# CORROSION AND CORROSION INHIBITION OF STEEL IN AQUEOUS MEDIA

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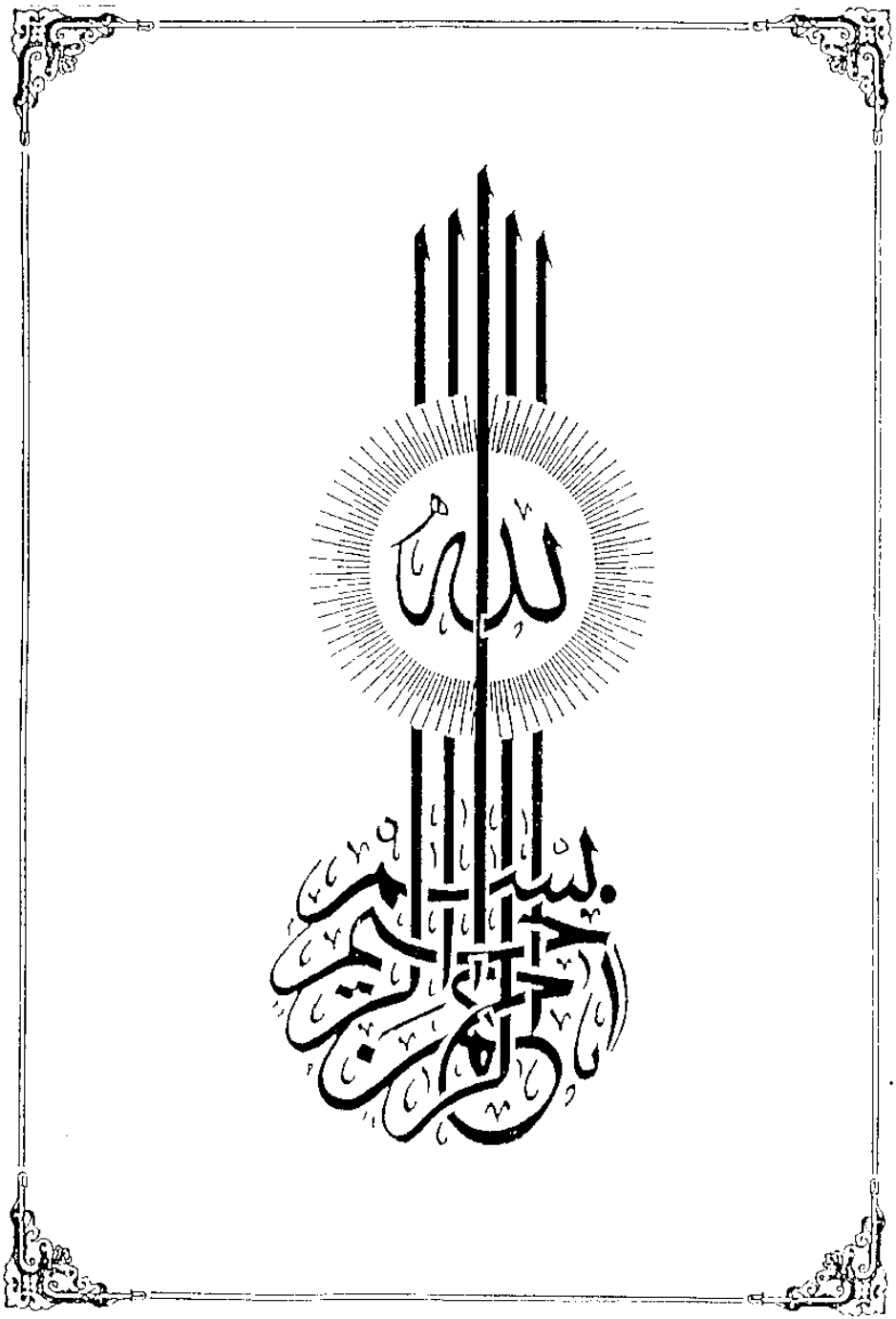

