

# “MATERIAL BEHAVIOUR UNDER CORROSIVE ENVIRONMENT — GUIDE FOR MATERIAL SELECTION”

By

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## ABSTRACT

In this paper, the behaviour of engineering materials as influenced by fluid velocity, operating temperature, humidity and duration of exposure to chemical and/or electro-chemical action is carefully studied, corrosive environment being prevalent. Moreover, metallurgical factors examined include grain size, alloying elements and degree of purity of metal, as well as heat and surface treatment.

The designer is herein provided with guidelines for the selection of materials and relevant manufacturing processes most suitable for given conditions of operation.

## 1. INTRODUCTION

Corrosion, for various atmospheres, may well account for more failures on a cost and tonnage basis than any other failure, with an estimated cost of several billion dollars in the United States alone (1). Atmospheres can be classified as industrial, marine, and rural. Corrosion is primarily due to moisture and oxygen but can also be accentuated by contaminants such as sulphur compounds and sodium chloride. Corrosion of steel at seaside amounts to some 400 to 500 times that encountered in a desert area. On the other hand, industrial environment can be 50 to 100 times more corrosive than desert environment. Industrial atmospheres are more corrosive than

rural atmospheres, primarily because of sulphur gases generated by the burning of fuels. Figure (1) illustrates the wide variation in corrosion depth (penetration) for structural carbon steel under different environmental conditions (2).

The selection of proper metal or alloy for specified corrosive environment is looked upon as one of the most common methods of combating corrosion. In alloy selection, a number of natural metal corrosive combinations is readily available; these usually represent maximum level of corrosion resistance for least expenditure. Some of these natural combinations are listed in relevant technical literature (1 & 2).

## **2. EFFECT OF ENVIRONMENTAL FACTORS**

Factors related to environment include temperature, oxygen concentration, pressure, solar radiation, relative humidity, velocity of flow, presence of impurities or pollutants, biological factors as well as mechanical effects. Table (1) comprises a listing of the effects of each of these factors, a number of which is further discussed hereunder.

### **2.1 Effect of Temperature**

Temperature is one of the most important single factors in corrosion. In many cases corrosion increases rapidly with increase in temperature. By way of example, the corrosion behaviour of 18/8 Cr/Ni steel in nitric acid, as displayed in Figure (2), shows that the corrosion rate increases to several thousand miles per year as a result of a temperature increase of some 50°C, (1). Numerous cases also show that raising the temperature from normal room temperature to about 75°C may lead to a tenfold increase in corrosion rate (1). It must be emphasized, however, that the effect of temperature is not clearly defined since it has an effect on relative humidity and consequently an indirect effect on corrosion (3). Moreover, the effect of temperature increase is rather complex as the diffusivity of oxygen molecules increases while the solubility decreases. Though data on these influences is rather scarce, yet the net mass transport of oxygen would increase with temperature (4) until a maximum is reached at about 75°C at which value the concentration falls while approaching the boiling point. It follows then that the corrosion rate would attain a maximum at 75°C and would decrease with further increase in temperature.

The interaction between environmental factors, viz. solution velocity and

temperature, as obtained by Zembura (5), are reproduced in Figure (3). It has been found that for copper in air-saturated 0.1  $\text{NH}_2\text{SO}_4$ , the controlling process is that of oxygen reduction up to a temperature of 50°C. At 75°C the process is controlled, however, by diffusion. Increasing solution velocity has been found to exert a significant influence on corrosion rate, this diminishing at temperature values below 50°C. It is thus evident how unwise it is to separate various parameters such as concentration, velocity and temperature should the dominating mechanism be sought.

## 2.2 Effect of Oxygen

At ordinary temperatures, dissolved oxygen is necessary for causing appreciable corrosion of iron in water. In air-saturated water, although the initial corrosion rate is very high, yet it diminishes over a period of days as the iron oxide film is formed on the surface to serve as a barrier to the diffusion of oxygen thus slowing down the corrosion process (6). Similar behaviour is also observed for outdoors. This is illustrated by figures relating to the rate of rusting, for the first and second years, also for the sixth to fifteenth years, Table (2). After few years of exposure the rate of rusting diminishes significantly; this is quite evident for low alloy steels (3). At a later stage, a steady state of corrosion rate is usually reached.

## 2.3 Effect of Relative Humidity

The relative humidity of the atmosphere represents one of the most important environmental variables which affect the corrosion rate of materials. Table (3) shows, by way of example, the effect of relative humidity on filiform corrosion of enamelled steel. Such data indicates that filiform corrosion occurs primarily in the range 65 to 95% relative humidity. Should the humidity be lower than 65%, the metal would be unaffected, while above some 90% humidity corrosion would primarily appear as blistering (1).

