PR7892   **CORROSION ENGINEERING**   **L T P C**
                                                                        3 0 0 3

OBJECTIVES
- To enlighten the engineering students about the scope and cost of corrosion
- To make the engineering students to understand the various types of corrosion under normal to severe corrosive environments in manufacturing industrial sectors.
- To develop the skills among the students about corrosion testing of materials and devices of Aerospace, Automobile, refinaries and electronic equipments.
- To familiarize the students in selection of materials, corrosion monitoring and prevention, developing the specialized skills in manufacturing the durable materials for various industries for long term application.

UNIT I   INTRODUCTION AND CORROSION PRINCIPLES   9
Introduction-Definition-Corrosion engineering-Scope in industries-Cost of corrosion-corrosion damage-Classification of corrosion (wet & dry)-electrochemical corrosion-electrochemical reactions-effects of oxidizers-velocity-temperature-concentration-Galvanic coupling (Dissimilar materials coupling) - metallurgical aspects-metallic properties-economic considerations-importance of corrosion inspection-new instruments.

UNIT – II   FORMS OF CORROSION ON ENGINEERING DEVICES   9
Introduction-two metal Corrosion-emf-Galvanic series-Distance area principle, characteristics, mechanism, velocity of pitting corrosion (autocatalytic, shape and growth)-Intergrannular corrosion (weld decay, knife line attack)-Selective leaching (dezincification and graphitation)-erosion corrosion-surface film-turbulence-impingement-stress corrosion-cracking-crack-morphology-stress effect-time to cracking-Hydrogen embrittlement-fracture mechanism-prevention.

UNIT-III   CORROSION TESTING OF ENGINEERING MATERIALS AND
**   DEVICES   9**
Introduction-classification-purpose-sample preparation-Exposure testing-Duration-planned interval tests for erosion corrosion-crevice-pitting-intergrannular-pitting and stress corrosion cracking-NACE test methods-Slow strain rate-linear polarization-cyclic voltametry-electronic instrumentation-AC impedance-in sea water testing-in vivo-testing-Huey and Streicher tests for stainless steel and sensitized steels-corrosion of plastics and elastomers-summerizing data-interpretations of data.

UNIT-IV   EFFECTS OF CORROSIVE ENVIRONMENTS AND AGEING STUDIES OF
**   ENGINEERING MATERIALS AND DEVICES   9**
Introduction-atmosphere-seawater-fresh water-soils-corrosion of aerospace-automobile-electronic equipments-nuclear-thermal solar power plants-Ageing studies of Class1-class2-class 3 materials in ambient, medium and severe corrosive environments & manufacturing industries- case studies.

UNIT-V   MODERN APPROACHES FOR CORROSION PREVENTION   9
Introduction- selection of materials-alternate environments- proper design rules-metallic coatings-anodic and cathodic-applications-galvanizing of steel sheet-metal cladding-electroplating-objectives-theory-procedures on metals and non metals-electroplating of nickel and chromium for automobile and other industries –cleaning methods of samples before and after electro plating-metals spray coatings- corrosion control standards.

TOTAL: 45 PERIODS

TEXT BOOKS
1. Mars G.Fontana Corrosion Engineering (Third edition) McGraw Hill Education (India) private Limited. Chennai , India
2. P.C.Jain & Monika Jain Engineering Chemistry, Dhanpat Rai & Sons, Delhi, India.

REFERENCES.
1. Pierre R. Roberge Handbook of corrosion Engineering, McGraw Hill Professional (1999)
2. Volkan Cicek, Corrosion Engineering, John Wiley & Sons (2014)
3. Volkan Cicek, Bayan Al-Numan,Corrosion Chemistry, John Wiley & sons (2011)

INTRODUCTION TO CORROSION

CHAPTER 1.1

PR 7892
CORROSION ENGINEERING

Definition

As per IUPAC,   •

Corrosion is an irreversible interfacial reaction of a   •
material (metal, ceramic, polymer) with its
environment which results in its consumption or
dissolution into the material of a component of the
environment. Often, but not necessarily, corrosion
results in effects detrimental to the usage of the
material considered. Exclusively physical or
mechanical processes such as melting and
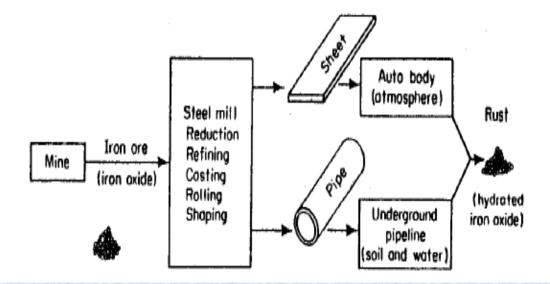evaporation, abrasion or mechanical fracture are not
included in the term corrosion

Corrosion Engineering

Corrosion may be defined in several ways:

1)Destruction or Deterioration of a material because of reaction with its environments.

2)Destruction of materials by means other than straight mechanical.   Or

3) it is extractive metallurgy in reverse.

Also

Corrosion may be defined as the destruction of a metal or an alloy because of chemical or electrochemical reaction with its surrounding environment or medium.

Metallurgy in reverse

Corrosion damages

The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over design. It can also jeopardize safety and inhibit technological progress.
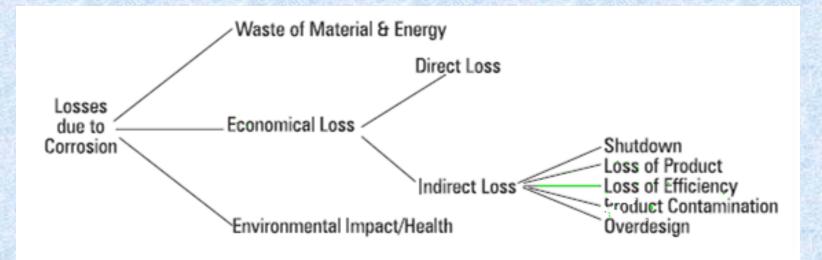
Corrosion in some cases is desirable , for example chemical machining or chemical milling (widely used in aircraft and other applications).Anodizing of aluminum is another beneficial corrosion process used to obtain better and more uniform appearance in addition to a protective corrosion product on the surface.

Losses due to Corrosion

FIVE GOOD REASONS TO STUDY CORROSION

(1) Materials are precious resources of a country. Our material resources of iron, aluminum, copper, chromium, manganese, titanium, etc. are dwindling fast. Some day there will be an acute shortage of these materials. An impending metal crisis does not seem anywhere to be a remote possibility but a reality. There is bound to be a *metal crisis* and we are getting the signals. To preserve these valuable resources, we need to understand how these resources are destroyed by corrosion and how they must be preserved by applying corrosion protection technology.

(2)Engineering knowledge is incomplete without an understanding of corrosion. Aero planes, carriers cannot be designed without any recourse to the corrosion behavior of materials used in these structures.
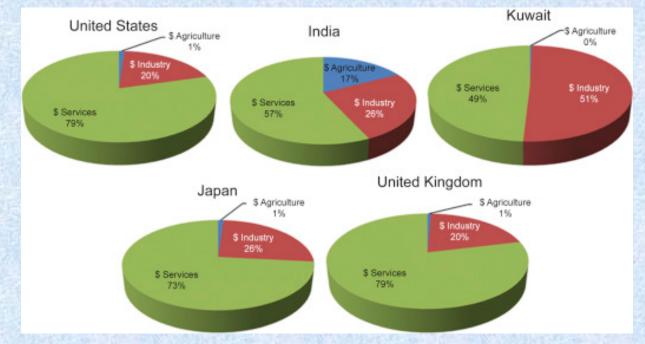
(3) Several engineering disasters, such as crashing of civil and military aircraft, naval and passenger ships, explosion of oil pipelines and oil storage tanks, collapse of bridges and decks and failure of drilling platforms and tanker trucks have been witnessed in recent years. Corrosion has been a very important factor in these disasters. Applying the knowledge of corrosion protection can minimize such disasters. In USA, two million miles of pipe need to be corrosion-protected for safety.

(4) The designing of artificial implants for the human body **requires a complete understanding of the corrosion science and engineering. Surgical implants must be very corrosion-resistant because of corrosive nature of human blood.**

(5) Corrosion is a threat to the environment. For instance, water can become contaminated by corrosion products and unsuitable for consumption. Corrosion prevention is integral to stop contamination of air, water and soil. The American Water Works Association needs US$ 325 billion in the next twenty years to upgrade the water distribution system.

Cost of Corrosion

In a study led by R. Bhaskaran at Lovely Professional University, Phagwara, Punjab, India and N.S. Rengaswamy at Central Electrochemical Research Institute, Karaikudi, India
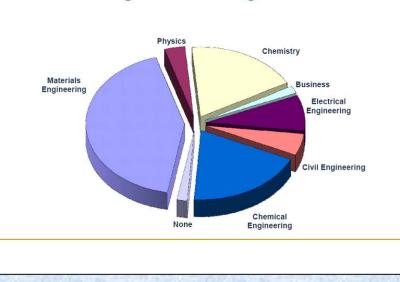
The India study gave one of the most detailed sector breakdowns of any of the national costs of corrosion. The direct cost of corrosion for India was USD 26.1 billion or 2.4 percent of India GDP. The avoidable cost of corrosion was USD 9.3 billion or 35 percent of the direct cost of corrosion.

Corrosion Engineering : **Is the application of science and art to prevent or control corrosion damage economically and safely.**

Corrosion engineer : **His job is to protect corrosion of various metallic structures , e.g.: corrosion protection of SHIPS , PIPE LINES , INDUSTRIES …etc. Corrosion Engineering is supposed to have the knowledge of Metallurgy , Electro-Chemistry , Mechanical behaviors of Materials , Electrical Engineering , corrosion test , the nature of corrosive environments and the knowledge of Cost analysis .**

Distribution of disciplines in which active corrosion engineers have graduated

What would be expected from Corrosion Engineer.

❖Ensuring maximum life of new equipment.

❖Preservation of existing equipment.

❖Protecting or improving the quality of a product in order to maintain or improve a competitive position.

❖Avoiding costly interruptions of production.

❖Reducing or eliminating losses of valuable products by spillage or leaks.

❖Refitting of equipment withdrawn from service because of corrosion.

❖Reducing hazards to life and property that might be associated with corrosion:

√ Explosions of pressure vessels or piping systems.

√ release of poisonous or explosive gases or vapors.

Environments : Practically all environments are corrosive to some degree. Examples are air and moisture . Environment means the condition of corrosion e.g.: Water , Water + Air , Water + Cl_2 ,

Water + H_2S .

CLASSIFICATION OF CORROSION

CHAPTER 1.2

PR7892 CORROSION ENGINEERING

Classification of corrosion :

Corrosion has been classified in many different ways . One method divides corrosion in to low - temperature and high – temperature corrosion . Another separates corrosion in to direct combination (or oxidation) and electro – chemical corrosion . The preferred classification here is (1) Wet corrosion and (2) Dry corrosion .

►Wet corrosion :- Occurs when a liquid is present . This is usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far .

Wet Corrosion : chemical reaction of a metal with the atmosphere in presence water

$Fe + H_2O \longrightarrow$ **No Corrosion**

$Fe + H_2O + Oxygen \longrightarrow Fe(OH)_2$ **Or** $Fe(OH)_3$

Chlorides   may be wet Cl_2 **[** $H_2O + Cl_2 \longrightarrow HCl + HOCl$ **]**

Salts like $NaCl$ **,** $MgCl$ **,** $CaCl_2$ **, ….. etc**

$NaCl + H_2O \longrightarrow NaOH + HCl$

corrosion by $H_2O + O_2$ **at room temp. is about 1/20 th to that of** H_2O **+ chlorides**

► **Dry Corrosion : Occurs in absence of a liquid phase or a above the dew point of the environment . Vapors and gases are usually the corrodents . Dry corrosion is most often associated with high temperatures .   like Oxidation of metals**

$$Fe + O_2 \longrightarrow Fe_2O_3 \ , Fe_3O_4 \ , FeO$$

Dry chlorine is practically non-corrosive to ordinary steel , but moist chlorine dissolved in water , is extremely corrosive and attacks most of common metals and alloys. The reverse is true for Titanium – dry chlorine gas is more corrosive than wet chlorine .

Sulfides H_2S it is very highly corrosive substance.

Dry – forms Iron sulfide

H_2S

Wet – forms Oxy – sulfides
($H_2S + H_2O$) + hydrogen embrittlements

SO_2 : has no corrosion effect but in presence of moisture and oxygen at forms sulfides.

18.4 Standard Electrode Potential

TABLE 18.1	Standard Reduction Potentials at 25°C		
	Reduction Half-Reaction		(V)

	Reduction Half-Reaction		(V)	
Stronger oxidizing agent ↑	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87	**Weaker reducing agent**
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2\,e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
Weaker oxidizing agent	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	**Stronger reducing agent** ↓
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Electro – Chemical Process :

There are two reactions taking place at the same time,

   a) Anodic reaction (Oxidation).

   b) Cathodic reaction (Reduction).

$$Fe \longrightarrow Fe^{+2} + 2e \quad (\text{ anodic reaction })$$

$$1/2 O_2 + H_2O + 2e \longrightarrow 2(OH)^- \quad (\text{ Cathodic reaction })$$

$$2Fe + 3/2 O_2 + 3H_2O \longrightarrow 2Fe(OH)_3 \quad [\text{ Rust }]$$

Anodic and Cathodic reaction have to take place at the same rate other wise the rate of corrosion would became slow .

Normally the Cathodic reaction is the rate controlling process .There are various types of Cathodic reactions possible under different conditions :

$$M \longrightarrow M^{+2} + 2e \quad \text{anodic}$$

Cathodic reactions:

1) Hydrogen evolution $2H^+ + 2e \longrightarrow H_2 \quad (\text{ gas })$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

   Or

$$Zn \longrightarrow Zn^{+2} + 2e \quad \text{(anodic)}$$

$$2H_+ + 2e \longrightarrow H_2 \quad \text{(Cathodic)}$$

2) Oxygen reduction

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$$

[in acidic medium with oxygen]

3) Oxygen reduction $O_2 + H_2O + 4\,e \longrightarrow 4(OH)$

[in neutral or basic medium] This is the most kind reaction happens

4) Metal Ion reactions

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$
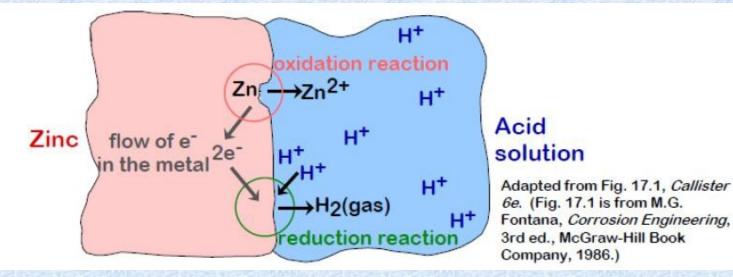
$$M^{+3} + e \longrightarrow M^{+2}$$

5) Metal deposition

$$M^{+} + e \longrightarrow M\downarrow$$

An overall electrochemical reaction must consist of at least one oxidation and one reduction reaction, and will be the sum of them; often the individual oxidation and reduction reactions are termed half-reactions. There can be no net electrical charge accumulation from the electrons and ions; that is, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.