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# CHAPTER 1

## GENERAL INTRODUCTION
## and
## OBJECT AND SCOPE OF THE PRESENT WORK

## GENERAL INTRODUCTION

Most metals, if exposed to natural environments without protection, will react with constituents in the environment to form corrosion products typical of the ores from which they originally were extracted. It is a well established fact that corrosion is electrolytic in character[1-4] and depends upon the operation of electrochemical reactions on the metal surface. The overall corrosion process consists of separate and faradaically equivalent anodic and cathodic reactions. Generally, these two reactions are not the reverse of each other but are different :

Anodic reaction : $Fe \longrightarrow Fe^{++} + 2e$

Cathodic reaction (in near neutral solutions) :

$$2\,e^- + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow 2\,OH^-$$

The driving force for the corrosion reaction is determined by the difference in potential between the anodic and the cathodic sites on the surface of the metal. The corrosion process depends on various factors. Both metallurgical and environmental factors are known to affect

the rate as well as the [illegible] of corrosion. The [illegible] metal factors that influence corrosion are: [illegible] ture of the medium, its chemical composition, [illegible] solution, the presence of additives, a - tion [illegible] correcly to the metal, the temperature and the pressure.

On the other hand, metallurgical factors are those connected to the metal itself such as the chemical nature of the metal, its structure and surface conditions.

Corrosion behaviour of steel in neutral and alkaline solutions of different anions :

Of prime importance for the present study is the differentiation between factors that lead to continious dissolution on one hand or to inhibition or eventual passivation on the other hand in the near neutral and alkaline media. The corrosion behaviour of steel in the presence of different salt solutions has been widely investigated, and it is beyond the scope of this study to review in detail the reported studies. References will be limited to those studies in which the corrosive

or inhibiting properties of anions are explained on some physical grounds. The action of anions especially in neutral and alkaline solutions on iron or steel surfaces has been sought to be explained on the basis of the theories discussed below.

Theories of corrosion:

The following is a short presentation of the various theories to explain the phenomenon of corrosion and the mechanism of inhibition.

According to the film-formation theory, suggested by Evans and his coworkers[1a], the solubility of the corrosion products decides whether a certain anion would inhibit corrosion or accelerate it. An insoluble film on a metallic surface acts as a barrier to the progress of corrosion. The immunity of lead and silver in sulphate and chloride solutions respectively, are taken to support this idea. Thus, sulphate and chloride ions exert an inhibiting action although they are normally considered as typical corrosion-accelerators. The corrosion of iron in KF solutions was studied by Chapman[5]. He found that corrosion in dilute solutions

was as high as in KCl solutions of equal molarities. As the concentration of $K^+$ was raised to 0.8 M corrosion rapidly ceased. This was attributed to the suppression of the solubility of $Fe_2$ in the presence of excess $Cl^-$ ions. Accordingly, the corrosion products, which in dilute solutions was regarded as being soluble, had to be passed in concentrated media with the film forming compounds which inhibit corrosion.

According to Evans[1a], when a metal is immersed in an aqueous medium, water molecules surround the metal surface to form water phalanx, which at anodic sites, is oriented in such a way that the oxygen part of the water molecule is nearest to the metal and the hydrogen part lies furtherst from it. In very dilute solutions, this water phalanx is most nearly complete. When anions are present in solution, they displace the water molecules from the metal surface due to the negative charge of these anions. In presence of adsorbed anions on the metal surface, current transfer is limited to the motion of metal cations towards the solution side. Accordingly, the metal may pass into solution and suffers corrosion. There is, however, also the possibility that the metal cation moves into positions between oxygen atoms of the

phalanx, displacing protons from the water molecules and forming a solid oxide or hydroxide on the surface. Spots and rings of colour on a specimen immersed in a mildly inhibitive salt solution represent places where the film is weak. In the case of iron, the material composing these colour-rings was at one time regarded as hydroxide, $(Fe(OH)_3)$ or $(FeO(OH))$, but it is probably $\delta$-$Fe_2O_3$. According to Evans it will be noticed that whilest the pushing off of $H^+$ ions from a phalanx of water molecules might produce either an oxide or hydroxide-film, the pushing off of $H^+$ ions from a phalanx of $OH^-$ ions can only lead to an oxide film.

Since oxide-films are generally more protective than the hydroxide-films this may be one reason why alkaline conditions favour inhibition. In addition, the depressed solubility of the film-substance in an alkaline solution is also an important factor. According to Evans[1a], decission between corrosion and inhibition depends upon the effect of the anion on the condition of the film formation.

