

## STAINLESS STEEL AND CORROSION

### HOW STAINLESS STEEL IS AFFECTED BY, AND RESISTS, CORROSION

Steel is the most utilized material of construction. However, natural forces cause steel, an unnatural form of iron, to revert to its natural oxide. This is corrosion.

The primary property of stainless steel is corrosion resistance and may be considered as the only reason why we use the material. Some may say that they use stainless steel for hygiene properties or for aesthetics, but it is the resistance to corrosion which allows stainless steels to have these essential benefits.

Stainless steels, because of their resistance to corrosion, are often used in highly aggressive conditions, which will cause most alternative materials to fail rapidly.

Therefore, an understanding of the basic mechanisms of corrosion will assist in selecting the correct stainless steel for use in a variety of situations and conditions.

### CORROSION

Essentially there are two forms of corrosion.

- Wet (aqueous) corrosion
- Dry (gaseous) corrosion

This paper will cover the more common mechanisms of Wet (aqueous) corrosion of stainless steel which can consist of one, or more, of the following forms of attack

- General corrosion
- Galvanic corrosion
- Atmospheric corrosion
- Erosion/abrasion corrosion
- Intergranular corrosion
- Pitting corrosion
- Crevice (shielded) corrosion
- Microbiologically induced corrosion (MIC)
- Stress corrosion cracking (SCC)

These different forms of corrosion are sometimes thought to affect only stainless steels. This is not the case. Carbon steels, low alloy steels and many other metals and alloys may also undergo similar forms of corrosive attack, but often in different environments.

Dry, or gaseous corrosion will be covered in an upcoming module addressing the high temperature use of stainless steels.

Some forms of corrosion are easily visible or readily identifiable (e.g. general and pitting corrosion), whereas others are not always easily detectable nor apparent (e.g. stress corrosion cracking, SCC).

### WET (AQUEOUS) CORROSION

This is an attack on the metal by aggressive substances generally dissolved in water to give a corrosive solution (electrolyte). A damp film or dust containing dissolved aggressive substances also results in a corrosive electrolyte.

The severity and extent of the corrosion depends on

- The concentration of such aggressive substances in the corrosive solution.
- The temperature of the corrosive solution.
- The presence and nature of contaminants and trace elements within the solution.

### THE CONCENTRATION

This is generally both known and controlled. Care should be taken to avoid conditions where the concentration can vary, e.g.

- Condensation and evaporation
- Concentration in crevices as this may result in unexpected, severe or localised corrosion attack.

### THE TEMPERATURE

This is usually known and uniform. Care must be taken to prevent higher localised temperatures. A typical example of such a condition is that prevailing under heat transfer, for example, solar heaters or heating coils.

super-heated corrosive solution that exists at the metal surface, through which the heat is transferred. It is the

temperature of this film which must be taken into account, as it gives rise to far more aggressive conditions than those related to the average bulk temperature.

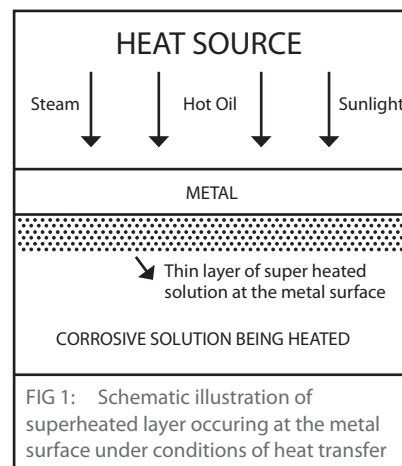


FIG 1: Schematic illustration of superheated layer occurring at the metal surface under conditions of heat transfer

### THE PRESENCE AND NATURE OF CONTAMINANTS

Because all aqueous corrosion is electrochemical there is always an equilibrium between the reactions at the metal surface and those within the corrosive solution. Even trace amounts of contaminants can affect this balance and therefore either aggravate or counteract and lower the severity of the corrosion.

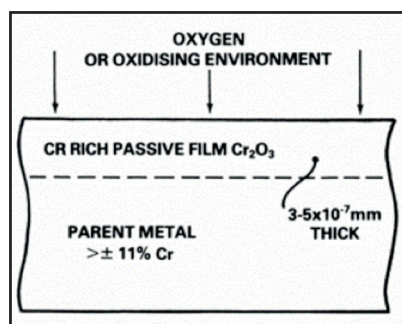
### STAINLESS STEEL

Stainless steel is a generic term covering a family of chromium (Cr) containing alloys. The chromium content is usually between 11 and 30%. Other alloying elements which increase

the corrosion resistance of stainless steel may also be added, such as, nickel (Ni), molybdenum (Mo), copper (Cu), titanium (Ti) and niobium (Nb).

This has been covered in detail in Module 1 of the Information Series.

