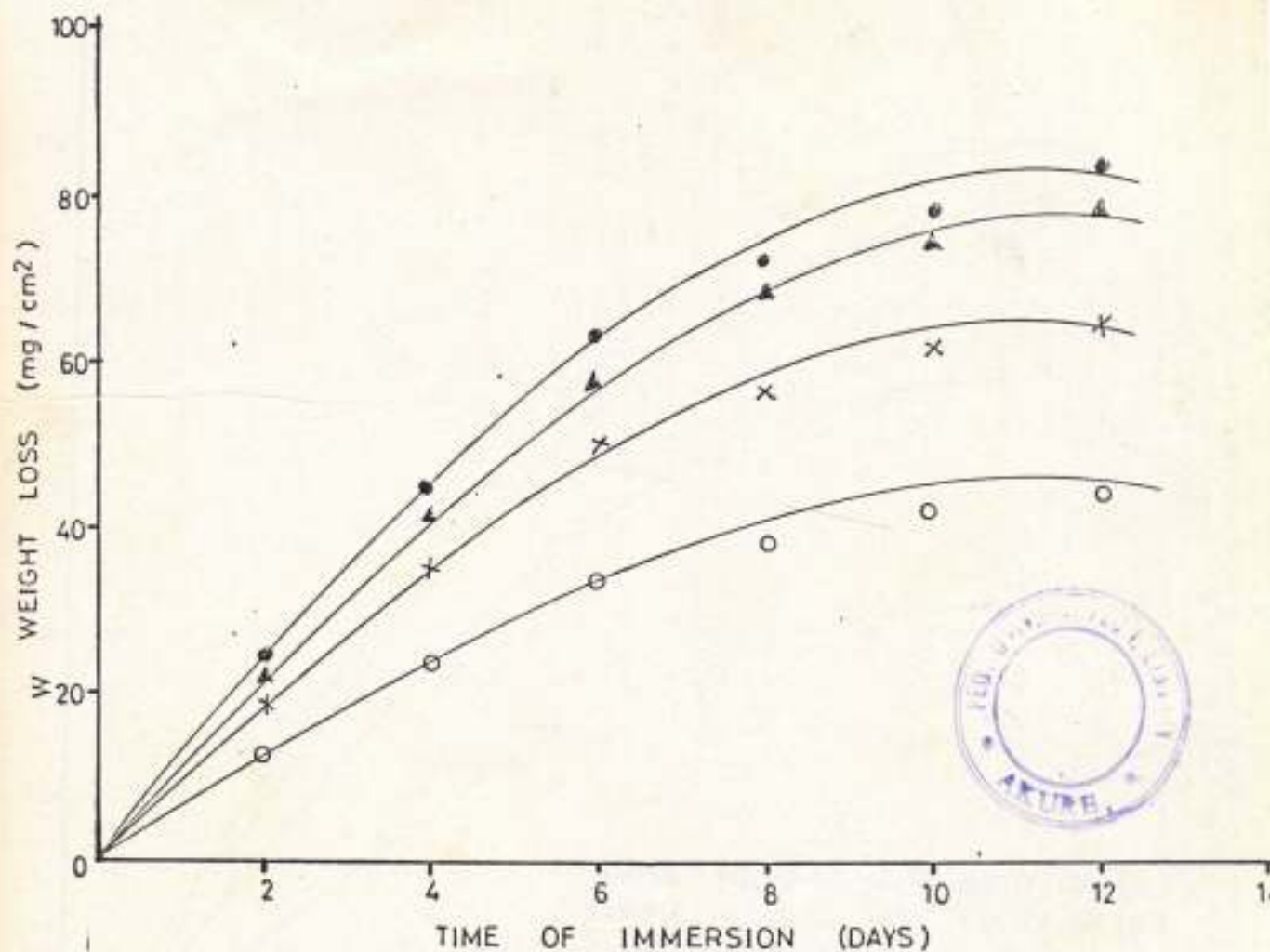
In this study, the surface roughness of a sample is assumed to correspond to the emery grade with which the samples was polished. In this regard therefore, figures 20, 21 and 22 present the effect of surface roughness on the corrosion (in weight loss per unit area) of Dead mild steel, mild steel and medium carbon steel respectively in 3% NaCl. The graphs consist of plots for samples in which corrosion process was inhibited by Sodium Nitrate, Nitrite, Dichromate, and Benzoate as well as for samples that are not inhibited.

4.2.3 Electrochemical Potential Test

The potential variation of Dead mild steel, mild steel and medium carbon steel samples with immersion time in 3% NaCl, without the use of an inhibitor, and when Sodium Nitrate, Nitrite, Dichromate and Benzoate inhibitors are used respectively (for samples of various surface roughness) are presented in figures, 23 - 25, 26 - 28, 29 - 31, 32 - 34 and 35 - 37.

4.2.4 Surface Roughness Variation With Inhibition Efficiency

The effect of surface roughness of Dead mild steel, mild steel and medium carbon steel samples on the inhibition efficiencies of Sodium Nitrite, Nitrate, Dichromate and Benzoate respectively are shown in figures 38, 39 and 40.



KEY

- — SAMPLE POLISHED WITH EMERY GRADE 1
- ▲ — SAMPLE POLISHED WITH EMERY GRADE 2
- X — SAMPLE POLISHED WITH EMERY GRADE 3
- — SAMPLE POLISHED WITH EMERY GRADE 4

FIG. 5: VARIATION OF WEIGHT LOSS OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, WITHOUT USING AN INHIBITOR.

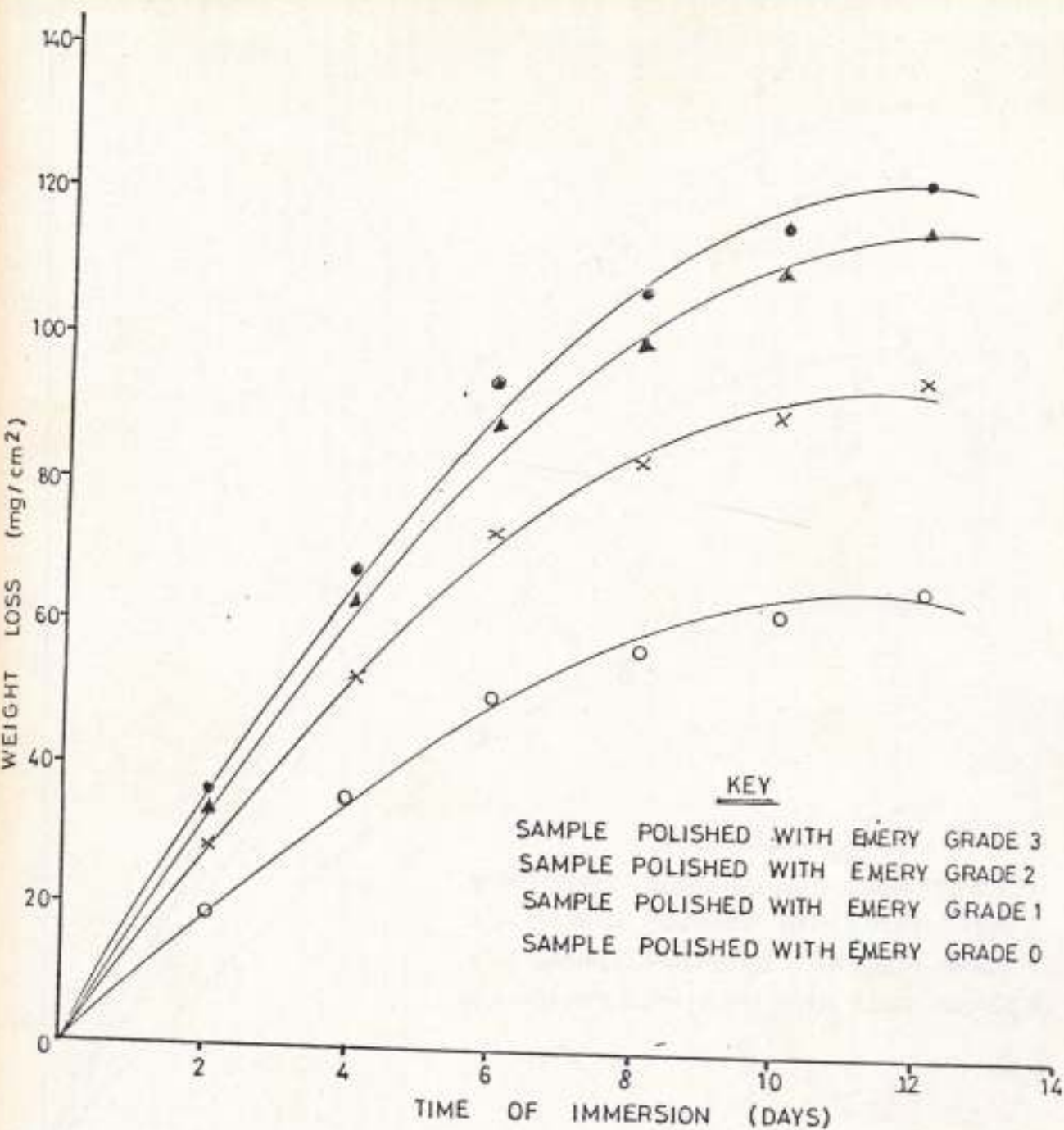


FIG. 6: VARIATION OF WEIGHT LOSS OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, WITHOUT USING AN INHIBITOR.

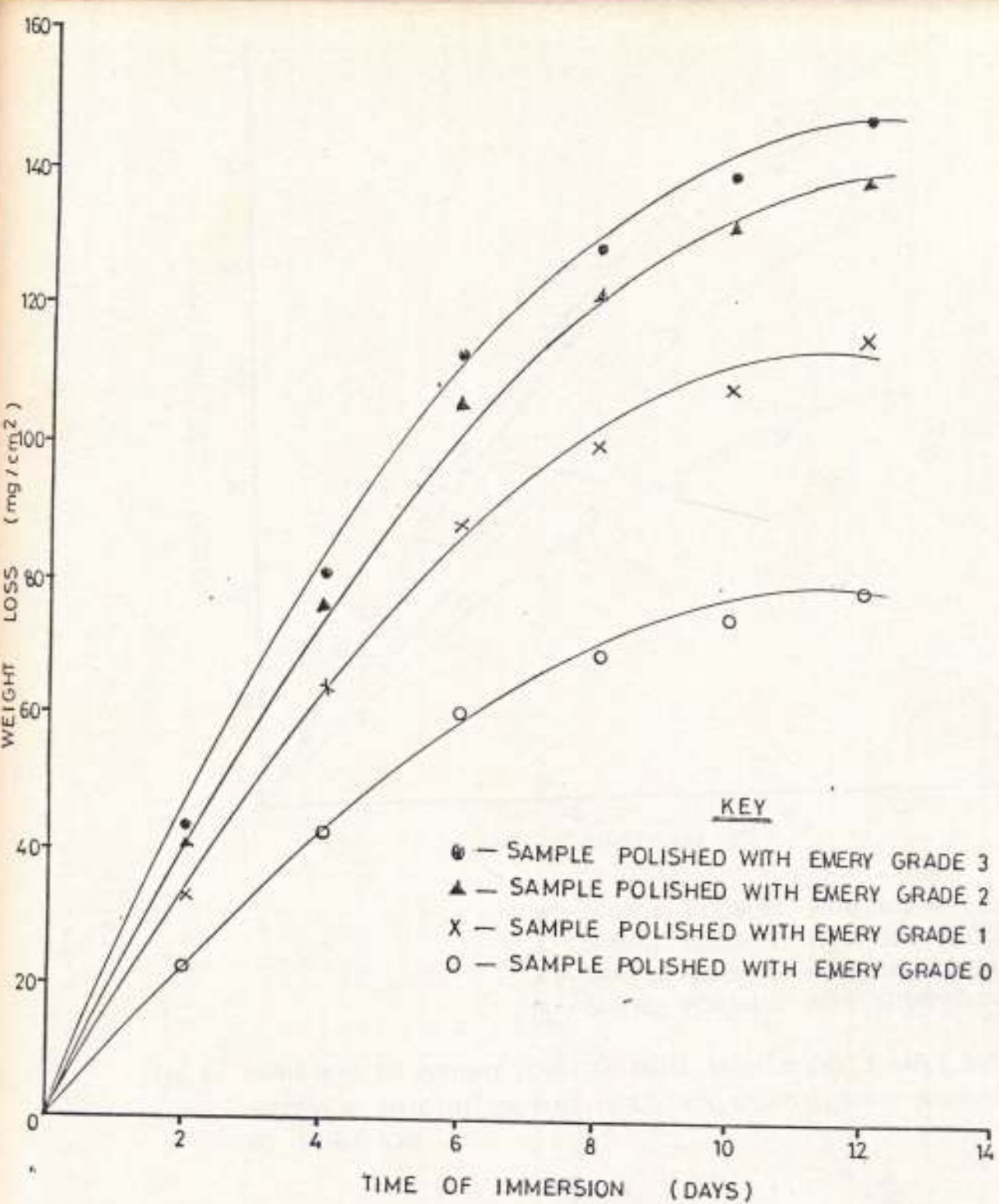


FIG. 7: VARIATION OF WEIGHT LOSS OF MEDIUM CARBON STEEL WITH IMMERSION TIME IN 3% NaCl, WITH USING AN INHIBITOR :

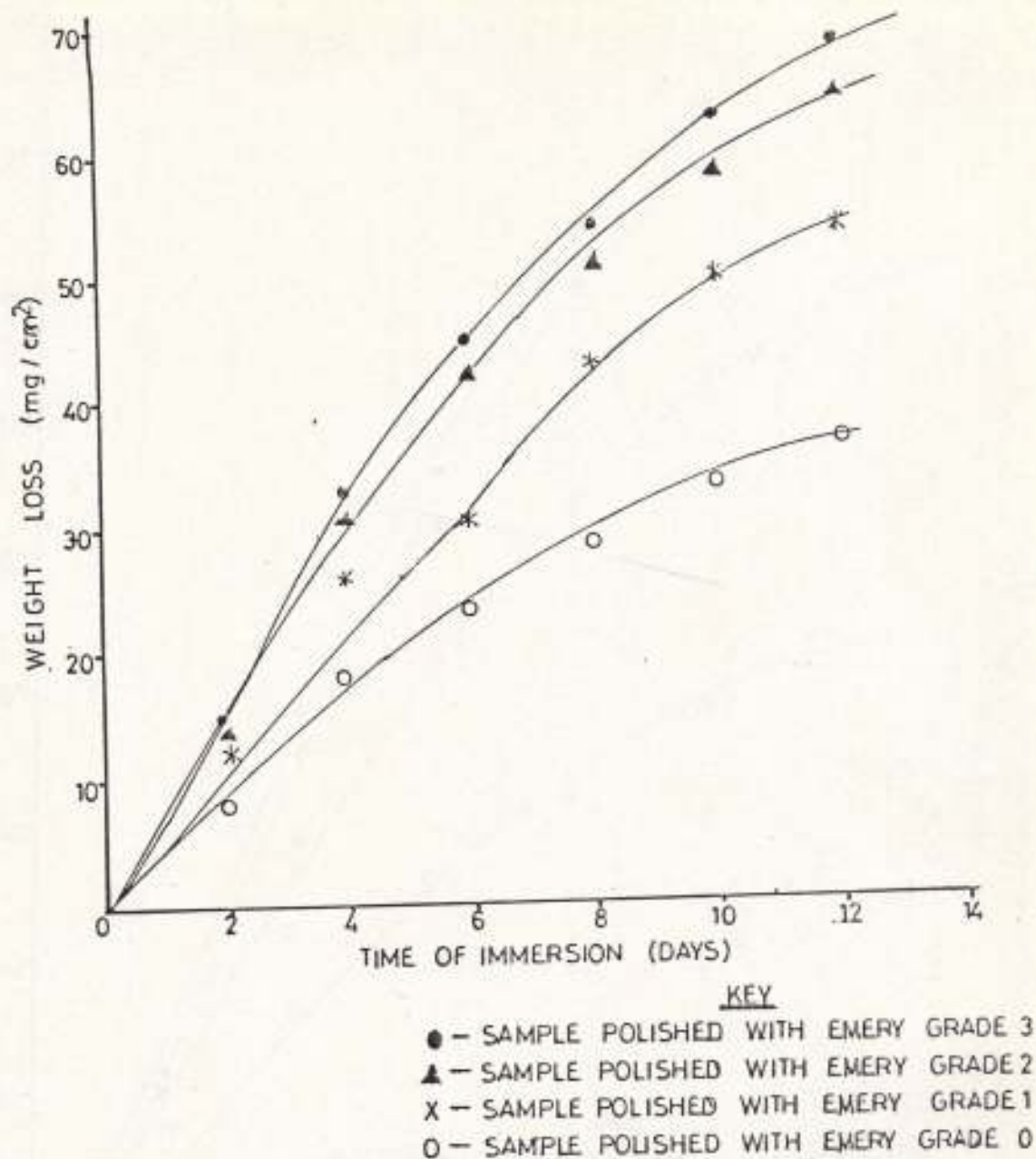


FIG. 8: VARIATION OF WEIGHT LOSS OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRATE AS INHIBITOR.