## 2.4 Effect of Velocity

Velocity of environment often strongly influences the mechanisms of corrosion reactions. At high velocity values, especially with solutions containing solids in suspension, mechanical wear would also emerge. Higher velocity may either strengthen or weaken corrosion attack, depending on relevant mechanism involved. More severe attack on steel results from increasing the supply of oxygen,

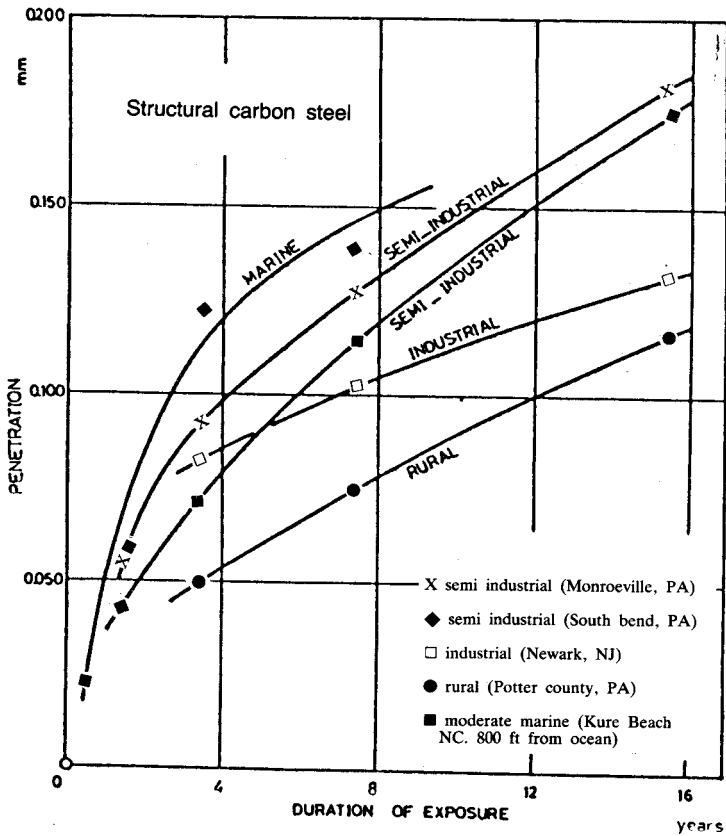


Fig. (1): Effect of environmental conditions on general penetration of structural Carbon steel.

**Table (1): Typical Environmental Influences on Corrosion.**

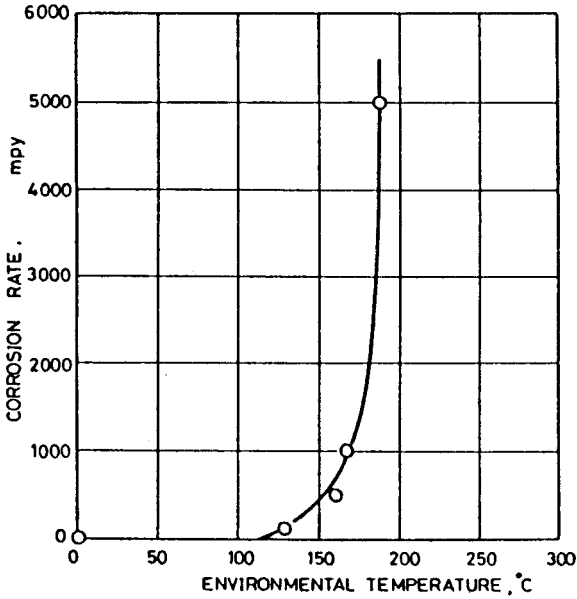
<b>Environmental Variable</b>	<b>Influence on Corrosion</b>
Temperature/ Pressure	Increase corrosion activities
Relative humidity	Promotes corrosion attack
Wind velocity	Accelerates erosion
Mechanical effects	Promote corrosion fatigue and fretting corrosion
Solar radiation	Promotes coating degradation
Impurities/Pollutants	Promote corrosion
Biological factors	Promote corrosion
Stray current	May cause localized corrosion

**Table (2): Variation of the Rate of Rusting with Duration of Exposure.**

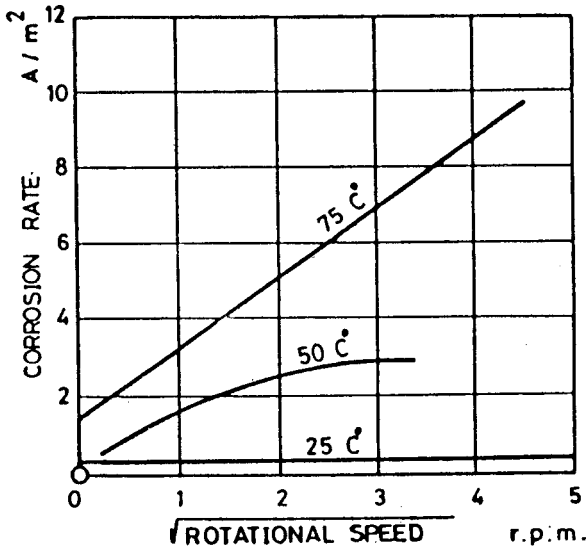
Steel	Rate of rusting (mm/y)		Ratio B/A
	A 1st & 2nd years	B 6th to 15th years	
Ordinary mild steel (Cu 0.02%)	0.129	0.094	0.73
Low-alloy steel (Cr 1.0%; Cu 0.6%)	0.077	0.025	0.33

**Table (3): Effect of Relative Humidity on Filiform Corrosion Enamelled Steel.**

Relative Humidity	Appearance
0-65%	No corrosion
65-80%	Very thin filaments
80-90%	Wide corrosion filaments
93%	Very wide filaments
95%	Mostly blisters, scattered filiform
100%	Blisters



**Fig. (2): Corrosion rate of 18/8 Cr/Ni steel (in 65% Nitric acid) as aggravated by temperature.**



**Fig. (3): Effect of rotational speed on the rate of a copper disk in air-saturated 0.1 NH<sub>2</sub>, SO<sub>4</sub> for various values of temperature.**

carbon dioxide, or hydrogen sulphide in contact with metal surface. Furthermore, velocity may increase diffusion or transfer of ions by reducing the thickness of the stagnant film at the surface. Figure 4(a) shows how the relative motion of sea water can increase the corrosion rate. In natural fresh water, however, the velocity of water first increases the corrosion rate by bringing more  $O_2$  to the surface, while at sufficiently high velocities, adequate oxygen may well reach the surface to cause partial passivity (6). In this case, the corrosion rate would decrease again after its initial rise, Figure 4(b). On the other hand, higher velocities may, in some cases, lead to reduced attack as they prevent the deposition of silt or dirt which would otherwise cause crevice corrosion.