The various different groups of stainless steel are schematically reflected in the Stainless Steel Family Tree, alongside.



## PASSIVITY

Passivity is the built-in mechanism which stainless steels possess to combat corrosion. It is defined as a state in which a metal or alloy loses its chemical reactivity and becomes inert.

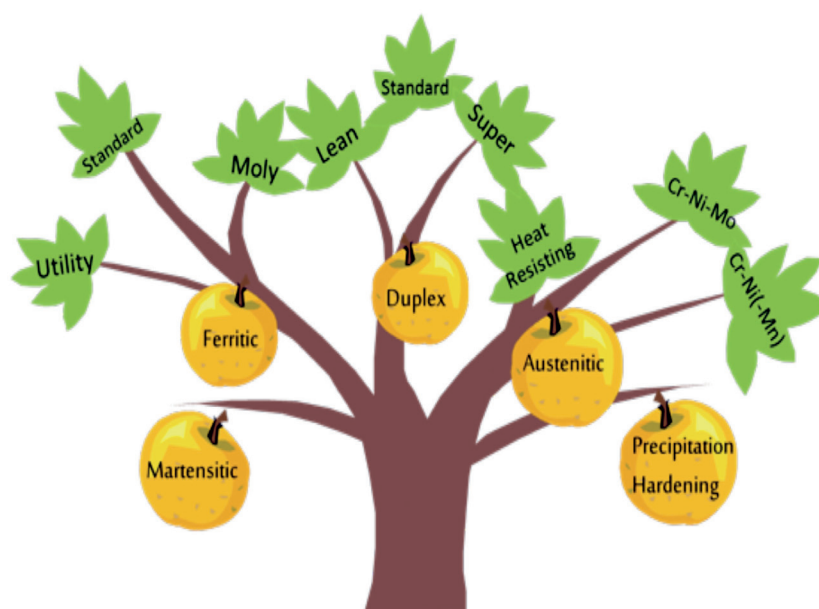
A chromium content of more than approximately 11% gives stainless steel this passivity, due to the formation of an extremely thin but uniform, continuous, tenacious and stable chromium-rich oxide film on the surface.

The formation and properties of the passive film are enhanced by increasing the chromium content and also by adding certain other elements, particularly molybdenum and nitrogen. The improved passivity which results extends the use of stainless steels into more corrosive applications.

The key to the corrosion resistance of stainless steels is this passive layer and care must be taken to ensure that, if damaged in any way, it should be allowed to repair itself.

The passive layer can be damaged or removed **mechanically** (scratching, machining or polishing), **thermally** (by welding or heat treatment) or **chemically** (by contamination with iron particles or salt). If this happens, the corrosion resistance of the steel may become compromised.

The passive film will re-form spontaneously in an oxygen containing environment (provided that the surface has been thoroughly cleaned or descaled) to restore the corrosion resistance of the stainless steel, but this does not happen instantaneously. In addition, any contamination or thermal



discolouration needs to be removed before passivation can take place.

**Passivation** is the chemical treatment of a stainless steel with a mild oxidant, such as a nitric acid solution, for the purpose of enhancing the spontaneous formation of the protective passive film. Such chemical treatment is generally not necessary for the formation of the passive film, but will generate a more rapid and complete passivity.

**Thermal contamination** can be removed mechanically (by grinding/polishing) or chemically by pickling. Pickling is an acid treatment to remove high temperature oxide films resulting from welding, heat treatment, hot working or other high temperature operations. Mixed acids solutions, such as nitric+hydrofluoric acid solutions, are most widely used by fabricators of stainless steel equipment and removes both metallic contamination and high temperature scales. These scales are not only undesirable for aesthetic reasons, they also result in a reduced corrosion resistance of the underlying stainless steel surface layer. Passivation alone will not remove the scale. Chemical passivation alone is, however, able to remove **ferrous contamination** and re-form the passive layer. Note that chemical passivation is not necessarily required as a separate step after pickling. All that is required is that the stainless steel equipment is properly rinsed with clean water and dried.

In the case of the passive layer being destroyed by **mechanical damage**, the passivity can be restored by passivation, as detailed above.

Care must be taken to maintain and preserve the integrity of the passive film.

■ Avoid mechanical damage and contamination.

■ Repair any affected areas, for example;

- high temperature scale adjacent to a weld, by pickling
- mechanically damaged or ground areas, by optional passivation
- contaminated areas by passivation.

■ Ensure a constant and sufficient availability of oxygen or oxygen containing agent.

## FORMS OF CORROSION

A number of different mechanism of corrosion of stainless steel are recognised. The underlying mechanism of all aqueous corrosion is electrochemical in nature, but the initiation of corrosion, often due to a breakdown of the passive layer, may be caused in different ways, depending on particular conditions.