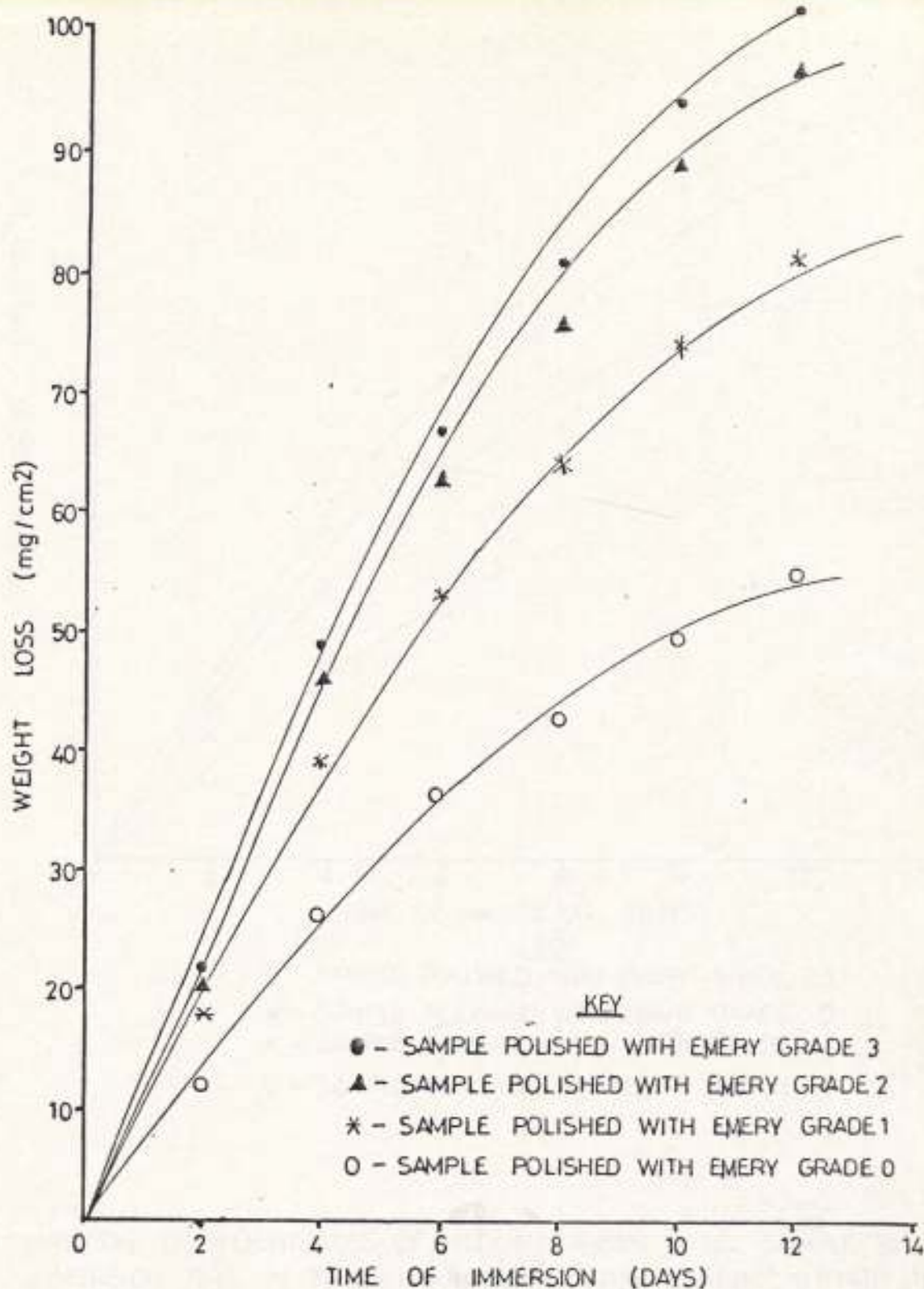


FIG.9: VARIATION OF WEIGHT LOSS OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRATE AS INHIBITOR.

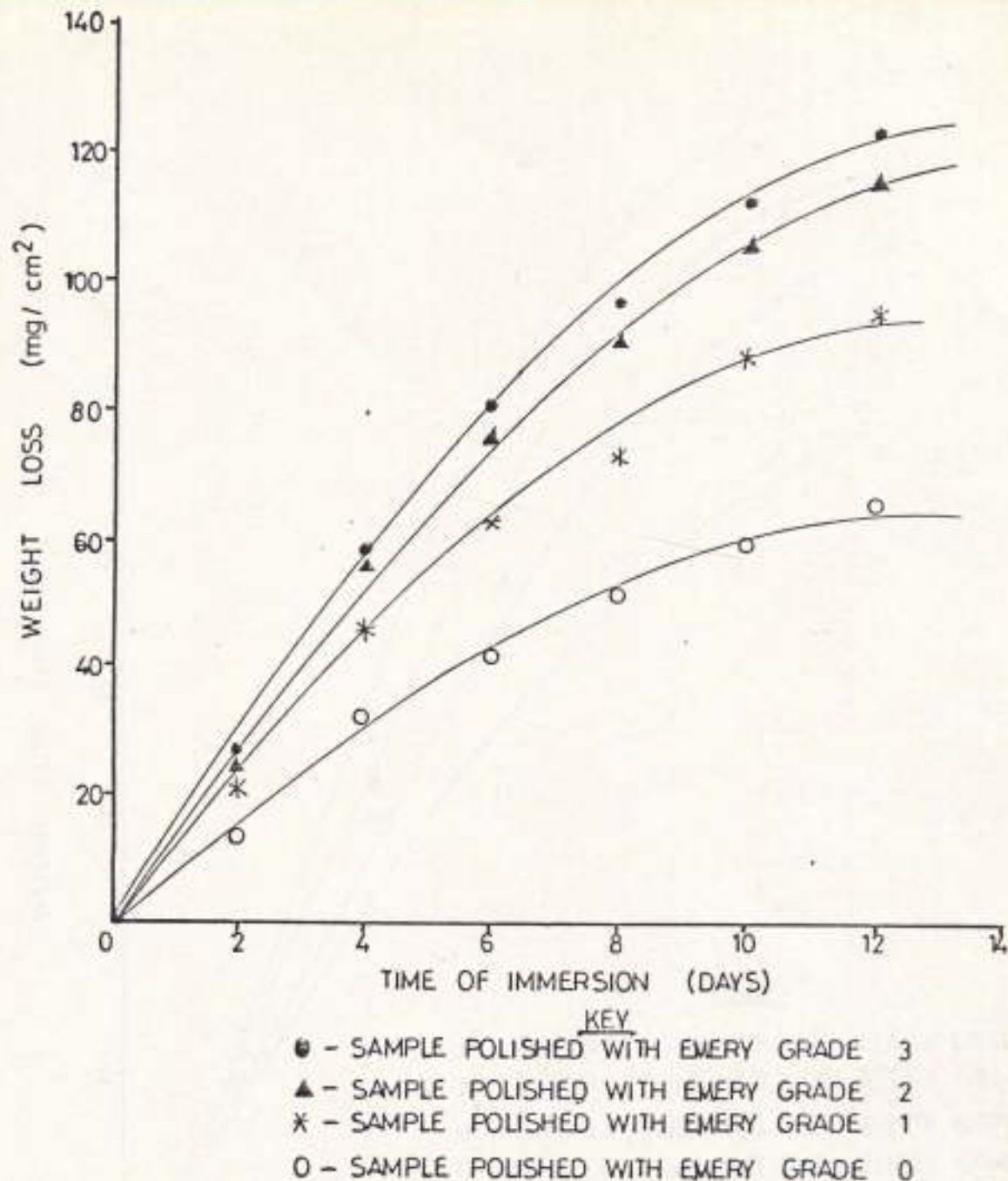


FIG.10: VARIATION OF WEIGHT LOSS OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRATE AS INHIBITOR.

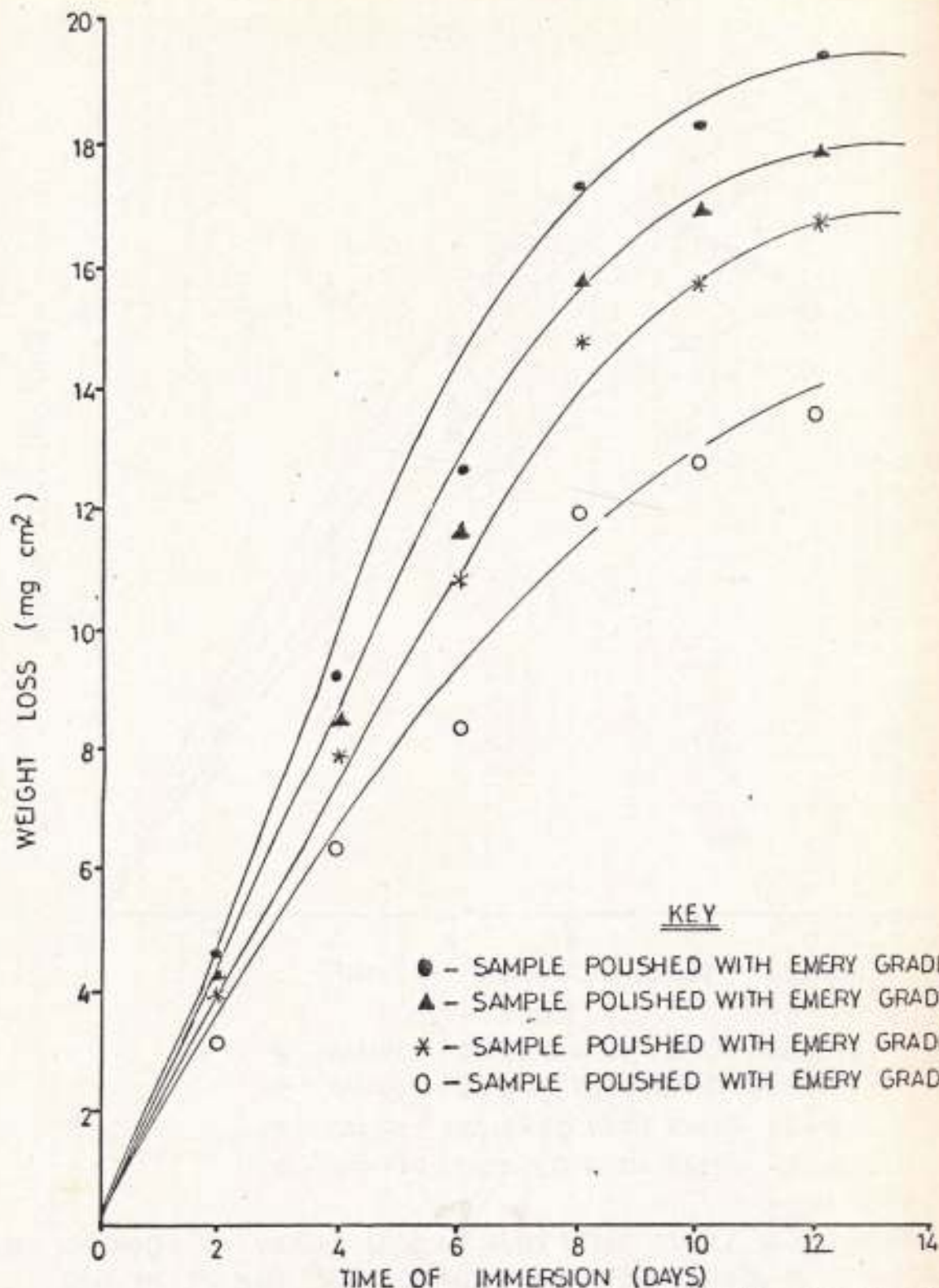
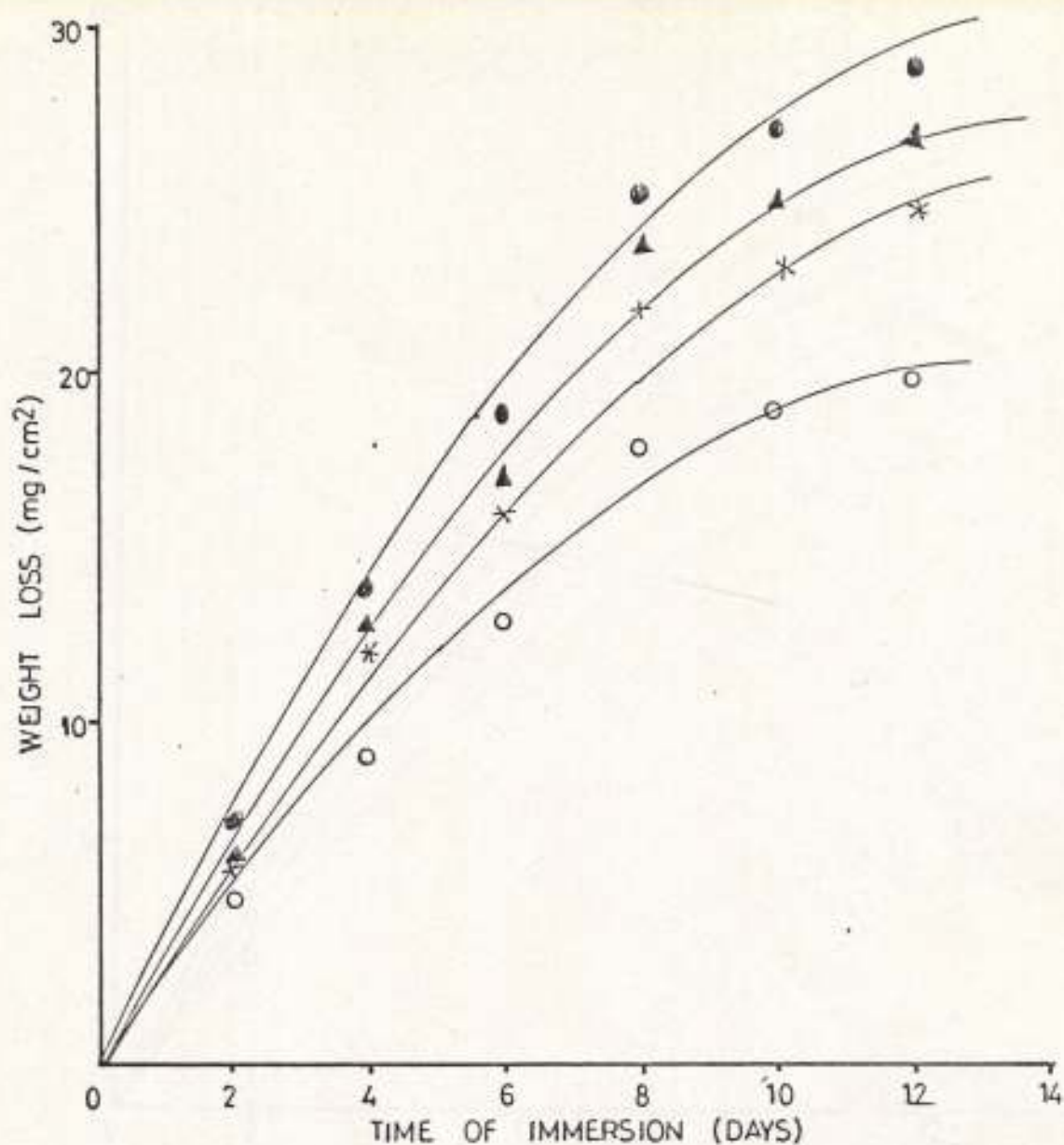


FIG. 11: VARIATION OF WEIGHT LOSS OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRITE AS INHIBITOR.



KEY

- - SAMPLE POLISHED WITH EMERY GRADE 3
- ▲ - SAMPLE POLISHED WITH EMERY GRADE 2
- * - SAMPLE POLISHED WITH EMERY GRADE 1
- - SAMPLE POLISHED WITH EMERY GRADE 0

FIG.12: VARIATION OF WEIGHT LOSS OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRITE AS INHIBITOR.

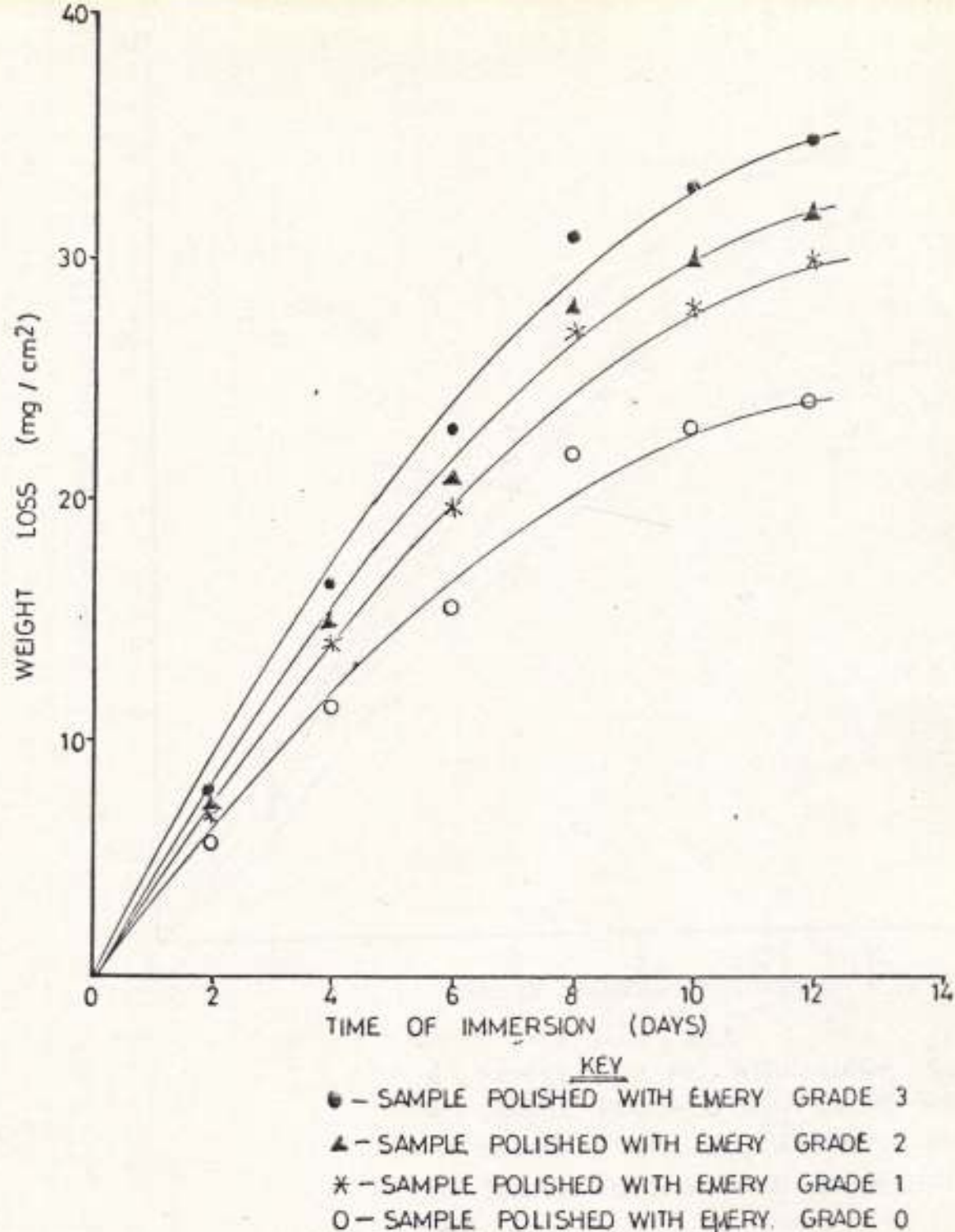
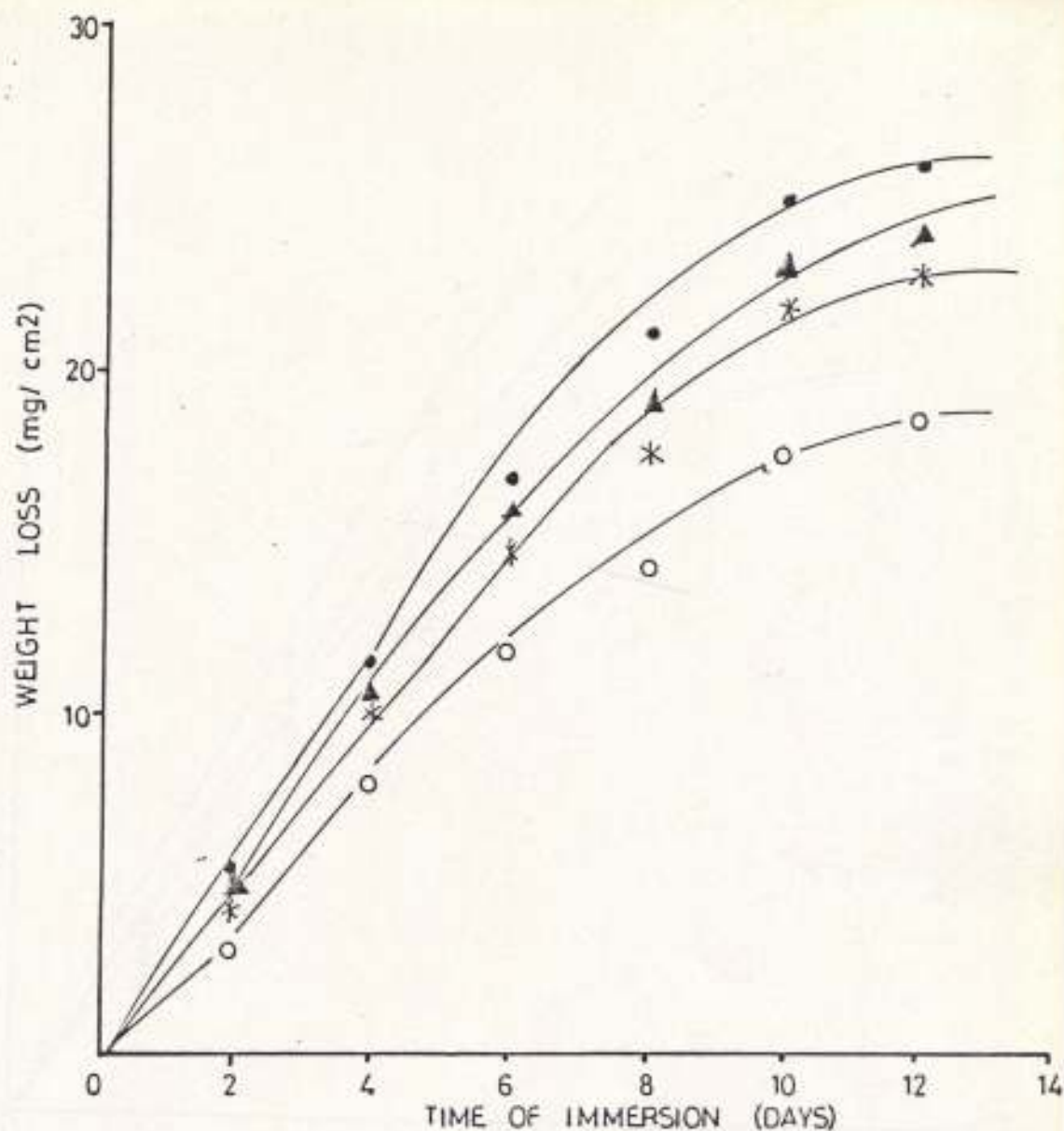