### **3. EFFECT OF METALLURGICAL FACTORS**

Before discussing the effect of these factors on corrosion, it is deemed quite useful to first review the different types of galvanic cells as, in many situations, galvanic cell formation is highly dependent on the metallurgical conditions of the material under consideration.

Table (4) summarizes the conditions under which galvanic cells may form (7). Three types of cells are herein dealt with, viz. cells with unlike electrodes, stress cells and concentration cells. The first type involves unlike electrodes in which the more noble phase serves as the cathode while the less noble phase acts as the anode. It is worth noting that corrosion reactions need not involve different metals, but may take place between two phases of a microstructure thereof.

In the stress cell, a distorted, higher-energy zone, such as a grain boundary, a dislocation line, or a cold-worked metal serves as an anode, while the strain or stress-free region constitutes the cathode. The concentration cell which arises from differences in electrolyte composition, accentuates corrosion by producing an anode at which the oxygen concentration is lower. The exposed oxygen-rich areas are cathodic, while the inaccessible locations acting as anodes are subjected to corrosion. As scale or rust builds up and restricts the supply of oxygen, such inaccessible locations become even more anodic with rapid formation of corrosion pits.

#### **3.1 Effect of Cold Work**

Cold-worked commercial steel has been found to corrode in natural waters at the same rate as that for annealed steel (8). In acids, however, cold working increases



the corrosion rate to several fold, e.g. Figures (5) and (6). Many authors have traditionally ascribed this effect to residual stress within the metal, which stress tends to increase the corrosion rate. It was suggested by Uhlig (9) that the observed increase in the corrosion rate is apparently caused by the segregation of carbon or nitrogen atoms at sites of imperfection, as produced by plastic deformation, rather than by the presence of the imperfections themselves. Results displayed in Figures (5) and (6) support this interpretation.

Subsequent heat treatment of cold-worked steel at 100°C induces additional diffusion of interstitial carbon atoms to imperfections in the metal lattice, thus increasing corrosion rate. Heat treatment at higher temperatures reduces the density of imperfection sites; this is accompanied by precipitation of carbides or nitrides with increasing particle size. The net outcome would be reduction in corrosion.

### 3.2 Effect of Heat Treatment

Thermal and mechanical treatments as well as fabrication processes, such as welding, can seriously affect the microstructure and consequently the corrosion resistance of materials. For steels frequently used in annealed or normalised conditions, the most important structural parameter that can be significantly influenced by heat treatment is the grain size. In studying the effect of ferrite grain size on stress-corrosion, it is clear from Figure (7) that coarse-grained steels fracture at appreciably lower stresses than those with smaller grain size. The effect of cooling rates from the austenitising temperature is more marked than the grain size effect as achieved by varying the austenitising temperatures (3). Water quenching from 920°C appears to render steel more susceptible to cracking than oil quenching. Further decrease in the cooling rate through air cooling to furnace cooling would lead to an additional increase in cracking resistance. It should be herein pointed out that these trends are only relative and that even with very slow cooling, many mild steels still display high susceptibility to stress corrosion.

The effect, on cracking tendencies of steel, of tempering which follows quenching is shown to largely depend on the tempering temperature. Although, some discrepancies exist between relevant results published by different authors (10 & 11), it seems reasonable to conclude that, in general, susceptibility to cracking diminishes with tempering temperature should a certain minimum be

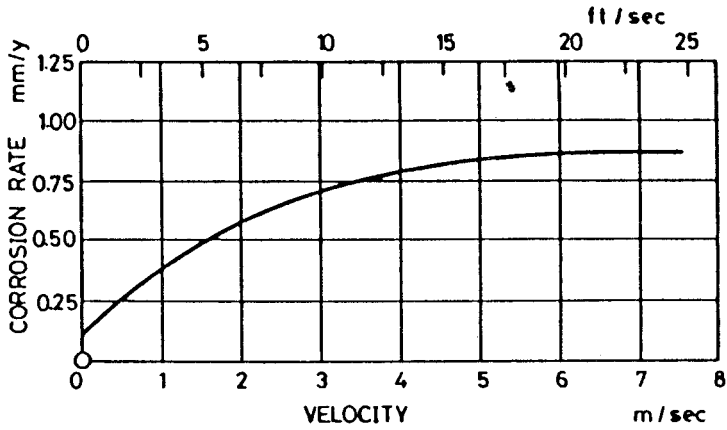


Fig. (4-a): Corrosion rate of steel in sea water as affected by velocity of flow.

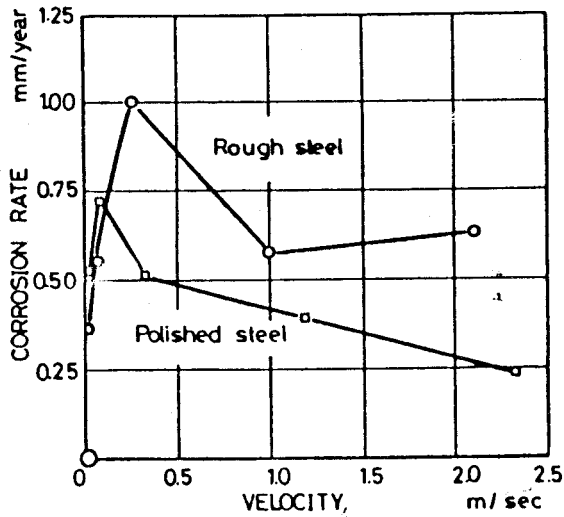


Fig. (4-b): Effect of velocity on corrosion rate of mild steel tubes with different finishes.