Example 1: Zinc metal immersed in an acid solution containing H+

Adapted from Fig. 17.1, *Callister 6e.* (Fig. 17.1 is from M.G. Fontana, *Corrosion Engineering*, 3rd ed., McGraw-Hill Book Company, 1986.)

➤**zinc will experience oxidation or corrosion according to,**

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

➤ **H+ ions are reduced according to,**

$$2H^+ + 2e^- \longrightarrow H_2 \, (gas)$$

➤ **The total electrochemical reaction**

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2 \, (gas)$$

Example 2: **Oxidation or rusting of iron in water, which contains dissolved oxygen, This process occurs in two steps:**

➢ **Fe is oxidized to Fe^{2+} [as $Fe(OH)_2$]**

$$Fe + \tfrac{1}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

➢ **Fe^{2+} to Fe^{3+} [as $Fe(OH)_3$]**

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2Fe(OH)_3$$
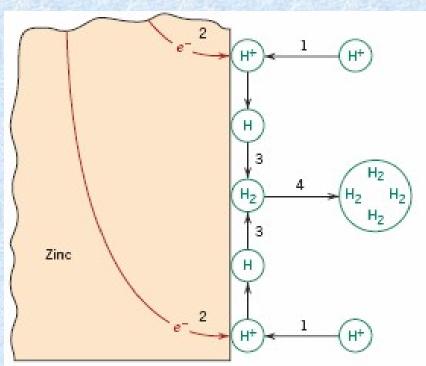
Polarization :-

The rate of an electro-chemical reaction is limited by various physical and chemical factors. Hence an electro-chemical reaction is said to be polarized or retarded by these environmental factors.
Polarization can be divided in to two different types :

1)Activation Polarization : It is controlled by the reaction sequence at metal – electrolyte interface. This is like the hydrogen evolution reaction on zinc during corrosion in acid solution .

Step 1: adsorb or attracted H⁺ to the surface .
Step 2: electron transfer to H⁺ .
Step 3: reduce the H⁺ to H_2 .
Step 4: hydrogen molecules combine to form
        a bubble of hydrogen gas .

The speed of reduction of hydrogen ions will be controlled by the slowest of these steps.

2)Concentration Polarization : **It is controlled by the diffusion in the electrolyte . For the case of hydrogen evolution , the number of H^+ in the solution is quite small, and the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface . Reduction rate controlled by bulk solution rather than at the metal surface.**

Activation polarization usually is controlling factor during corrosion in media containing a high concentration of active aspects .(concentrated acids). **Concentration polarization** generally predominates in the dilute acids , aerated salt solutions .
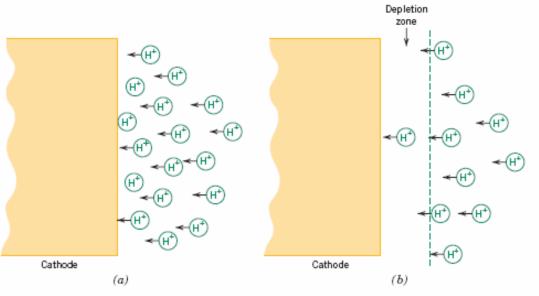
Figure 17.8 For hydrogen reduction, schematic representations of the H^+ distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd

Passivity :-

The phenomenon is rather difficult to define because of its complex nature and specific conditions under which it occurs.
Passivity refers to the loss chemical reactivity experienced by certain metals and alloys under particular environmental conditions.
Fe ,Ni , Si , Cr , Ti , Al , and their alloys can be passive in certain conditions.
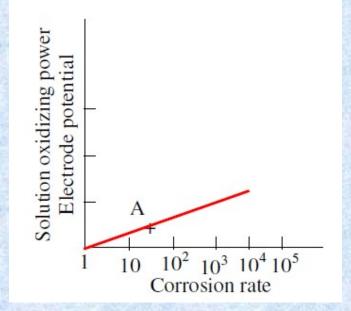
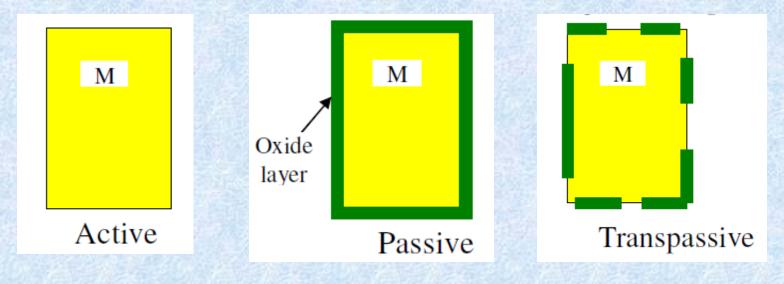Fig. (1) Corrosion rate of the a metal as a Function of solution oxidizing power (electrode potential) active metal (non-passive)
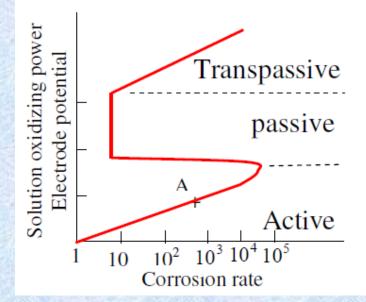
Fig. (2) Corrosion characteristics of an active-passive metal as function of solution oxidizing power

Fig.(1) refer to active metal in air-free acid solution it is corrode and corrosion rate increase by adding oxygen or ferric ions.
Fig.(2) illustrates the typical behavior of a metal of which demonstrates passive effects .

There are three regions, Active , Passive & Transpassive.
Active region : the behavior of a normal metal.
Passive region: If more oxidizing agent is added the corrosion rate suddenly decrease, this mean that this region begin.
Transpassive region: with further increase in oxidizing agents the corrosion rate again increase with increasing oxidizer power.

Active

Oxide layer

Passive

Transpassive

Rate of corrosion :-

The most common methods used are 1 –
Weight loss in mg or gram.
2 - % weight change.
   Poor – sample shape and exposure Time influence results.
3 – Milligram / sq. decimeter / day . (mdd).
4– Grams / sq. decimeter / day . 5 -
Grams / sq. centimeter / hour 6 -
Grams / sq. meter / hour .
7 - Grams / sq. inch / hour .
8 - Moles / sq. centimeter / hour .
   Good – but expressions do not give penetration rates .
9- Inch / year   . 10 -
Inch / month .
11 – mm / year most common method . K= 87.6
Better – expressions give penetration rates.

Corrosion Penetration Rate,   CPR = $\dfrac{KW}{\rho A t}$

where W is the weight loss after exposure time t; ρ and A represent the density and exposed specimen area

12 – Mils per Year (MPY) 1 mil = 1/ 1000 in . K=534

Best – expresses penetration Without decimals or large numbers.

Factors effecting on corrosion rates :

1) Environments effects: It is desirable to change process variables.

(i) Effect of Oxygen and Oxidizers : **The effect of oxidizers on corrosion Rate can be represented by the graph Shown here .**

Examples
Region 1
Corrosion rate Oxidizer
Monel alloy in HCl + O_2 (Ni + Cu alloys)
 Cu in H_2SO_4 + O_2
  Fe in H_2O + O_2
Regions 1 – 2
  18Cr-8Ni in H_2SO_4 + Fe^{+3}
  Ti in HCl + Cu^{+2}

Region 2
 18Cr-8Ni in HNO_3
Hastelloy C in $FeCl_3$ (Ni alloy with alloying elements)
Region 2 – 3
   18Cr-8Ni in HNO_3 + Cr_2O_3
Region 1 – 2 – 3
  18Cr-8Ni in concentrated H_2SO_4 + HNO_3 mixtures at elevated temperatures.
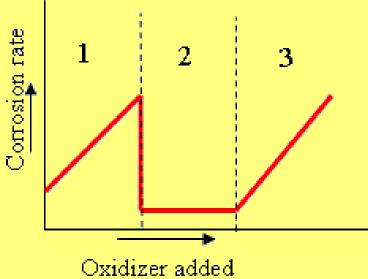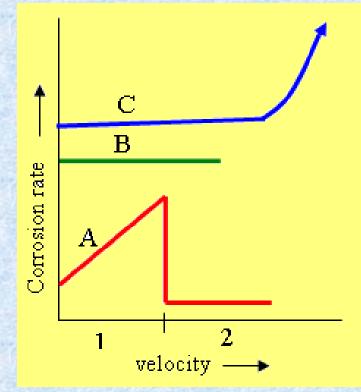
(ii) Effects of Velocity : Mean the velocity of medium .
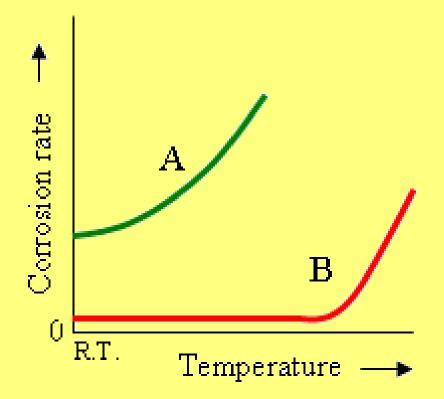
The effects of velocity on corrosion rate are, like the effect of oxidizer additions, complex and depend on the characteristics of the metal and the environment to which it is exposed. If rate of corrosion is controlled by **Activation polarization** then there is no effect of velocity. If the process is diffusion controlled **(concentration polarization).** Then the corrosion rate increase with increasing velocity.

Examples
 Curve A
Corrosion rate velocity

       1:   Fe in $H_2O + O_2$
            Cu in $H_2O + O_2$
   1 − 2 :   18Cr-8Ni in $H_2SO_4 + Fe^{+3}$
            Ti in $HCl + Cu^{+2}$

Curve B :

    Fe in dilute HCl
   18Cr-8Ni in H_2SO_4

Curve C :

    Pb in dilute H_2SO_4
    Fe in concentrated H_2SO_4

(iii) Effect of Temperature: **Temp. increases the rate of almost all chemical reactions. By increasing Temp. the conductivity of the metal and the medium increases and also the diffusion rate in the medium increase. Therefore the corrosion rate also increases .**

Examples
Curve A :
    18Cr-8Ni in H_2SO_4
    Ni in HCl
    Fe in HF
Curve B :
    18Cr-8Ni in HNO_3
    Monel in HF
    Ni in NaOH
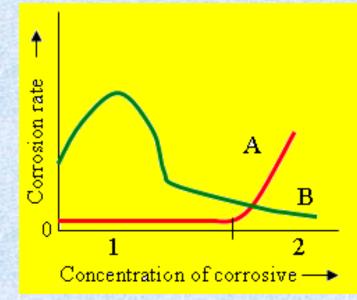
(iV) Effects of Corrosion Concentration : (concentration of corrosive medium). Many materials which exhibit passivity effects are only negligible affected by wide changes in corrosive concentration (curve A) . The reduction in rate after a Maximum is due to the difficulty in ionization with the increase in concentration of corrosive medium (curve B).

Examples
Curve A :
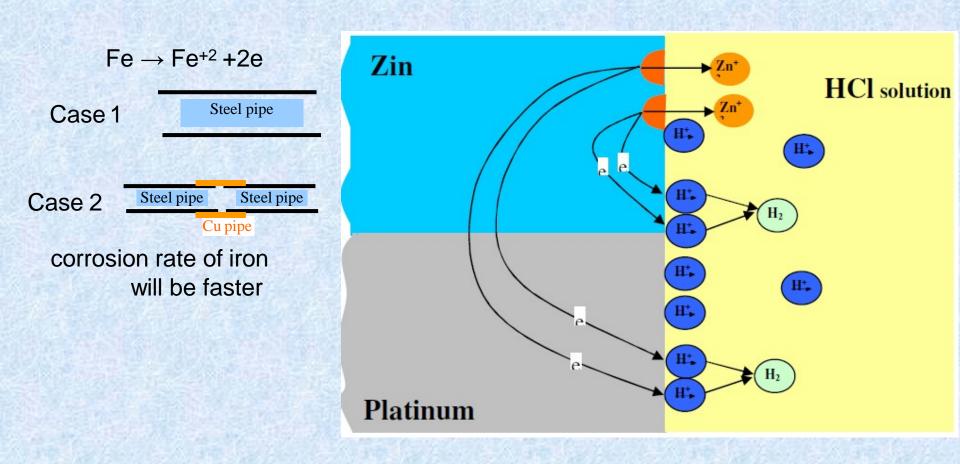
   1 :   Ni in NaOH
           18Cr-8Ni in HNO3
           Hastelloy B in HCl
           Ta in HCl

  1 – 2 : Monel in HCl
           Pb in H_2SO_4

Curve B :

     Al in acetic acid and HNO_3
     18Cr-8Ni in H_2SO_4 , &   Fe in H_2SO_4
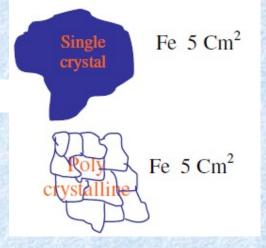
(V) Effects of Galvanic Coupling : **By this we mean , when two dissimilar metals are in contact each other . Under this condition the corrosion rate of one metals stops and the corrosion rate of the other metal becomes faster . This depends on the Electro-Potential of the two metals.**

$Fe \rightarrow Fe^{+2} + 2e$

Case 1

Steel pipe

Case 2

Steel pipe   Steel pipe

Cu pipe

corrosion rate of iron will be faster

2) Metallurgical Aspects:

Polycrystalline Would corrode much faster than single crystal. And is due to the presence of grain – Boundaries in Polycrystalline grain boundaries are the regions of high Energy their for their Chemical reactivity is higher than the rest of materials.

1Effect of Grain boundary.

2- Metal purity.

2 Effect of various phases in the alloys presence of phases alloys have the same effect as Galvanic – coupling in .

3   Different metals.

4   Residual stresses.

5   The strain hardening deformation.

ELECTRO-CHEMICAL CORROSION

CHAPTER 1.3

PR7892
CORROSION ENGINEERING

Electro-chemical Considerations :

For metallic materials, the corrosion process is normally electrochemical, that is **a chemical reaction** in which there is transfer of **electrons** from one chemical species to another. Metal atoms characteristically lose or give up electrons in what is called an **oxidation reaction**. The site at which oxidation takes place is called the **anode**; oxidation is sometimes called an **anodic reaction.**

The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed **a reduction reaction.** The location at which reduction occurs is called the **cathode.**

Corrosion Cell : For Corrosion to take place ,the information of a corrosion cell is essential. A corrosion cell essentially comprised of the following four components.
 1) Anode   . 2) Cathode . 3) Electrolyte   .   &
 4) Metallic path.

