

The  $\text{FeSO}_4$  formed accelerate corrosion, once rusting has started, corrosion cannot be stopped even after  $\text{SO}_2$  is removed from air.

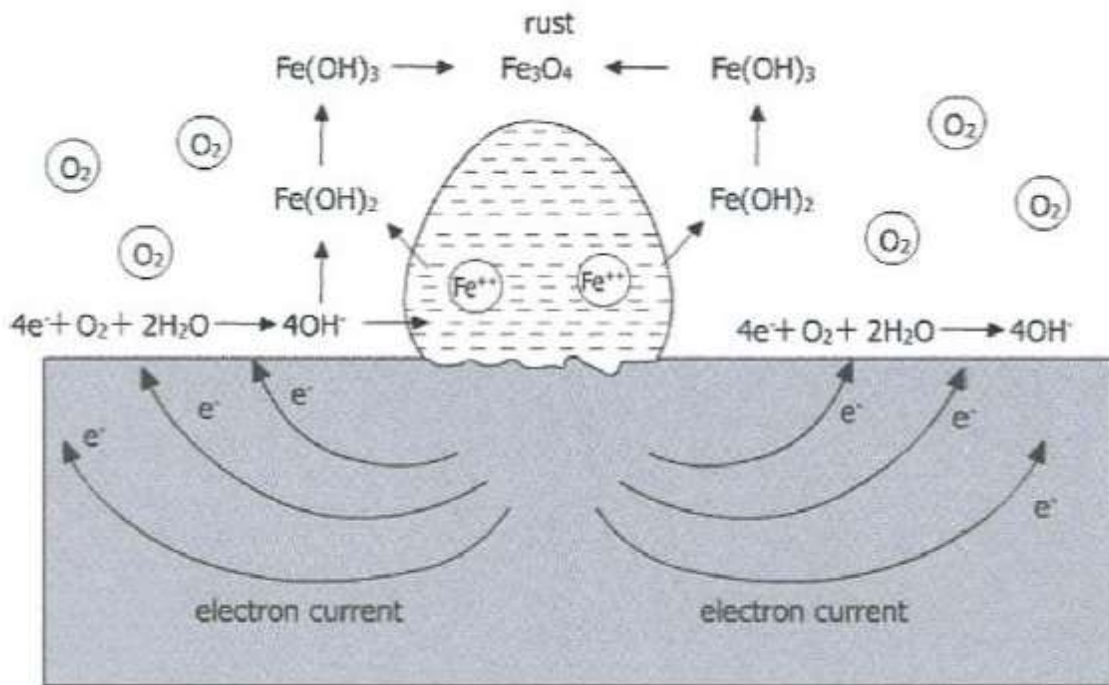
- 2) Effect of humidity: Corrosion can be caused in the atmosphere when more than 60% of the humidity is present, as this is the value in equilibrium with saturated  $\text{NaCl}$  solution and  $\text{NaCl}$  is commonly present on surfaces. In the presence of such humidity, an invisible thin film of moisture is formed on the surface of a metal. The thin film of moisture acts as an electrolyte for the passage of current. Structures which are exposed to open air, are affected by damp environments. Beyond 80% relative humidity, a sharp increase in the rate of corrosion is observed.
- 3) Water layer: If visible water layers are formed on the metal surface, corrosion initiates. Splashing of seawater, rain and drops of dew provide the wet environment. The water layer on the metal surface acts as an electrolyte and provides a passage for the flow of current, similar to the situation in a corrosion cell.
- 4) Dew formation: If the dew becomes acidic, due to the presence of  $\text{SO}_2$ , it increases the rate of corrosion. Automobiles left open in the air may be subject to corrosion through acidic dew formation.
- 5) Corrosion products: If the corrosion product on the metal surface is microporous, it can condense the moisture, below the critical value. Corrosion proceeds rapidly in such a case, even if the moisture content is below the critical limit.

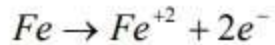
### **Mechanism of uniform corrosion**

Corrosion mechanism in aqueous solution has been amply demonstrated. A very thin layer of electrolyte is present. It is probably best demonstrated by putting a small drop of seawater on a piece of steel. On a metal surface exposed to atmosphere, only a limited quantity of water and dissolved ions are present,

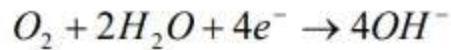
whereas the access to oxygen present in the air is unlimited. Corrosion products are formed close to the metal surface, unlike the case in aqueous corrosion, and they may prevent further corrosion by acting as a physical barrier between the metal surface and environment, particularly if they are insoluble as in the case of copper or lead. The following is a simplified mechanism of aqueous corrosion of iron.

At anodic areas, anodic reaction takes place:

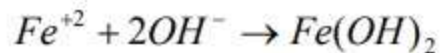




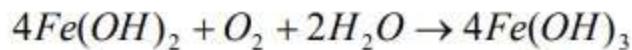
At cathodic areas reduction of Oxygen takes place



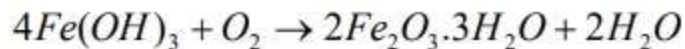
The OH ions react with iron ions , produced at the anode



With more access to Oxygen in the air ,  $Fe(OH)_2$  oxidizes to  $Fe(OH)_3$



Ferrous hydroxide is converted to hydrated ferric oxide or rust by oxygen



Rust ( $Fe_2O_3 \cdot 3H_2O$ ) is formed halfway between the drop center and the periphery .the electrons flow from the anode (drop center) to cathode (periphery) in the metallic circuit. The current flow is shown in above figure. The ferrous ions on the surface of iron are soluble whereas those in solution are oxidized by oxygen to insoluble hydrated oxides of ferric called rust. The rust is formed away from the corroding site.

The corrosion rate is very high if the ferrous ion is oxidized to ferric oxide rapidly.  $Fe(OH)_3$  is insoluble and if it forms away from a metal surface, the corrosion reaction speeds up as equilibrium is to be maintained by supplying more ferrous ions ( $Fe^{+2}$ ) from the surface. If, however,  $Fe(OH)_3$  is formed on the surface of a metal very rapidly, the corrosion is prevented (a passive film).

**Example of uniform corrosion:**

- a) Tarnishing of silver ware.
- b) Tarnishing of electrical contacts.
- c) Rusting of steels in open air.
- d) Corrosion of offshore drilling platforms.

- e) Corrosion of galvanized steel stairways.
- f) Failure of distillation columns.
- g) Corrosion of electronic components.
- h) Corrosion of underground pipes (composite asphalt coated).
- i) Corrosion of automobile bodies.
- j) Corrosion of heat exchanger tubes.
- k) Corrosion of structural steels.

Corrosion allowance: A popular remedy is to make a corrosion allowance. After calculating the rate of corrosion penetration and knowing how much thickness of the metal would be reduced after a specified period, an equivalent amount of thickness maybe added to prevent the loss of designed thickness. A corrosion allowance is, therefore, made at the design stage to prevent the loss of thickness by general corrosion. For instance, if the predicted rate of corrosion for a new carbon-steel product cooler is 4 mpy, as the unit is designed for 15 years, the required corrosion allowance is 4 mpy x 15 years = 60 mils (0.060 in).