## GENERAL CORROSION

In general corrosion, the attack is uniform over the entire surface and is similar to that generally seen on mild steel. General corrosion of stainless steels is normally observed in highly corrosive reducing acid environments, often associated with the chemical and mining industries.

It is the least dangerous form of corrosion because the rate of corrosion is measurable and predictable and can therefore be allowed for when

designing for a required life or safety factor.

General corrosion rates are measured and reported in different units as;

- a corrosion current in milliamp per square centimetre (mA/cm<sup>2</sup>)
- a penetration of thickness in millimetre per year (mm/year)
- a loss of thickness in milli-inches (mils) per year (mpy)
- a loss of mass in grams per square metre per day (g/m<sup>2</sup> • day)

Conversion between the units for the corrosion of iron (Fe) is as follows:

The severity of attack or suitability of material is indicated in different ways. General corrosion rates are often determined under laboratory conditions using chemically pure

solutions. More meaningful results are obtained if plant solutions are used, or if the corrosion rates are determined under in- service conditions.

The most common indicator, and that used in a number of different “corrosion manuals”, is that of a band of corrosion rates, as indicated in Table 1 below: These bands are used in drawing up iso-corrosion graphs, used by corrosion engineers to predict safe operating conditions in various chemical environments, as illustrated in Tables 2 and 3 below. Typically a band of “0” is considered to be safe, that of “2” is unacceptably high, while “1” is an intermediate area and should be treated with caution.

Reported general corrosion rates often

	mA/cm2	mm/year	mpy	g/m2 • day
mA/cm2	1	11.6	456	249
mm/year	0.063	1	39.4	21.6
mpy	0.00219	0.0254	1	0.547
g/m2 • day	0.00401	0.0463	1.83	1

TABLE 1: SEVERITY OF ATTACK AND SUITABILITY OF MATERIAL FOR DIFFERENT CORROSION RATES

CORROSION RATE	CORROSION RATE
<b>Band 0</b> <0,1mm/yr (<5mpy)	<b>Highly resistant</b>
<b>Band 1</b> 0,1-1,0mm/yr (5-50 mpy)	<ul style="list-style-type: none"><li>• Transition from highly resistant to severe corrosion.</li><li>• Metastable.</li><li>• Consider use with care.</li></ul>
<b>Band 2</b> >1,0mm/yr (>50mpy)	<b>Severe corrosion</b> <b>Not suitable</b>

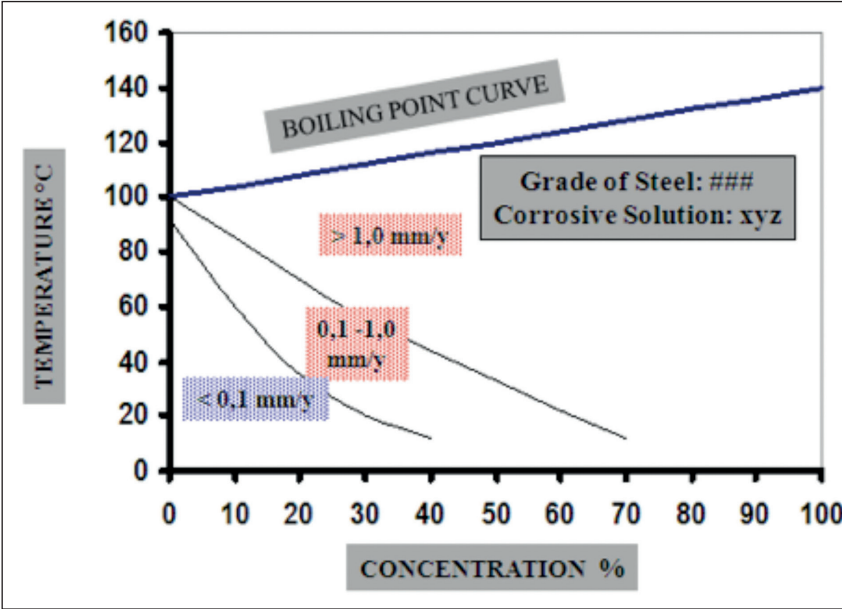


Table 2: Generic isocorrosion graph

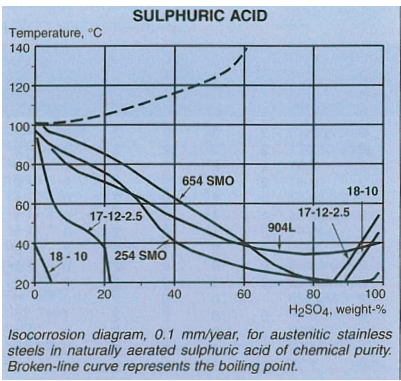


Table 3: Isocorrosion graph showing suitability of different stainless steel grades in sulphuric acid

have a notation of “Op”. This indicates that an additional corrosion mechanism is likely to occur (pitting corrosion in this example) and care must be exercised.