Anode (-ve of cell): One of the two dissimilar metal electrodes in an electrolytic cell. Electrons are released at anode , which is the more reactive metal .Electrons move through the wire in to the cathode.
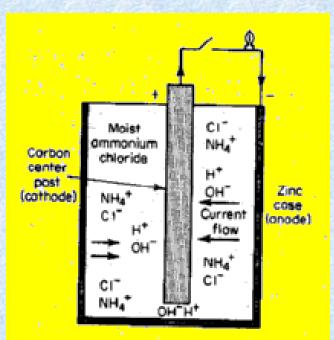
Cathode (+ve of cell) : The other Electrode in the electrolytic cell .Reduction takes place at cathode and electrons are consumed .

Electrolyte (e.g. salt solution) : It is the electrically conductive solution for corrosion to occur. Positive electricity passes from anode to cathode through the electrolyte as cations .

Metallic path : The two electrodes are connected externally by a metallic conductor. Current flow from (+) to (-) which really electrons flowing from (- e) to (+e).

Current flow : Conventional current flows from anode (-) to cathode (+) as Zn++ ions through the solution. The circuit is completed by passage of electrons from the anode to the cathode through the wire (outer current).
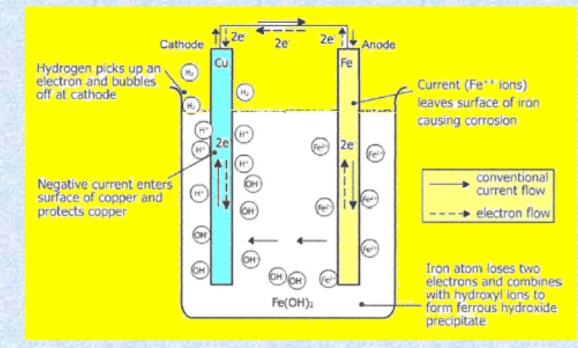
Electron Flow : The circuit is completed by negative ions (-) Which migrate from cathode (+) , through the electrolyte , towards the anode (-).

Example :
In the dry Battery
Zinc casing acts as anode.
Carbon electrode acts as cathode.
Moist ammonium chloride acts as
Electrolyte .
 e.g. Zn ions dissolve from a zinc
anode and thus carry positive
current away from it ,
through the Aqueous electrolyte.

$$Zn + 2H^+ \longrightarrow Zn^{+2} + H_2 \uparrow$$

Anodic And Cathodic Reactions

Anodic reactions characteristics :

(1) Oxidation of metal to an ion with a charge.
(2) Release of electrons.
(3) Shift to a higher valence state.

The process of oxidation in most metals and alloys represents corrosion. If oxidation is stopped , corrosion is stopped.

Cathodic reactions characteristics :

The Process of reductions which occur at the cathode represents protection .Electrons released by the anodic reactions are consumed at the cathode surface. Unlike an anodic reaction , there is a decrease in valence state. (most common Cathodic reactions mentioned above).
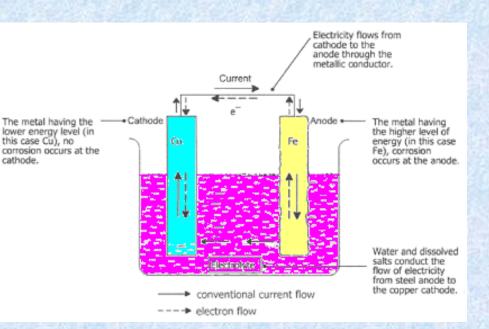
Types of Corrosion Cells :

There are several types of corrosion cells:

(1) Galvanic cells
(2) Concentration cells
(3) Electrolytic cell
(4) Differential temperature cells.

(1) Galvanic cells :

The galvanic cell may have an anode or cathode of dissimilar metals in an electrolyte or the same metal in dissimilar conditions in common electrolyte.
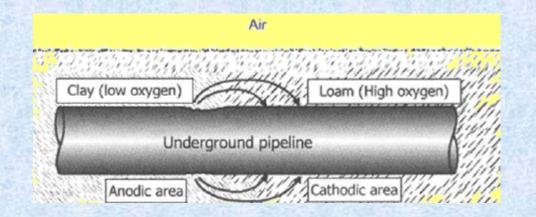
(2) Concentration Cells :

This is similar to galvanic cells except the anode and cathode are of same metals in a heterogeneous electrolyte. A pipe in soil, Concentration cells may be set up by:

(a) Variation in the amount of oxygen in soils.

(b) Differences in moisture content of soils.

(c) Differences in compositions of the soil.

Concentration cells are commonly observed in underground corroding structures, such as buried pipes or tanks.

There are three general types of concentration cell corrosion:

1)Metal Ion Concentration Cells

In the presence of water, a high concentration of metal ions will exist under faying surfaces and a low concentration of metal ions will exist adjacent to the crevice created by the faying surfaces. An electrical potential will exist between the two points. The area of the metal in contact with the low concentration of metal ions will be cathodic and will be protected, and the area of metal in contact with the high metal ion concentration will be anodic and corroded.

2)Oxygen Concentration Cells

A water solution in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points.Corrosion will occur at the area of low-oxygen concentration (anode).
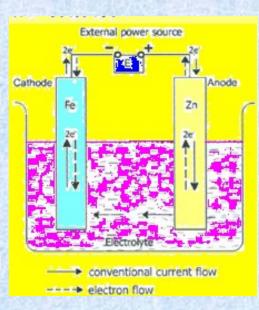
3)Active-Passive Cells

Metals that depend on a tightly adhering passive film (usually an oxide) for corrosion protection; e.g., austenitic corrosion-resistant steel, can be corroded by active-passive cells. The corrosive action usually starts as an oxygen concentration cell; e.g., salt deposits on the metal surface in the presence of water containing oxygen can create the oxygen cell.

The inequality of dissolved chemicals causes a potential difference which establishes anode in the more concentrated region and cathode in the less concentrated region.

(3) Electrolytic Cells :

This type of cell is formed when an external current is introduced into the system. It may consist of all the basic components of galvanic cells and concentration cells plus an external source of electrical energy. Notice that anode has a (+) polarity and cathode has (-) polarity in an electrolytic cell, where external current is applied. This is the type of cell set up for electrically protecting the structures by Cathodic protection. The polarity of an electrolytic cell is opposite to that in a galvanic (corrosion) cell.

(4) Differential Temperature Cells :

This type of cell is formed when two electrode of same metals present in different temperatures , causing in different potential ,high temp. electrode will be the cathode and the lower temp. will be the anode . (e.g. heat exchangers & condensers).

The Electro Motive Series (EMF)

When a metal is immersed in an electrolyte, a dynamic equilibrium is established across the interface with a potential difference between the metal and electrolyte. If a metal is immersed in a solution of its own ions , such as Zn in $ZnSO_4$ solution ,or copper in $CuSO_4$ the potential obtained is called the reversible potential (E_{rev}).

If the metals are in their standard stats , such that activities of the metallic ions are equal to unity or gases are at 1 bar pressure , the potentials obtained are called ' Standard Electrode Potentials ' . A standard potential refers to the potential of pure metal measured with reference to a hydrogen reference electrode (H_2 / H^+) which is arbitrarily defined as Zero .It is not possible to establish a reversible potential for alloys containing two or more reactive components , so only pure metals are listed in table below .
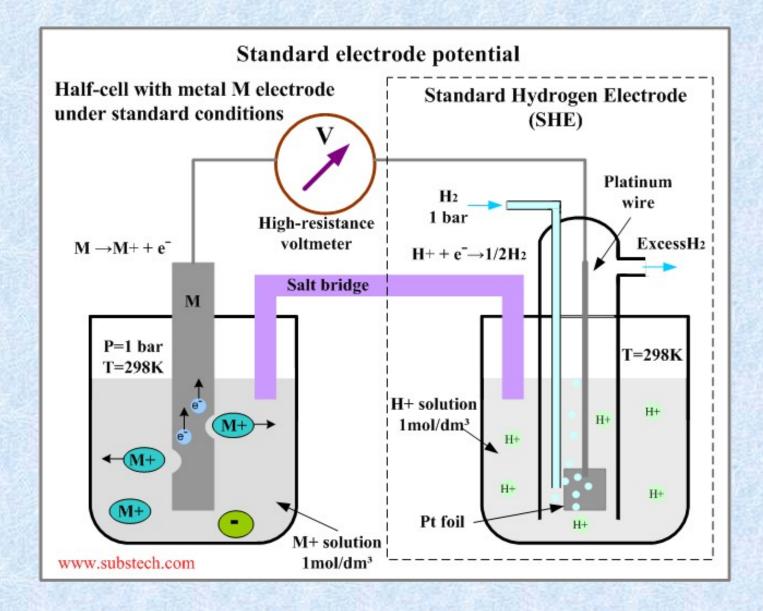
Standard electrode potential

Half-cell with metal M electrode under standard conditions

Standard Hydrogen Electrode (SHE)

V

High-resistance voltmeter

$M \rightarrow M+ + e^-$

$H+ + e^- \rightarrow 1/2 H_2$

H₂ 1 bar

Platinum wire

Excess H₂

Salt bridge

M

P=1 bar T=298K

T=298K

H+ solution 1mol/dm³

Pt foil

M+ solution 1mol/dm³

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Table 17.1   The Standard emf Series
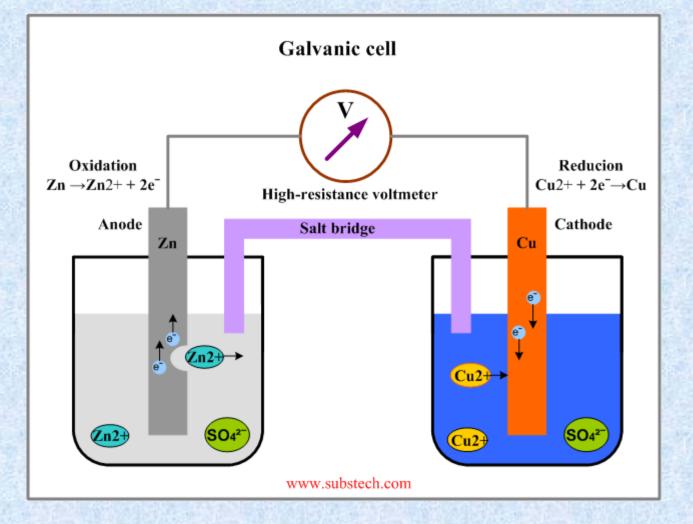
	Electrode Reaction	Standard Electrode Potential, V^0(V)
	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
↑	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
Increasingly inert	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
(cathodic)	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
Increasingly active	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
(anodic)	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
↓	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
	$Na^+ + e^- \longrightarrow Na$	−2.714
	$K^+ + e^- \longrightarrow K$	−2.924

Galvanic series : In actual corrosion problems , galvanic coupling between metals in equilibrium with their ions rarely occurs. In general , the positions of metals and alloys in the galvanic series agree closely with their constituent elements in the emf series .

This represents the relative reactivities of a number of metals and commercial alloys in seawater.

Table 17.2   The Galvanic Series

Platinum
Gold
Graphite
Titanium
Silver
⌈ 316 Stainless steel (passive)
⌊ 304 Stainless steel (passive)
⌈ Inconel (80Ni–13Cr–7Fe) (passive)
⌊ Nickel (passive)

Increasingly inert (cathodic)

⌈ Monel (70Ni–30Cu)
│ Copper–nickel alloys
│ Bronzes (Cu–Sn alloys)
│ Copper
⌊ Brasses (Cu–Zn alloys)
⌈ Inconel (active)
⌊ Nickel (active)
Tin
Lead

Increasingly active (anodic)

⌈ 316 Stainless steel (active)
⌊ 304 Stainless steel (active)
⌈ Cast iron
⌊ Iron and steel
Aluminum alloys
Cadmium
Commercially pure aluminum
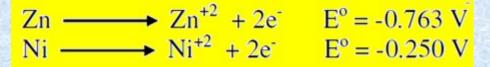Zinc
Magnesium and magnesium alloys

Example 1 : A galvanic cell consist of (Zn) electrode in($ZnSO_4$) solution with (1 mole) concentration . The other is of (Ni) electrode in ($NiSO_4$) solution with (1 mole) concentration . The two electrodes are separated with porous partition to prevent mixing of the two solutions . The two electrodes are contacted with conductive wire . Find.

a) On which electrode the oxidation reaction will be .
b) Which electrode will be the anode .
c) Which electrode will corroded .
d) what is the EMF for this galvanic cell , circuit close.

Solution :

The half cells reactions are :

$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^o = -0.763 \text{ V}$$
$$Ni \longrightarrow Ni^{+2} + 2e^- \qquad E^o = -0.250 \text{ V}$$

(a) Oxidation reaction will take place on Zn electrode .Because the potential deference in Zn half cell more negative (- 0.763 V) compare with (-0.250 V) for Ni half Cell .

(b) From previous answer, Zn electrode is the anode , because the oxidation reaction take place on anode electrode.

(c) In galvanic cell , the anode electrode is the corroded electrode , for that Zn electrode will corroded.

(d) Cell potential is the sum of the two half cells potential.

$$
\begin{array}{lll}
\text{Anode reaction} & Zn \longrightarrow Zn^{+2} + 2e^- & E^o = -0.763 \text{ V} \\
\text{Cathode reaction} & Ni \longrightarrow Ni^{+2} + 2e^- & E^o = +0.250 \text{ V} \\
\hline
& Zn + Ni^{+2} \longrightarrow Zn^{+2} + Ni & E^o_{cell} = -0.513 \text{ V}
\end{array}
$$

The result of the Cell reaction . Ni potential changed with respect to standard potential cell .This is due to its potential in the EMF series . Also if we connect Pt electrode with Cu electrode we get :

$$Pt \longrightarrow Pt^{'2} + 2e^- \qquad E^\circ = +1.200 \text{ V}$$
$$Cu \longrightarrow Cu^{+2} + 2e^- \qquad E^\circ = +0.337 \text{ V}$$

By subtraction the lower potential from the higher we get

Reduction
$$Pt \longrightarrow Pt^{+2} + 2e^- \qquad E^\circ = +1.200 \text{ V}$$
Oxidation
$$Cu \longrightarrow Cu^{+2} + 2e^- \qquad E^\circ = -0.337 \text{ V}$$
$$E^\circ_{cell} = +0.8633 \text{ V}$$

If the galvanic Cell contain two electrodes , One of them with (- ve) potential and the other with (+ ve), such as Zinc with Copper .