The general practice is to allow 1/8 in, or 3.2 mm minimum corrosion allowance.

$$\text{Estimation of remaining life (years)} = \frac{\text{Remaining corrosion allowance(mils)}}{\text{Present corrosion (mpy)}}$$

For example, consider a crude oil tower overhead pipeline. Due to some accident, the crude tower was shutdown. The general wall thickness measured was 0.14 in on a 35 in diam. carbon steel overhead line. The minimum thickness required is 0.15 in. The current corrosion rate is 40 mils/year. Another shutdown for inspection is scheduled to take place after two years. Use the above equation to estimate the remaining life.

$$2 \text{ years} = \frac{\text{corrosion allowance remaining}}{40 \text{ mpy}}$$

**So corrosion allowance remaining = 80 mils (0.080 in)**

**The required remaining thickness = 0.15 in + 0.080 in = 0.23 in.**

The best solution, therefore, would be to install reinforcing plates of above 0.20 inch in thickness.

**How to prevent uniform corrosion?** Uniform corrosion or general corrosion can be prevented through a number of methods:

- 1) Use thicker materials for corrosion allowance
- 2) Use paints or metallic coatings such as plating, galvanizing or anodizing
- 3) Use Corrosion inhibitors or modifying the environment
- 4) Cathodic protection (Sacrificial Anode or Impressed Current -ICCP) and Anodic Protection

## 3-2 Galvanic Corrosion or Dissimilar Metal Corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Contact between dissimilar metals occurs frequently but is often not a problem. The aluminum head on a cast iron block, the solder on a copper pipe, galvanizing on a steel purlin and the steel fastener in an aluminum sheet are common examples.

### What causes galvanic corrosion?

For galvanic or dissimilar or electrolytic corrosion to occur, three conditions must be met:

- ✚ The metal join must be wet with a conductive liquid
- ✚ There must be metal to metal contact
- ✚ The metals must have sufficiently different potentials

### Factors effect on galvanic corrosion

#### 1-Wetting the join

The conductive liquid (or electrolyte) could be rainwater or water absorbed into surface deposits if the relative humidity (RH) is high enough or even simple condensation. If the deposits are sea salt, then they will start to dissolve if the RH exceeds 34% because of the magnesium chloride. The greater the conductivity the more severe the galvanic effects. Salt or industrial pollution significantly increases the conductivity of water so galvanic effects are normally more severe near the coast or in heavy industrial areas. Low conductivity, pure rainwater will only cause slight galvanic effects. One complication is that during evaporation, water films become more conductive so initially benign water may cause quite active galvanic

effects as the liquid in the crevice under a bolt or clamp becomes more concentrated. Water may be excluded by design or the use of adhesive sealants or by painting the noble metal for 30 to 50mm beyond the join to prevent charged atom (ion) transport in any thin water film. Painting the active metal (carbon steel or aluminum or zinc) can cause deep holes at coating defects.

## **2-Metal to metal contact**

Galvanic corrosion can only occur if the dissimilar metals are in electrical contact. The contact may be direct or by an external pipe or wire or bolt. If the dissimilar metals are insulated from each other by suitable plastic strips, washers or sleeves then galvanic corrosion cannot occur. Paint is not a reliable electrical insulator especially under bolt heads or nuts or washers or near edges of sheets of metal. The paint is usually damaged on installation or by subsequent movement. Note that the chromium oxide film layer on the stainless steel is very thin and not an electrical insulator. Therefore the chromium oxide film will not prevent galvanic corrosion.

## **3-Potential differences**

All metals dissolve to some extent when they are wetted with a conductive liquid. The degree of dissolution is greatest with active or sacrificial metals such as magnesium and zinc and they have the most negative potential. In contrast, noble or passive metals such as gold or graphite are relatively inert and have a more positive potential. Stainless steel is in the middle although it is more noble than carbon steel. The potential can be measured with a reference electrode and is used to construct a galvanic series as shown on page 2 (ASTM Standard G82).

When two metals are connected and in contact with a conducting liquid, the more active metal will corrode and protect the noble metal. Zinc is more negative than steel and so the zinc coating of galvanized steel will corrode to protect the steel at scratches or cut edges. The stainless steels, including 304 and 316, are more

positive than zinc and steel, so when stainless steel is in contact with galvanized steel and is wet, the zinc will corrode first, followed by the steel, while the stainless steel will be protected by this galvanic activity and will not corrode. The rate of galvanic attack is governed by the size of the potential difference.

The graph shows that stainless steels have two ranges of potential. The usual, passive behavior is shown by the light hatching. However, if the passive film breaks down, the stainless steel corrodes and its potential is in the dark bar range.

As a rule of thumb, if the potential difference is less than 0.1 volt, then it is unlikely that galvanic corrosion will be significant.

If all three conditions are met then galvanic corrosion is probable and the rate of corrosion will be influenced by the relative area and the current density delivered by the noble metal.

#### **4-Relative wetted surface area**

If a noble metal like stainless steel has a large surface area in contact with the electrolyte while the sacrificial metal (such as aluminum) has a very small surface area in contact with the electrolyte, then the stainless steel will generate a large corrosion current which will be concentrated on a small area of sacrificial metal. The aluminum will corrode quickly, and so aluminum fasteners in stainless steel are not acceptable. However, a stainless screw in aluminum is frequently used although corrosion of the aluminum immediately around the stainless is quite possible. This is because the ratio of wetted noble fastener in an active metal might change from a 1:50 ratio to 1:1 during drying after a rainstorm. If contaminants are significant this means that avoiding dissimilar metal pairs may be a preferred option to prevent galvanic attack.

Galvanized fasteners in stainless steel will also lose zinc more rapidly than standalone exposures. An added disadvantage is that the corrosion product will turn from white to orange when the corrosion reaches the zinc-iron alloy near the



bottom of the galvanized layer. After that, corrosion of the carbon steel fastener commences - again at a faster rate than standalone exposures.

As a rule of thumb, if the wetted area of the corroding metal is 10 times the wetted area of the noble metal, then galvanic effects are not serious although the larger the ratio the less the effect.

### **5-Available current density**

Stainless steel has an effective passive film so the available corrosion current able to be carried by charged atoms (ions) is quite low. If the behavior of a copper/steel and a stainless steel/steel couple is compared, the copper/steel coupling is a more significant galvanic problem despite the similar potential separation of 0.35 volts.

Examples of acceptable galvanic pairs include:

- ❖ The copper alloy potential is more active than the stainless steel and it provides cathodic protection current to limit pitting of the stainless steel shaft or crevice attack at the bearing sleeve. The depth of loss of the copper alloy is low because it has a very large area compared to the exposed shaft.
- ❖ Galvanized steel pipe hangers are used to hang stainless steel piping externally around chemical plants. The surface area ratio is bad with large area of stainless steel to small area of active zinc/steel but the rainwater is usually of quite low conductivity and 20 year service life is normal.
- ❖ In the water industries, galling between stainless steel threads and nuts has been avoided by using aluminum bronze nuts on stainless steel studs or bolts. Although aluminum bronze is more active than stainless steel, the conductivity of the water, and hence the corrosion rate, is generally quite low. The nuts will require replacement but only at times of major overhaul.
- ❖ The potential difference between passive 304 and passive 316 is small so galvanic corrosion of the 304 is not expected, even with large area ratios.

Unacceptable material pairs include: a rubber seal with a carbon black loading so high (for UV resistance) that it is conductive and causes galvanic attack of a stainless screw or pin. Gaskets incorporating graphite have caused similar problems for stainless steel flanges and must not be used for seawater regardless of the stainless steel alloy.