In aerated solutions of oxidizing anions, i.e. chromate and nitrite, the protective film is mainly

a sufficiently high rate at the cathodic sites on the metal surface. This is in agreement with the opinion of Kolotyrkin[13] that inhibitors need not to participate in forming the passive film. Their action-according to kolotyrkin is to increase the overall rate of the cathodic reaction and to shift the steady state potential to the positive direction leading to the onset of passivity. A similar idea of Uhlig[14] stated that any phenomenon through which the metal aquires a potential nobler than the Flade potential will produce passivity. According to these authors, the inhibtor should be an oxidising agent and able to create a stable redox potential. The passivator should also be present in sufficient concentration in order to develop a sufficiently noble potential for the redox system. Passivity is thus favoured by noble redox potentials, high limiting diffusion currents for the reduction of the passivator, as well as low Tafel slopes.

The effect of benzoate, phthalate and phosphate as corrosion inhibitors for iron in presence of air[15] was taken to demonstrate that the reduction of the inhibitor is not a prerequisite for passivation, and that inhibition is mainly due to the reduction of

oxygen in presence of these inhibitors. In absence of the inhibitor, oxygen acts as a corrosive agent. Gatos[16] has shown that benzoates and cinnamates do not inhibit the corrosion of iron coupled to a more noble metal and that during inhibition of iron, only one-tenth of a monolayer is formed on the surface of the metal. It appears from these observations that the phosphate, phthalate, cinnamate or any such ion could be adsorbed on the anodic sites of the metal surface only when the positive charge on the metal is increased by the cathodic reduction of oxygen. In a study of the cathodic polarization of passive iron in chromate and pertechnetate solutions, Cartledge[17] found that only a small fraction of the total current could be associated with the reduction of the inhibitors. However, it is worth remarking that not all the oxidising agents function as inhibitors. The electrochemical polarization theory seems to oversimplify the action of the different types of inhibitors in both neutral and alkaline media and is obviously of limited application, i.e. only to reducible ions. Thus the electrostatic polarization theory, though logically sound, is not borne out in all systems.

According to the adsorption theory by Uhlig[18], any substance adsorbed on the metal surface and capable of sharing electrons with the underlying metal would act as an inhibitor. The adsorbed species may (i) block the active site or (ii) displace from the surface any catalyst for the anodic dissolution reaction or (iii) by virtue of the net charge of the adsorbed ion have some effect on the potential and corrosion of the metal. Thus, for example, the corrosion of the 18-8 stainless steel in 6.3 N hydrochloric acid solution was found to decrease to 1/470 its value when carbon monoxide was introduced into solution[19,20]. In this case the protective film-formation could neither be responsible for inhibition nor is the phenomenon related to the elevation of the hydrogen overpotential since carbon monoxide causes the shift of the corrosion potential to the noble direction. According to the adsorption theory, a passivator possesses a high affinity for the metal and a high activation energy for the reaction with it[21]. The uptake of chromium[22-25] and organic inhibitors[26] from aqueous solutions on the surface of steels was found to follow typical adsorption isotherms. Both primary and secondary adsorption has been suggested to

take place on the surface of the metal. In one case the adsorbed film was said to be composed of an inner close-packed layer of oxygen atoms of covalent radius of 0.7 Å on top of which a chemisorbed close-packed layer of oxygen molecules with a radius of 1.2 Å was placed[18]. Hydroxide radicals or water molecules were assumed to participate to some extent in the passive film structure. This model could explain the measured quantities of adsorbed oxygen and accounted, theoretically, for the Flade-potential which could not be properly explained on the basis of an oxide film[27].

Wroblewska[28] reviewed the uses of organic and inorganic corrosion inhibitors. $KTeO_4$ completely prevents oxidation of Fe even at such concentrations that the adsorption of $TeO_4^-$ ions is sufficient for the formation of a monomolecular layer.

De[29] has formulated a general theory of inhibition by adsorption, in both neutral and acid solutions, based on the electrocapillary properties of anions. It is well known that capillary-active anions are preferentially adsorbed on mercury along the positive branch of the electrocapillary curve, depressing it