FIG.13: VARIATION OF WEIGHT LOSS OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRITE AS INHIBITOR.



KEY

- - SAMPLE POLISHED WITH EMERY GRADE 3
- ▲ - SAMPLE POLISHED WITH EMERY GRADE 2
- ✕ - SAMPLE POLISHED WITH EMERY GRADE 1
- - SAMPLE POLISHED WITH EMERY GRADE 0

FIG.14: VARIATION OF WEIGHT LOSS OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION USING SODIUM DICHROMATE AS INHIBITOR.

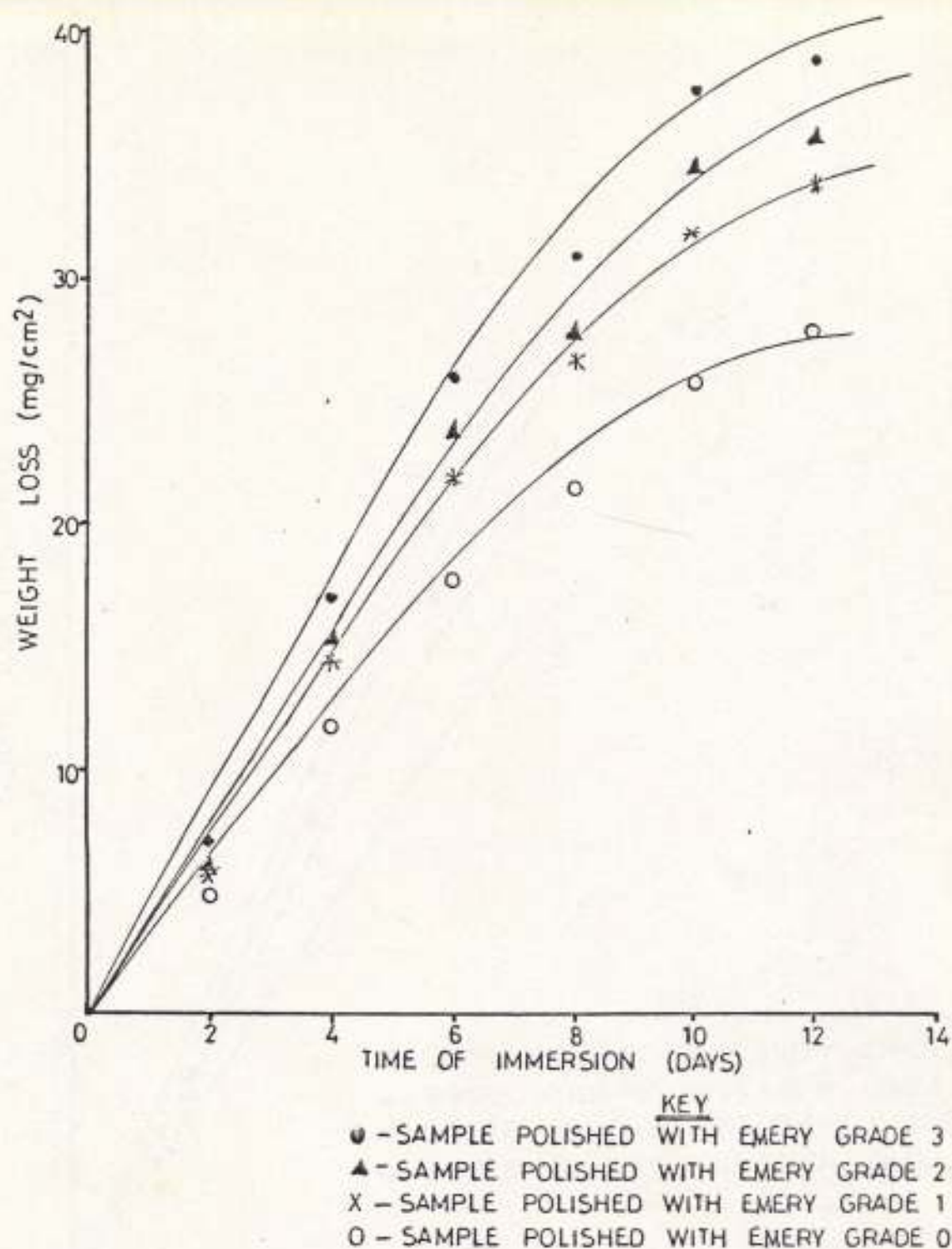


FIG. 15: VARIATION OF WEIGHT LOSS OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM DICHROMATE AS INHIBITOR.

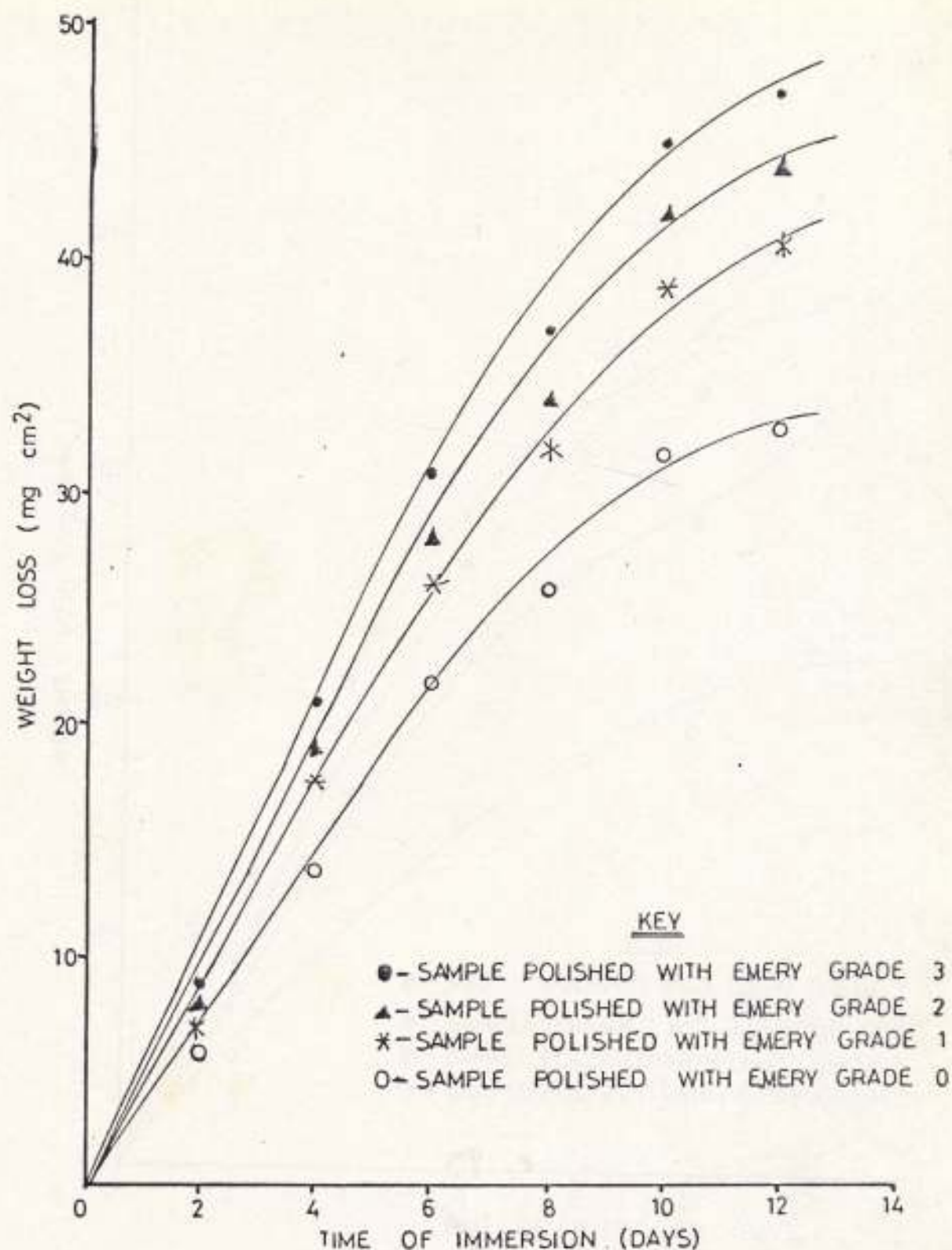


FIG. 16; VARIATION OF WEIGHT LOSS OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM DICHROMATE AS INHIBITOR.

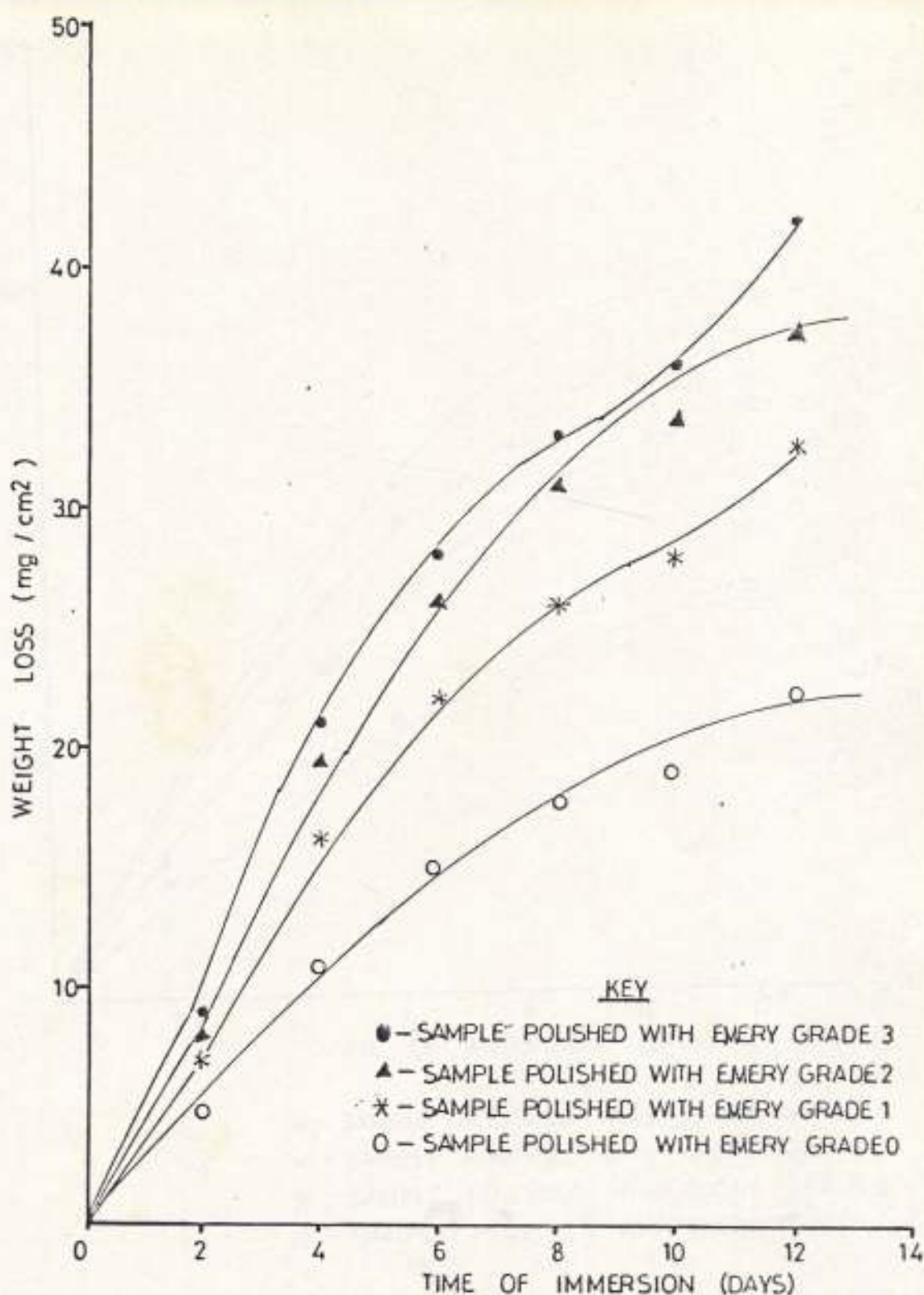


FIG.17: VARIATION OF WEIGHT LOSS OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM BENZOATE AS INHIBITOR.