## Galvanic Series



## Mechanisms

What causes galvanic corrosion? Different metals and alloys have different electrochemical potentials (or corrosion potentials) in the same electrolyte. When the corrosion potentials of various metals and alloys are measured in a common electrolyte (e.g. natural seawater) and are listed in an orderly manner (descending or ascending) in a tabular form, a Galvanic Series is created. It should be emphasized that the corrosion potentials must be measured for all metals and alloys in the same electrolyte under the same environmental conditions (temperature, pH, flow rate etc.), otherwise, the potentials are not comparable

The potential difference (i.e., the voltage) between two dissimilar metals is the driving force for the destructive attack on the active metal (anode). Current flows through the electrolyte to the more noble metal (cathode) and the less noble (anode) metal will corrode. The conductivity of electrolyte will also affect the degree of attack. The cathode to anode area ratio is directly proportional to the acceleration factor.

## Prevention

**How to prevent galvanic corrosion?** Galvanic corrosion can be prevented through a number of methods:

- Select metals/alloys as close together as possible in the galvanic series.
- Avoid unfavorable area effect of a small anode and large cathode.
- Insulate dissimilar metals wherever practical
- Apply coatings with caution. Paint the cathode (or both) and keep the coatings in good repair on the anode.
- Avoid threaded joints for materials far apart in the galvanic series.

### 3-3 CREVICE CORROSION

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion.

#### Theory of Crevice Corrosion

Corrosion requires energy. During corrosion the reacting components go from a higher to a lower energy state and release the energy needed for the reaction. In the dry corrosion the metal and the oxygen combine to produce the oxide on the surface because the reaction leads to a compound (the oxide) at a lower energy level. The oxide layer shields the metal from the oxygen and forms a barrier. The oxide will not react with the oxygen in the air or the metal. The barrier makes it difficult for oxygen in the air to contact the metal and it eventually grows so thick that the movement of electrons and ions across it stop. Provided the oxide layer does not crack, or is not removed, the metal is protected from further corrosion.

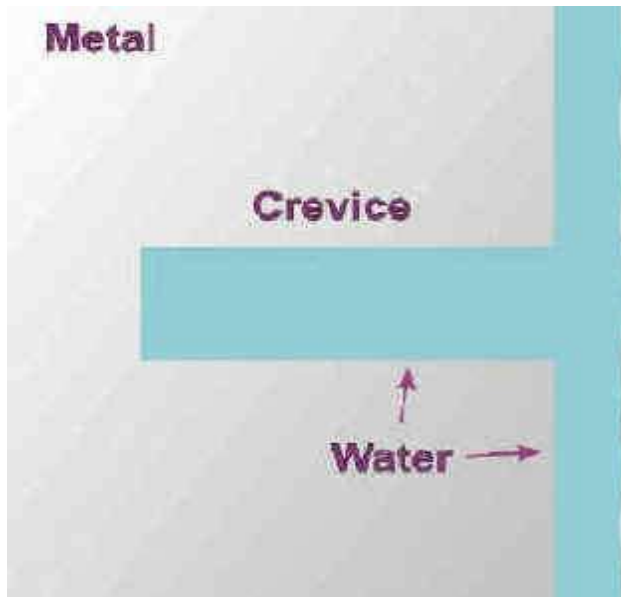
#### Mechanisms of crevice corrosion

The Fontana and Greene model describes crevice corrosion mechanism. This model consists of three stages.

**Stage 1:** Corrosion occurs as normal both inside and outside the crevice:



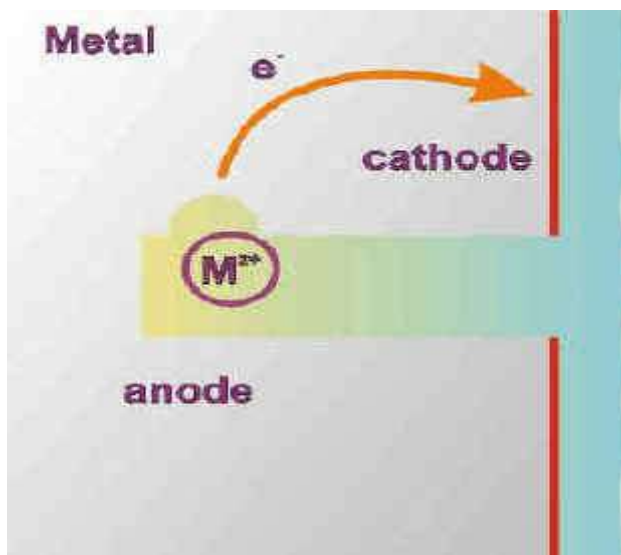
The positively charged metallic ions are electrostatically counterbalanced by  $OH^{-}$ .



**Stage 1**

At time zero, the oxygen content in the water occupying a crevice is equal to the level of soluble oxygen and is the same everywhere.

**Stage 2:** at this stage, the cathodic reaction inside the crevice consumed most of the oxygen available.



**Stage 2**

Because of the difficult access caused by the crevice geometry, oxygen consumed by normal uniform corrosion is very soon depleted in the crevice. The corrosion reactions now specialize in the crevice (anodic) and on the open surface (cathodic).

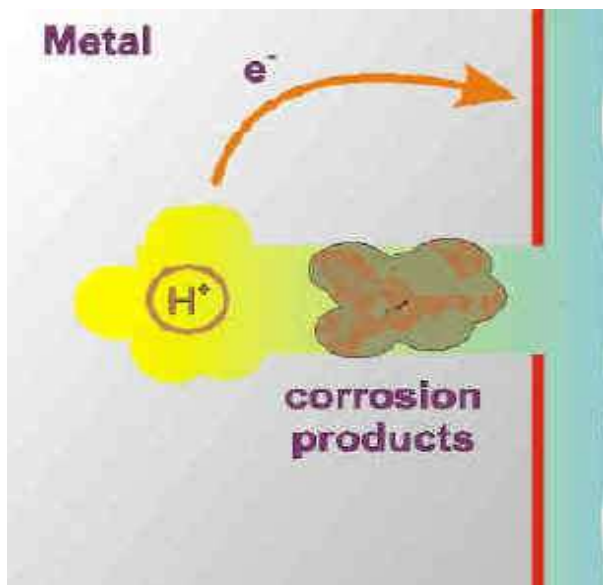
**Stage 3:** Cl<sup>-</sup> and OH<sup>-</sup> diffuse into the crevice to maintain a minimum potential energy. Metal chloride is formed. Hydrolysis of metal chloride lowers pH and



More Mn<sup>+</sup> ions attack more Cl<sup>-</sup> leads to lower pH inside crevice, metal dissolution accelerates and more Mn<sup>n+</sup> ions will be produced that will lower pH.

### Stage 3

The **crevice development** a few more accelerating factors fully develop:



1. The metal ions produced by the anodic corrosion reaction readily hydrolyze giving off protons (acid) and forming corrosion products.
2. The acidification of the local environment can produce a serious increase in the corrosion rate of most metals.
3. The corrosion products seal even further the crevice environment.
4. The accumulation of positive charge in the crevice becomes a strong attractor to negative ions in the environment.

### Factors affecting crevice corrosion

There are several factors that are responsible for crevice corrosion initiation in stainless steel alloys. These parameters need to be considered when modeling of crevice corrosion is of interest. The main factors and their combined effect on crevice corrosion can be listed as:

#### 1- Oxide films

Almost all passive films have multilayer structures, usually with the inner oxide and the outer hydroxide layer. The oxide layer is a barrier against cations transfer, and on the hydroxide layer the exchange with the electrolyte takes place. The resistance of stainless steels to localized corrosion is a function of the thickness and composition of the passive film on the metal surface. Stainless steels exhibit an

oxide film usually 1-5 nm thick which provides resistance to localized corrosion on the metal surface. The stability of passive film formed on austenitic stainless steels is dependent on alloy composition, temperature, and the exposed environment. For example the presence of chromium and molybdenum in the oxide increases crevice corrosion resistance of stainless steel alloys. The corrosion initiation usually begins at the potential where the breakdown of the passive film occurs.