Reported general corrosion rates, as indicated above, should be used as guidelines only and full account should be taken of:

- Service conditions/variations.
- State of the metal surface/maintenance of passivity.
- The corrosive solution in respect of uniformity/variation in terms of concentration, temperature and contaminants.

Stainless steels exhibit very low general corrosion rates in many highly aggressive, corrosive environments. They are not totally immune or impervious, but are versatile materials of construction offering attractive and viable life cycle costs.

Under some conditions the surface may exhibit signs of staining i.e. visible rusting. It is very seldom that such staining indicates corrosion rates equivalent to those of plain carbon (mild) steel and, even if left untreated, minimal metal loss will occur. A simple cleaning process will usually remove the staining and restore the surface appearance. However the cause should be investigated, especially if severe dark staining is evident, as it is an indication that passivity has broken down.

## GALVANIC CORROSION

Galvanic corrosion can occur when two different metals are in electrical contact and are immersed in the same corrosive solution.

The galvanic series (or electro potential series) determines the nobility of metals and semi-metals. When two metals are submerged in an electrolyte, while electrically connected, the less





noble (base) will experience galvanic corrosion. The rate of corrosion is determined by the electrolyte and the difference in nobility. The difference can be measured as a difference in voltage.

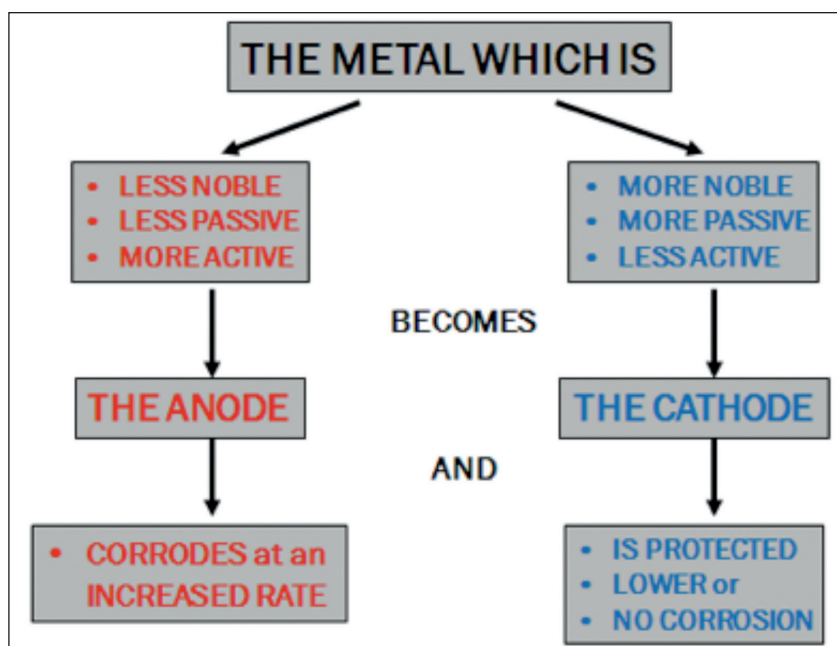
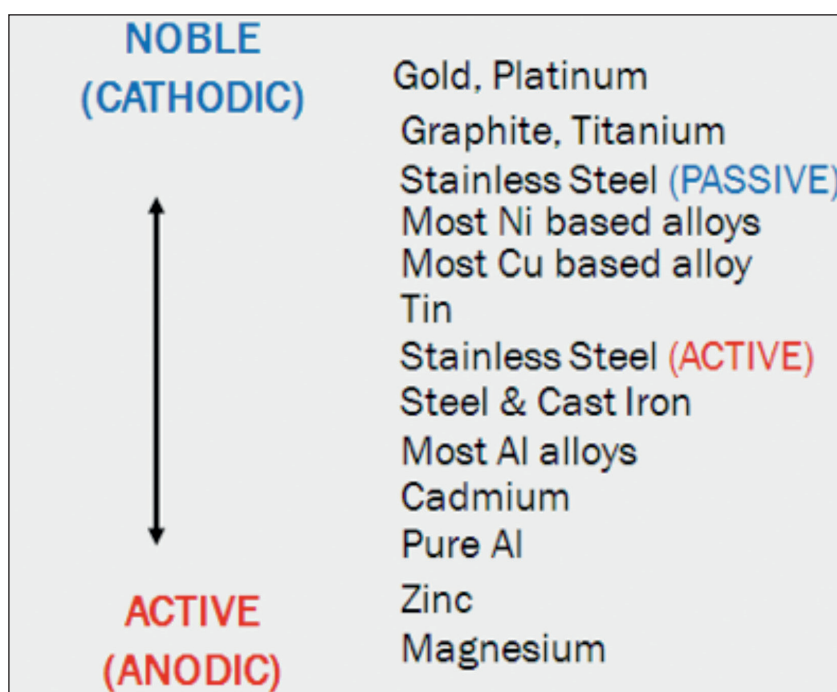
The adjacent image illustrates the galvanic series for seawater (in decreasing order of electrical activity). Metals nearer the bottom of the table are less noble and have a greater tendency to lose electrons than the more noble metals found higher on the list.