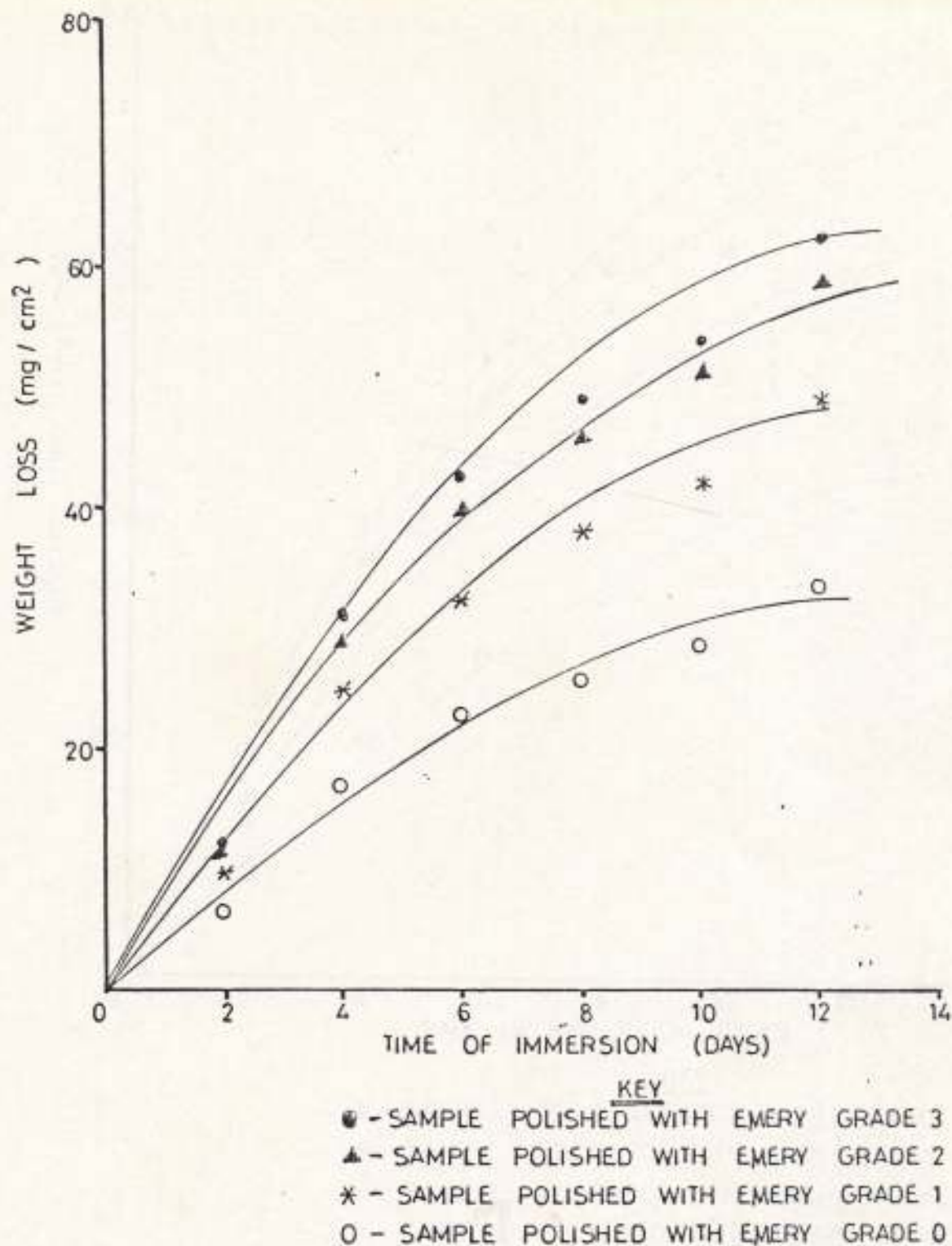
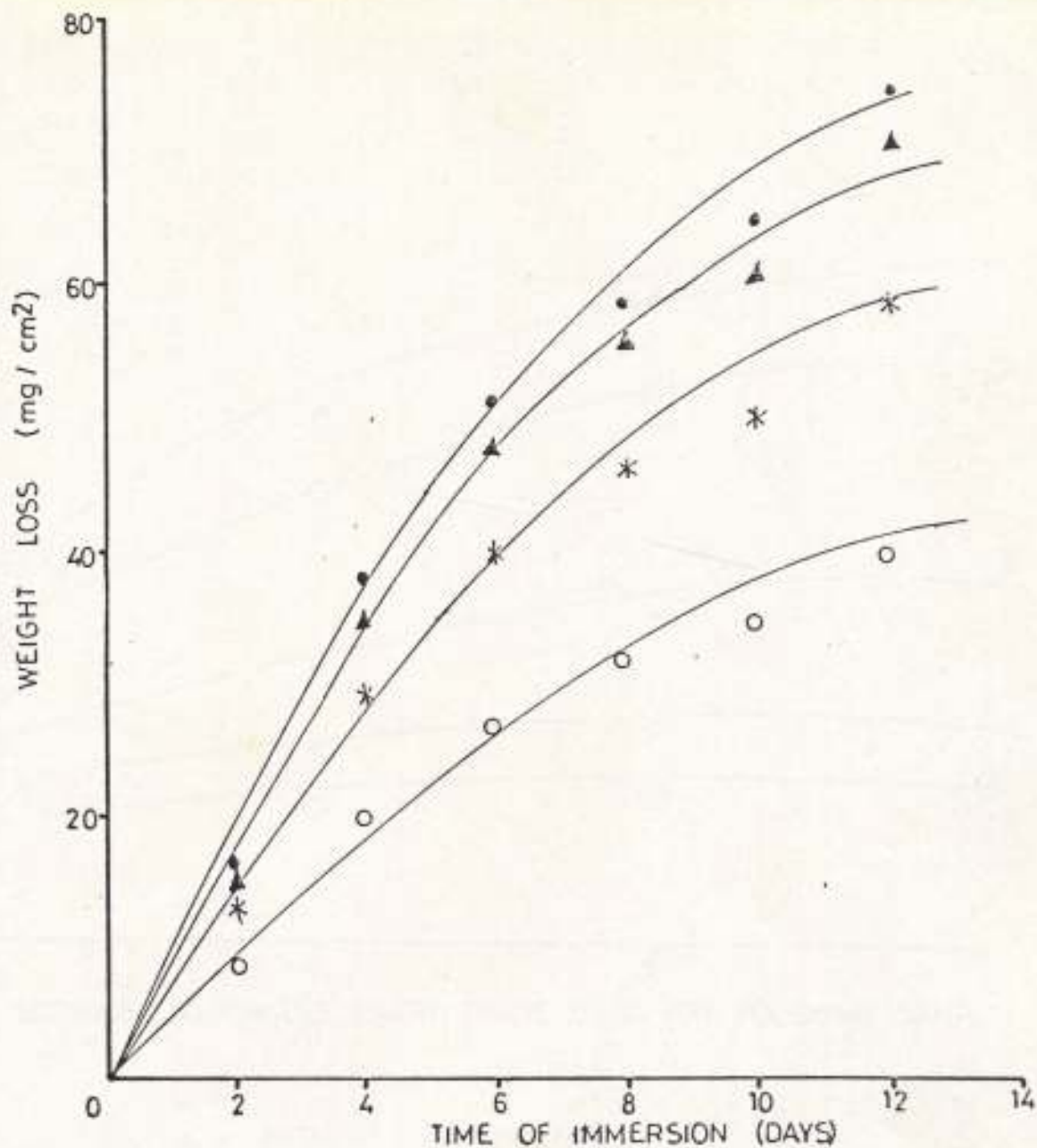


FIG.18: VARIATION OF WEIGHT LOSS OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION USING SODIUM BENZOATE AS INHIBITOR.



- KEY
- - SAMPLE POLISHED WITH EMERY GRADE 3
 - ▲ - SAMPLE POLISHED WITH EMERY GRADE 2
 - * - SAMPLE POLISHED WITH EMERY GRADE 1
 - - SAMPLE POLISHED WITH EMERY GRADE 0

FIG.19: VARIATION OF WEIGHT LOSS OF MEDIUM CARBON STEEL WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM BENZOATE AS INHIBITOR.

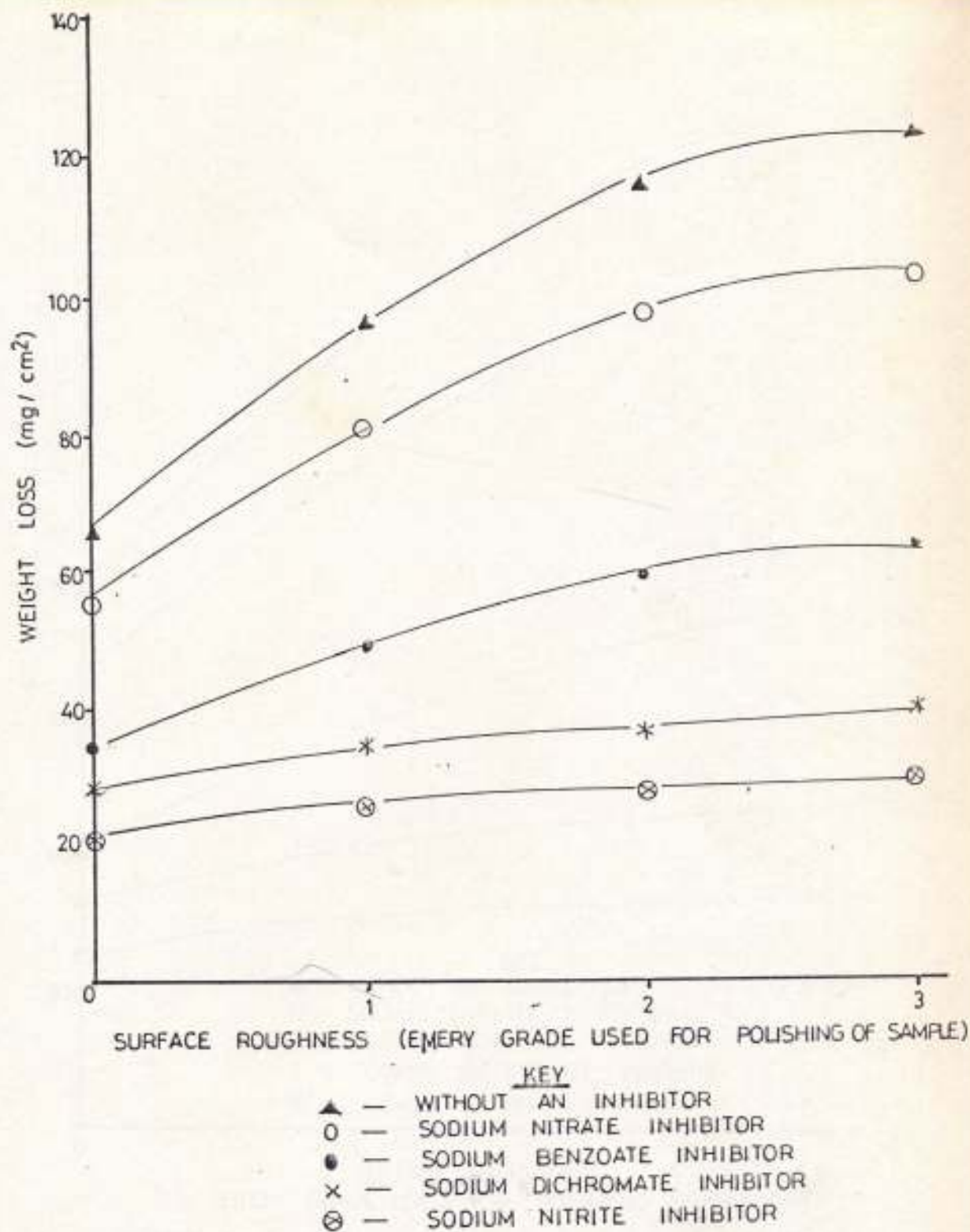


FIG.21: EFFECT OF SURFACE ROUGHNESS ON THE CORROSION OF MILD STEEL IN 3% NaCl SOLUTION.



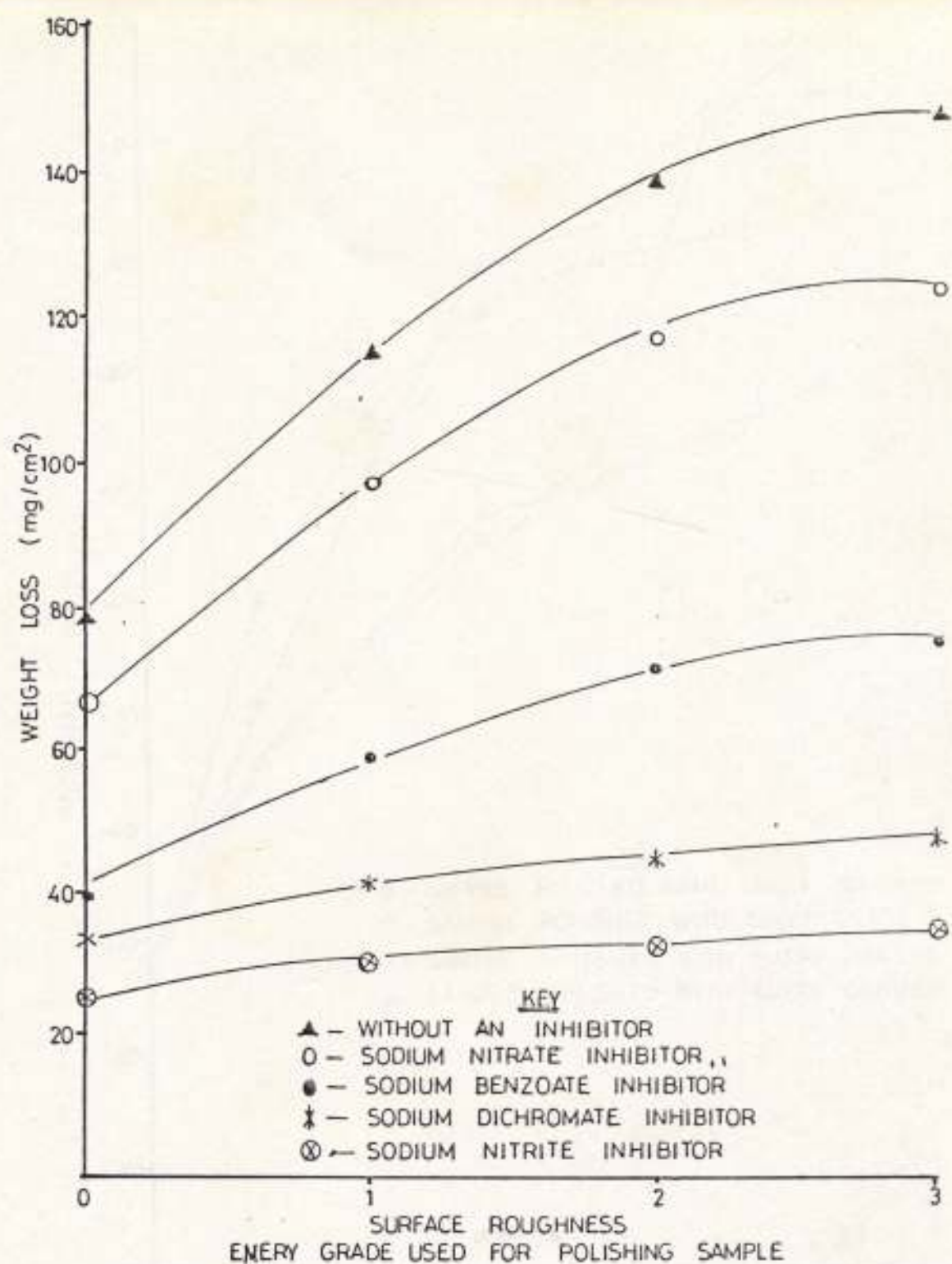


FIG 22 EFFECT OF SURFACE ROUGHNESS ON THE CORROSION OF MEDIUM CARBON STEEL IN 3% NaCl SOLUTION.

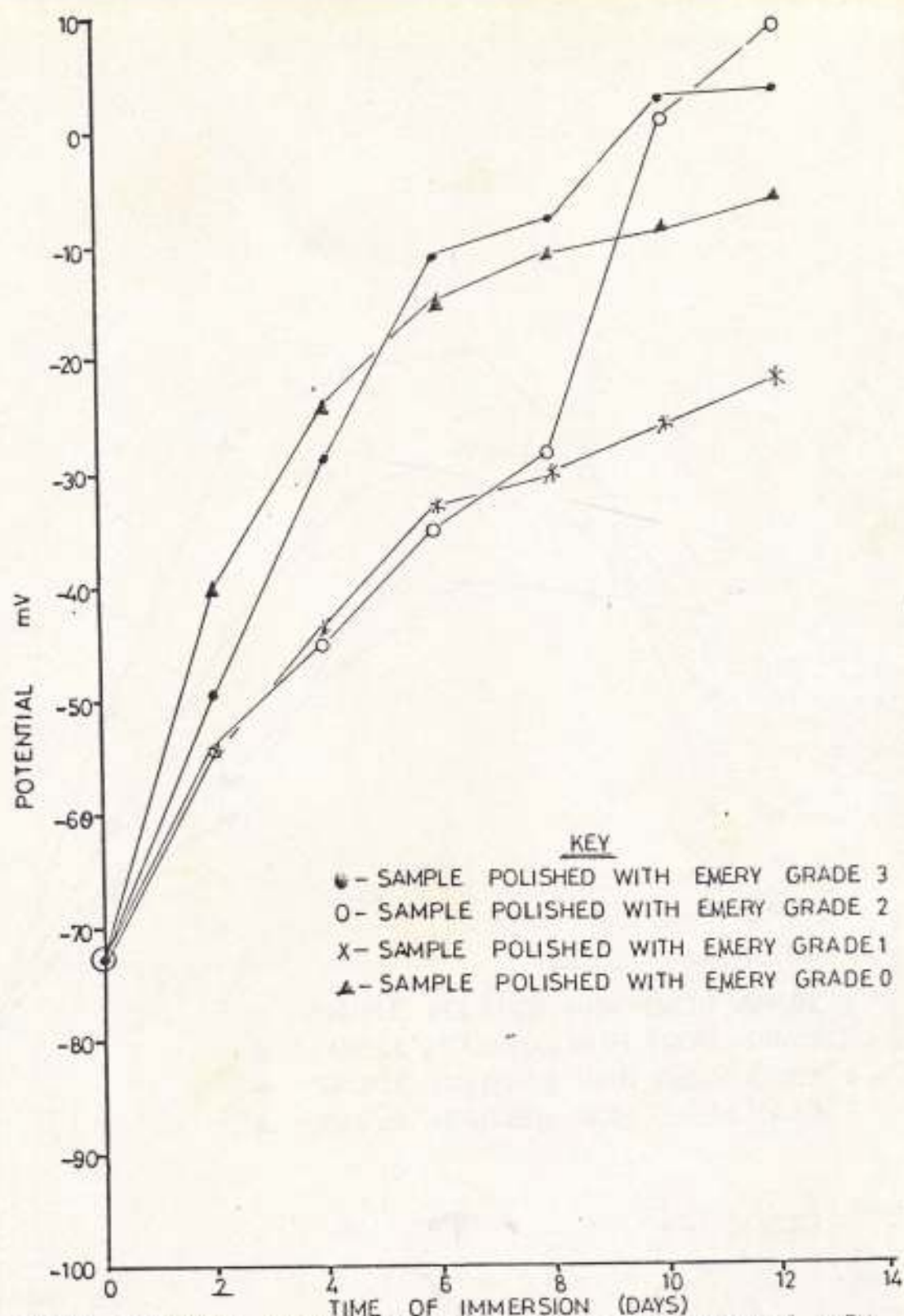


FIG.23. POTENTIAL VARIATION OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, WITHOUT USING AN INHIBITOR.

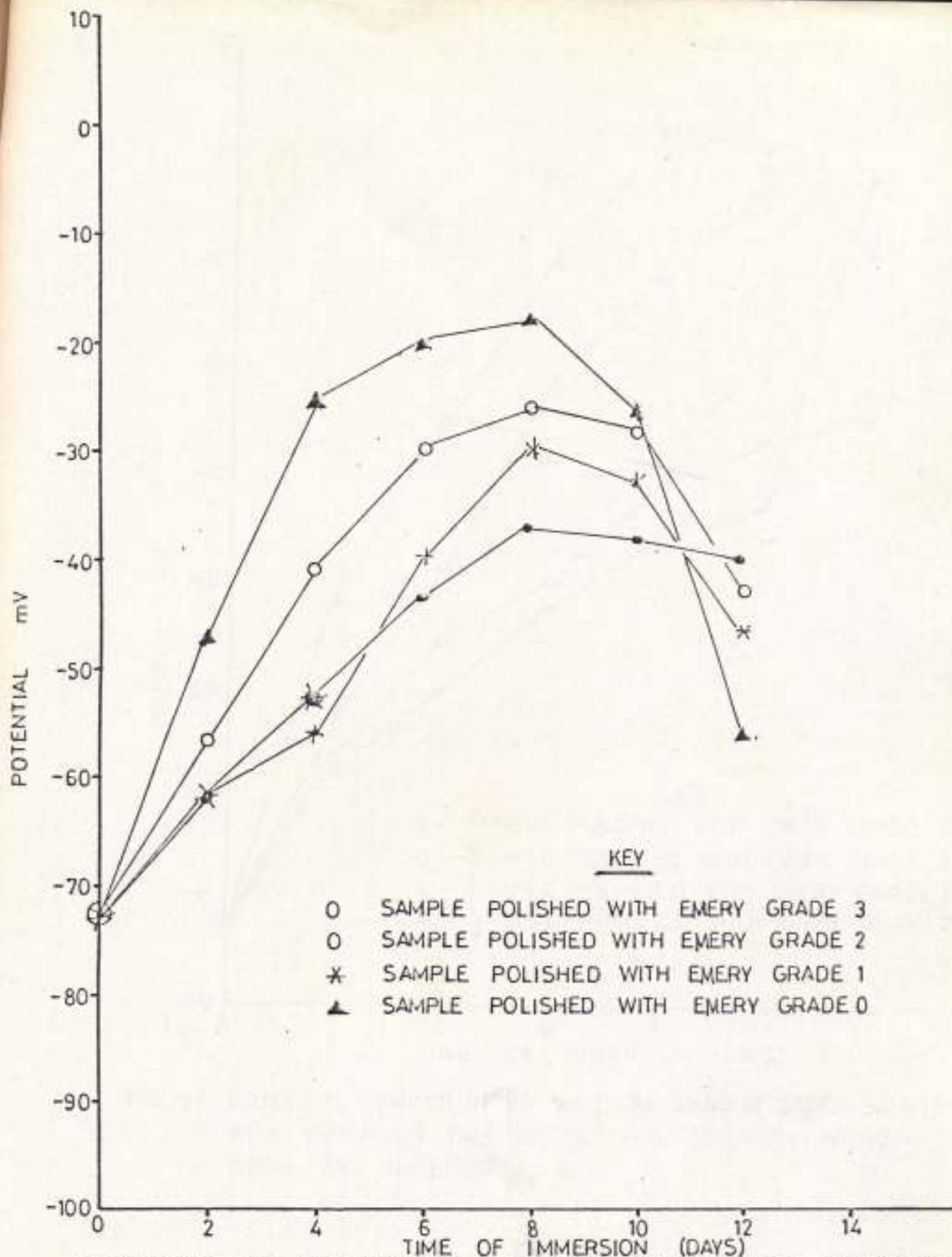


FIG.24: POTENTIAL VARIATION OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, WITHOUT USING AN INHIBITOR.