When the effect of oxide films to crevice corrosion is studied, the transport of different metallic constituents, matter and charge through the film must be considered. The interaction between the film and the environment can include many different reactions e.g. adsorption, surface complex formation and re-precipitation of various cations at different pH levels and locations of the oxide film. Oxide penetration and thinning mechanisms also should be considered.

## 2- Alloying elements in metals

The presence or absence of certain alloying elements in stainless steel results in higher or lower crevice corrosion initiation and propagation resistance, and the influence of these elements vary with temperature and pH. Stainless steels containing relatively high levels of molybdenum, nickel and chromium (elements which are known to increase resistance to depassivation) are less prone to localized corrosion. The beneficial effect of chromium and nickel ions is based on stabilization of passive film by shifting the corrosion potential (during crevice corrosion initiation) or the critical crevice potential into the noble direction. Therefore usually stainless steels that have high molybdenum, nickel and chromium levels require very low pH and high chloride ion concentration to cause a breakdown of their passive film. Also copper ions and the synergistic action of nitrogen and molybdenum in stainless steels increase the resistance of alloys to passive film breakdown. Detrimental effect on the corrosion resistance of metals shows elements such as sulphur and manganese.

Also other metal structure related factors as alloying elements affect the crevice corrosion sensitivity. Examples of these are second-phase particles, solute segregated grain boundaries, flaws, cold work and the degree of surface roughness. The locations of these factors implicate which areas are sensitive to localized corrosion initiation.

### 3- Repassivation

Under certain circumstances, the increasing corrosion partial current that follows a nucleation of a corroding pit may cease. While the repassivation of the corroding surface decreases the growth of pits, the increasing Ohmic potential drop along the depth of the pit also results in the pit being stable at a low anodic current density at the bottom. This is because, as the pit deepens, the diffusion of the cations out of the pit reduces, thus decreasing the rate at which these ions dissolve from the substrate. At some point, the pit stops growing and is considered 'dead'. It is necessary to determine whether the presence of different phases or other microstructural features in the local neighborhood would have any influence on Whether a pit repassivates or not. Repassivation kinetics is considered critical in determining the localized corrosion resistance of metals and alloys, and in influencing the accumulated damage.

### 4- Geometry

Crevice geometry has great influence to crevice corrosion sensitivity. Increasing the crevice tightness and depth the chances for crevice corrosion initiation increase. The width and depth of the crevice control the access of oxygen into the crevice and affect the internal gradients of concentration, potential distribution, etc. Not every crevice existing on the metal structure suffers of localized corrosion. There is certain optimum crevice widths at which the given material is resistant to crevice corrosion. In sufficiently wide crevices, the access of oxygen and the exchange with the external solution is not significantly affected. In very narrow



crevices, on the other hand, the concentration gradients are so steep that the breakdown of passivity can occur even close to the mouth of the crevice. In this case, deeper regions will be free of a corrosion attack. However, a wider gap creates smaller IR drop in the crevice electrolyte than a tighter gap, thus resulting in more chances of crevice corrosion initiation. Also in some cases deep crevices may restrict propagation because of a voltage drop through the crevice solution. The use of higher-alloy stainless-type material offers the advantage of providing resistance over a broader range of conditions. Most practical crevices have crevice gaps on the order of 0.1-10 mm, and lengths of 1-10 mm. To simplify calculations and modeling it is usually assumed that crevices have ideal dimensions; perfectly vertical side walls and uniform crevice gaps. Practical crevices and crevices fabricated for experiments by pressing two pieces of material together, however, do not have ideal dimensions. It has been reported that sub-crevices created by irregular crevice wall morphology have a significant impact on the ion concentration distributions inside a crevice, and that these sub-crevices dominate the crevice corrosion behavior of stainless steel type 304 and titanium alloy 825. It has also been proposed that for a crevice depth of 0.1 cm, a gap of less than 0.01 mm might be required for initiation of crevice corrosion of type 304 stainless steel in natural water with 1000 mg/l chloride ion content.

### **5- Temperature, pH and chemical environment**

During the corrosion process, increase in temperature accelerates the reaction kinetics of metal dissolution and related reduction reactions causing the breakdown of the passive region. An increase in temperature causes higher conductivity of electrolytes thus leading to a corresponding increase in the rate of electrochemical reaction and anodic current. However few studies have indicated that for AISI 304 and 316 stainless steels immersed in naturally aerated seawater for 28 days at 10, 25 and 50°C, it was observed that corrosion was more severe at 25°C than at 10 or

50°C. Reason for this “unusual” behavior could be that at a higher temperature of 50°C, oxygen solubility is reduced, which decreases the external cathodic reaction rate, and in the end lowers the corrosion rate. The acidity or the alkalinity of the corrosion environment significantly affects the corrosion behavior of metals in many ways. In the case of crevice corrosion the migration of anionic species (e.g. Cl<sup>-</sup>) from the bulk solution to the crevice to preserve electro-neutrality and the hydrolysis of the dissolved metal ions lowers the pH in the crevice solution. This acidification and chloride build-up in the crevice during active stages of crevice corrosion is aggressive to most metals and tends to prevent repassivation and promote corrosion. Also the bulk environment chloride levels and acidity affect the crevice electrolyte pH and chloride level.

Corrosion inhibitors in the electrolyte have the opposite effect to crevice corrosion, since they slow down the corrosion reactions. The availability of redox species is an important factor in crevice corrosion, since it controls the rate of reduction and dissolution reactions. During localized corrosion, some salts precipitate on the corroding substrate as a result of reactions between dissolved anions and species in the electrolyte in the pit or crevice. Precipitation occurs when the product of the ionic reactants exceeds the solubility product. The corrosive microenvironment under surface deposits is very different from the bulk solution, e.g. pH of these microenvironments tends to be very acidic.

## COMBATING CREVICE CORROSION

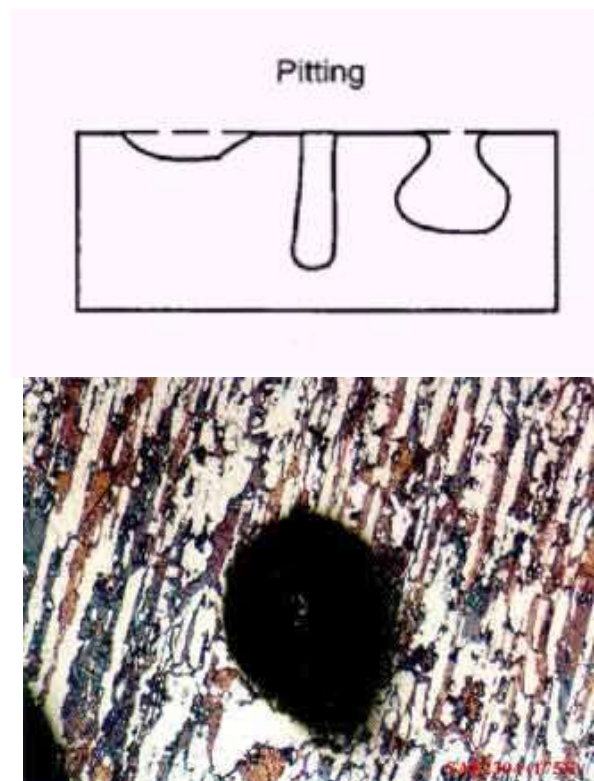
Methods and procedures for combating or minimizing crevice corrosion are as follows:

1. Use welded butt joints instead of riveted or bolted joints in new equipment.
2. Close crevices in existing lap joints by continuous welding, caulking, or soldering.
3. Design vessels for complete drainage; avoid sharp corners and stagnant areas.
4. Inspect equipment and remove deposits frequently.
5. Remove solids in suspension early in the process, if possible.
6. Remove wet packing materials during long shutdowns.
7. Provide uniform environments, if possible, as in the case of backfilling a pipeline trench.
8. Use "solid," nonabsorbent gaskets, such as Teflon, wherever possible.
9. Weld instead of rolling in tubes in tube sheets.