Note that stainless steel appears twice in this galvanic series. This represents the stainless steel in the active state, with no passive film and in the passive state, with the passive film intact.

The relative surface area of two metals is an important factor when evaluating galvanic corrosion. If the surface area of the more noble metal is small compared with the surface area of the less noble metal, the more noble metal will not significantly accelerate the corrosion of the larger area of the less noble metal.

In the first example below, the large area of stainless steel sheet will dramatically increase the corrosion rate of the carbon steel fasteners resulting in a rapid failure.

In the second example below, the stainless steel fasteners will not accelerate the corrosion of the steel plate because the area of the anode (carbon steel) is large compared to the cathode (stainless steel fasteners).



## PITTING CORROSION

Pitting corrosion, or pitting, is a form of extremely localised corrosion that leads to the creation of small holes in the metal. The driving power for pitting corrosion is the depassivation of a small area, which becomes anodic while the balance of the product (a much larger area) becomes cathodic, leading to very localised galvanic corrosion. The corrosion penetrates the mass of the metal, with limited diffusion of ions.

In stainless steels, pitting corrosion is generally caused by halide ions (which are usually chlorine ions, as these are found in sea water, soils and many raw materials). These halide ions:

- Attack localised weak points in the passive film,
- Destroys passivity in a very small area, forming
  - Micro-anodes,
  - Extremely unfavourable 'galvanic effect'.

There are several preventive approaches to avoid pitting. Examples are listed below:

- Proper material selection e.g. using 316, or duplex stainless steels containing Mo or N and having a higher pitting resistance compare to 304. In other words, use higher alloyed stainless steels for increased resistance to pitting corrosion.
- Control pH, chloride concentration and temperature.
- Agitation of stagnant fluid.

## PITTING RESISTANCE EQUIVALENT (PRE) – RELATIVE PITTING RESISTANCE

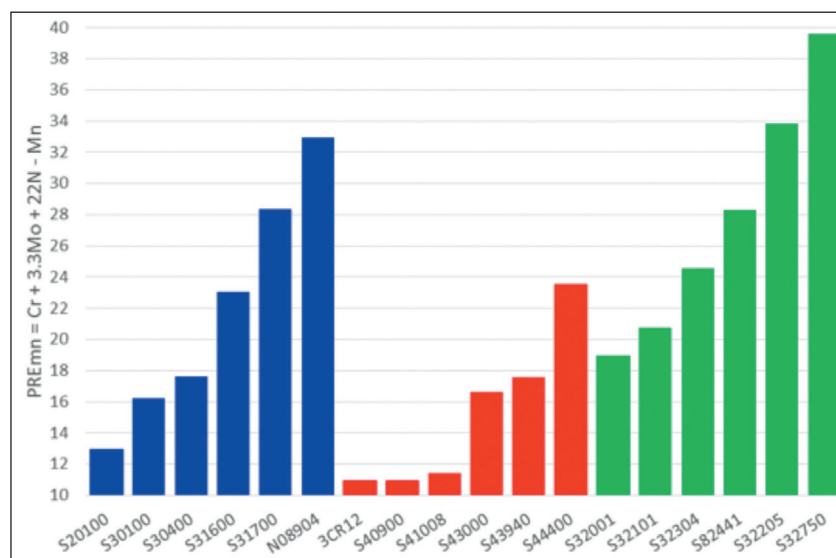
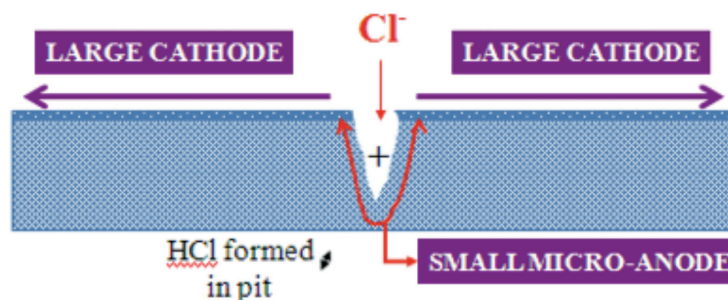
The pitting resistance equivalent number (PRE or PREN) is a measure of the relative pitting corrosion resistance of stainless steel in a chloride-containing environment. The pitting resistance of stainless steel is primarily determined by its composition. The elements which have a significant impact are chromium, molybdenum and nitrogen.