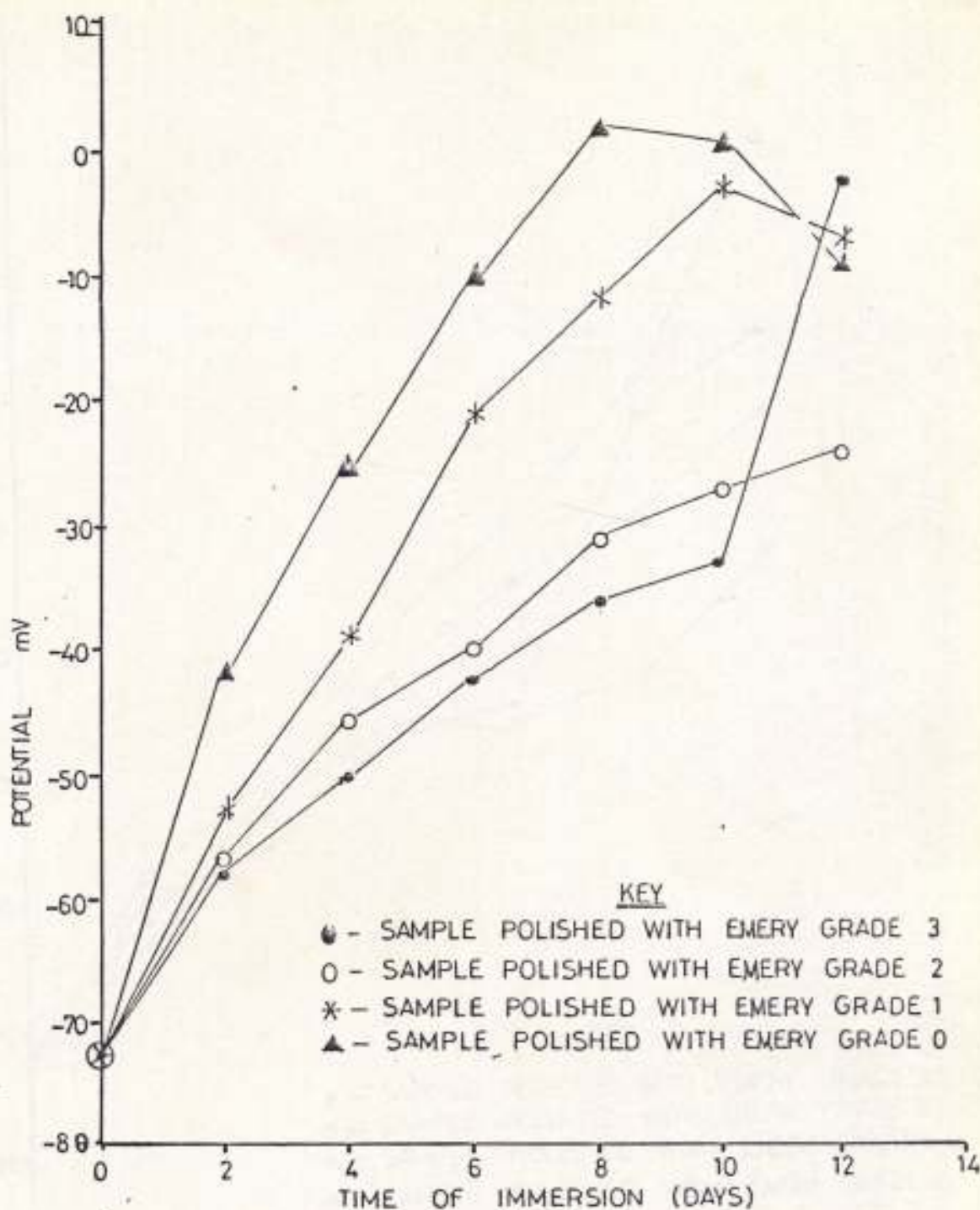


FIG.25: POTENTIAL VARIATION OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, WITHOUT USING AN INHIBITOR.

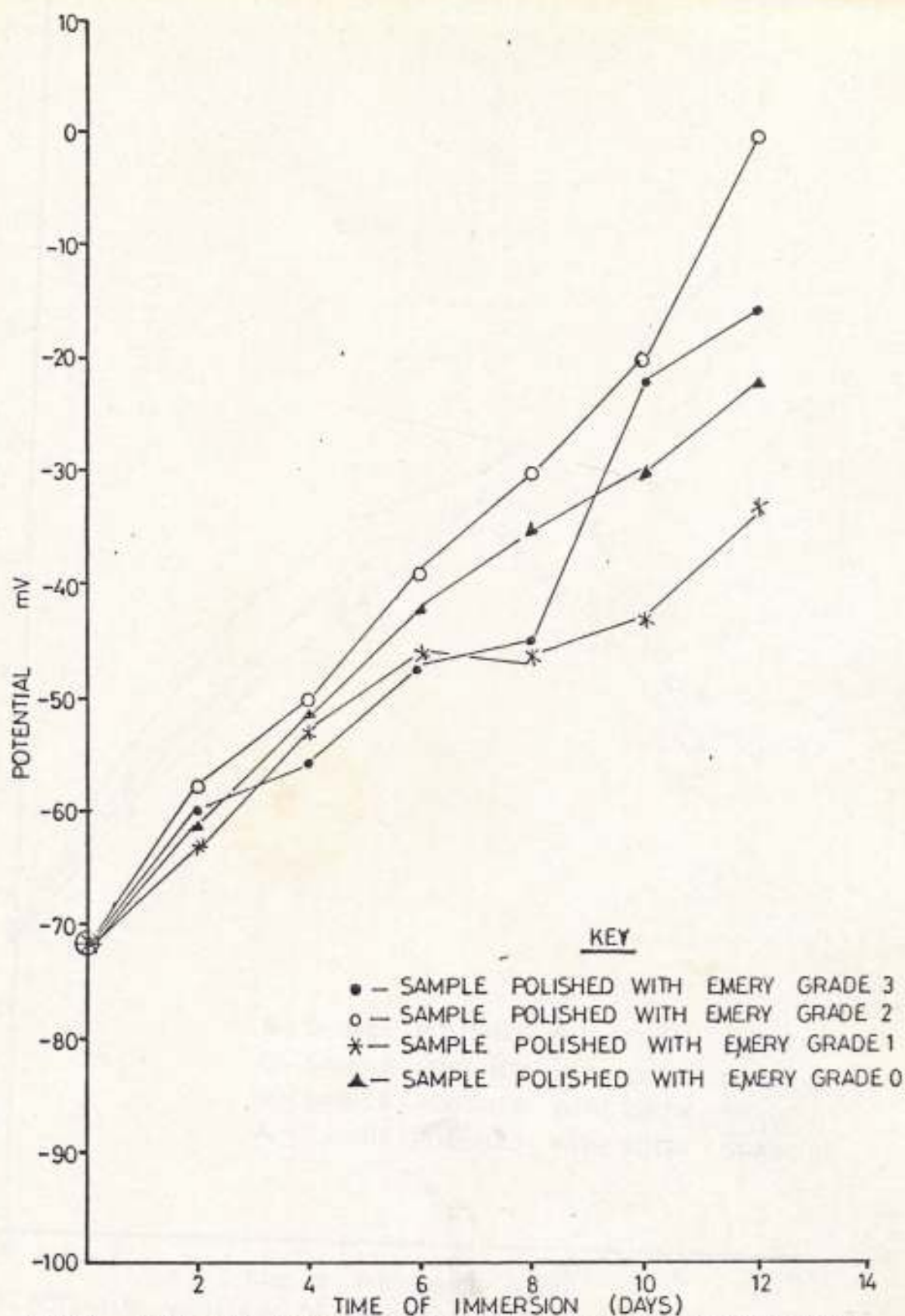


FIG 26 POTENTIAL VARIATION OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRATE AS INHIBITOR.

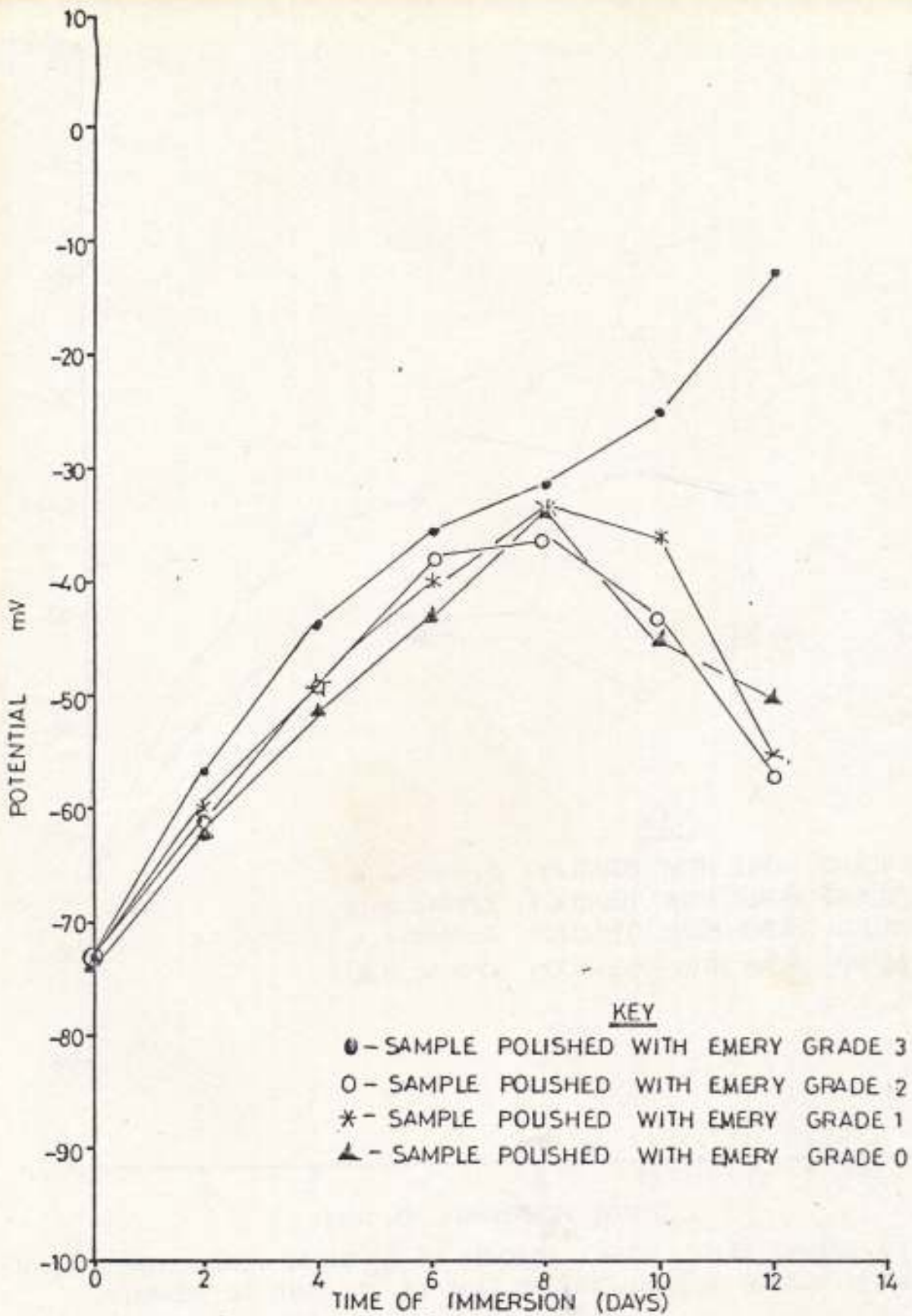


FIG.27: POTENTIAL VARIATION OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl, USING SODIUM NITRATE AS INHIBITOR.

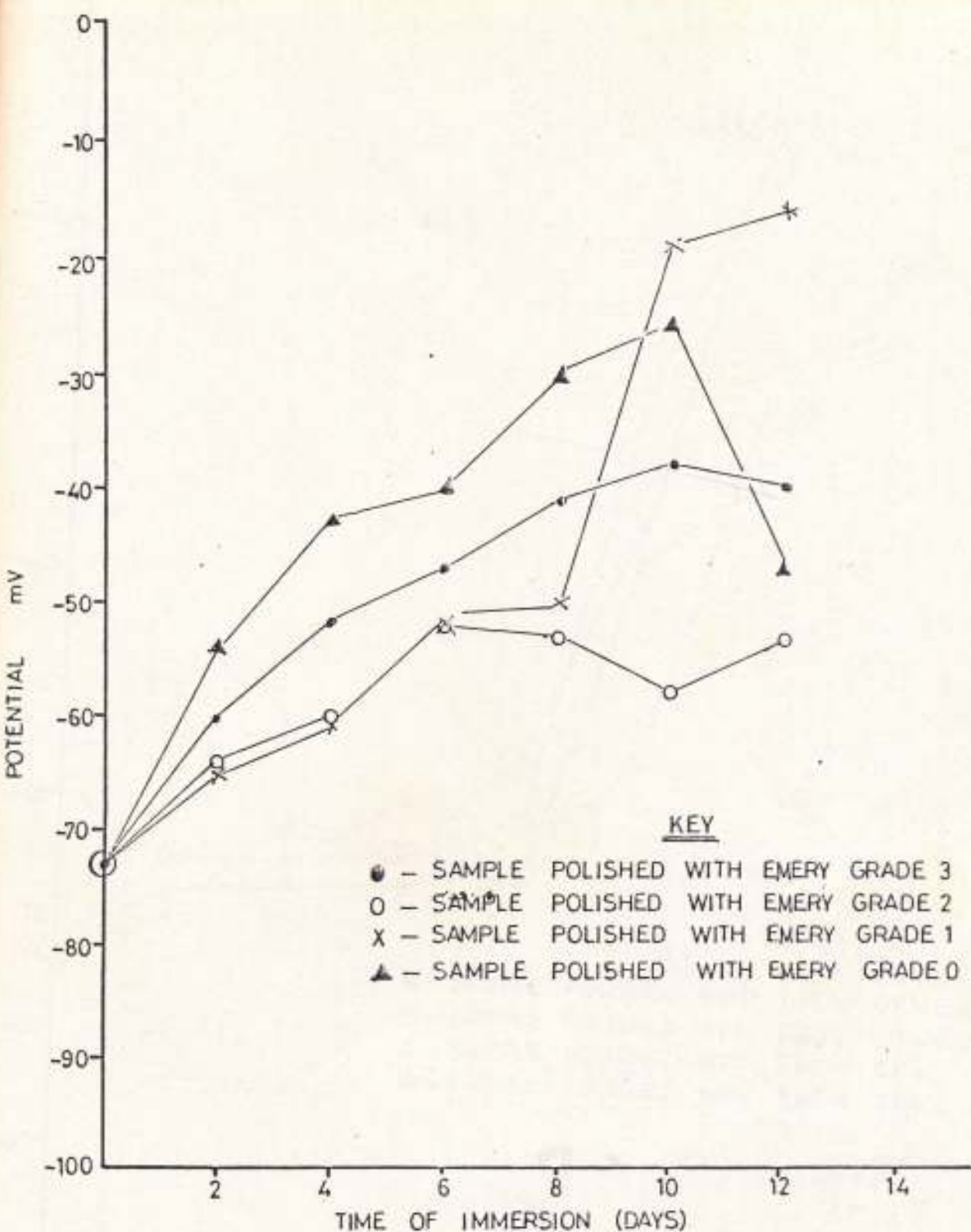


FIG. 28: POTENTIAL VARIATION OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRATE AS INHIBITOR.

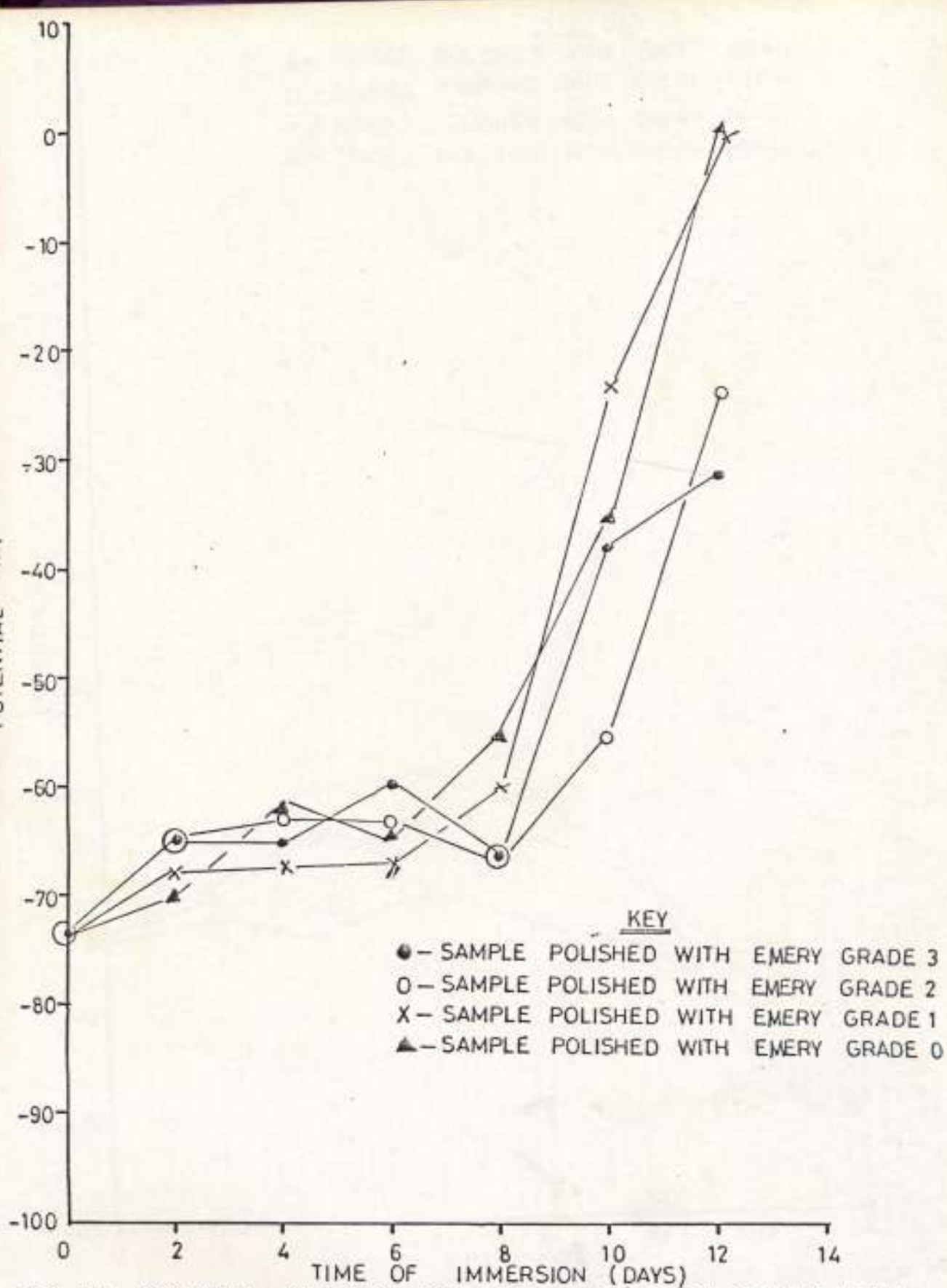


FIG. 29: POTENTIAL VARIATION OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRITE AS INHIBITOR.