### 3-4 PITTING CORROSION

**Pitting corrosion** is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. Pitting corrosion, which, for example, is almost a common denominator of all types of localized corrosion attack, may assume different shapes. Pitting corrosion can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped

**Pitting corrosion** is an electrochemical oxidation-reduction (redox) process, which occurs within localized holes (cells) on the surface of metals coated with a passive film.



## Types of Pitting Corrosion:

### Trough Pits

Narrow, deep



Shallow, wide



Elliptical



Vertical grain attack



### Sideway Pits

Subsurface



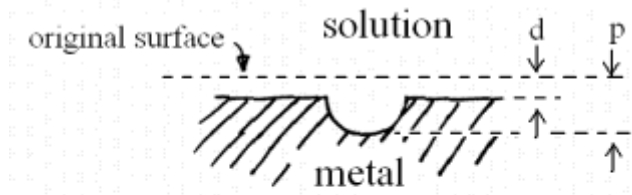
Undercutting



Horizontal grain attack



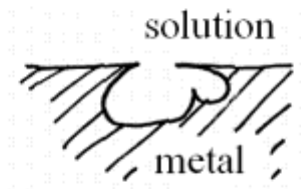
**PITTING: Extreme localized attack, may perforate metal sheet/plate . . . etc.**



$$\text{“Pitting factor”} = \frac{p}{d}$$

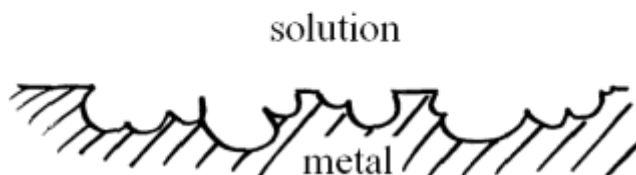
$p$  = deepest penetration

$d$  = average penetration from weight loss;



“Undercutting”

pit opening usually < 1 mm.



Pits may overlap to give the

## Pitting Resistance Equivalent Numbers (PREN)

**Pitting resistance equivalent numbers (PREN)** are a theoretical way of comparing the pitting corrosion resistance of various types of stainless steels, based on their chemical compositions.

They typically take the form

$$\text{PREN} = \text{Cr} + m \text{Mo} + n \text{N}$$

Where '**m**' and '**n**' are the factors for molybdenum and nitrogen.

The most commonly used version of the formula is

$$\text{PREN} = \text{Cr} + 3.3\text{Mo} + 16\text{N}$$

$$\text{PREN} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N}$$

Where (**W**) Tungsten is known to have an effect on the pitting resistance and for some grades a modified formula is used

### Pitting is an insidious and destructive form of corrosion:

- ❖ Difficult to detect (pits may be small on surface, may be covered with deposit);
- ❖ Can cause equipment to fail (by perforation) with very little weight loss.
- ❖ Difficult to measure as pit depth and distribution vary widely under identical conditions.
- ❖ “Incubation” period may be months or years.

## Mechanisms:

**What causes pitting corrosion?** For a defect-free "perfect" material, pitting corrosion is caused by the ENVIRONMENT (chemistry) that may contain aggressive chemical species such as chloride. Chloride is particularly damaging to the passive film (oxide) so pitting can initiate at oxide breaks.

The environment may also set up a differential aeration cell (a water droplet on the surface of a steel, for example) and pitting can initiate at the anodic site (center of the water droplet).

For a homogeneous environment, pitting IS caused by the MATERIAL that may contain inclusions (MnS is the major culprit for the initiation of pitting in steels) or defects. In most cases, both the environment and the material contribute to pit initiation.

The ENVIRONMENT (chemistry) and the MATERIAL (metallurgy) factors determine whether an existing pit can be repassivated or not. Sufficient aeration (supply of oxygen to the reaction site) may enhance the formation of oxide at the pitting site and thus repassivate or heal the damaged passive film (oxide) - the pit is repassivated and no pitting occurs. An existing pit can also be repassivated if the material contains sufficient amount of alloying elements such as Cr, Mo, Ti, W, N, etc... These elements, particularly Mo, can significantly enhance the enrichment of Cr in the oxide and thus heals or repassivates the pit.

**Pit initiation.** An initial pit may form on the surface covered by a passive oxide film as a result of the following:

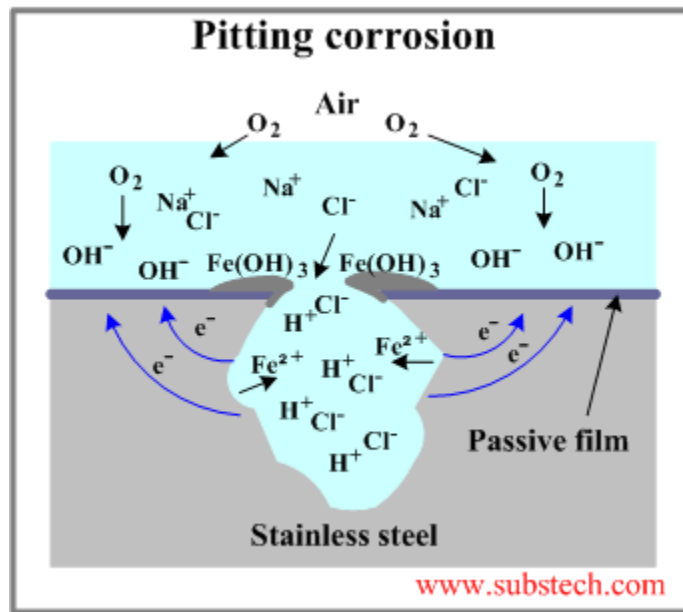
Mechanical damage of the passive film caused by scratches. Anodic reaction starts on the metal surface exposed to the electrolyte. The passivated surrounding surface act as the cathode.

Particles of a second phase (non-metallic inclusions, intermetallic inclusions, metallic particles, Micro segregation) emerging on the metal surface. These

particles precipitating along the grains boundaries may function as local anodes causing localized galvanic corrosion and formation of initial pits.

Localized stresses in form of dislocations emerging on the surface may become anodes and initiate pits.

Non-homogeneous environment may dissolve the passive film at certain locations where initial pits form.



**Pit growth.** In presence of chloride ions pits are growing by autocatalytic mechanism. Pitting corrosion of a stainless steel is illustrated in the figure.

Anodic reactions inside the pit:



The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:





As a result of these reactions the electrolyte enclosed in the pit gains positive electrical charge in contrast to the electrolyte surrounding the pit, which becomes negatively charged.

The positively charged pit attracts negative ions of chlorine  $\text{Cl}^-$  increasing acidity of the electrolyte according to the reaction:



PH of the electrolyte inside the pit decreases (acidity increases) from **6** to **2-3**, which causes further acceleration of corrosion process.

Large ratio between the anode and cathode areas favors increase of the corrosion rate.

Corrosion products ( **$\text{Fe}(\text{OH})_3$** ) form around the pit resulting in further separation of its electrolyte.