$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^\circ = -0.763 \text{ V}$$
$$Cu \longrightarrow Cu^{+2} + 2e^- \qquad E^\circ = +0.337 \text{ V}$$

In this case ,if we subtract Cu potential from Zn potential the result is :

Oxidation
$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^\circ = -0.763 \text{ V}$$
Reduction
$$Cu \longrightarrow Cu^{+2} + 2e^- \qquad E^\circ = -0.337 \text{ V}$$
$$E^\circ_{cell} = -1.100 \text{ V}$$

We change reduction sign to get the cell potential difference .

Example 2 : Write the reactions of the anodic half cell (oxidation)
and Cathodic half cell (reduction) . For the following
electrodes and electrolytes , by using standards potential
values :

(a) Zinc and copper electrodes are immersed in dilute (CuSO4).
(b) Copper electrode is immersed in water saturated with oxygen.
(c) Iron electrode is immersed in water saturated with oxygen.
(d) Magnesium electrode is immersed in water saturated with oxygen.

Solution :

(a)
$$Zn \longrightarrow Zn^{+2} + 2e^- \qquad E^0 = - 0.763 \text{ V}$$

Oxidation (Anodic reaction)

$$Cu^{+2} + 2e^- \longrightarrow Cu \qquad E^0 = - 0.337 \text{ V}$$

Reduction (Cathodic reaction)

Changing the sign of Cathodic reaction , we observed that Zinc reaction
possess more negative , so it is the anode and oxidation reaction
occurred on it.

b) May be there is a low rate corrosion or may be there is no corrosion , because the potential difference between Cu oxidation (0.337 V) and that formed in water from hydroxide ion (0.401 V) is very small .

c)

$$Fe \longrightarrow Fe^{+2} + 2e \qquad E^o = -0.440 \text{ V}$$

Oxidation (Anodic reaction)

$$O_2 + 2H_2O + 2e^- \longrightarrow 4OH^- \qquad E^o = -0.401 \text{ V}$$

Reduction (Cathodic reaction)

Iron potential's difference is more negative, so it is the anode and oxidation reaction occurred on it.

d)

$$Mg \longrightarrow Mg^{+2} + 2e^- \qquad E^o = -2.36 \text{ V}$$

(Anodic reaction)

$$O_2 + 2H_2O + 2e^- \longrightarrow 4OH^- \qquad E^o = -0.401 \text{ V}$$

(Cathodic reaction)

Mg is more negative in potential, so it is the anode and oxidation reaction occurred on it.

Galvanic Cell with Electrolytes that are not one molar :-

Most of electrolyte solutions of the real galvanic cells are not to be (1 mole) .But they are always dilute solutions , which they are less than (1 mole) .If the ions concentrates in the electrolyte surround to the anode electrode is less than 1 mole , the reaction motive force to dissolve or corrode the anode will be higher .Because there is less concentrate of ions that causes the reverse reaction .There for it will be more negative of electro-chemical series on the anodic half cell.

$$M \longrightarrow M^{+n} + ne^-$$

Truly the metal ion concentration effects **(C_{ion})** on the standards potential of the electrochemical series **(E^o)**at **(25°)**Temperature are given by Nernst equation for the half anodic cell reaction .Where there is one kind of ions are produced . Nernst equation can be written as follow :

$$E = E^o + \frac{RT}{nF} \ln\left[\frac{a_{products}}{a_{reactives}}\right]$$

$$E = E^o + 2.3 \frac{8.3\,J/K^o.mole \text{ X } (25+273)K^o}{n \text{ X } 96,500\,coulomb} \log C_{ion}$$

$$E = E^0 + \frac{0.0592}{n} \log C_{ion}$$

Where are :

E = New electrochemical potential for the half cell .

E^o = standard electrochemical potential for the half cell .

n = No. of electrons transferred (the valence).

C_{ion} = molar concentrations of the ions .

R = gas constant = 8.3 J/K^o/mole.

T = Temperature = 25 + 273 = 298 K^o.

F = Faraday constant = 96,500 coulomb .

For the Cathodic reaction , the final potential sign must be inverses .

Example 3:

A galvanic cell in (25 C^o) temp. it is formed from Zinc electrode in   (0.10 mole $ZnSO_4$) solution , the other electrode is of Nickel in (0.05 mole $NiSO_4$) solution .The two electrodes are separated with porous wall and connected with external wire. What is the value of the cell potential, when the circle is connected

Solution :

First we suppose that the solutions are in (1 mole) concentrate. So
the potentials of Zn & Ni be in standard value of EMF serious . Zn electrode
will be the anode because its potential(- 0.763 v) is more negative in the
electrochemical cell of Zn – Ni Than of Ni (- 0.250 v).
Then using Nernst equation to correct the potentials of the cell .

$$E = E^O + \frac{0.0592}{n} \log C_{ion}$$

Anode reaction

$$E_A = -0.763\ V + \frac{0.0592}{2} \log 0.10$$
$$= -0.763\ V - 0.296\ V$$
$$= -0.793\ V$$

Cathodic reaction

$$E_c = -(-0.250\ V + \frac{0.0592}{2} \log 0.05)$$
$$= +0.250\ V + 0.0385\ V$$
$$\text{emf of Cell} = E_A + E_C = -0.793\ V + 0.288\ V$$
$$= -0.505\ V$$

In the modern theory principles we shall take the free energy to solve
Nernst equation .

FORMS OF CORROSION

CHAPTER 1.1

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Forms of corrosion

It is convenient to classify corrosion by the forms in which it manifests itself , the basis for this classification being the appearance of the corroded metal. In most cases the naked eye is sufficient , but sometimes magnification is helpful or required . Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment . There are eight forms of corrosion.

1)Uniform or General Corrosion

It is uniform thinning of a metal without any localized attack. This kind of corrosion happen mostly in one phase materials and is unformed throughout the surface. Corrosion dose not penetrate very deep inside. This kind of corrosion can be happened in most environments , such as dry and wet atmospheres , acids , brines … etc .

Uniform Attack is a form of electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit.

2

Mechanism of uniform Corrosion

Corrosion mechanism in aqueous solution has been amply demonstrated. In atmospheric corrosion which also exemplifies uniform corrosion, 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 comparing the atmospheric corrosion with aqueous corrosion , the following differences are observed: 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 limited. 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 the anodic areas , anodic reaction takes place:

$$Fe \longrightarrow Fe^{+2} + 2\,e \quad (\text{anodic reaction})$$

3

At the Cathodic areas, reduction of oxygen takes place:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

The OH ions react with the Fe++ ions produced at the anode :

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

With more access to oxygen in the air , Fe(OH)$_2$ oxidizes to Fe(OH)$_3$ and later it losses its water :

$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4\,Fe(OH)_3$$

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

$$4\,Fe(OH)_2 + O_2 \longrightarrow 2\,Fe_2O_3.\,H_2O + 2\,H_2O$$
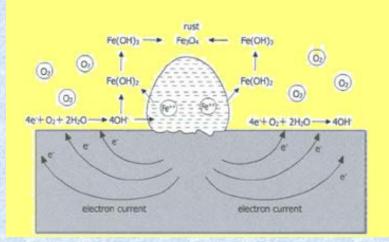
Rust (Fe$_2$O$_3$. H$_2$O) is formed halfway between the drop center and the periphery which is alkaline. The electrons flow from the anode (drop center) to cathode (periphery in the metallic circuit. As shown in the figure below .

4

Aqueous Corrosion

Rust is a generic term to describe a series of different oxides, $Fe(OH)_2$, $Fe(OH)_3$, $FeO(OH)$, $Fe_2O_3.H_2O$ that forms when iron corrodes. The common form of Rust is a Red products:Fe_2O_3. Rust forms due to a reaction between the iron and water; either water condensing from air or rain.The oxygen in the air dissolves in the water and causes rust to form.There are always two distinct chemical reactions in a corrosion process, the basic is:

1)Anodic Dissolution of Metal (Iron) that goes into solution (water)

$$..: Fe ~-----> ~ Fe^{2+} + ~ 2e$$

2)Cathodic Reduction of Oxygen dissolved in water

$$O_2 + 2H_2O + 4e^- ----> ~ 4OH^-$$

The final reaction is:

$$Fe^{2+} + 2OH^- ~-----> ~ Fe(OH)_2$$

This oxide will then further reacts with oxygen to give the final red product:$Fe_2O_3.H_2O$

5
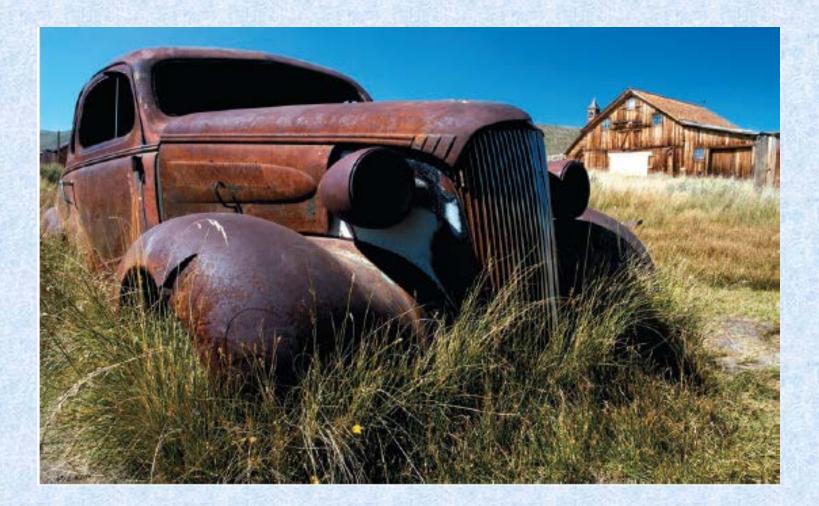
Examples include general rusting of steel and iron and the tarnishing of silverware. The life of equipment can be accurately estimated .

Uniform corrosion can be prevented or reduced by :-
1)proper materials , including coatings .
2)inhibitors .
3)Cathodic protection .

General corrosion of the reactor vessel head
(note: this exterior general corrosion was indicative of a much more serious local corrosion problem due to a leak in the pressure boundary)

6

7

8

FORMS OF CORROSION

CHAPTER 2.2

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1

2) Galvanic or Two-Metal corrosion

Galvanic corrosion occurs when two metals or alloys are electrically coupled while exposed to an electrolyte.

The more reactive metal in the particular environment will experience corrosion, the more inert metal, will be protected from corrosion.

For *example*, steel screws corrode when in contact with brass in a marine environment; or if copper and steel tubing are joined in a domestic water heater, the steel will corrode in the vicinity of the junction.

2

For Education Purpose Only
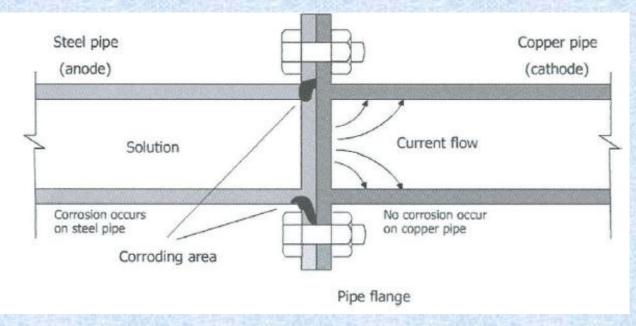
Mechanism of Galvanic corrosion

For the formation of a galvanic cell, the following components are required :

    (1) A cathode. (2) An anode. (3) An electrolyte.
    (4) A metallic path for the electron current .

In case of copper and steel pipe joint , Iron is more negative potential in the emf series (-0.440 V).It is the anode ,moisture acts an electrolyte and metal surface provides a metallic path for electron current to travel. A piece of copper is the cathode .Galvanic cell will formed and galvanic corrosion proceeds .

3

Factors affecting galvanic corrosion

The following factors significantly affect the magnitude of galvanic corrosion:-

(A) Position of metals in the Galvanic series : For galvanic corrosion. The magnitude of galvanic corrosion primarily depends on how much potential difference exists between two metals. For a particular environment, the metals selected should be close to each other in galvanic series to minimize galvanic corrosion . (Al should be joined to Fe).

4

Table 17.2   The Galvanic Series

Platinum
Gold
Graphite
Titanium
Silver
316 Stainless steel (passive)
304 Stainless steel (passive)
Inconel (80Ni–13Cr–7Fe) (passive)
Nickel (passive)

Increasingly inert (cathodic)

Monel (70Ni–30Cu)
Copper–nickel alloys
Bronzes (Cu–Sn alloys)
Copper
Brasses (Cu–Zn alloys)
Inconel (active)
Nickel (active)
Tin
Lead

Increasingly active (anodic)

316 Stainless steel (active)
304 Stainless steel (active)
Cast iron
Iron and steel
Aluminum alloys
Cadmium
Commercially pure aluminum
Zinc
Magnesium and magnesium alloys

5
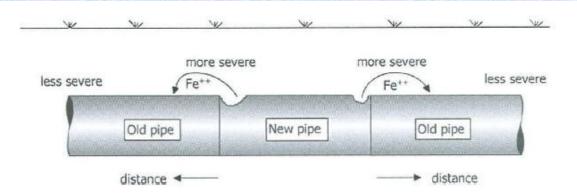
(B) The Nature of Environment : The environment that surrounds the metal must be consider . Water containing copper ions like seawater is likely to form galvanic cell on a steel surface of the tank. The marine environments , galvanic corrosion may be accelerated due to increased conductivity of the electrolyte. Galvanic corrosion of buried material is reduced because of the increased resistivity of soil. Tantalum is very corrosion resistant metal. It is anodic to platinum and carbon , but the cell is active only at high temperatures. Zn is anode with respect to iron at room temp. with presence of water , but if the water temperature became higher (60 -75 C^o). The polarity will reverse and iron will be anode (corroded).

(C) Area , Distance and Geometric Effects :

Effect of Area : The anodic to Cathodic area is extremely important as the magnitude of galvanic corrosion is seriously affected by it .An unfavorable area ratio consists of a large cathode and a small anode .Corrosion of anodic area may be 10 or 100 times greater than if the anodic and Cathodic areas were equal in size .

Effect of Distance : It is a known principle that the solution conductivity varies inversely with the length of the conduction path. The greatest galvanic damage is likely to encountered near the junction of two metals and severity would be decreased with increased length .

6

Effect of Geometry : Geometry of components and their design also influence galvanic corrosion . As current does not flow around the corners , the geometry of the circuit affects the degree of galvanic corrosion .Any obstacle to polarization would accelerate galvanic corrosion .

The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte. For a given cathode area, a smaller anode will corrode more rapidly than a larger one.

7

Measures taken to reduce galvanic corrosion are:

1 - If coupling of dissimilar metals is necessary, choose two that are close together in the galvanic series.