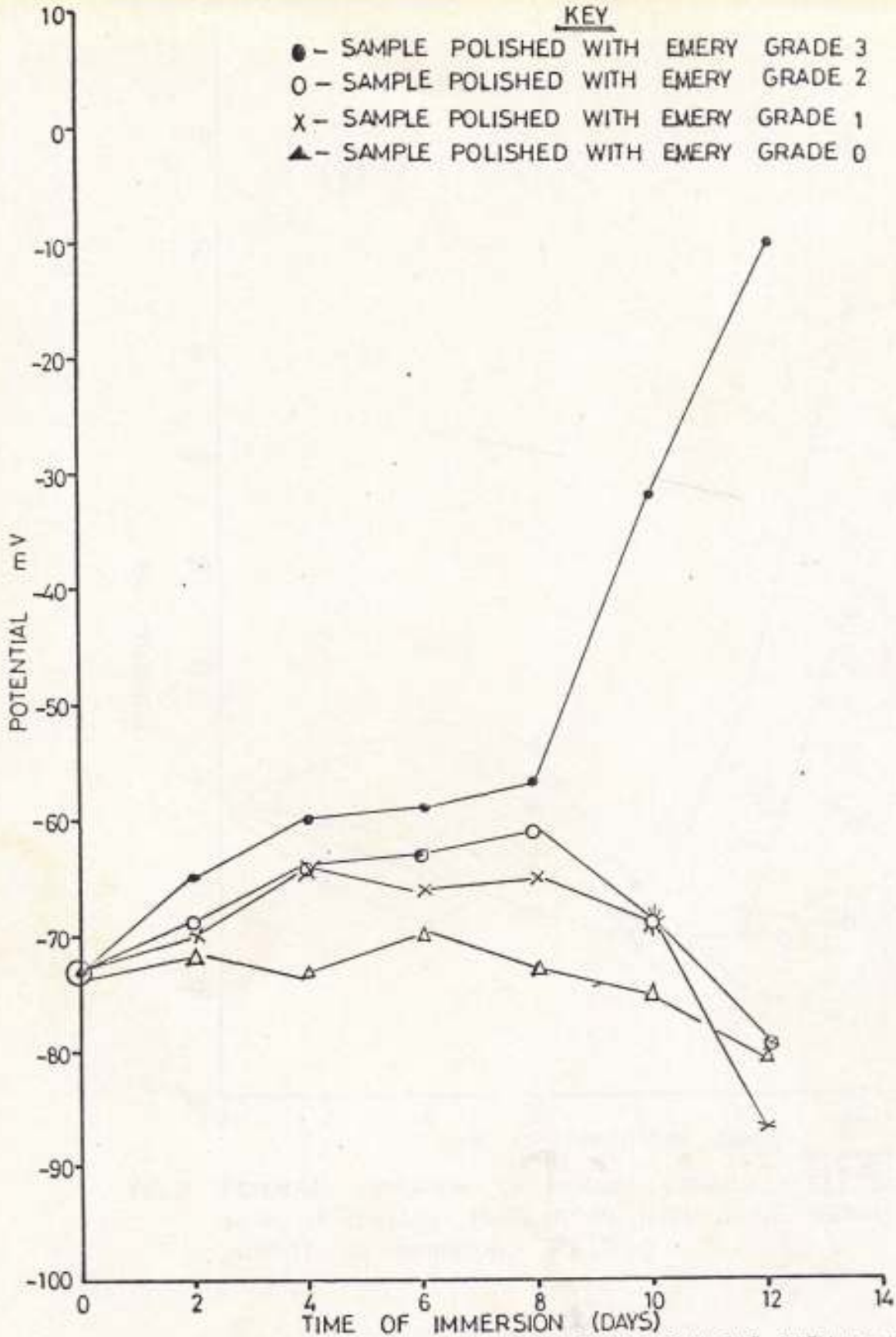


FIG. 30: POTENTIAL VARIATION OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM NITRITE AS INHIBITOR

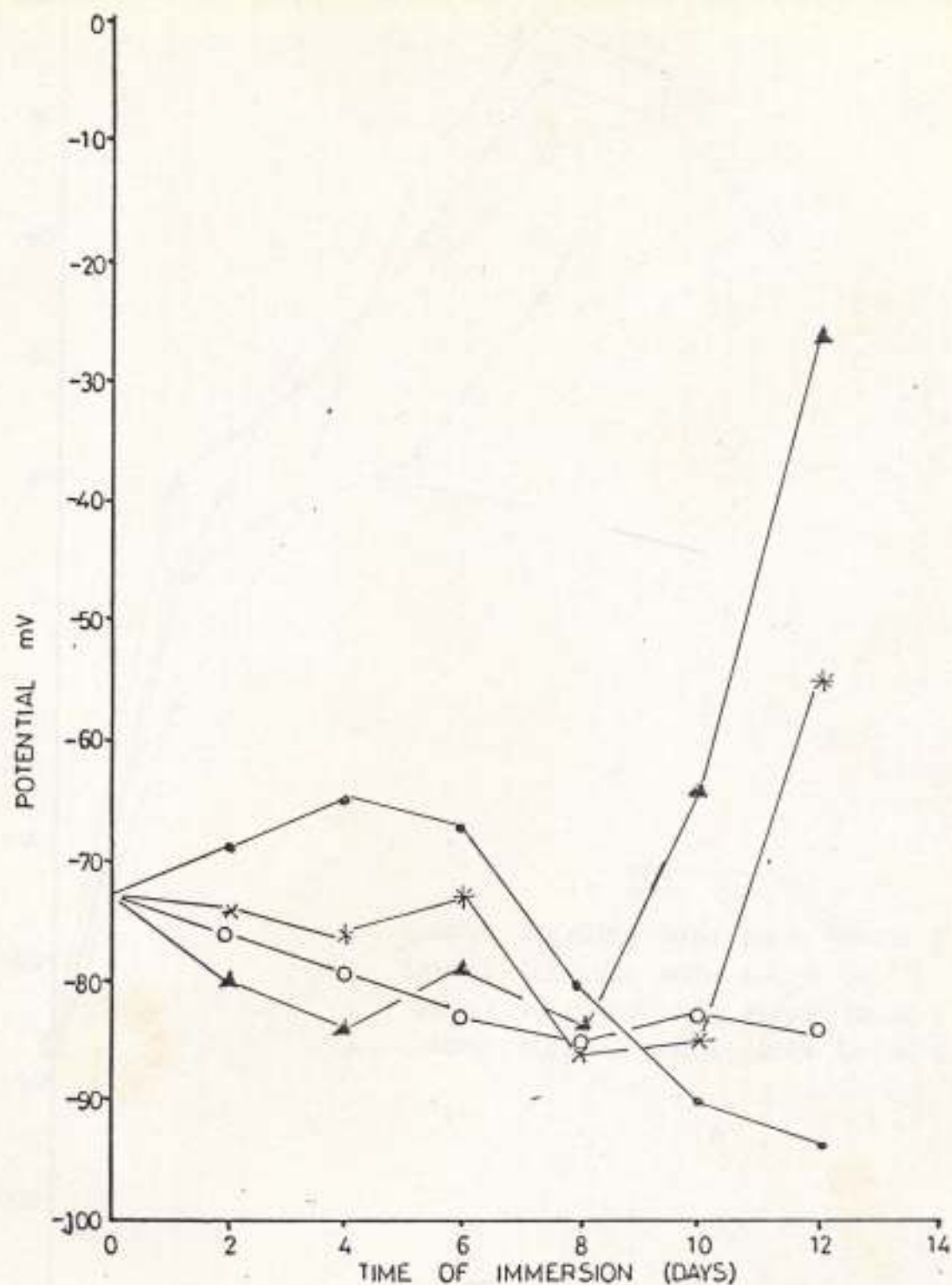


FIG.31: POTENTIAL VARIATION OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl, USING SODIUM NITRITE AS INHIBITOR.

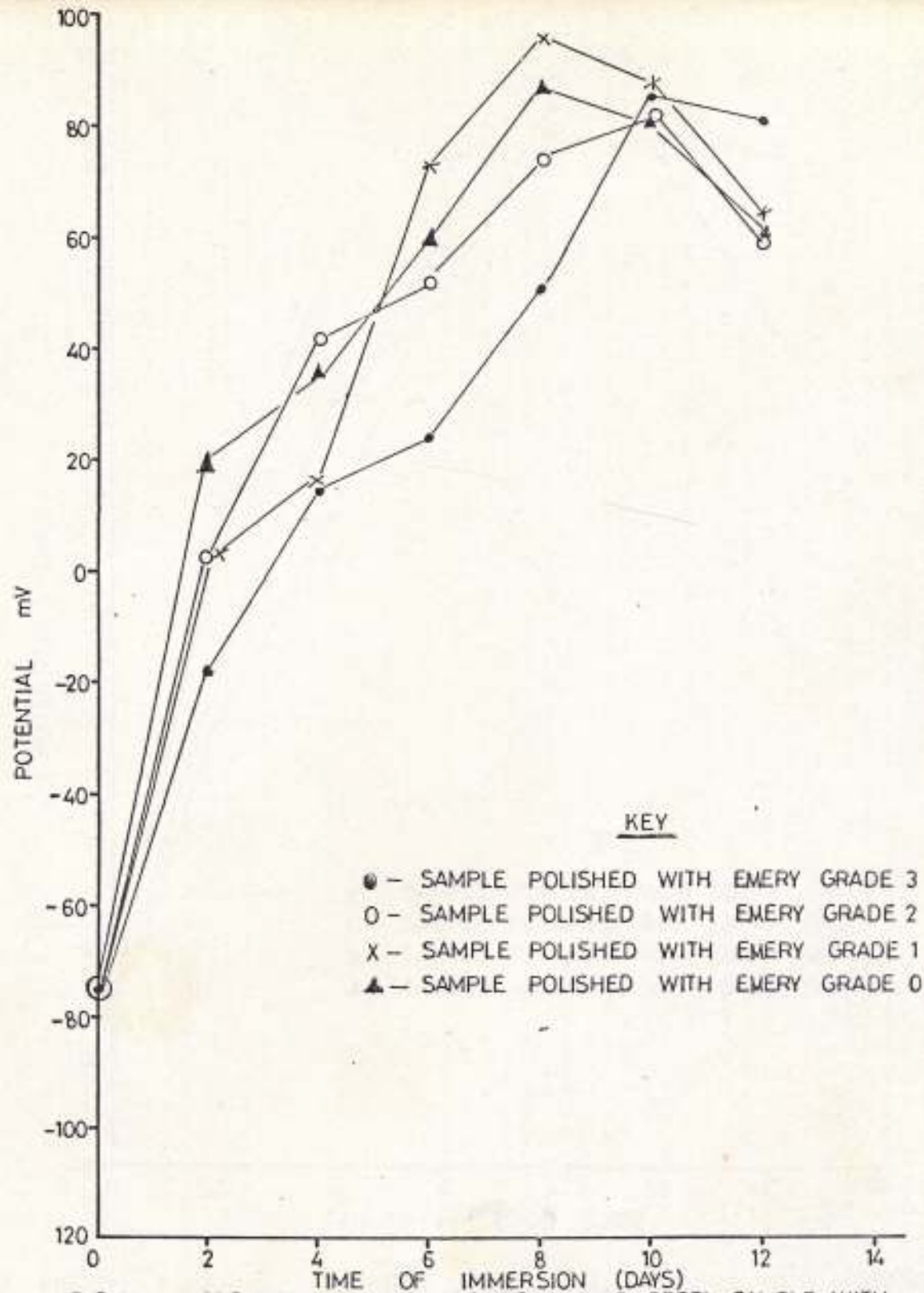


FIG 32 POTENTIAL VARIATION OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM DICHROMATE AS AN INHIBITOR.

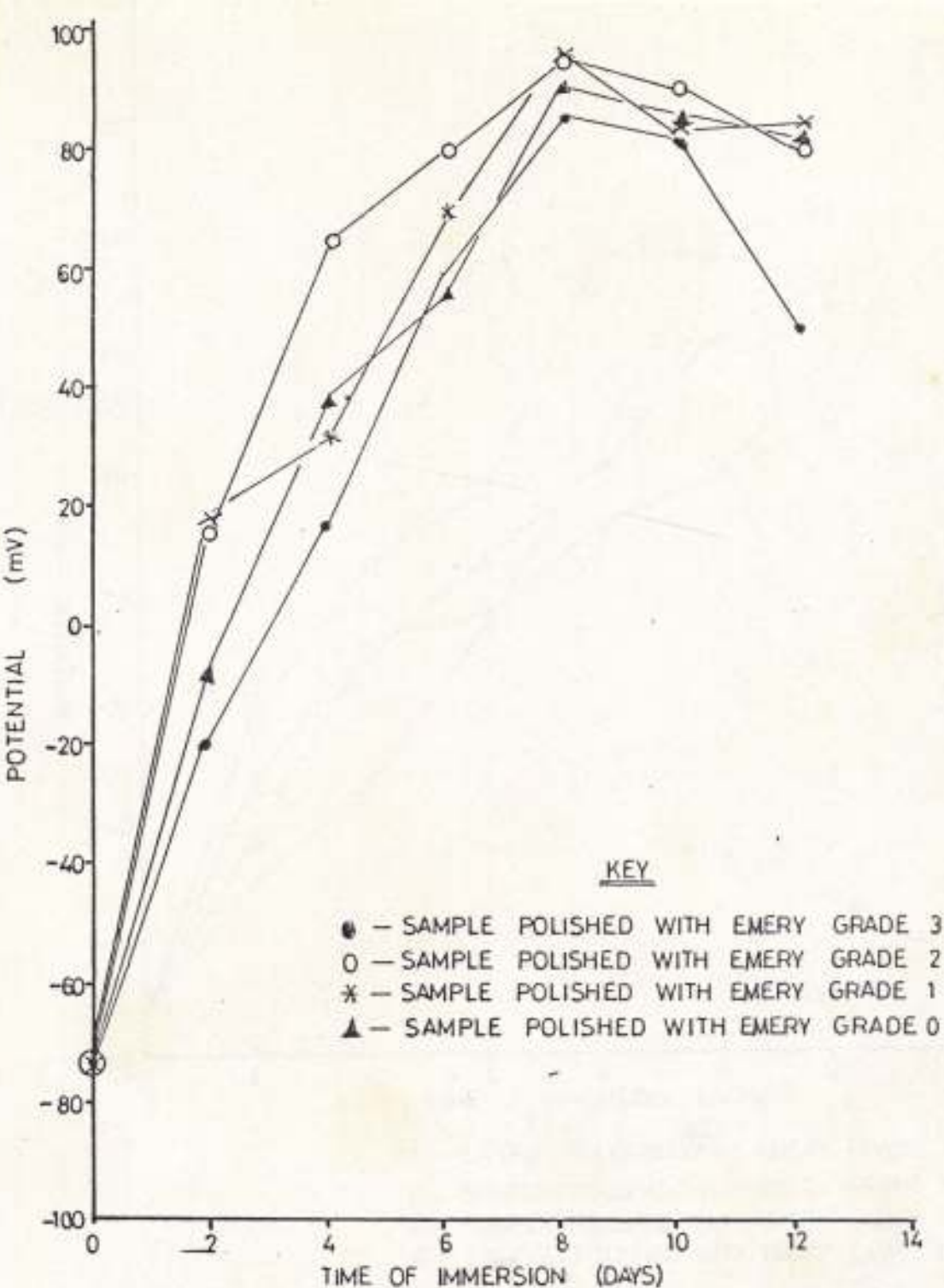


FIG. 33: POTENTIAL VARIATION OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM DICHROMATE AS INHIBITOR.