Remember:

- inside pit - anodic, rapid dissolution
- outside pit - cathodic,  $\text{O}_2$  reduction
- most  $\text{M}^+$  will hydrolyze, form  $\text{H}^+$
- positive charges attract  $\text{Cl}^-$  ions
- $\text{H}^+$  and  $\text{Cl}^-$  accelerate metal dissolution
- high ionic concentrations in pit make  $\text{O}_2$  solubility very low

- high density of solution within pits means pits are more stable when growing downwards
- Static environment accelerates process.

**Some alloys developed especially to resist pitting.**

### **Effects of alloying on pitting resistance of stainless steel alloys**

<b>Element</b>	<b>Effect on pitting resistance</b>
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and niobium	Decreases resistance in $\text{FeCl}_3$ , other mediums no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

### **Means of pitting corrosion control:**

- Selection of appropriate material
- Providing stirring of the electrolyte
- Control of the electrolyte composition (PH, chloride ions)
- Corrosion inhibitors
- Cathodic protection
- Corrosion protection coatings

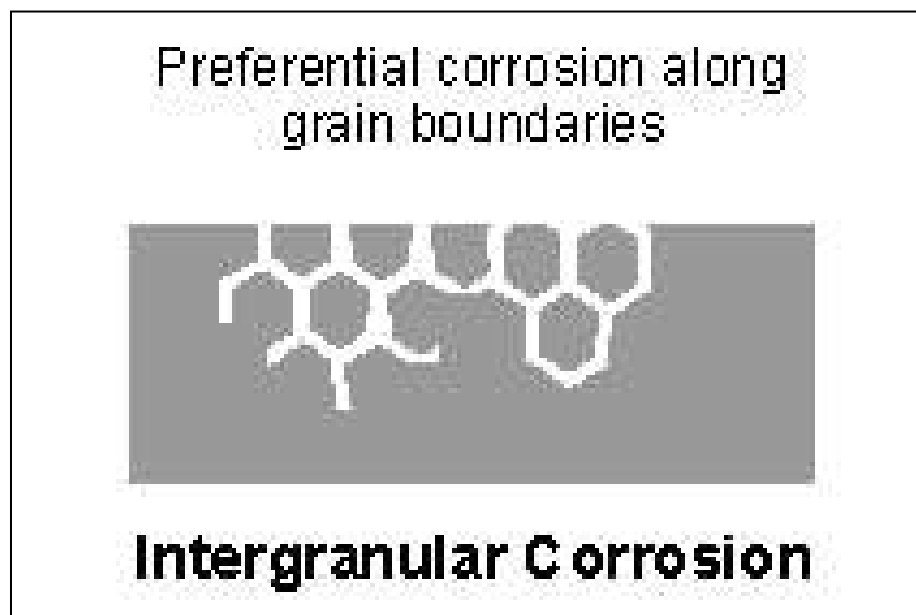
### **How to avoid Pitting corrosion?**

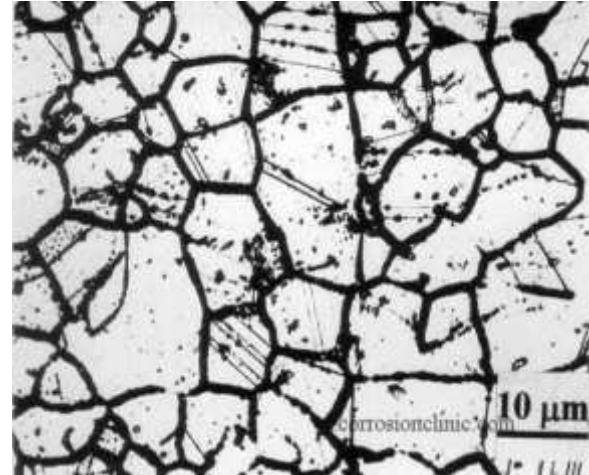
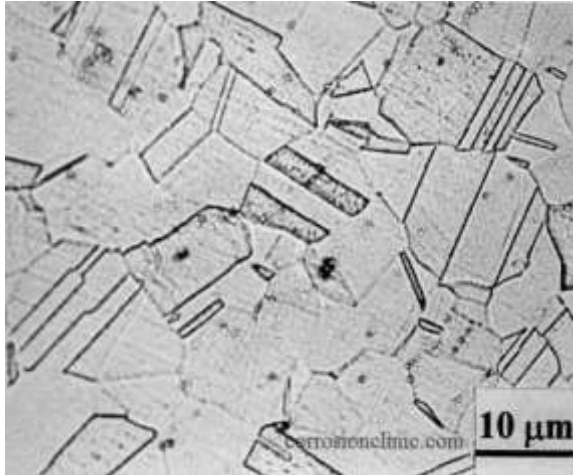
But how do you avoid this type of corrosion? In these cases it is necessary the **choice of alloys with high amounts of chromium, nickel and molybdenum.** These **items have a passive layer much more stable and durable.** To avoid the process of pitting, you are still advised to avoid environments containing high amounts of **chlorine ions** and halides in general

### 3-5 Intergranular corrosion

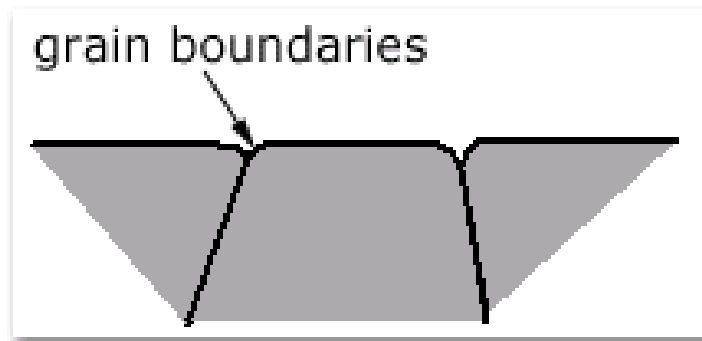
Intergranular corrosion is sometimes also called "intercrystalline corrosion" or "interdendritic corrosion". In the presence of tensile stress, cracking may occur along grain boundaries and this type of corrosion is frequently called "intergranular stress corrosion cracking (**IGSCC**)" or simply "intergranular corrosion cracking".

"Intergranular" or "intercrystalline" means between grains or crystals. As the name suggests, this is a form of corrosive attack that progresses preferentially along interdendritic paths (the grain boundaries). Positive identification of this type of corrosion usually requires microstructure examination under a microscopy although sometimes it is visually recognizable as in the case of weld decay.



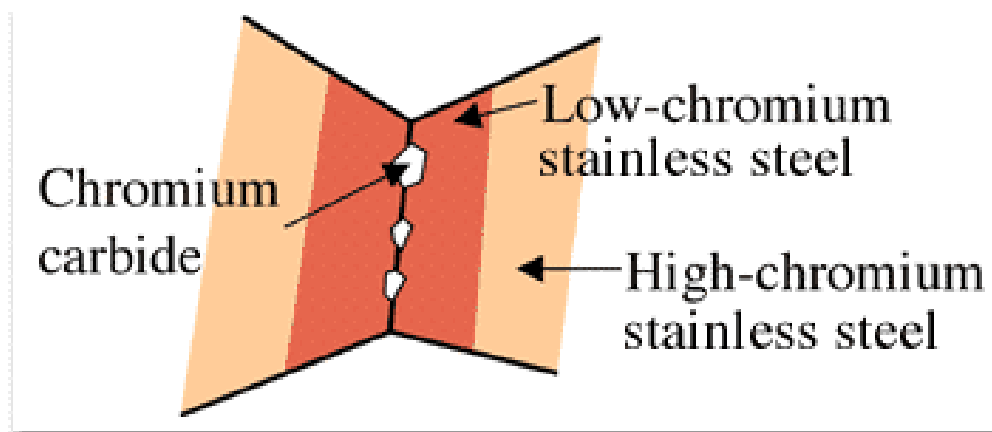


The photos above show the microstructure of a type 304 stainless steel. The figure on the left is the normalized microstructure and the one on the right is the "sensitized" structure and is susceptible to intergranular corrosion or intergranular stress corrosion cracking.