2 - Avoid an unfavorable anode-to-cathode surface area ratio; use an anode area as large as possible.

3 - Electrically insulate dissimilar metals from each other.

4 - Electrically connect a third, anodic metal to the other two; this is a form of Cathodic protection.

8

FORMS OF CORROSION CHAPTER 2.3 3)CREVICE CORROSION

3) Crevice Corrosion

This is a localized form of corrosion, caused by the deposition of dirt, dust, mud and deposits on a metallic surface or by the existence of voids , gaps and cavities between adjoining surfaces. An important condition is the formation of a differential aeration cell for crevice corrosion to occur .This type of attack is usually associated with small volumes of stagnant solution .

Causes :

(a) Presence of narrow spaces between metal-to-metal or non-metal to metal components.
(b) Presence of cracks , cavities and other defects on metals.
(c) Deposition of barnacles, befouling organisms and similar deposits.
(d) Deposition of dirt, mud or other deposits on a metal surface .

Materials and Environment: **The conventional steels, like SS304 and SS316, can be subjected to crevice corrosion in chloride containing environments, such as brackish water and sea water. Water chemistry plays a very important role. Factors affecting crevice corrosion are :**

(a) Crevice Type .

Crevice type means whether the crevice is between metal- to-metal, metal to non-metal or a marine growth, like barnacles or other marine bio fouling organisms, on the metal surface. It is important to know whether factors affecting crevice are man-made or natural in order to select appropriate methods for prevention.

(b) Alloy Composition .

It is important to know whether or not the alloy is resistant to crevice corrosion . Example Hastelloy and Inconel were highly resistant to crevice corrosion in ambient and elevated temperature seawater. The alloying elements in various grade of steel affect both the electrochemical and chemical processes, such as hydrolysis, passive film formation, passive current density and metal dissolution .

(c) Passive Film characteristics .

The type of passive film formed is important, as the breakdown of a passive film results in the onset of crevice corrosion.
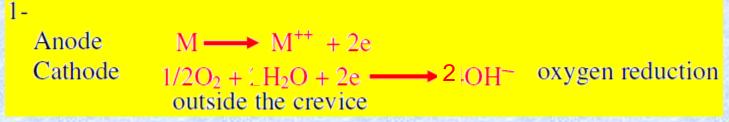
(d) Geometry of Crevice .

The magnitude of crevice corrosion also depends on the depth of the crevice, width of the gap, number of crevices and ratio of exterior to interior crevice. And there are another factors such as (e) Effect of Temperature , (f) Bulk Solution Composition , (g) Mass Transfer in and out of Crevice , and (h) Oxygen .

Mechanism Of Crevice Corrosion :

The phenomenon of crevice corrosion is extremely complex . Most of the mechanism is based on certain type of concentration cells .

1) A difference in metal ions exists between the crevice and the outside, a corrosion cell is formed .The area with low metal concentration becomes the anode and the other cathode .

2) A high concentration of oxygen on the surface outside the crevice and a low oxygen concentration inside a crevice creates differential aeration cell ,which initiates crevice corrosion. The mechanism is as follow:

1-

Anode $M \longrightarrow M^{++} + 2e$

Cathode $1/2 O_2 + 2 H_2O + 2e \longrightarrow 2 OH^-$ oxygen reduction
              outside the crevice

2- After some time, the oxygen in the crevice is consumed , but the concentration of oxygen at the cathode remains unchanged, hence the reaction continues unabated.

3- Within the crevice , the following processes continue to occur .

$$Cr \longrightarrow Cr^{+++} + 3e$$ **Chromium contained in the stainless steel.**

$$Fe \longrightarrow Fe^{++} + 2e$$ **To preserve electro-neutrality, the chloride ions**

are attracted by Cr⁺⁺⁺ or Fe⁺⁺ ions and metallic chlorides are formed:

$$Cr^{+++} + 3\,Cl^- \longrightarrow CrCl_3$$

$$Fe^{++} + 2\,Cl^- \longrightarrow FeCl_2$$

4- Hydrolysis of these chlorides takes place immediately which results in the production of acid conditions in the pit. Hydrolysis increases the level of acidity in the crevice. The geometry of a crevice limits the exchange of solution between the structure and the crevice in the bulk, thus creating acid conditions in the pit. The above is generalized by:

$$M^+ + Cl^- + HOH \longrightarrow MOH + HCl$$

In case of 18-8 stainless steel ;

$$CrCl_3 + 3HOH \longrightarrow Cr(OH)_3 + 3HCl$$
$$FeCl_2 + 2HOH \longrightarrow Fe(OH)_2 + 2HCl$$
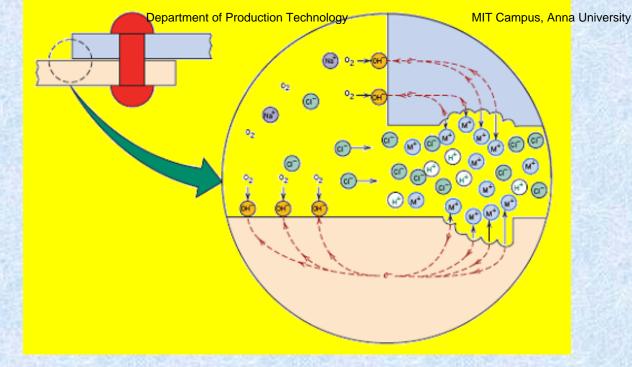
It can be observed that acid is produced and hence acid conditions are produced inside the crevice . The PH may attain a value of as low as 1.0 inside the crevice. Once the acid conditions are generated, the process continues until the reaction is terminated. The mechanism described above is self-generative and once it starts, it continues.

Coutesy of NASA

The above mechanism is, however purely qualitative and dose not provide an explanation of the following:

1) Why crevice corrosion take place even in non-aggressive environments?

2) What is the critical concentration of chloride ions necessary to induce crevice corrosion?

3) The major emphasis is on the formation of a differential aeration cell, whereas other differential cells also may affect crevice corrosion.

4) The relationship of time, chloride concentration and passivity is not explained clearly.

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 or plant flow sheet, if possible.**
6. **Remove wet packing materials during long shutdowns.**
7. **Provide uniform environment, if possible as in the case of backfilling a pipeline trench.**
8. **Weld instead of rolling in tubes sheets.**
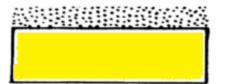
FORMS OF CORROSION
CHAPTER 2.3.1
FILIFORM CORROSION
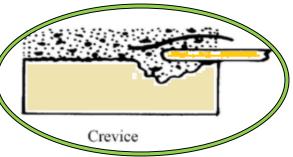
Uniform

Intergranular

Galvanic

Crevice

Pitting

Surface cracks   Internal voids

Hydrogen damage

Stress corrosion

Corrosion fatigue

Hydrogen induced cracking

Fretting   Erosion   Cavitation

Cavitation, erosion and fretting

Filiform corrosion:
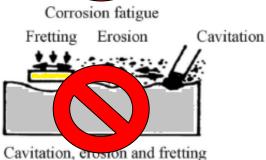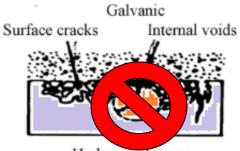
Filiform corrosion **is a type of localized corrosion that is often associated with aluminum and magnesium alloys that have an organic coating.**

This type of corrosion has occurred on other coated metals such as zinc, iron and steel. Filiform corrosion tends to occur at high humidity, e.g. greater than about 75% and temperatures at or slightly above room temperature.

The corrosion appears as thread-like filaments under the coating. The corrosion products cause the coating to bulge giving the surface the appearance a skin to that of a lawn riddled with mole tunnels. The filaments proceed from points where the coating is no longer continuous. Numerous coating systems are susceptible.
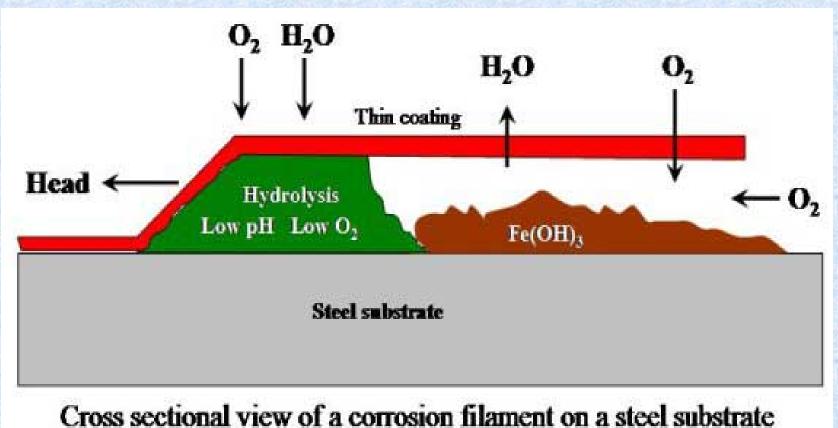
Condensates containing halides, sulfates, carbonates, or nitrates have been associated with Filiform corrosion. Damage to the metal tends to be limited but the effect on appearance tends to be detrimental.

<u>Filiform corrosion:</u>

Filiform corrosion occurs under surface layers such as paint. It depends on the relative moisture of the air and the quality of the surface treatment preparation prior to coating.

Filiform corrosion has the appearance of thin threadlike attacks progressing along the surface beneath a surface layer. The mode of attack is similar to pitting corrosion in that the front of the attack is supported by moisture which penetrates the surface layer and becomes depleted of oxygen making the area anodic.

Filiform corrosion mainly has an aesthetic effect, but the corrosion products formed may cause deformation in narrow crevices or delimitation of surface treatment. .

Filiform corrosion:

The mechanism of Filiform corrosion is shown in the figure below:-.

Cross sectional view of a corrosion filament on a steel substrate

<u>Filiform corrosion:</u>

The mechanism has a number of characteristics that are similar to Crevice corrosion, e.g. differential aeration and hydrolysis of metal ions resulting in increasing acidity in the region of dissolution. This type of corrosion has the following characteristics.

1. **The coating allows oxygen and water to migrate through it.**
2. **The concentration of dissolved oxygen becomes highest at the back of the head near the region of the tail. This region becomes the cathode.**
3. **Oxygen becomes depleted at the head. This region becomes the anode.**
4. **Corrosion is driven by the potential difference between these regions, a potential difference which can rise to several tenths of a volt.**
5. **Metal ion formation and dissolution proceeds at the head while oxygen is reduced closer to the tail.**

<u>Filiform corrosion:</u>

Filiform corrosion gives the appearance of a series of small worms under the paint surface. It is often seen on surfaces that have been improperly chemically treated prior to painting.

<u>Filiform corrosion:</u>

Thus, the worm-like or thread-like structure that is formed has two parts that participate in the corrosion process, the front of the head in which metal dissolves and the region behind the head in which oxygen is reduced. Farther back is an inactive region in which metal oxide and metal hydroxide have formed a precipitate. Hydrogen bubbles can be formed if the head becomes very acidic. The propagating head region continues to move under the coating into new areas leaving behind a thin trail of corrosion under the coating. The threads can measure less than 1 millimeter across. Multiple threads or worms can appear under the coating. When two propagating heads meet, the propagation tends to stop. When a propagating head approaches the inactive tail it tends to be deflected. The corroding alloy can affect the appearance of the filament.

<u>Filiform corrosion:</u>

For example, Filiform corrosion of aluminum or magnesium can result in a whitish precipitate forming in the tail. Filiform corrosion of iron can result in a head containing a greenish fluid (Fe(II)) and a tail containing a redish precipitate (Fe(III)).

The occurrence of Filiform corrosion has been reported to be decreased by the following approaches

- **Application of more than one layer of a coating.**
- **Use of a chromate containing conversion coating or primer on aluminum.**
- **Use of a zinc containing primer on steel.**
- **Reducing the relative humidity or maintaining a low relative humidity when storing items made of susceptible alloys**

Filiform corrosion:

According to one recent investigation, a reduction of the Cu content in the
aluminum alloy below 0.3% reduces Filiform corrosion substantially. The use of
an inhibiting primer or a conversion coating can also be effective. However
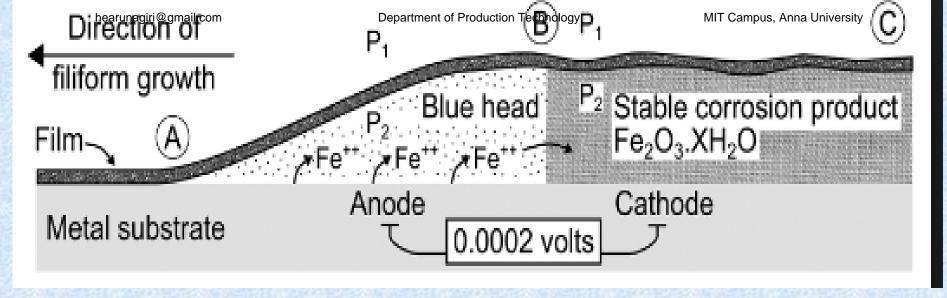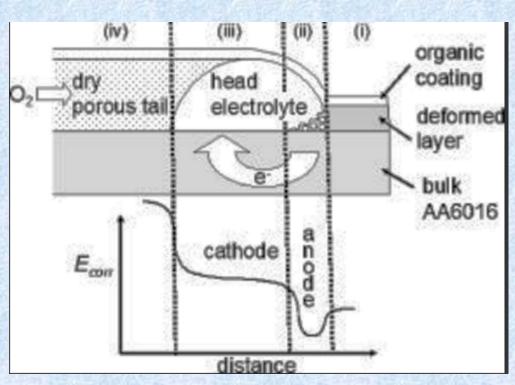anodizing used as a pre-treatment seems to be the best solution.

<u>Filiform corrosion:</u>
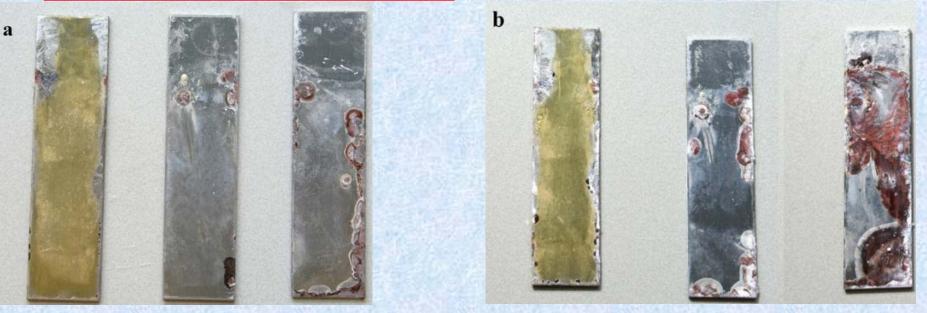
Fig. 2. Three different coatings on Al2024 after 1 week (a) and 7 weeks (b) immersion in 5 wt.% NaCl solution. The left sample is coated with PBDMA based latex, the middle with PSMA based latex and the right with polyester.