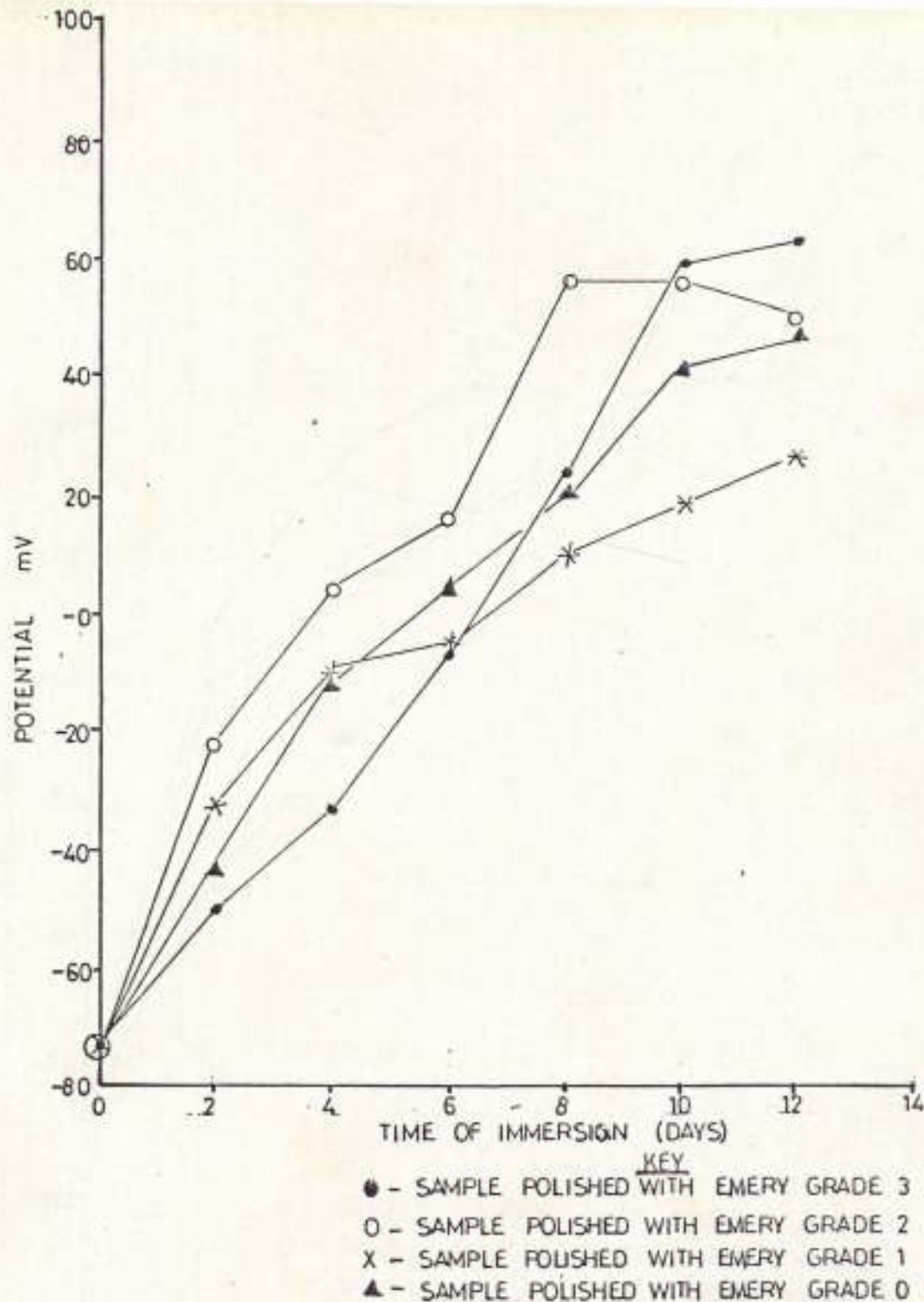


FIG.34: POTENTIAL VARIATION OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM DICHROMATE AS INHIBITOR.

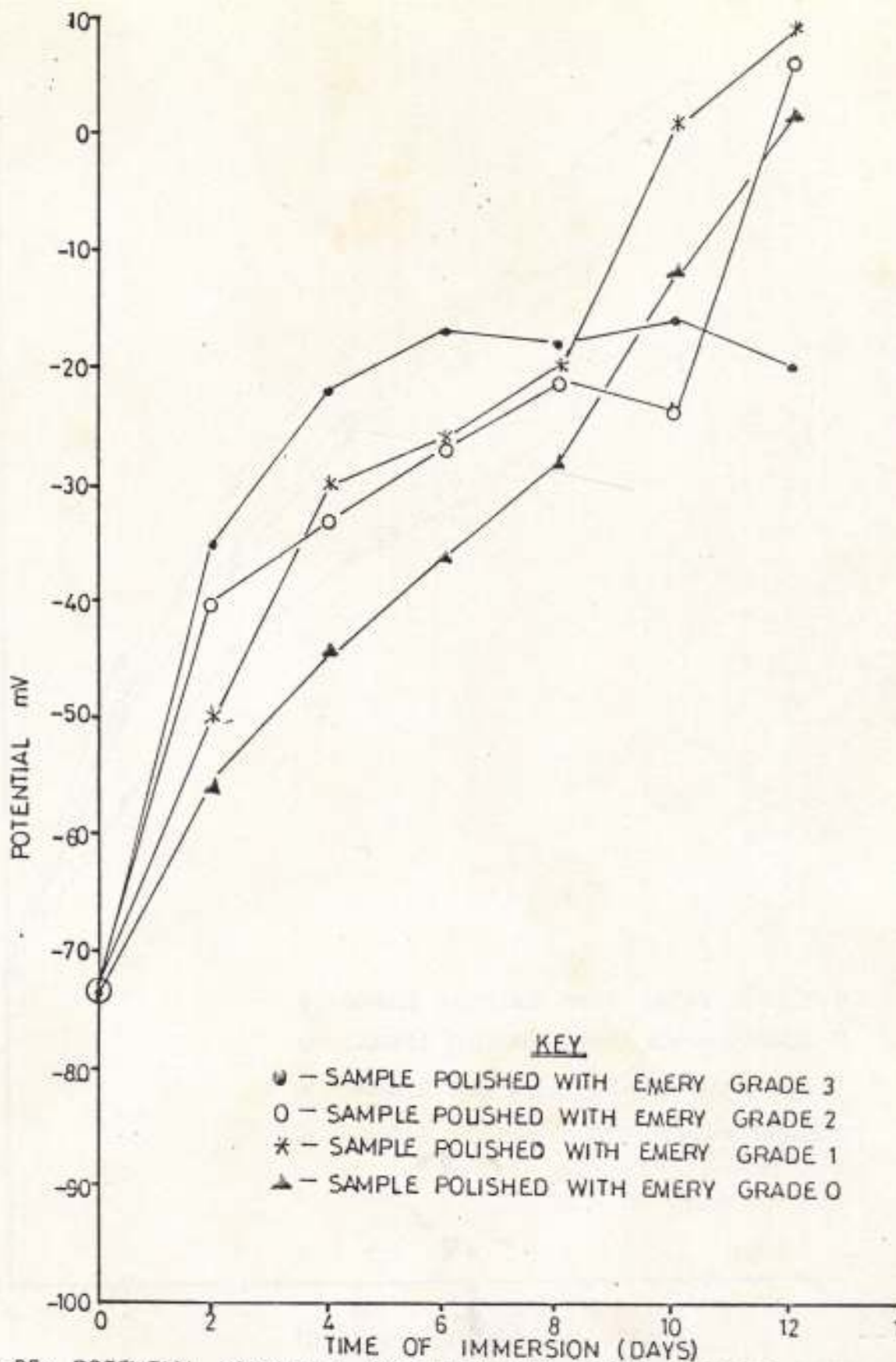


FIG. 35: POTENTIAL VARIATION OF DEAD MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM BENZOATE AS INHIBITOR.

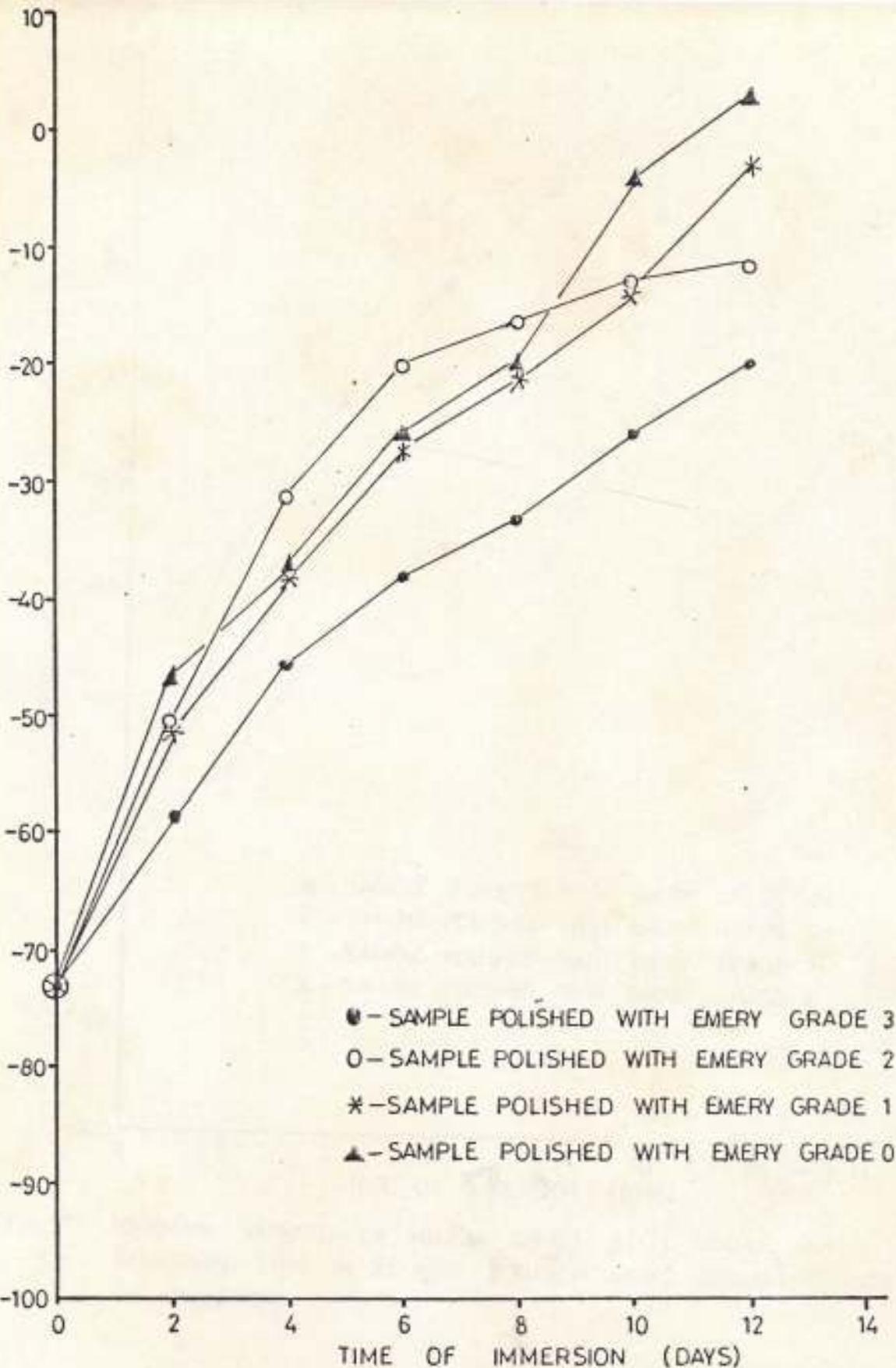


FIG.36; POTENTIAL VARIATION OF MILD STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION, USING SODIUM BENZOATE AS INHIBITOR.

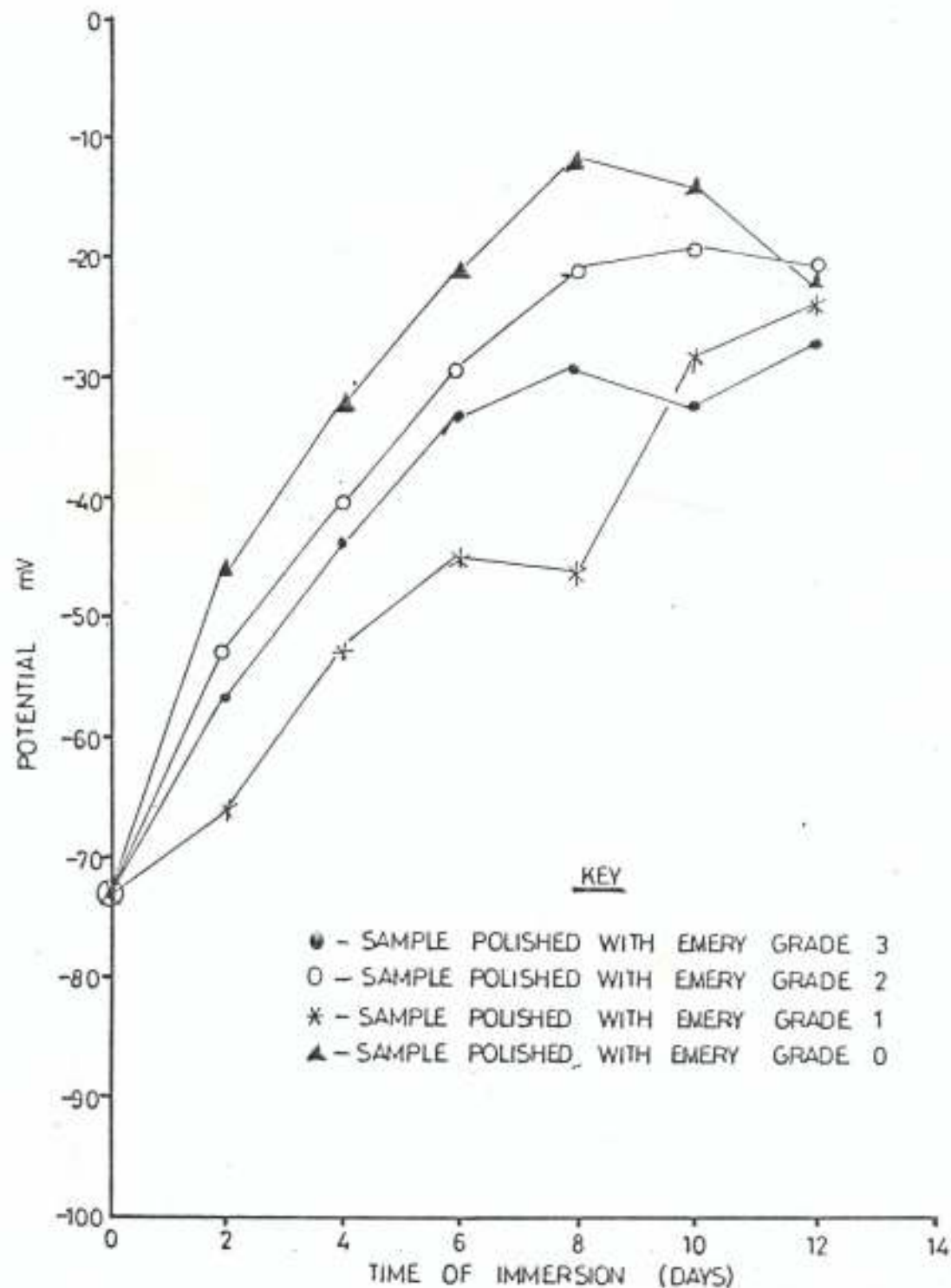


FIG.37: POTENTIAL VARIATION OF MEDIUM CARBON STEEL SAMPLE WITH IMMERSION TIME IN 3% NaCl SOLUTION USING SODIUM BENZOATE AS INHIBITOR.

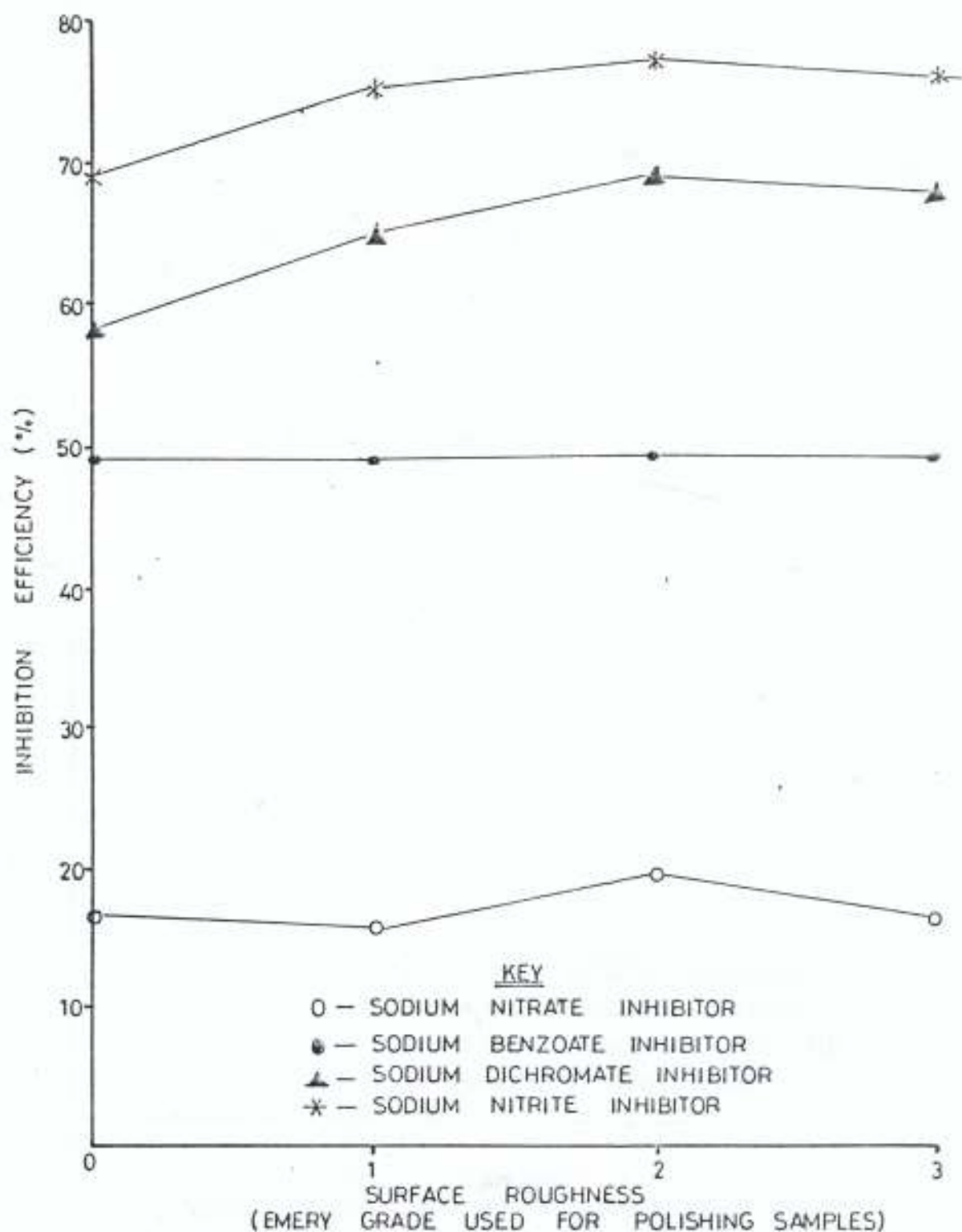


FIG. 38: EFFECT OF SURFACE ROUGHNESS OF DEAD MILD STEEL SAMPLES ON THE INHIBITION EFFICIENCY OF INHIBITORS USED IN 3% NaCl SOLUTION.