- The atoms in the grain boundaries are in a distorted lattice.
- The higher energies of grain boundary atoms make them slightly more reactive than grains.

In stainless steels the problem occurs after the metal is heated to between  $425^{\circ}\text{C}$  and  $870^{\circ}\text{C}$ . During the heating, the chromium in the stainless steel reacts with carbon in the steel and forms particles of chromium carbide at the grain boundaries. The regions near the grain boundaries become depleted in chromium. This means that the regions around the grain boundaries are no longer protected by the chromium passivation, and therefore corrode intergranularly.



## Mechanisms

**What causes intergranular corrosion?** This type of attack results from local differences in composition, such as coring commonly encountered in alloy castings. Grain boundary precipitation, notably chromium carbides in stainless steels, is a well-recognized and accepted mechanism of intergranular corrosion. The precipitation of chromium carbides consumed the alloying element - chromium from a narrow band along the grain boundary and this makes the zone anodic to the unaffected grains. The chromium depleted zone becomes the preferential path for corrosion attack or crack propagation if under tensile stress.

Intermetallics segregation at grain boundaries in aluminum alloys also causes intergranular corrosion but with a different name - "exfoliation".

## Prevention

How to prevent intergranular corrosion? Intergranular corrosion can be prevented through:

- ❖ Use low carbon (e.g. 304L, 316L) grade of stainless steels
- ❖ Use stabilized grades alloyed with titanium (for example type 321) or niobium (for example type 347). Titanium and niobium are strong carbide-formers. They react with the carbon to form the corresponding carbides thereby preventing chromium depletion.
- ❖ Use post-weld heat treatment.

### 3-6 Selective leaching Or Dealloying:

**What is dealloying ?** Dealloying is the selective corrosion of one or more components of a solid solution alloy. It is also called parting, selective leaching or selective attack. Common dealloying examples are decarburization, decobaltification, denickelification, dezincification, and graphitic corrosion.

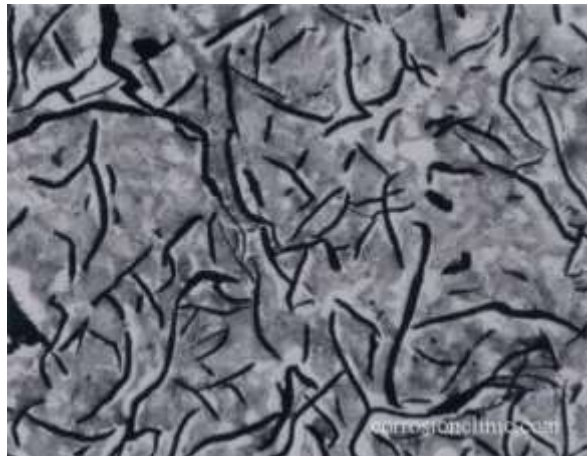
**Decarburization** is the selective loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface.

**Decobaltification** is selective leaching of cobalt from cobalt-base alloys, such as Stellite, or from cemented carbides.

**Denickelification** is the selective leaching of nickel from nickel-containing alloys. Most commonly observed in copper-nickel alloys after extended service in fresh water.

**Dezincification** is the selective leaching of zinc from zinc-containing alloys. Most commonly found in copper-zinc alloys containing less than 85% copper after extended service in water containing dissolved oxygen.

**Graphitic corrosion** is the deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion products leaving the graphite intact. Graphitic corrosion should not be confused with another term graphitization, which is used to describe the formation of graphite in iron or steel, usually from decomposition of iron carbide at elevated temperatures.



Graphitic corrosion of a gray cast iron valve

## Mechanisms

**What causes dealloying?** Different metals and alloys have different electrochemical potentials (or corrosion potentials) in the same electrolyte. Modern alloys contain a number of different alloying elements that exhibit different

corrosion potentials. The potential difference between the alloying elements is the driving force for the preferential attack on the more "active" element in the alloy.

In the case of dezincification of brass, zinc is preferentially leached out of the copper-zinc alloy, leaving behind a copper-rich surface layer that is porous and brittle.

### **Danger**

- The alloy may not appear damaged
- May be no dimensional variations
- Material generally becomes weak – hidden to inspection

### **Prevention**

**How to prevent dealloying?** Dealloying, selective leaching and graphitic corrosion can be prevented through the following methods:

- A.** Select metals/alloys that are more resistant to dealloying. For example, inhibited brass is more resistant to dezincification than alpha brass; ductile iron is more resistant to graphitic corrosion than gray cast iron.
- B.** Control the environment to minimize the selective leaching
- C.** Use sacrificial anode cathodic protection or impressed current cathodic protection



### 3-7 Erosion Corrosion

Erosion corrosion is an acceleration in the rate of corrosion attack in metal due to the relative motion of a corrosive fluid and a metal surface. The increased turbulence caused by pitting on the internal surfaces of a tube can result in rapidly increasing erosion rates and eventually a leak. Erosion corrosion can also be aggravated by faulty workmanship. For example, burrs left at cut tube ends can upset smooth water flow, cause localized turbulence and high flow velocities, resulting in erosion corrosion. A combination of erosion and corrosion can lead to extremely high pitting rates.

Erosion-corrosion is most prevalent in soft alloys (i.e. copper, aluminum and lead alloys). Alloys which form a surface film in a corrosive environment commonly show a limiting velocity above which corrosion rapidly accelerates. With the exception of cavitation, flow induced corrosion problems are generally termed erosion-corrosion, encompassing flow enhanced dissolution and impingement attack. The fluid can be aqueous or gaseous, single or multiphase.

**There are several mechanisms described by the conjoint action of flow and corrosion that result in flow-influenced corrosion:**

**Mass transport-control:** Mass transport-controlled corrosion implies that the rate of corrosion is dependent on the convective mass transfer processes at the metal/fluid interface. When steel is exposed to oxygenated water, the initial corrosion rate will be closely related to the convective flux of dissolved oxygen towards the surface, and later by the oxygen diffusion through the iron oxide layer. Corrosion by mass transport will often be streamlined and smooth.

**Phase transport-control:** Phase transport-controlled corrosion suggests that the wetting of the metal surface by a corrosive phase is flow dependent. This may occur because one liquid phase separates from another or because a second phase forms from a liquid. An example of the second mechanism is the formation of discrete bubbles or a vapor phase from boiler water in horizontal or inclined tubes in high heat-flux areas under low flow conditions. The corroded sites will frequently display rough, irregular surfaces and be coated with or contain thick, porous corrosion deposits.

**Cavitation:** Cavitation sometimes is considered a special case of erosion-corrosion and is caused by the formation and collapse of vapor bubbles in a liquid near a metal surface. Cavitation removes protective surface scales by the implosion of gas bubbles in a fluid. Calculations have shown that the implosions produce shock waves with pressures approaching 415 MPa. The subsequent corrosion attack is the result of hydro-mechanical effects from liquids in regions of low pressure where flow velocity changes, disruptions, or alterations in flow direction have occurred. Cavitation damage often appears as a collection of closely spaced, sharp-edged pits or craters on the surface.