(Temperature: 21°C, Duration: 48 hr. tests)

**Table (4): Summary of Galvanic Cells (7).**

	<b>Examples</b>	<b>Anode (oxidation)</b>	<b>Cathode (reduction)</b>
		<b>Basal phase</b>	<b>Nobler phase</b>
<b>Electrode Composition</b>	Zn versus Fe Fe versus H <sub>2</sub> H <sub>2</sub> versus Cu Pearlite	Zn Fe H <sub>2</sub> Ferrite	Fe H <sub>2</sub> Cu Carbide
<b>Stress cells</b>	Boundaries Grain size Imperfections Strains Stresses	<b>Higher energy</b>	<b>Lower energy</b>
		Boundaries Fine-grain Defect Cold-worked Loaded areas	Grain Coarse-grain Perfect Annealed Nonloaded areas
<b>Solution concentration</b>	Electrolyte Oxidation Dirt or scale	<b>Lower concentration</b>	<b>Higher concentration</b>
		Dilute solution Low O <sub>2</sub> Covered areas	Con. solution High O <sub>2</sub> Clean areas

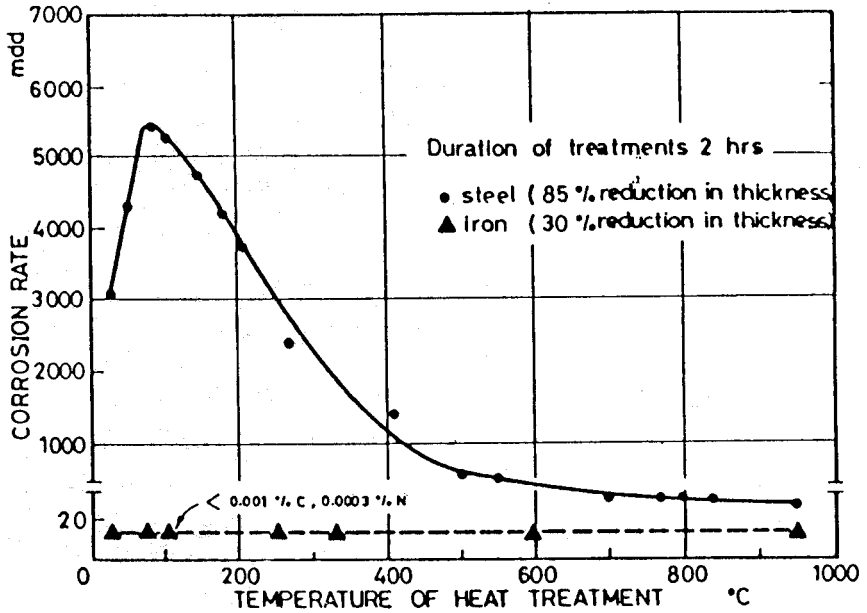


Fig. (5): Effect of heat treatment of cold-worked steel (0.076% and of iron on corrosion rate in deaerated 0.1 HCL at 25°C.

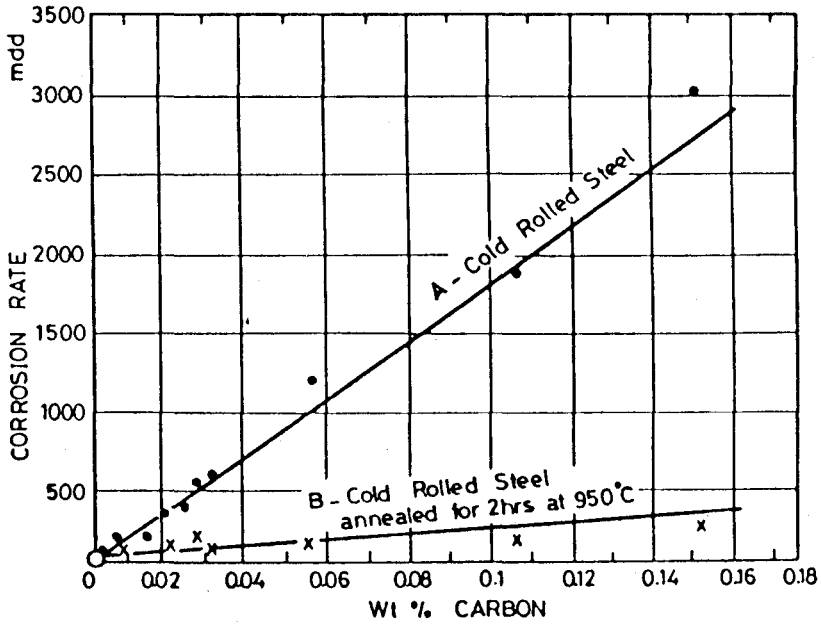


Fig. (6): Effect of carbon content on corrosion rate in deaerated 0.1 N HCL at 25°C:

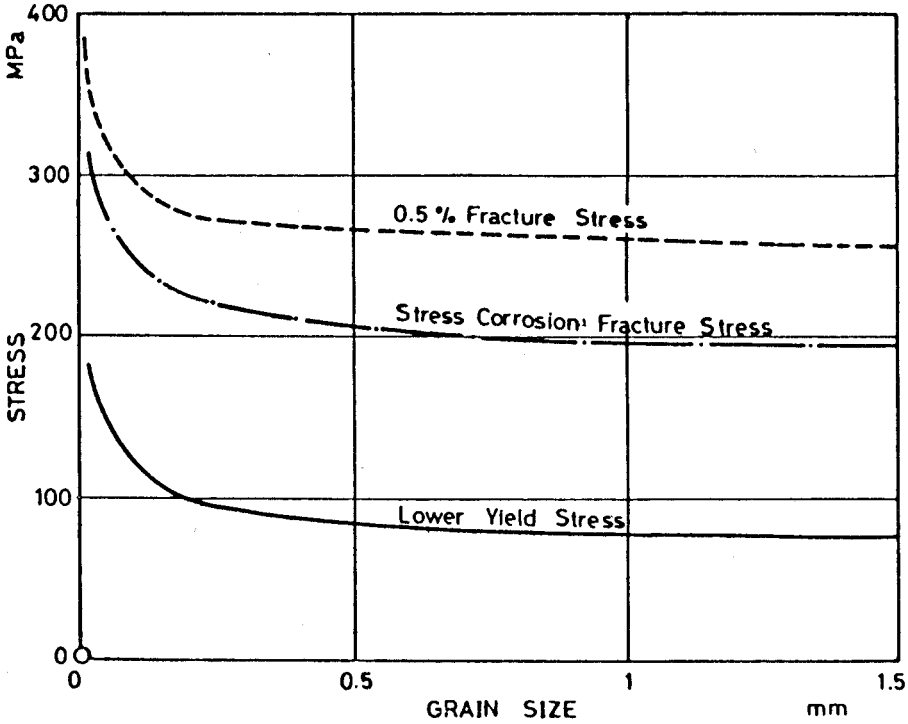
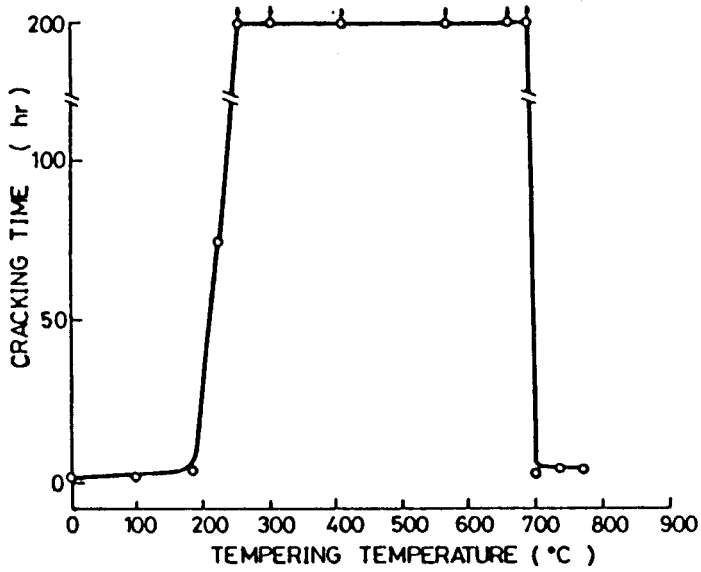


Fig. (7): Effect of ferrite grain size on yield and fracture stresses for 0.08% C steel in 8 NCa (NO<sub>3</sub>)<sub>2</sub>. (Based on Data Obtained from Ref (3)).



**Fig. (8): Effect of 30 min. tempering (following quenching from 950°C cracking of 0.06% C steel in boiling calcium nitrate-ammonium nitrate solution.**

exceeded. The work of Houdrement et al (10) agrees with most other workers in showing that tempering above about 300°C enhances cracking resistance of steel and that maximum benefit may be attained with tempering temperatures of some 600°C or above. On the other hand, the results of Uhlig and Sava (12) indicate that full benefit of tempering may be obtained at temperatures ranging from 250°C to 700°C, depending on steel composition and duration of tempering, Figure (8).

In a recent study, some of the effects of microstructure and heat treatment on the environmental cracking behaviour of duplex stainless steels in chloride-containing environments are discussed (13). It has been revealed that the resistance of these materials to stress corrosion cracking (SCC) increases with ferrite content between 0 and some 40%, Figure (9). With higher ferrite content, however, resistance to SCC decreases. Much of the beneficial effect of ferrite in the 0 to 40% ferrite range is attributed to the higher resistance of the ferrite phase to SCC crack propagation. It is concluded (13), however, that heat treatment which leads to an increase in the amount of ferrite displays a generally detrimental effect on cracking susceptibility at ambient temperature, presumably because the ferrite phase being more sensitive to hydrogen. Low temperature heat treatment which simulates service aging of cold-worked material, seems to have no detrimental effect; on the contrary such treatment may possibly have some beneficial effect on cracking susceptibility.

### **3.3 Effect of Alloying Elements**

Alloying has long been known to provide an effective means of improving the resistance of metals to attack by corrosive environments at either low or high temperatures. For example, it was found that the most efficient alloying elements for improving the oxidation resistance of iron in air are chromium and aluminium. Use of these elements together with nickel and silicon additions proved to be particularly effective. Figures (10) and (11) illustrate the beneficial effects of alloyed silicon and chromium on the corrosion behaviour of iron and low-carbon steel respectively. A further example on the general effect of low-alloy additions on the rusting of structural steel is reproduced in Figures (12) to (14). From the extensive data available for the influence of alloying elements on corrosion resistance, e.g. (15), the following features are worth noting:

- i Copper: additions up to about 0.2% indicate marked improvement; further additions bring, however, little or no improvement.