Filiform corrosion:

Fig. 3. Corrosion of steel substrates after 1 week of immersion in 5 wt.% NaCl (aq) solution, coated with a PBDMA based coating (a) and filiform corrosion underneath a PSMA based coating (b).
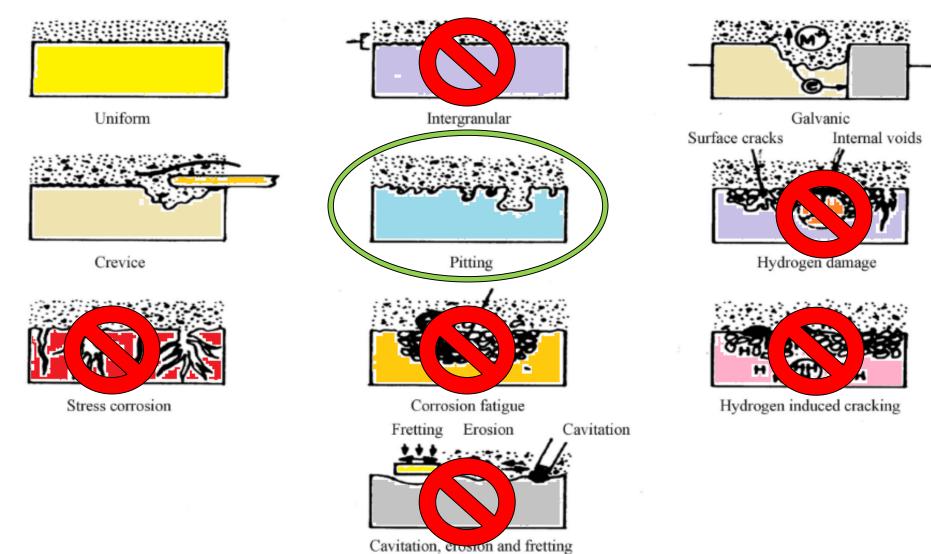
FORMS OF CORROSION
CHAPTER 2.4
PITTING CORROSION

Uniform

Intergranular

Galvanic

Crevice

Pitting

Surface cracks   Internal voids

Hydrogen damage

Stress corrosion

Corrosion fatigue

Hydrogen induced cracking

Fretting   Erosion   Cavitation

Cavitation, erosion and fretting

Pitting Corrosion

It is a form of localized corrosion of a metal surface where small areas corrode preferentially leading to formation of cavities or pits, and bulk of the surface remains un -attacked. Metals which form passive films , such as aluminum and steel are more susceptible to this form of corrosion. It causes failure by penetration with only a small percent weight-loss of the entire structure.

__Environment :__ **Generally the most conductive environment for pitting is the marine environment. Ions such as Cl^- , Br^- and I^- in appreciable concentrations tend to cause pitting of steel . Thiosulfate ions also induce pitting of steels. Aluminum also pits in a same environments of steel . Present of dust or dirt particles in water may lead to pitting corrosion in copper pipes transporting seawater. With soft water pitting in copper occurs in the hottest part of system , whereas with hard waters pitting occurs in the coldest part of the system.**

<u>Conditions:</u> the most important condition is that the metal must be in passive state for pitting to occur. Metals which become passive by film formation have a high resistance to uniform corrosion. The process of pitting destroys this protective film at certain sits resulting in the loss of passivity and initiation of pits on metal surface .

The following are the conditions for pitting to occur:-

1) Breaks in the films or other defects .(lack of film homogeneity)

2) The presence of halogen ions ,such as Cl^-, Br^-,and I^- and even $S_2O_3^-$

3) Stagnant conditions in service. (pumps serve in seawater with longer

   life than kept out of service).

<u>Mechanism</u>

   In order for pitting to take place, the formation of anode is a prerequisite. With the formation of an anode, a local corrosion cell is developed. The anode may be formed as a result of :-

   1) Lack of homogeneity at the metal corrosive interface , which caused by presence of impurities, grain boundaries, niches, rough surface ,…etc. The difference in the environments can cause formation of concentration cells on the metal surface.

2) Destruction of a passive film. Resulting to formation a small anode, results in several anode sits and the surrounding surface acts as cathode. Thus, an unfavorable area ratio results.
3) Deposit of debris or solids on the metal surface. This generally leads to the formation of anodic and Cathodic sites.
4) Formation of an active – passive cell with a large potential difference.
5) The formation of small anode on the passive steel surface, leads to the formation of the above cell.

Conditions:

(1) The passive metal surrounding the anode is not subject to pitting as it forms the cathode and it is the site for reduction of oxygen.
(2) The corrosion products which are formed at the anode cannot spread on to the cathode areas. Therefore, corrosion penetrates the metal rather than spread, and pitting is initiated.
(3) There is a certain potential characteristic of a passive metal, below which pitting cannot initiate. This is called pitting potential (E_p).

Pitting Processes

1) The formation of anodic sits by disruption of the protective passive film on the metal surface.

$$M \longrightarrow M^{n+} + ne$$

This is balanced by the Cathodic reaction of oxygen on the adjacent surface

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

2) Due to the continuing metal dissolution , an excess of positive ions (M$^+$) is accumulated in the anodic area. The process is self-stimulating and self-propagating. To maintain charge neutrality negative ions (anions), like chloride, migrate from electrolyte (for example seawater or a 5% NaCl solution).

$$M^+Cl^- + H_2O \longrightarrow MOH + H^+ + Cl^-$$

(OH$^-$) ions also migrate to neutralize the positive charges. This process is called hydrolysis.
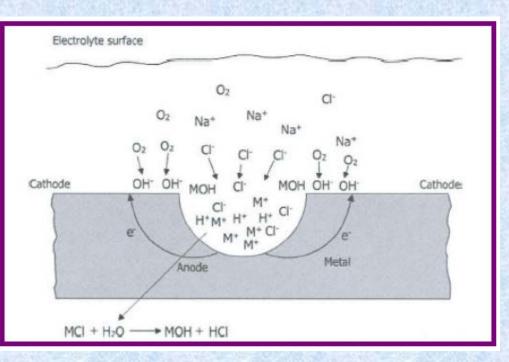
3) The presence of (H$^+$) ions and chloride content , prevents Repassivation. The above process generates free acid and the pH value at the bottom of pit is substantially lowered (1.5-1.0).

(4) The increase in the rate of dissolution at the anode increases the rate of migration of the chloride ions and the reaction becomes time dependent and continues, resulting in the formation of more and more M^+Cl^- , generation of more and more H^+Cl^- by hydrolysis.

(5) The process continues until the metal is perforated. The process is autocatalytic and it increases with time resulting in more and more dissolution.

(6) Finally, the metal is perforated and the reaction is terminated.

As shown above ,basically three processes are involved :

1 – Pitting Initiation .
2 – Pitting Propagation .
3 – Pitting Termination.

Prevention : **The methods suggested for combating crevice corrosion generally apply also for pitting or using inhibiters e.g Chromates(CrO_4)$^{-2}$, Phosphates(PO_4)$^{-3}$, Silicates(SiO_4)$^{-4}$.**

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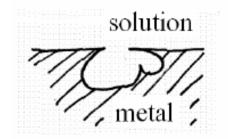
Pitting is an insidious and destructive form of corrosion:

➤ **Difficult to detect (pits may be small on surface, but extensive below surface from undercutting; 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 (nominally) identical conditions.**

➤ **"incubation" period may be months or years.**
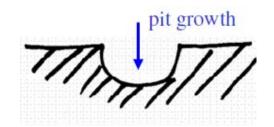
"Pitting factor" = $\frac{p}{d}$

d = average penetration from weight loss;

p = deepest penetration
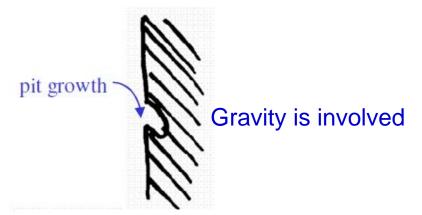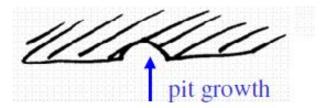
"Undercutting"
pit opening usually < 1 mm.

Pits may overlap to give the appearance of rough, general wastage.

Pits usually occur upward, facing horizontal surface.

Gravity is involved

and less frequently on vertical surfaces.

rarely on downward-facing surfaces.

Some alloys developed especially to resist pitting.

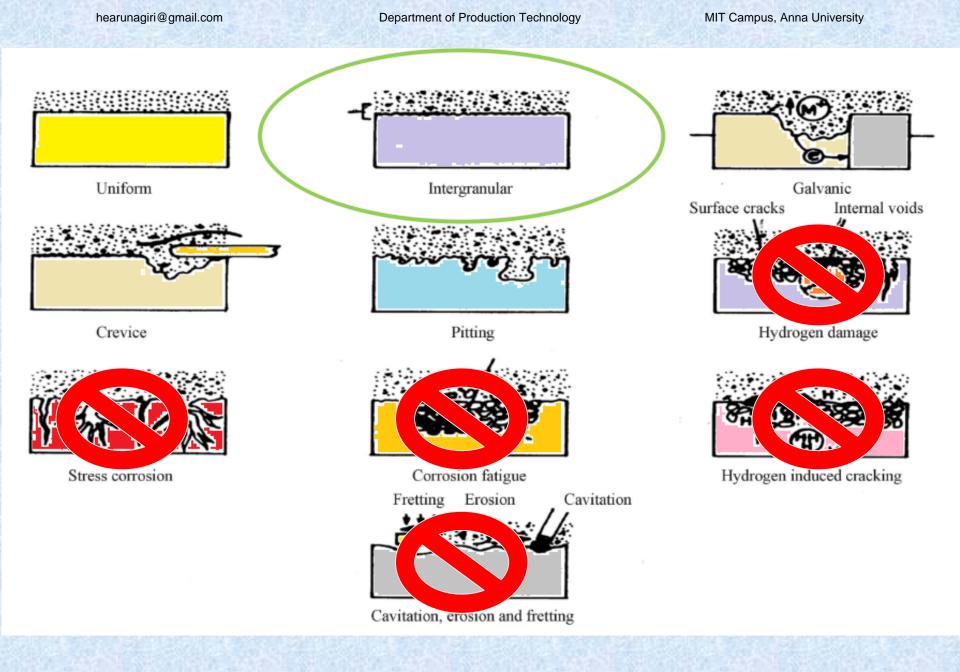**Effects of alloying on pitting resistance of stainless steel alloys.**

Element	Effect on pitting resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with Molybdenum
Titanium and niobium	Decreases resistance in $FeCl_3$, other medium no effect
Sulfur and selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases
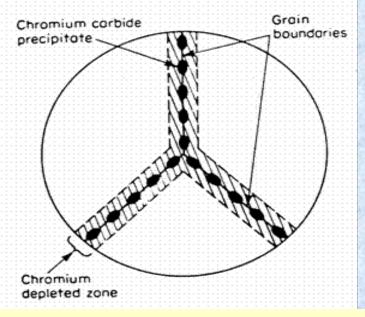
FORMS OF CORROSION CHAPTER 2.5 INTERGRANNULER CORROSION
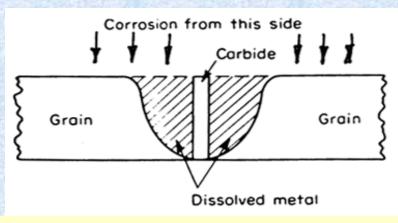
Uniform

Intergranular

Galvanic

Surface cracks   Internal voids

Crevice

Pitting

Hydrogen damage

Stress corrosion

Corrosion fatigue

Hydrogen induced cracking

Fretting   Erosion   Cavitation

Cavitation, erosion and fretting

Intergrannular Corrosion Or Sensitization

intergrannular corrosion , can be caused by impurities at the grain boundaries, enrichment of one of alloying elements, or depletion of one of these elements in grain boundary areas. Small amounts of iron in aluminum ,wherein the solubility of iron is low , have been shown to segregate in grain boundaries and cause intergrannular corrosion.

Depletion of chromium in grain boundary regions results in intergrannular corrosion of stainless steels. Cr is added to steels to make them "stainless". Th elements in grain boundary Cr-rich oxide film (based on Cr_2O_3) is thin, adherent and very protective. __BUT__ if heated into range 510-790°C, the steels "sensitize" and become prone to IGA.
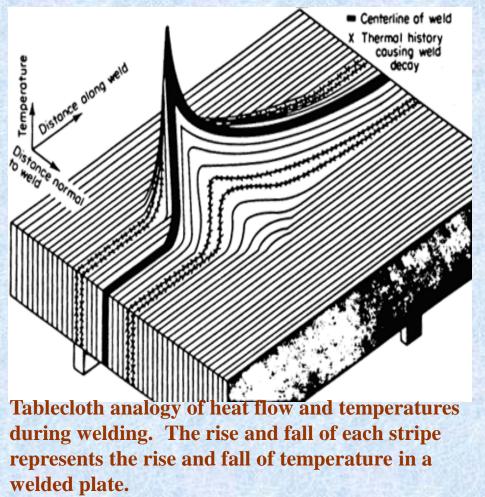
Chromium carbide precipitate

Grain boundaries

Chromium depleted zone

Diagrammatic representation of a grain boundary in sensitized type 304 stainless steel.

Corrosion from this side

Carbide

Grain

Grain

Dissolved metal

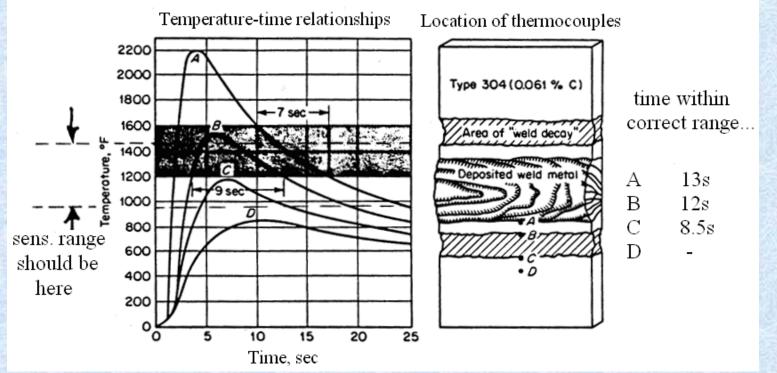**Cross section of area shown the sensitization.**

Sensitization involves the *precipitation* of Cr carbide ($Cr_{23}C_6$) at the grain boundaries; at the high temperature its solubility is virtually zero. The C diffuses readily, and the disorder in the boundaries provides nucleation sites. This depletes the boundaries of Cr.