## Mechanisms

### What causes Erosion Corrosion?

The mechanical effect of flow or velocity of a fluid combined with the corrosive action of the fluid causes accelerated loss of metal. The initial stage involves the mechanical removal



of a metal's protective film and then corrosion of bare metal by a flowing corrosive occurs. The process is cyclic until perforation of the component occurs.

Erosion-corrosion is usually found at high flow rates around tube blockages, tube inlet ends, or in pump impellers. The photo shows erosion corrosion of a cast aluminum pump casing due to excessively high flow rate of the coolant.

Cavitation-corrosion is a special form of erosion-corrosion. It is caused by water bubbles produced by a high-speed impeller, which then collapse and cause pits on the metal surface.

### **Erosion Corrosion vs. Flow-Accelerated Corrosion**

In the corrosion literature, erosion corrosion and flow-accelerated corrosion have been frequently used interchangeably. There does not exist a well-defined boundary between the two. Some argue that there is a subtle difference between Erosion Corrosion and Flow-Accelerated Corrosion. In FAC, fluid flow removes magnetite ( $\text{Fe}_3\text{O}_4$ ) layer, exposing steel to corrosion, leading to wall thinning. There is no or thinner magnetite on surface at FAC location due to the flow effect than at locations not subjected to FAC.

## **Prevention and Prediction**

**How to prevent Erosion Corrosion?** Erosion corrosion can be prevented through:

- streamline the piping to reduce turbulence
- control fluid velocity
- using more resistant materials
- using corrosion inhibitors or cathodic protection to minimize erosion corrosion

### 3-8 Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) is the cracking induced from the combined influence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. The problem itself can be quite complex.

Cold deformation and forming, welding, heat treatment, machining and grinding can introduce residual stresses. The magnitude and importance of such stresses is often underestimated. The residual stresses set up as a result of welding operations tend to approach the yield strength. The build-up of corrosion products in confined spaces can also generate significant stresses and should not be overlooked. SCC usually **occurs in certain specific alloy-environment-stress combinations**.



**intergranular SCC of an Inconel heat exchanger tube with the crack following the grain boundaries**

Usually, most of the surface remains unattacked, but with fine cracks penetrating into the material. In the microstructure, these cracks can have an intergranular or a transgranular morphology. Macroscopically, SCC fractures have a brittle appearance. SCC is classified as a catastrophic form of corrosion, as the detection of such fine cracks can be very difficult and the damage not easily predicted. Experimental SCC data is notorious for a wide range of scatter. A disastrous failure may occur unexpectedly, with minimal overall material loss.

The micrograph above (X500) illustrates intergranular SCC of an Inconel heat exchanger tube with the crack following the grain boundaries.

The micrograph below (X300) illustrates SCC in a 316 stainless steel chemical processing piping system. Chloride stress corrosion cracking in austenitic stainless steel is characterized by the multi-branched "lightning bolt" transgranular crack pattern.

SCC in a 316 stainless steel chemical processing piping system; photo courtesy The catastrophic nature of this severe form of corrosion attack has been repeatedly illustrated in many news worthy failures, including the following: Swimming pool roof collapse in Uster, Switzerland \* EL AL Boeing 747 crash in Amsterdam Stress Corrosion Cracking (SCC) Chloride SCC **One of the most important forms of stress corrosion** that concerns the nuclear industry is **chloride stress corrosion**.

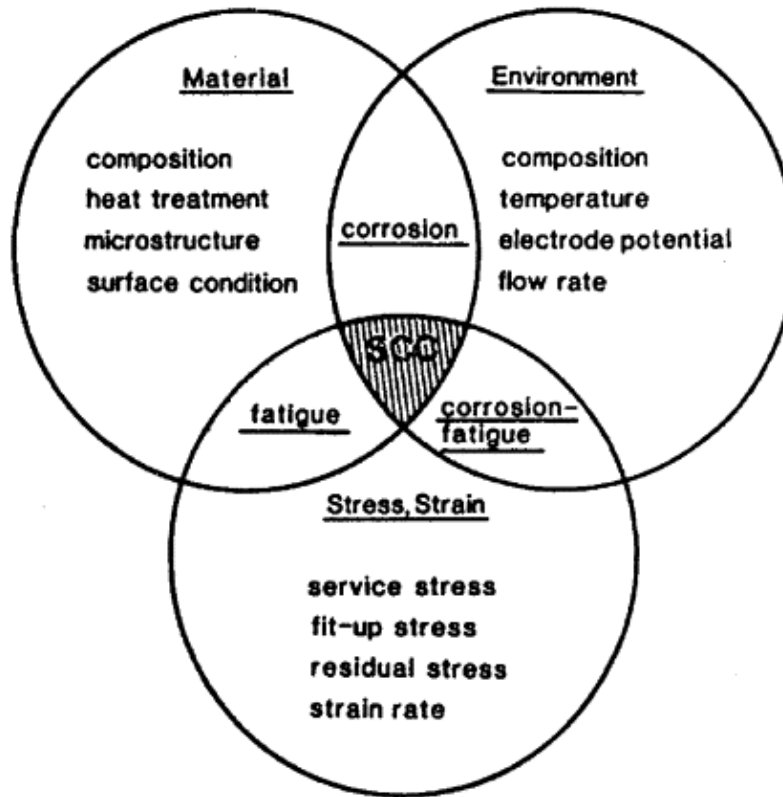
**Chloride stress corrosion** is a type of intergranular corrosion and occurs in austenitic stainless steel under tensile stress in the presence of oxygen, chloride ions, and high temperature. It is thought to start with chromium carbide deposits along grain boundaries that leave the metal open to corrosion. This form of corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and use of low carbon steels.



**SCC in a 316 stainless steel chemical processing piping system; photo courtesy**

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Stress corrosion cracking (SCC) is interpreted to take place due to specific combinations of susceptible materials in suitable corrosion environments under adequate stress, specifically under constant stress, Figure below. The equivalent mechanism for crack growth under cyclic stresses is called corrosion fatigue (CF), and crack growth here depends upon the stress ratio.



Factors affecting EAC. Note that the specific conditions are required for cracking to occur

## Mechanisms

**What causes stress corrosion cracking?** Stress corrosion cracking results from the conjoint action of three components: (1) a susceptible material; (2) a specific chemical species (environment) and (3) tensile stress. For example, copper and its alloys are susceptible to ammonia compounds, mild steels are susceptible to alkalis and stainless steels are susceptible to chlorides.

There is no unified mechanism for stress corrosion cracking in the literature. Various models have been proposed which include the following:

- Adsorption model: specific chemical species adsorbs on the crack surface and lowers the fracture stress.

- Film rupture model: stress ruptures the passive film locally and sets up an active-passive cell. Newly formed passive film is ruptured again under stress and the cycle continues until failure.
- Pre-existing active path model: Pre-existing path such as grain boundaries where intermetallics and compounds are formed.
- Embrittlement model: Hydrogen embrittlement is a major mechanism of SCC for steels and other alloys such as titanium. Hydrogen atoms diffuse to the crack tip and embrittle the metal.

## Prevention

**How to prevent stress corrosion cracking?** Stress corrosion cracking can be prevented through:

- ❖ Avoid the chemical species that causes SCC.
- ❖ Control of hardness and stress level (residual or load).
- ❖ Introduce compressive stress by shot-peening for example.
- ❖ Use of materials known not to crack in the specified environment.
- ❖ Control operating temperature and/or the electrochemical potential of the alloy.