The formula, which quantifies their respective contribution, is:

$$PREN = CR + 3.3MO + 16N$$

This is the most common PRE formula that is used. A more accurate PRE formula that is becoming more commonly used is PRE<sub>mn</sub>, which takes into account the negative effect of manganese.

## Pitting Corrosion



$$PRE_{mn} = CR + 3.3Mo + 22N - Mn$$

The chart above shows the relative pitting corrosion resistance of some of the most common stainless steels. Ferritics are shown in red, austenitics in blue and duplex stainless steels in green.

The graph can be used as a tool for material selection and material substitution. For example, it can be seen that 304, 441 (S43940) and 2001 have similar pitting resistances and can thus be used in similar environments. Similarly, 316, 444 and 2304 are similar, have better pitting resistance and for example are suitable in marine atmospheres.

■ Originally the PRE was used as an indication of resistance to pitting in sea water:

- If > 36, then resistant to pitting in marine environments including splashing.
- PRE > 40 is required for sea water immersion.

## CREVICE CORROSION

Crevice corrosion refers to corrosion occurring in confined spaces in which



the access of the corrosive to the stainless steel surface is limited. These spaces are generally called crevices.

The corrosion resistance of a stainless steel is dependent on the presence of the passive film, but it is possible under certain conditions for this passive film to break down, for example in halide solutions or reducing acids. However, areas where the passive film can break down can also be the result of the way components are designed, for example under gaskets, in sharp re-entrant corners or associated with incomplete weld penetration or overlapping surfaces. These can all form crevices which can promote corrosion.

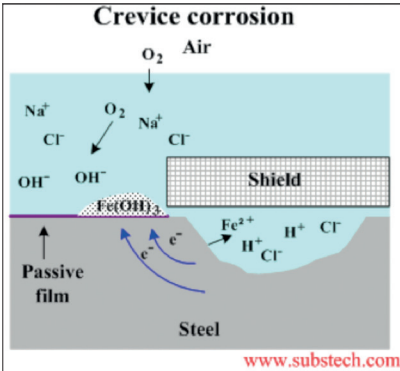
To function as a corrosion site, a crevice has to be of sufficient width to permit entry of the corrodent, but narrow enough to ensure that



the corrodent remains stagnant. Accordingly, crevice corrosion usually occurs in gaps a few micrometres wide and is not found in grooves or slots in which circulation of the corrodent is possible. This problem can often be overcome by paying attention to the design of the component, in particular to avoiding formation of crevices or at least keeping them as open as possible, or by using flexible washers or gaskets which form a perfect seal.

Crevice corrosion is a very similar mechanism to pitting corrosion; alloys resistant to one are generally resistant to both. Crevice corrosion can be viewed as a less severe form of localised corrosion when compared with pitting. The depth of penetration and the rate of propagation in pitting corrosion are generally significantly greater than in crevice corrosion.

Crevices can develop a local chemistry which is very different from that of the bulk fluid.



## ATMOSPHERIC CORROSION

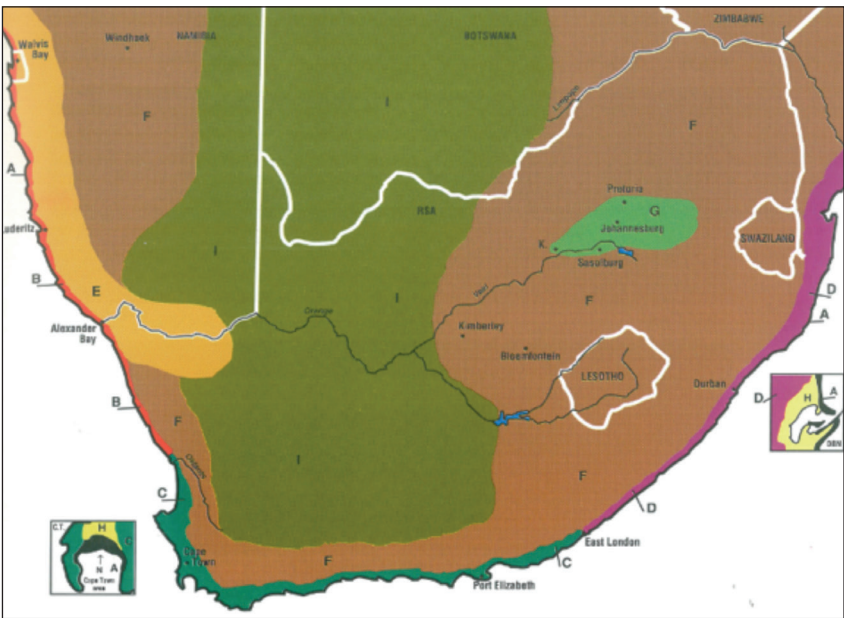
Atmospheric corrosion is:

- The corrosion of metals exposed to air and its pollutants.
- An electrochemical process where a film of electrolyte forms on the metal surface.
- When air pollutants such as SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub> and salts dissolve in a film of water and increase its conductivity and corrosivity.