Sensitization by welding, or "Weld Decay"

During welding, the weld "bead" and the metal on either side pass through the temperature range for sensitization. Temperature and time are crucial for carbide precipitation: sensitized areas are on either side of the bead.

Tablecloth analogy of heat flow and temperatures during welding. The rise and fall of each stripe represents the rise and fall of temperature in a welded plate.
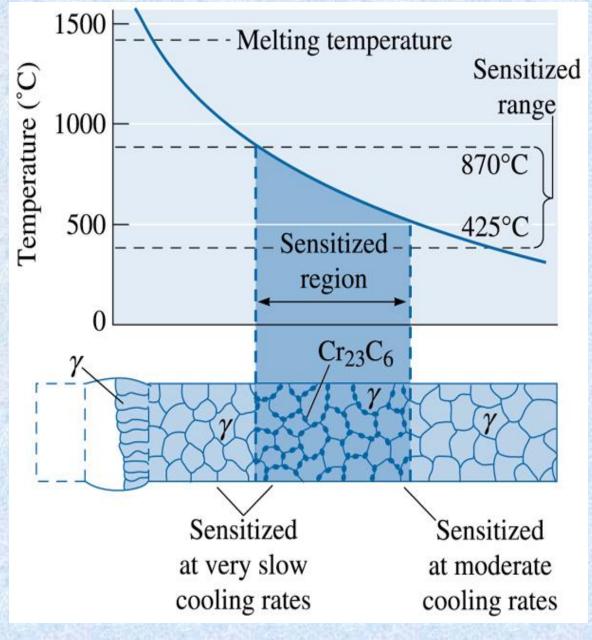
Temperatures during electric-arc welding of type 304 stainless steel.

Actual measurements made with thermocouples at points ABCD. Fontana says metal at and between points B and C within sensitizing range for some time.

Sensitized SS can be used in many environments which are not too aggressive or where selective corrosion not a problem (domestic, architecture)

The peak temperature surrounding a stainless-steel weld and the sensitized structure produced when the weld slowly cools .
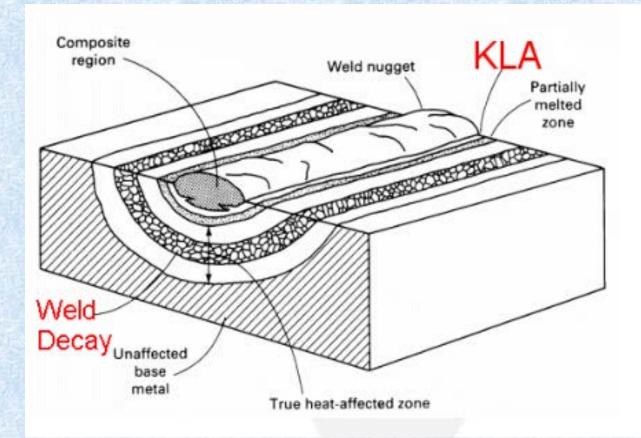
KNIFE LINE ATTACK

What is knife-line attack? Knife-Line Attack (KLA) is a form of intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.

The corrosive attack is restricted to extremely narrow line adjoining the fusion line. Attack appears razor-sharp (and hence the name of "knife-line" attack). It is possible to visually recognize knife-line attack if the lines are already formed along the weld.

KNIFE LINE ATTACK

SELECTIVE LEACHING

This process, also called "dealloying" or "selective leaching", involves the selective dissolution of one of the elements in a single phase alloy or one of the phases in a multiphase alloy

Numerous alloys are susceptible to selective corrosion in certain conditions. For example, denickelization can occur in Cu-Ni alloys, and dealuminization in aluminium bronzes, while the graphitization phenomenon in grey cast irons is due to slow dissolution of the ferrite matrix.

DEZINCIFICATION

The most well known example for selective leaching is the dezincification of brass (e.g. 70Cu - 30Zn). In this case, the brass takes on a red coppery tinge as the zinc is removed. It also becomes porous and very brittle, without modification to the overall dimensions of the part.

This problem can be overcome by choosing an alloy that is less prone, such as a copper-rich cupro-nickel. Brasses with lower zinc contents or containing elements such as tin (1%) and/or small quantities of arsenic, antimony, or phosphorus have much greater resistance.
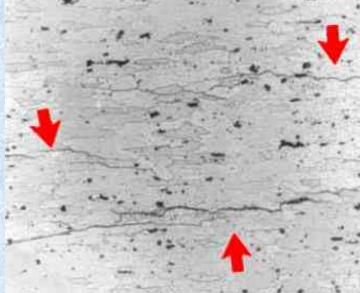
GRAPHITATION

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.

Minimizing IGA of SS

(1) Heat Treatment   "Quench-Annealing"
                    or ... "Solution-Annealing"
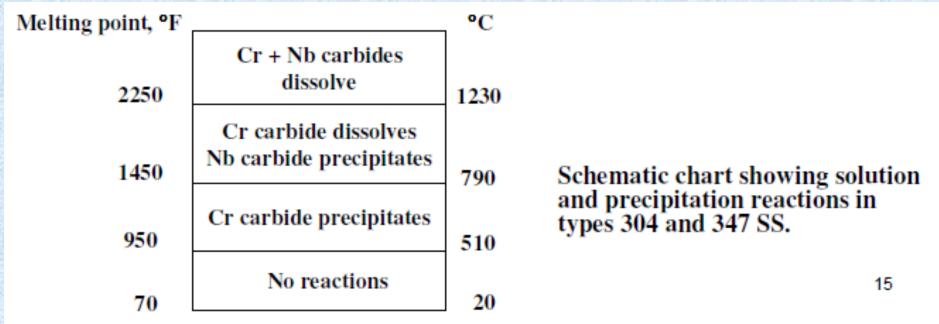   **or .... "Solution-Quenching"**

        Involves heating to above Cr carbide precipitation temperature to dissolve carbides, then water-quenching to cool through sensitization range rapidly.

        Most austenitic SS supplied in solution-quenching condition; if welded during fabrication, must be quench-annealed to avoid weld decay during subsequent exposure to corrosive environments. Solution-quenching of large components can be a problem.

(2) Alloy "Stabilization"
Elements that are strong carbide formers are added:
<blockquote>
Nb (or Nb+Ta)   type 347 SS
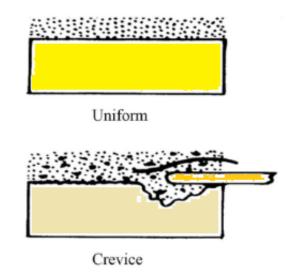**Ti   type 327 SS**
</blockquote>

Important to ensure that Nb (for example) carbide has precipitated, so that Cr Carbide cannot precipitate and reduce corrosion resistance at grain boundaries
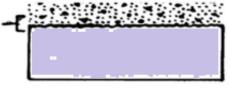
Melting point, °F		°C
2250	Cr + Nb carbides dissolve	1230
1450	Cr carbide dissolves Nb carbide precipitates	790
950	Cr carbide precipitates	510
70	No reactions	20

Schematic chart showing solution and precipitation reactions in types 304 and 347 SS.

15

REMEMBER - it is the Cr that provides the corrosion resistance, not the stabilizer.

FORMS OF CORROSION
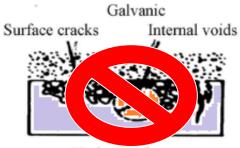# CHAPTER 2.6
EROSION CORROSION

Uniform

Intergranular

Galvanic

Crevice

Pitting

Surface cracks   Internal voids

Hydrogen damage

Stress corrosion

Corrosion fatigue

Hydrogen induced cracking

Fretting   Erosion   Cavitation

Cavitation, erosion and fretting

EROSION CORROSION :

Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface. Generally this movement is quite rapid, and mechanical wear effects or abrasion are involved.
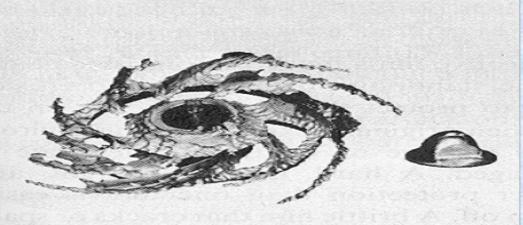
Removal of the metal may be:

➢ as corrosion product which "slips off" the surface because of the high fluid shear and bares the metal beneath.

➢ as metal ions, which are swept away by the fluid flow before they can deposit as corrosion product.
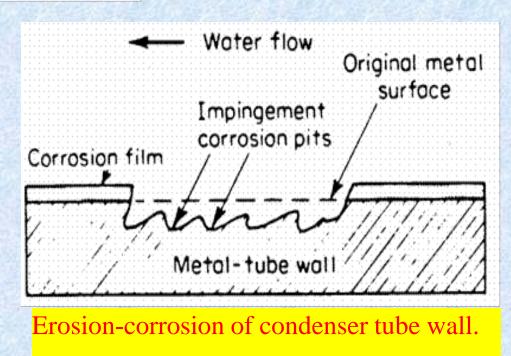
erosion is the straightforward wearing away by the mechanical abrasion caused by suspended particles. e.g., sand-blasting, erosion of turbine blades by droplets .

erosion-corrosion also involves a corrosive environment the metal undergoes a chemical reaction.

Erosion-corrosion produces a distinctive surface finish: grooves, waves, gullies, holes, etc., all oriented with respect to the fluid flow pattern . . . "scalloping"...

Erosion-corrosion of stainless alloy pump impeller.
Impeller lasted ~ 2 years in oxidizing conditions;
after switch to reducing conditions, it lasted ~ 3 weeks!

Erosion-corrosion of condenser tube wall.

Most metals/alloys are susceptible to erosion-corrosion. Metals that rely on protective surface film for corrosion protection are particularly vulnerable, e.g.: Al , Pb , SS , CS. Attack occurs when film cannot form because of erosion caused by suspended particles (for example), or when rate of film formation is less than rate of dissolution and transfer to bulk fluid.
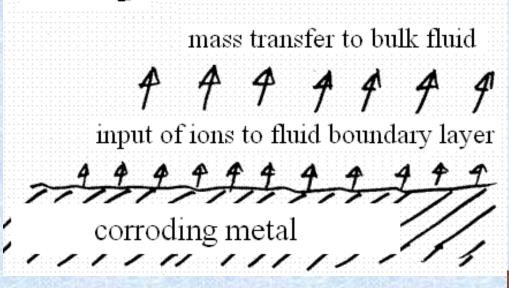
Erosion-Corrosion found in:

◇ aqueous solutions;
◇ gases;
◇ organic liquids;
◇ liquid metal.

If fluid contains suspended solids, erosion-corrosion may be aggravated.
Vulnerable equipment is that subjected to high-velocity fluid, to rapid change in direction of fluid, to excessive turbulence . . viz. equipment in which the contacting fluid has a very thin boundary layer

- high mass transfer rates.

fluid flow
→

mass transfer to bulk fluid
↑ ↑ ↑ ↑ ↑ ↑ ↑

input of ions to fluid boundary layer
↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑

corroding metal

Vulnerable equipment includes:

- pipes (bends, elbows, tees);
- valves;
- pumps;
- blowers;
- propellers, impellers;
- stirrers;
- stirred vessels;
- HX tubing (heaters, condensers);

- flow-measuring orifices, venturies;
- turbine blades;
- nozzles;
- baffles;
- metal-working equipment (scrapers, cutters, grinders, mills);
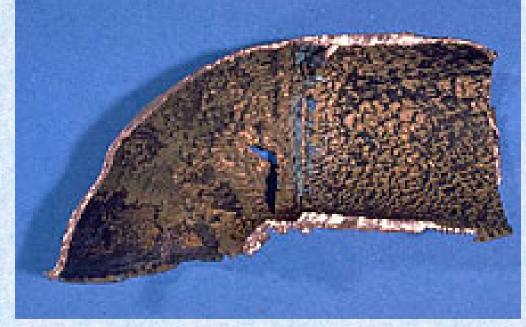- spray impingement components;
- etc.

5

Surface film effects

Protective corrosion-product films important for resistance to erosion-corrosion.

Hard, dense, adherent, continuous films give good resistance, provided that they are not brittle and easily removed under stress. Lead sulphate film protects lead against <u>DILUTE</u> H_2SO_4 under stagnant conditions, but not under rapidly moving conditions. pH affects films in erosion-corrosion of low-alloy steel. Scale generally granular Fe_3O_4 (non-protective). But at pH 6 & pH 10, scale $Fe(OH)_2$/$Fe(OH)_3$ . . . hinders mass transport of oxygen and ionic species.

Good resistance of Ti to erosion-corrosion in:
- ◇ **seawater**
- ◊ **Cl^- solutions;**
- ◊ **HNO_3;**
- ◊ **and many other environments.**

Resistance depends on formation and stability of TiO_2 films.
- Cu alloys.

"Horseshoe" type erosion-corrosion damage in a copper pipeline.

Prevention of Erosion-Corrosion

➤design (avoid impingement geometries, **high velocity,** etc.);

➤chemistry (e.g., in steam supply systems . . . for CS or low-alloy steel <u>add</u> O_2,

➤ maintain pH > 9.2, use morpholine rather than NH_3);

➤ materials (use Cr-containing steels);

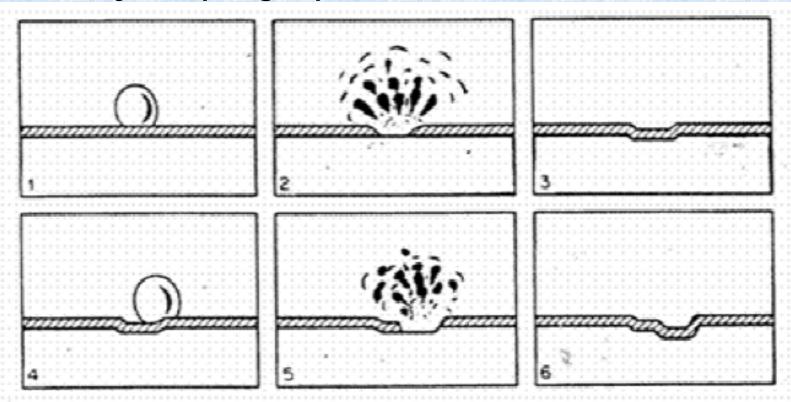➤ use hard, corrosion-resistant coatings.

CAVITATION DAMAGE

Cavitation-corrosion is particular form of erosion caused by the "implosion" of gas bubbles on a metal surface. It is often associated with sudden variations in pressure related to the hydrodynamic parameters of the fluid (e.g. hydraulic turbine blades, propellors, stirrer blades, etc.).

A regular hydraulic regime in the fluid is extremely important. A good surface condition decreases the number of potential sites for the formation of vapour bubbles. An increase in fluid pressure is often sufficient to maintain a single phase fluid, thus avoiding the formation of vapour bubbles. Plastic or rubber coatings have often proved to be effective, although the problems of adherence between the coating and the metal are frequently an obstacle.