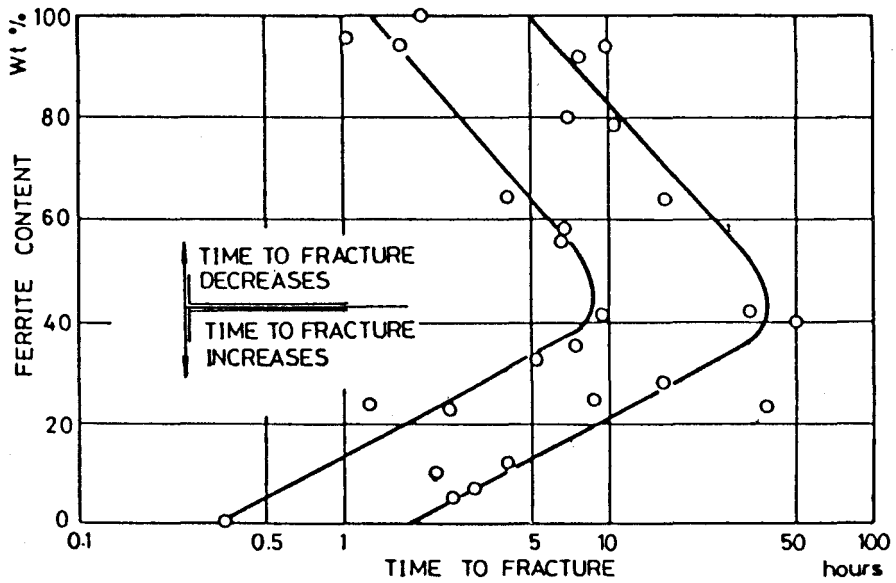


- ii Chromium: fractional percentages are shown to exert significant influence on corrosion rates.
- iii Phosphorus: highly beneficial when combined with copper. In practice, however, phosphorus content in excess of some 0.10% adversely affects mechanical properties.
- v Manganese: contribution to corrosion resistance not as yet well understood.
- vi Silicon: position similar to manganese.
- vii Molybdenum: so far with limited use, but may prove to be as effective as copper.

Various authors have shown that for regular commercial-quality steels in annealed and in normalised conditions, carbon content of steel plays a most significant role in determining intergranular cracking susceptibility. For austenitic steels, elements such as nitrogen would be held largely responsible for stress-cracking susceptibility. This is illustrated in Figure (13), (12), in which the addition of some 0.2 wt % nitrogen is shown to reduce time to failure from more than 200 hours down to less than 15 hours. On the other hand, the addition of carbon would lead to reduced susceptibility to cracking, Figure (14).

#### 4. HETEROGENEITIES IN METAL/ENVIRONMENT

Corrosion attack is generally uniform so long as the metal/environment is homogeneous, namely the metal being uniform in composition and the environment constituting uniform temperature, velocity, etc. Engineering metals have, scarcely such homogeneous structure. Grain boundaries, various phases and different mechanical and/or thermal treatments are heterogeneities that favour localized attack; metallographic etching of metals with a view to revealing structure is based on this concept. Typical forms of heterogeneities in metals are summarized in Table (5). Heterogeneities, which may develop during actual use of the component can lead to serious corrosion damage which is mainly localized, such as pitting, crevice, galvanic and intergranular corrosion, also stress corrosion cracking and corrosion fatigue (16).



**Fig. (9):** Effect of ferrite content on time to fracture for tensile specimens of various duplex alloys in boiling 42%  $Mg Cl_2$ . (Applied stress = 250 MPa).

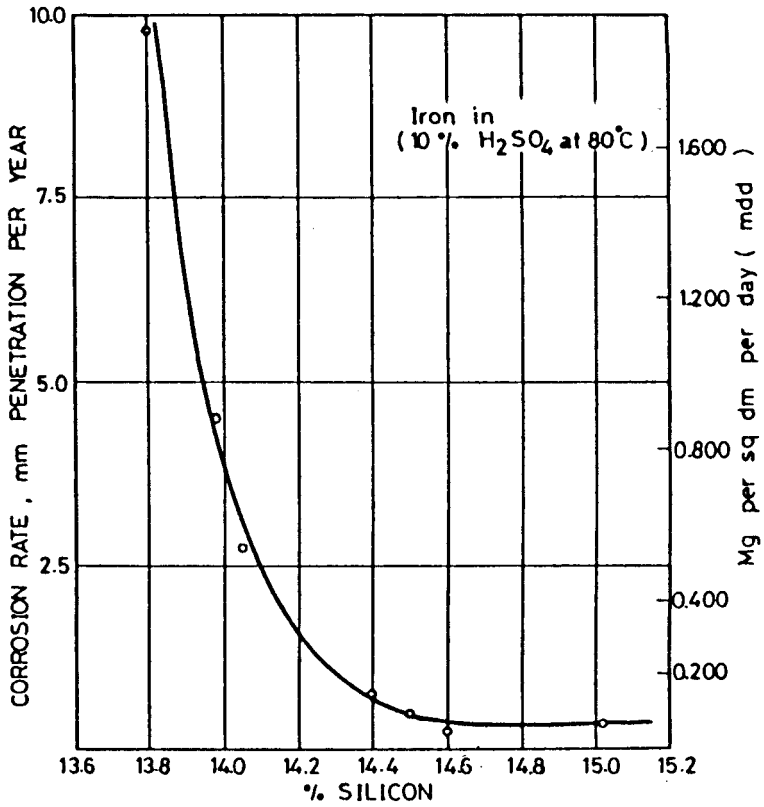


Fig. (10): Effect of silicon additions on the corrosion rate of iron.