Atmospheric corrosion is a serious worldwide problem affecting people in all walks of life. It is of concern to homeowners, architects, engineers, designers, maintenance personnel and accountants. All outdoor and indoor materials exposed to the elements are potentially subjected to degradation resulting from atmospheric conditions.

Damage caused by atmospheric corrosion can be dangerous as well as costly, for example:

- Bridges failing as a result of rusting



Code	Description	Map area.	Type of corrosion
A	Intertidal to 5km inland		Severe marine
B	Desert Marine (Mists)		Severe marine
C	Temperate marine		Marine
D	Sub-tropical marine		Medium to severe marine
E	Desert inland dry		Desert
F	Inland		Rural
G	Inland urban		Inland industrial++
H	Urban coastal		Marine industrial++
I	Inland arid		Semi desert

and consequent failure of steel parts, ■ Essential automobile parts failing from corrosion.

Costly repairs include repair and painting of bridges and towers, replacing of fencing and maintenance of building exteriors, to name a few.

Generally, atmospheric corrosion is defined by geographic location, local weather conditions and architectural design.

There are several factors to take into account in determining the degree of corrosion to be expected:

- Environment,
  - Rural, urban pollution, industrial pollution.
- Salt,
  - Coastal/marine exposure and distance from sea.
  - De-icing salt exposure (normally only in in Europe and North America).
- Weather,
  - Temperatures, humidity and rainfall.
- Design,

- Exposed surfaces facilitating rain cleaning.
- Surface finish of stainless steel and roughness.
- Maintenance,
  - Washing frequency.

The corrosion rate can be decreased by controlling the above five factors or by selecting a more corrosion resistant stainless steel. The corrosion map of South Africa is shown above.

## INTERGRANULAR CORROSION

Intergranular corrosion, sometimes known as sensitisation, is a form of corrosion where the boundaries of grains of the material are more susceptible to corrosion than that the rest of the grain.

This is most frequently caused during the welding of thick sections of high carbon stainless steel as a result of chromium carbide precipitation at the grain boundaries and chromium

depletion of the surrounding areas. The chromium depleted areas around the grain boundaries can be preferentially dissolved in certain corrosive environments. This is known as sensitisation and is summarised below.

Intergranular corrosion occurs where carbon content in the stainless steel is high, or where cooling rates in welding or heat treatment are slow. In most cases, modern steelmaking practice has reduced the carbon content to levels at which we seldom see sensitisation, except in extremely heavy fabrications. However, carbon contamination during fabrication or in service is now a more serious cause of this problem.

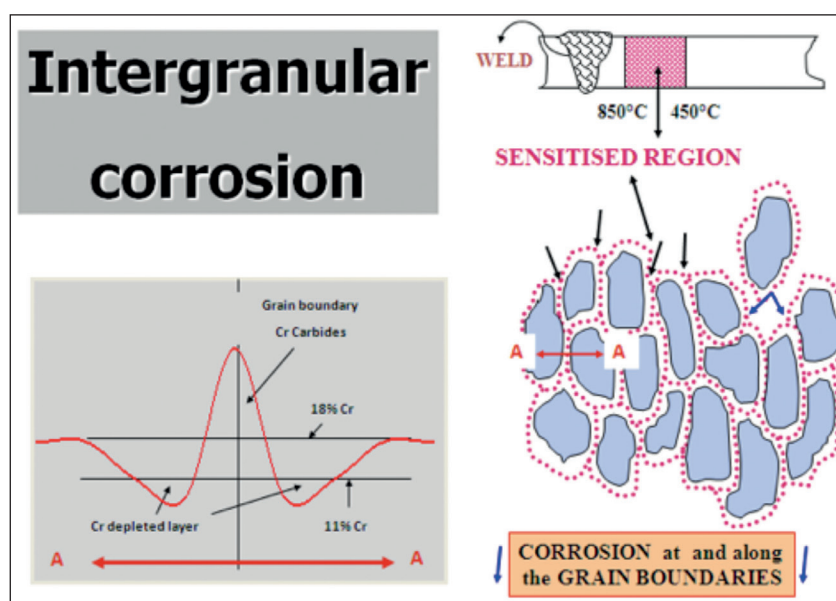
Intergranular corrosion can be prevented through:

- Using a low carbon (e.g. 304L, 316L) grade of stainless steels.
- Using stabilised grades alloyed with titanium, for example type 316Ti, niobium stabilised grades, for example 347, can also be used.
- Titanium and niobium are strong carbide-formers. They react with the carbon to form the corresponding carbides, thus tying up the carbon, thereby preventing chromium carbide formation and resultant chromium depletion at the grain boundaries.
- Using post-weld heat treatment to dissolve the carbides and put chromium back into solution.
- Ensuring that the welding processes used have sufficiently low heat inputs to increase the cooling rate.
- Ensuring that the stainless steel is not contaminated with carbonaceous materials, especially prior to welding or heat treatment.