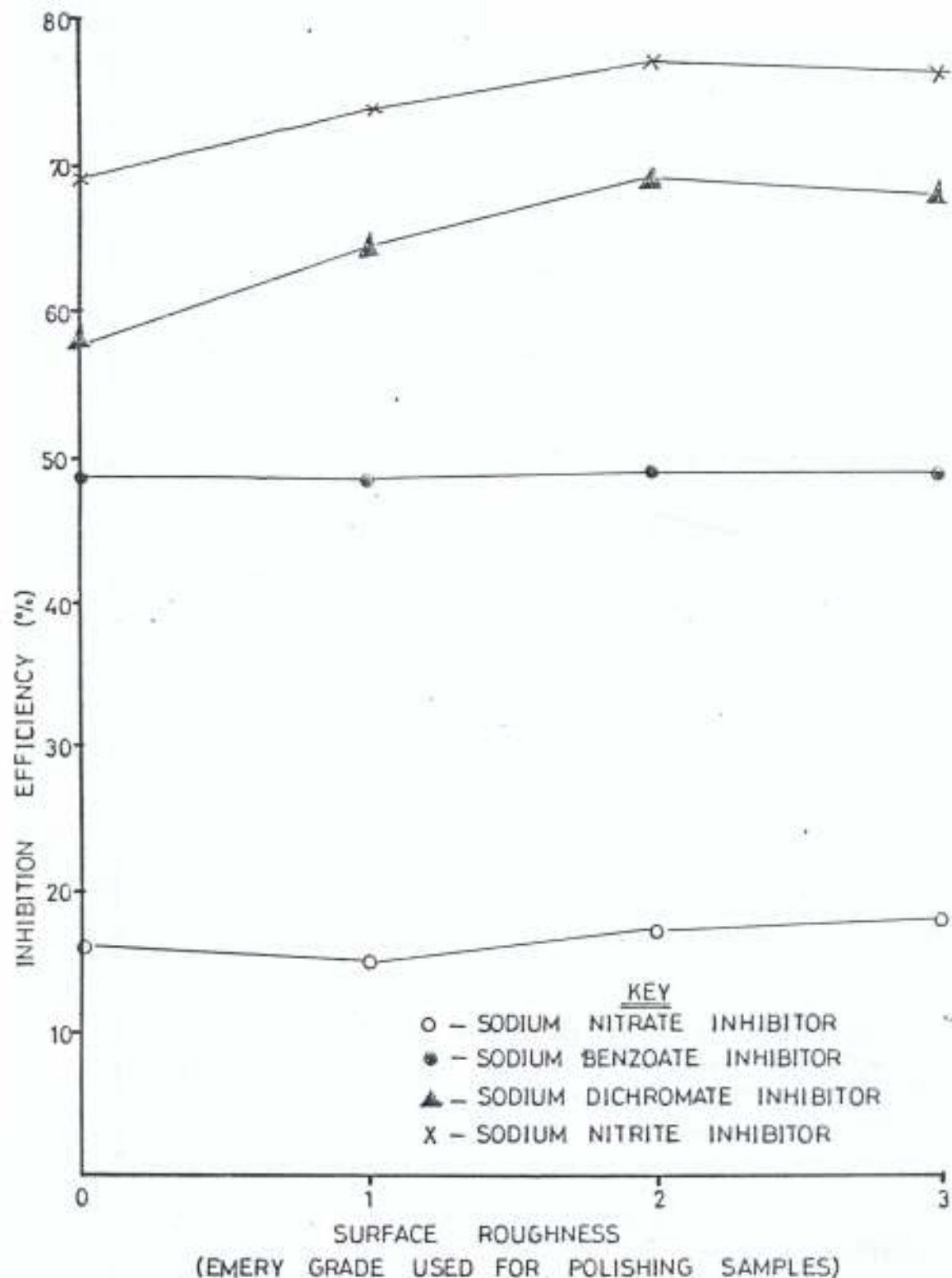


FIG.39: EFFECT OF SURFACE ROUGHNESS OF MILD STEEL SAMPLES ON THE INHIBITION EFFICIENCY OF INHIBITOR USED IN 3% NaCl SOLUTION.

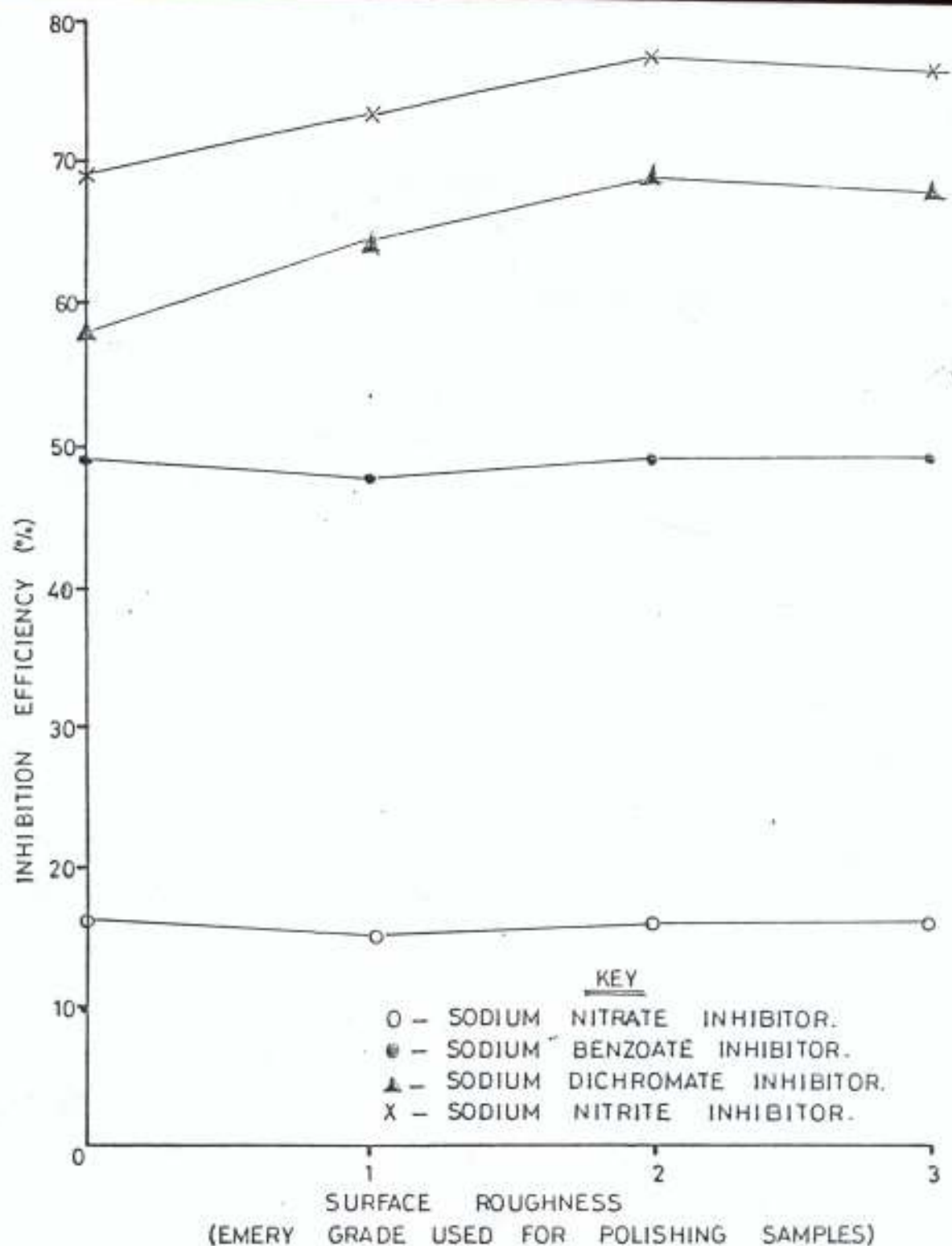


FIG.40: EFFECT OF SURFACE ROUGHNESS OF MEDIUM CARBON STEEL SAMPLES ON THE INHIBITION EFFICIENCY OF INHIBITORS USED IN 3% NaCl SOLUTION.

4.3.1 Weight Loss Variation with immersion Time

The weight loss of samples immersed in 3% NaCl was found to generally increase sharply with immersion time for the first six days, after which the rate of corrosion (in weight loss per unit surface area) starts to decrease.

This could be due to the fact that in the first few days, the oxide film on the samples has not been stabilized while in the later days, the inhibitors used have enhanced the formation of passivating oxide films on the samples, which do not allow diffusion of metal ions and this inhibits the anodic reaction i.e. metal dissolution. The fact that the graphs of weight loss versus immersion time (shown in figs 5-19) follows the parabolic law of oxidation, is a further proof that protective oxide films are formed on the samples.

Overall rate of corrosion is seen to vary with the surface roughness of the samples, the inhibitor used in the corroding medium and carbon content of the sample. This is imperative from the fact that the weight loss per unit surface area of sample of various surface roughness increases in the order of emery grades depicting that grade 3>2>1>0. We can therefore, say that the rate of weight loss of samples increases with increase in surface roughness.

On the other hand, it is obvious from the graphs that the rate of weight loss of samples in different inhibitors are in the decreasing order: sodium nitrate, sodium benzoate, sodium dichromate, sodium nitrite.

It is also interesting to note from graphs of figs 6 - 19, that the rate of weight loss of the samples decreases in the following order: Medium Carbon Steel, Mild Steel, Dead Mild Steel. Therefore, it would be correct to assume that the rate of corrosion of Carbon Steels in 3% NaCl increases with increase in carbon content of the steel

3.2 Weight Loss Variation With Surface Roughness

Figures 20, 21 and 22 show a general indication of increase of rate of weight loss with surface roughness for all the carbon steel samples. However, closer observation of the graphs shows that the gradient of the plots for samples inhibited with sodium dichromate and sodium nitrite is small compared to that of samples inhibited by sodium nitrate, sodium benzoate and that without an inhibitor. This implies that surface roughness has little effect on the inhibitive power of sodium dichromate and sodium nitrite.

3.3 Potential Variation With Immersion Time

The variation of the electrode potential of the carbon steel samples with immersion time (figs 23 - 37) show a rapid fluctuation of the potential, moving generally in the noble direction with increasing time.

This behaviour could be attributed to an overall thickening of the passivating oxide film due to a combination of locally increaseⁱⁿ pH and the presence of dissolved oxygen, while the fluctuation in the active direction could be attributed to sporadic film breakdown by large concentration of chloride ions (Cl^-). However, the vast rapid fluctuations of these potentials after a period of 6 days are inexplicable by the above factors.

4.3.4 Surface Roughness Variation With Inhibition Efficiency

Figures 38, 39 and 40 show that for samples inhibited with sodium nitrate, sodium dichromate and sodium nitrite, the inhibition efficiency initially rises as surface roughness increases from "0" to "2" and drops as the surface roughness increases from "2" to "3". This drop may be due to the fact that as the surface roughness increases, the corrosion rate also increases, therefore, the concentration of inhibitors required for inhibition increases, but since the concentration of the inhibitor remained constant with increase in surface roughness, it is imperative that the inhibition drops. For samples inhibited with sodium benzoate, it is observed that the percentage inhibition efficiency remained constant at 49% with variation in surface roughness.

It could also be seen from the graphs that the percentage inhibition efficiency of the inhibitors increases in the following order: sodium nitrate, sodium benzoate, sodium dichromate and sodium nitrite. This confirms the validity of the weight loss (with time) test, which gave an indication of a similar order of inhibition.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Based on the result from the research findings, the following conclusions may be drawn.

- (1) When sodium nitrite, sodium dichromate, sodium benzoate or sodium nitrate are used as inhibitor, they enhance the formation of passivating oxide film on the corroding metal, thus inhibiting the anodic reaction.
- 2) Corrosion rate generally increases with surface roughness.
- 3) Corrosion of carbon steels in 3% NaCl increases with increase in carbon content of the steel.

Surface roughness has little effect on the inhibitive power of sodium dichromate and sodium nitrite.

- 5) The electrode potential of carbon steel shows rapid fluctuation and moves generally in the noble direction with increasing time of immersion.
- 6) The inhibition efficiency of inhibitors generally rises as the surface roughness increases, but falls at a certain critical surface roughness where higher concentration of inhibitors are required.
- 7) The inhibition efficiency of inhibitors, on the corrosion of carbon steels in 3% NaCl increases in the order: sodium nitrate, sodium benzoate, sodium dichromate, sodium nitrite.

2. RECOMMENDATIONS

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

- 1) The nitrite and chromate inhibitors being more effective in 3% NaCl are recommended for use as corrosion inhibitors in this media for carbon steel of different surface roughness.

- 2) To generally inhibit corrosion effectively, where carbon steels are used in 3% NaCl, the surface roughness should be as fine as possible.
- 3) If the surface texture of carbon steels to be used in 3% NaCl environment, is very large, the concentration of inhibitors used should be high enough to obtain an optimum inhibition efficiency.
- 4) More detail study should be carried out on the effect of surface roughness on varying concentration of sodium dichromate and sodium nitrite as these have been found to be far more effective (as corrosion inhibitors) out of the four inhibitors studied.



REFERENCES

- Antropov, L. I. (1977), Theoretical Electrochemistry
Mir Publishers, Moscow.
- Bailey, F. W. J. (1972), Fundamentals of Engineering Metallurgy,
Cassell and Macmillan Publishers Limited, New York, p.39
- Bajah, S. T., Ehiemere N. and Ivowi U. M. O. (1982), Science Teachers
Association of Nigeria, Nigeria Integrated Science Project, Bk. 3,
Heinemann Educational Books, Nigeria Plc.
- Bockris, J. O. M., (1965), Journal of Electrochemical Society, Delft,
The Netherlands, 122, p. 1025.
- Bogatyreva, E. V. and Balezin, S. A. (1959). Journal of Applied chemistry
U.S.S.R., 32, p. 1094.
- Brasher, D. M. (1966), British Corrosion Journal, 1, p.3
- Brasher, D. M. (1969), British Corrosion Journal, 4, p. 122
- Brasher, D. M. and Mercer, A. D. (1968), British Corrosion Journal 3, p.
120- 129
- Brasher, D. M., Beynon, J. G., Rajagopalam, K. S. and Thomas J. G. N.,
(1970), British Corrosion Journal, 5, p.264
- Capp, J. A., (1914), Proc. Amer. Soc. Test Mater, 14, p.474
- Davies, D. E. and Slaiman, Q. J. M., (1977), Corrosion Science, 11, p.67
- Deltombe, E. and Pourbaix, M (1954), Proceedings of the 6th Meeting,
CITCE, Butterworths, London, P. 118
- Dix, E. H. (Jr) and Bowman, J. J. (1937), Amer. Soc. Test Matter. Spec.
Tech., Publ. No 32, P. 57
- Edwards, W. T., Le Surf, J. E. and Hayes, P. A., (1966), 2nd European
Symposium on Corrosion Inhibitors, University of Ferrara
- Epelboin, I., Kaddam, M. and Takenouri, H., (1972) Journal of Applied
Electrochemistry, 2, p.71
- Evans, U. R. (1960), the Corrosion and Oxidation of Metals, Arnold,
London.

- Freiman, L. I. Kolotyркиn, Y. M. (1969), *Protection of Metals*, 5, p. 113.
- Fujii, S. and Aramaki, K. (1966), *Proc. 3rd International Conference on Metallic Corrosion*, Moscow.
- Gilroy, D. and Mayne, J. E. D. (1965), *British Corrosion Journal*, 1, p. 102.
- Gouda, V. k. (1967), *Corrosion Science*, 7, p. 221.
- Hancock, P. and Mayne, J. E. D. (1958), *Journal of Chemical Society*, 4, p. 167.
- Hersch, P., Hare, J. B., Robertson, A. and Sutherland, S. M. (1961), *Journal of Applied Chemistry* 11, p. 251 and 265.
- Hoar, T. P. (1956), *Corrosion*, A symposium, University of Melbourne, p. 124.
- Ifeadi, C. N. and Nwankwo, J. N. (1987), *Oil Spill Incidents in Nigerian Petroleum Industry - a Critical Analysis*, Quarterly Magazine of the NNPC, Fourth Quarter, 8, No 4, p. 5- 11.
- Kubaschewski, O. and Brasher, D. M. (1959), *Trans. Faraday Soc.*, 55, p. 1200
- La Que, F. L. (1969), *Electrochemistry and Corrosion (Research and Tests)*, Acheson Memorial Address, *Journal of Electrochemical Society*, 116, P. 73C.
- Legault, R. A. and Walker, M. S. (1964), *Corrosion*, p. 282t.
- Mayne, J. E. O. and Ramshaw, E. H. (1960), *Journal of Applied Chemistry*, 10, p.419
- Mayne, J. E. O. and Page, C. L. (1970), *British Corrosion Journal*, 1, P.93.
- Mayne, J. E. O. and Page, C. L. (1972), *British Corrosion Journal*, 7, P. 111
- Muller, W. J. (1933), *Die Bedeckungstheorie de Passivitat der Metalle Und ihre Experimentalle Bergrundung*, Verlag Chemie, Berlin.
- Omar, I. H. (1987), *10th International Congress on Mettalllic Corrosion* , 13, P. 2723.

- Polino, G. W. (1970), Corrosion Science, 10, P.297
- Pourbaix, M. (1970), Corrosion, 26, P. 431
- Pourbaix, M. (1973), Lectures on Electrochemical Corrosion, Plenum Press, New York.
- Pryor, M. J. and Cohen, M. (1951), Journal of Electrochemical Society, 98, P. 263
- Pryor, M. J. and Cohen, M. J. (1953), Journal of Electrochemical Society, 100 p. 203
- Putilova, I. N., Balezin, S. A. and Baranmik, V. P., (1960), Metallic Corrosion Inhibitors Pergamon Press, London
- Ride, R. N. (1958), Symposium on Corrosion (Melbourne University), 267, P. 1955-56,
 . Published in Journal of Applied Chemistry, 8, P. 175
- Shreir, L. L. (1976), Metal/ Environment Reactions, Corrosion, V.1,
 (edited by Shreir L. L.)
- Shreir, L. L. (1976), Corrosion Control, Corrosion, v.2, (edited by Shreir, L. L.),
 P. 12 : 21 and 15 : 24
- Stanlar, W. (1962), Plant Engineering Handbook, 2nd Edition (edited by Stanlar W),
 U.S.A., P. 5 : 24
- Stern, M. and Geary, A. L. (1957), Journal of Electrochemical Society, 104, P. 56
- Trabanelli, G. and Carassati (1970), Advances in Corrosion Science and Technology,
 1, Plenum press, New York, London, P. 147
- Uhlig, H. H. (1971), Corrosion and Corrosion Control, John Willey and Sons Inc.,]
 2nd Edition, New York, P. 46
- Wesley, W. A. (1943), Pro. Amer. Soc. Tests Matter., 49. P.649
- Zucchini, B. L., Zucchi F. and Trabanelli, G., (1970), 3rd European Symposium on
 Corrosion Inhibitors, Ferrara.