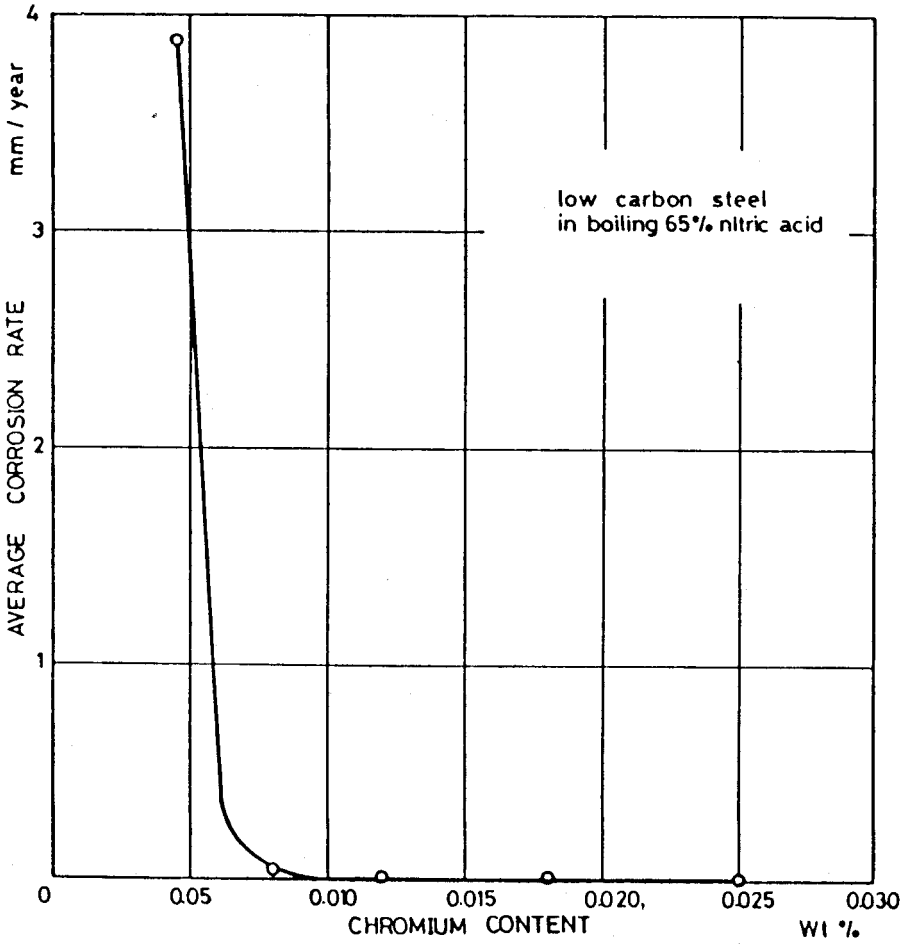


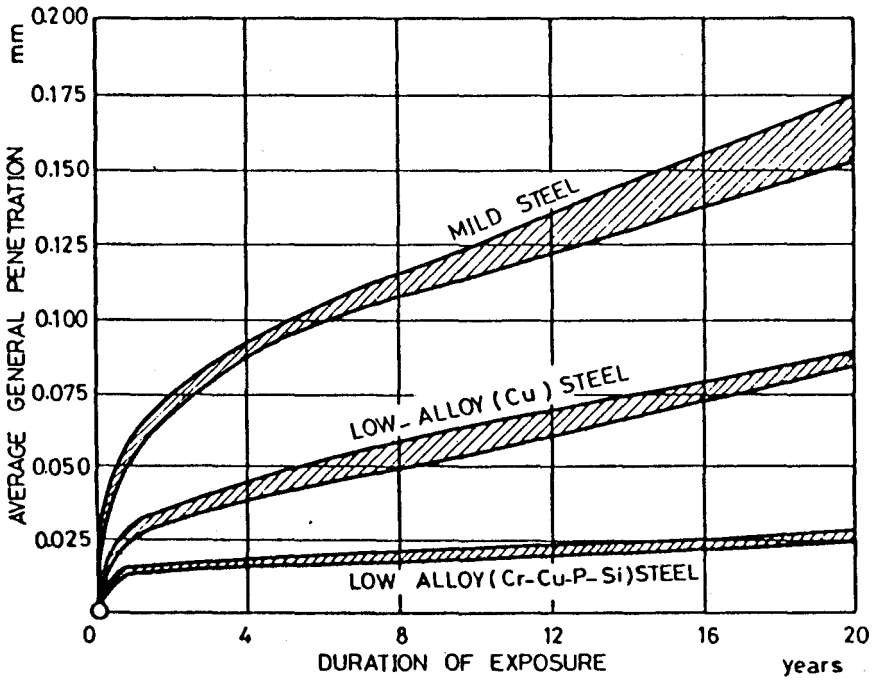
Fig. (11): Effect of chromium additions on the corrosion rate of low-carbon steel.