## MICROBIOLOGICALLY INFLUENCED CORROSION

Microbiologically Influenced corrosion (MIC) results from the microbiological activity of certain bacteria, often found in untreated water. It has the following consequences:

- It can cause very aggressive corrosive attack.
- It affects many different materials, not just stainless steel.
- There are two types of bacteria:
  - Aerobic: Requires environment containing oxygen.
  - Anaerobic: Requires environment free of (or low in) oxygen.
- Sulphate Reducing Bacteria (SRB). Sulphate-reducing bacteria are those



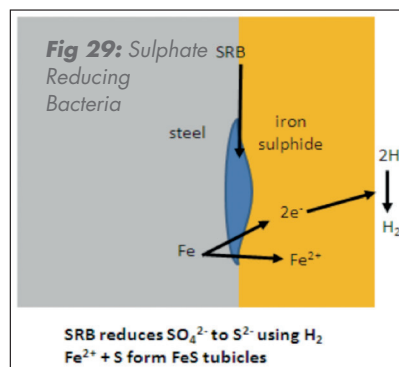
bacteria that can obtain energy by oxidising organic compounds or molecular hydrogen ( $H_2$ ) while reducing sulphate ( $SO_4^{2-}$ ) to hydrogen sulphide ( $H_2S$ ). In a sense, these organisms “breathe” sulphate rather than oxygen, in a form of anaerobic respiration.

Microbiologically influenced corrosion is a common problem in industrial processes due to the presence of microbes, adequate nutrients and corrosive by-products. Frequently MIC results in corrosion failures in waters of extremely low corrosivity and so it is often unexpected.

MIC is most frequently found in water cooling systems and heat exchangers and can result in extremely rapid perforation of tubes and vessels. It is also common in the mining industry due to the presence of these bacteria in underground mine waters.

Microbiologically influenced corrosion (also known as MIC) can be prevented through a number of methods such as:

- Regular mechanical cleaning if possible.
- Chemical treatment of the water with biocides to control the population of bacteria.



**Fig 30: Microbiologically Influenced Corrosion**

- Complete drainage and dry-storage.
- Use of higher alloyed stainless steels, although this may be the most expensive route.

## STRESS CORROSION CRACKING (SCC)

Stress corrosion cracking is a localised mechanism of corrosion that requires a tensile stress, a susceptible material and a specific environment.

Many metals can suffer SCC, but there has to be a tensile stress, a specific environment and a susceptible material. In the case of stainless steels, the key issue is the austenitic microstructure. This means that austenitic stainless steels, with nickel between 5% and





25%, can be susceptible to SCC. In stainless steels the specific environment is halide ions (chlorides, bromides and fluorides). SCC in austenitic stainless steels normally only occurs above about 50°C. Because super austenitics like 254SMO have very high nickel contents, they are resistant to stress corrosion cracking.

Duplex stainless steels can also suffer from SCC in extreme conditions, such as very high chloride levels or temperatures in excess of 100°C.

Ferritic stainless steels do not suffer from chloride induced SCC.

Stress corrosion cracking can be prevented through:

- Avoiding the chemical environment that causes SCC.

- Control of hardness and stress level (residual or load).

- Introducing compressive stress for example by shot-peening.

- Use of materials known not to crack in the specified environment.

- Control operating temperature

- Anti SCC lacquer – i.e. eliminate contact with the environment.

Failure in stainless steels is due to fine branching transgranular cracks.

## ABRASION & EROSION CORROSION

Erosion and abrasion corrosion are two mechanisms which involve a combination of mechanical and corrosive attack. Abrasive particles in suspension, travelling at high velocities, expose fresh metal surfaces which then suffer high rates of corrosion. stainless steels offer a high resistance due to the synergistic effect of wear plus corrosion (i.e. wear increases the corrosion rate and corrosion increases the wear rate).

Abrasion corrosion is characterised by low stress and low angle particle wear, for example coal sliding over a wear plate or slurry in a pipe line.

Erosion corrosion is characterised by high stress and high angle wear. For example slurry at a pipe bend or cavitation in a pump impeller, caused by collapse or implosion of air or gas bubbles at the metal surface.

This form of corrosion is best addressed by:

- Suitable selection of materials,

- Appropriate design,

- Change of environment,

- Application of corrosion-resistant coatings, and

- Cathodic protection.