**Table (5): Typical Forms of Heterogeneities in Metals.**

Type	Description
1. Atomic	(a) Point defects : vacancies and interstitials (b) Line defects : screw and edge dislocations (c) Disordered molecules at point of emergence of dislocations
2. Microscopic	(a) Grain boundaries — usually more reactive than grain interior (b) Phases — single or multiphase
3. Macroscopic	(a) Grain boundaries (b) Discontinuities on metal surface : scratches, cut edges, discontinuities in oxide films or in applied coatings (c) Bimetallic couples of dissimilar metals (d) Geometrical factors : general design, crevices. .... etc.

**Table (6): Material Selection Check-list.**

<p><b>1. General physical properties:</b></p> <ul style="list-style-type: none"><li>— Chemical composition</li><li>— Contamination of contents by corrosion products</li><li>— Corrosion characteristics in various environments</li><li>— Effect of cold working</li><li>— Effect of high temperature on corrosion resistance</li><li>— Effect on strength after exposure to hydrogen</li><li>— Position in electrochemical series</li><li>— Susceptibility to various types of corrosion</li></ul>
<p><b>2. Mechanical properties:</b></p> <ul style="list-style-type: none"><li>— Compression, tension, shear, fatigue, hardness, etc.</li></ul>
<p><b>3. Design limitations:</b></p> <ul style="list-style-type: none"><li>— Velocity</li><li>— Temperature</li><li>— Contents</li><li>— Geometric form</li><li>— Loading</li><li>— Protection methods</li><li>— Maintainability</li></ul>
<p><b>4. Fabrication:</b></p> <ul style="list-style-type: none"><li>— Corrosion effects of forming</li><li>— Corrosion effects of welding</li><li>— Corrosion effects of machining</li><li>— Uniformity of characteristics</li><li>— Protective coatings</li><li>— Quality of surface finish</li></ul>
<p><b>5. Economic considerations:</b></p> <p>Such as availability and cost</p>



**Fig. (12): Enhancing corrosion resistance of steel outdoors through low-alloy additions.**

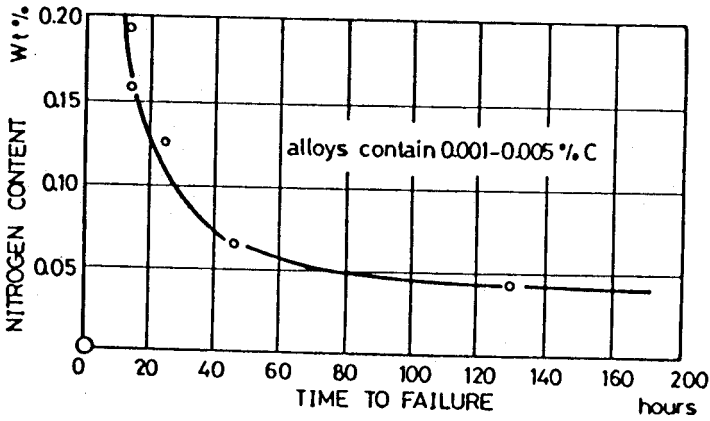


Fig. (13): Enhancing component life by reducing nitrogen content (Cold-rolled 19-20 Cr-Ni steel in boiling  $MgCl_2$ , at  $154^\circ C$ ).

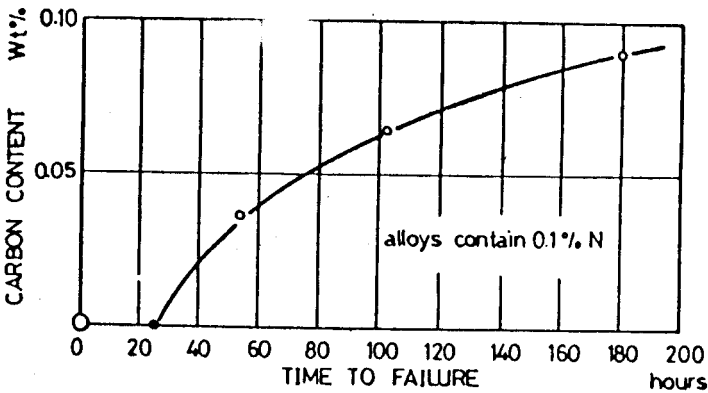


Fig. (14): Effect of carbon content on time to failure (Same material and medium as for Fig. 13).



## **5. MATERIAL SELECTION**

The susceptibility to various forms of corrosion can in many cases be reduced by the selection of suitable materials. Basically, the corrosion resistance of materials can be evaluated with due regard to the following considerations:

1. Type of corrosion to which the material is susceptible.
2. Experience gained during use of material under consideration.
3. Possibilities of effectively protecting material surface from corrosion.
4. Possible incompatibility problems with other contacting materials.
5. Adequacy of current corrosion prevention procedures. Availability of alternative methods or means.

It is evident that the selection of corrosion-resisting materials calls for expert knowledge, both in engineering and in corrosion control. Normally close cooperation between the designer and the corrosion or material engineer is needed. In the material selection check list given in Table (6), data obtained should serve in determining suitable materials and fabrication methods for the specific application under consideration. More emphasis is given, however, to material properties having direct impact on corrosion resistance. Several materials may be considered before relevant optimal choice is stuck; such material should not be expected to satisfy all required features, consequently a compromise has to be accepted.

## **6. CONCLUSION**

It is herein concluded that the selection of most suitable metals or alloys to work under specific corrosive environments constitutes one of the most effective methods of controlling or even preventing corrosion. In selecting such materials, heterogeneities in metals and/or environment should be critically examined. The designer is herein provided with a material selection check-list in an endeavour to enable him to place his design on a corrosion-conscious basis.

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