CAVITATION DAMAGE

Similar effect to E-C: mechanical removal of oxide film caused by collapsing vapor bubbles.
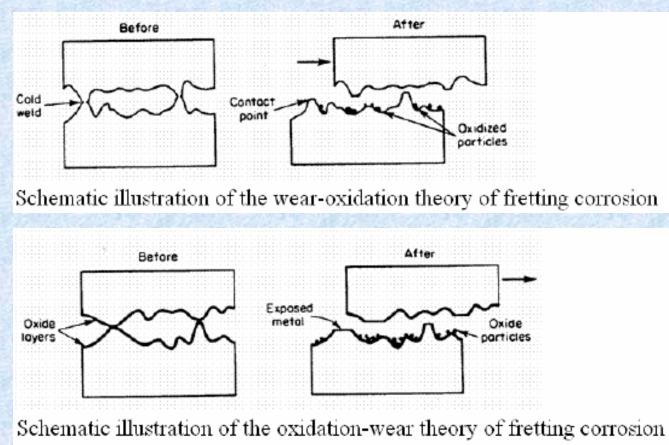

High-speed pressure oscillations (pumps, etc.) can create shock waves > 60,000 psi. Surface attack often resembles closely-spaced pitting.

FRETTING CORROSION

Similar to E-C but surface mechanical action provided by wear of another surface generally intermittent, low-amplitude rubbing.

Two theories . . . with same overall result . . .

Schematic illustration of the wear-oxidation theory of fretting corrosion

Schematic illustration of the oxidation-wear theory of fretting corrosion

Friction-wear at an axle-cylinder contact point.

Prevention of Fretting Corrosion

➤**lubricate**;
➤ **avoid** **relative motion (add packing, etc.)**;
➤ **increase** **relative motion to reduce attack severity**;
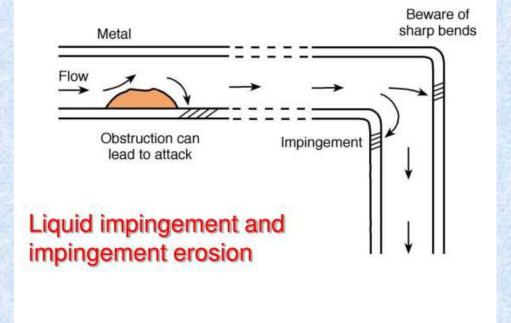➤ **select materials (e.g., choose harder component).**

Effect OF TURBULENCE

Many erosion corrosion failures occur because of turbulence or turbulent flow conditions exist. Turbulence results in greater agitation of the liquid at the metal surface than in case of laminar. Turbulence results in more intimate contact between the environment and the metal.
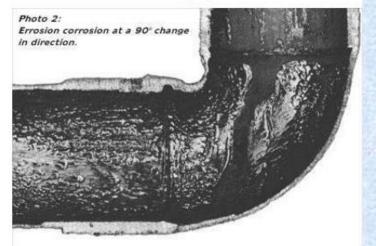
Effect OF IMPINGEMENT

Impingement corrosion is a form of erosion-corrosion generally associated with the local impingement of a high velocity, flowing fluid against a solid surface.

Impingement corrosion usually produces a pattern of localized attack with directional features.

Liquid impingement and impingement erosion

Erosion corrosion at pipeline elbow

Photo 2:
Errosion corrosion at a 90° change in direction.

FORMS OF CORROSION CHAPTER 2.7 STRESS CORROSION CRACKING (SCC)

9) Stress Corrosion Cracking (SCC):-
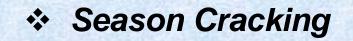
In this type of corrosion loss due to corrosion effects is negligible, but the metal gets cracked after some time .It is a localized action caused by the presence of corrosion medium and the tensile stress conditions. The greater the stress on the material, the quicker it will crack. (in fabricated components, there are usually RESIDUAL STRESSES from cold working, welding, surface treatment such as grinding or shot peening, etc., as well as APPLIED STRESSES from the service, such as hydrostatic, vapor pressure of contents, bending loads, etc.). Have enough localized tensile stress . For annealed metals, the external required stress for (SCC) may be as 10% yield stress .It has been found that SCC for metals happens in those media in which the same metals under normal conditions do not corrode. Stress corrosion cracking is fairly common for those metals and alloys which have high resistance against general corrosion . The most common examples of SCC are :-

➢season cracking" of brass.
➢ caustic embrittlements" of Carbon Steel.

❖ *Season Cracking*

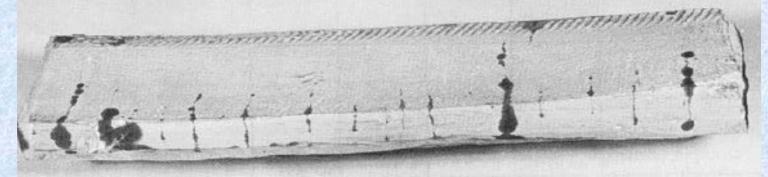**Occurs where brass case is crimped onto bullet, i.e., in area of high residual stress.Common in warm, wet environments (e.g., tropics).Ammonia (from decomposition of organic matter, etc.) must be present.**

Season Cracking of German ammunition

❖ *Caustic Embrittlements*

Early steam boilers (19th and early 20th century) of riveted carbon steel. Both stationary and locomotive engines often exploded.

Carbon steel plate from a caustic storage tank failed by caustic embrittlement.

Examination showed:

- **cracks or brittle failures around rivet holes.**
- **areas susceptible were cold worked by riveting (i.e., had high residual stresses).**
- **whitish deposits in cracked regions were mostly caustic (i.e., sodium hydroxide from chemical treatment of boiler water).**
- **small leaks at rivets would concentrate NaOH and even dry out to solid. SCC revealed by dye penetrate.**

Factors important in SCC:

☼ **environmental composition.**
☼ **stress.**
☼ **metal composition and microstructure.**
☼ **temperature.**

} necessary

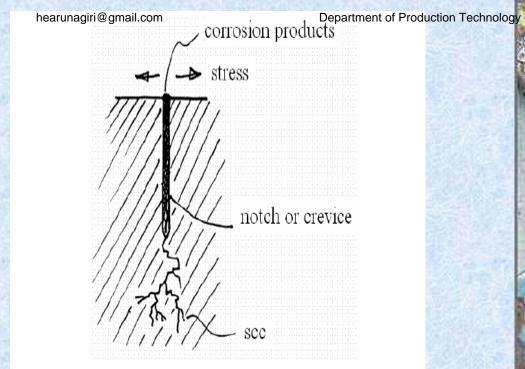**e.g.,**   **brasses crack in NH_3, not in Cl^-;**
SSs crack in Cl^-, not in NH_3;
SSs crack in caustic, not in H_2SO_4, HNO_3, CH_3COOH, . . . etc.

Environments that may cause stress corrosion of metals and alloys

Material	Environment	Material	Environment
Aluminum alloys	$NaCl-H_2O_2$ solutions	Ordinary steels	NaOH solutions
	NaCl solutions		$NaOH-Na_2SiO_2$ solutions
	Seawater		Ca, NH_3, and $NaNO_3$ solutions
	Air, Water vapor		
Copper alloys	NH_3 (g & aq)		Mixed acids ($H_2SO_4-HNO_3$)
	Amines		HCN solutions
	Water, Water vapor		Acidic H_2S solutions
Gold alloys	$FeCl_3$ solutions		Seawater
	Acetic-acid-salt solutions		Molten Na-Pb alloys
Inconel	Caustic soda solutions	Stainless steels	Acid chloride solutions
Lead	Lead acetate solutions		such as $MgCl_2$ and $BaCl_2$
Magnesium alloys	$NaCl-K_2CrO_4$ solutions		$NaCl-H_2O_2$ solutions
	Rural and coastal atmospheres		Seawater
			H_2S
	Distilled water		$NaOH-H_2S$ solutions
Monel	Fused caustic soda		Condensing steam from chloride waters
	Hydrofluoric acid		
	Hydrofluosilicic acid	Titanium alloys	Red fuming HNO_3, N_2O_4,
Nickel	Fused caustic soda		seawater, methanol-HCl

corrosion products

stress

notch or crevice

scc

N.B. small-radius notch tip and even smaller-radius crack tip are STRESS RAISERS

A "wedging action" by corrosion products of ~ 10 ksi (10,000 psi) can induce → ~ 300 ksi (300,000 psi) at the crack tip.

"Intergranular" SCC ("IGSCC")
Metallurgical Factors in IGSCC

In austenitic SS and Ni alloys, *sensitization* is of major importance in determining susceptibility to IGSCC . . . depletion of grain boundaries in Cr because of carbide precipitation makes them vulnerable to attack. e.g., IGSCC of recirculation piping in BWRs (type 304 SS) induced by ~ 200 ppb dissolved oxygen in the otherwise pure H_2O coolant resulted in a major replacement problem. Plants using L-grade experienced very much less SCC.

- Al alloys (e.g., with Mg and Zn) are also susceptible to IGSCC because of precipitation within grain boundaries . . . Mg-rich precipitates can denude the grain boundaries of Mg, make them susceptible to attack in aqueous media.

- <u>N.B</u>. In grain-boundary-precipitate mechanisms for inducing IGSCC, very local galvanic effects between precipitates and matrix are important:

-    some precipitates are ANODIC;

-    some precipitates are CATHODIC.

- Grain boundary segregation of alloy constituents or impurities (without precipitation of separate phases) can also induce IGSCC.

- e.g., Mg enrichment of grain boundaries in Al alloys is a factor in IGSCC promotes local dissolution and hydrogen entry (maybe to form hydride, MgH);

- also . . . grain boundary enrichment of impurities and/or C in Fe-base alloys,   Ni-base alloys and austenitic stainless steels can contribute to IGSCC;

-   segregation of P, Si, S, N, B reported; only clear link with IGSCC reported for P in austenitic SS in oxidizing aqueous solutions, for P in ferritic alloys in nitrate and caustic solutions.

Transgranular SCC

Lattice structure in metal/alloy matrix important: dislocation emergence, movement along slip planes under stress, and similar factors that can disrupt passivating films, will promote dissolution of metal at highly localized and strained areas.

Prevention of SCC

1. ***Lowering the stress*** below the threshold value if one exists. This may be done by annealing in the case of residual stresses, thickening the section, or reducing the load. Plain carbon steels may be stress-relief annealed at 590 to 650°C, and the austenitic stainless steels are frequently stress-relieved at temperatures ranging from 820 to 930°C.

2. ***Eliminating the critical environmental species*** by, for example, de-gasification, demineralization, or distillation.

3. ***Changing the alloy*** is one possible recourse if neither the environment nor stress can be changed. For example, it is common practice to use Inconel (raising the nickel content) when type 304 stainless steel is not satisfactory.   Although carbon steel is less resistant to general corrosion, it is more resistant to stress-corrosion cracking than are the stainless steels. Thus, under conditions which tend to produce stress-corrosion cracking, carbon steels are often found to be more satisfactory than the stainless steels. For example, heat exchangers used in contact with seawater or brackish waters are often constructed of ordinary mild steel.

4. ***Applying Cathodic protection*** to the structure with an external power supply or consumable anodes. Cathodic protection should only be used to protect installations where it is positively known that stress-corrosion cracking is the cause of fracture, since hydrogen embrittlement effects are accelerated by impressed Cathodic currents.

Prevention of SCC

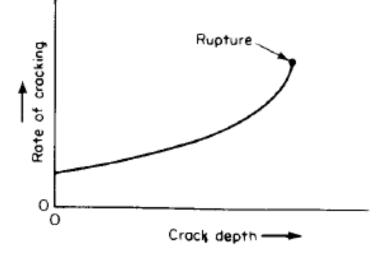**5. *Adding inhibitors* to the system if feasible. Phosphates and other inorganic and organic corrosion inhibitors have been used successfully to reduce stress-corrosion cracking effects in mildly corrosive media. As in all inhibitor applications, sufficient inhibitor should be added to prevent the possibility of localized corrosion and pitting.**

6. *Coatings* are sometimes used, and they depend on keeping the environment away from the metal - for example, coating vessels and pipes that are covered with insulation. In general, however, this procedure may be risky for bare metal.

7. *Shot-peening* (also known as shot-blasting) produces residual compressive stresses in the surface of the metal. Very substantial improvement in resistance to stress corrosion found as a result of peening with glass beads. Type 410 stainless was exposed to 3% NaCl at room temperature; type 304 to 42% $MgCl_2$ at 150°C; and aluminum alloy 7075-T6 to a water solution of $K_2Cr_2O_7$-CrO_3-NaCl at room temperature.
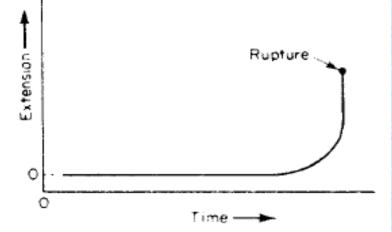
Prevention of SCC

Rate of stress corrosion crack propagation as a function of crack depth during tensile loading

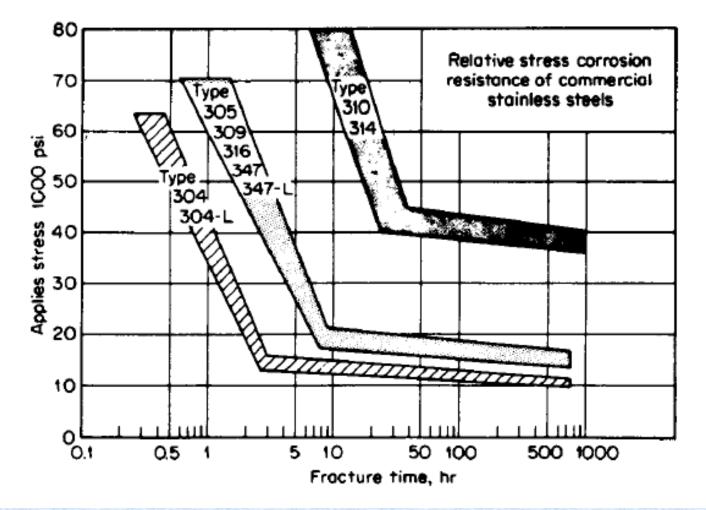**Specimen extension as a function of time during constant load stress corrosion cracking test**

Prevention of SCC

Specimen extension as a function of time during constant load stress corrosion cracking test

CORROSION TYPES
CHAPTER 2.8
HYDROGEN DAMAGE

Hydrogen Damage

It is a general term which refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen.
Hydrogen damage may be classified into four distinct types:
➢ hydrogen blistering.
➢ hydrogen embrittlements.
➢ decarburization.
➢ hydrogen attack.
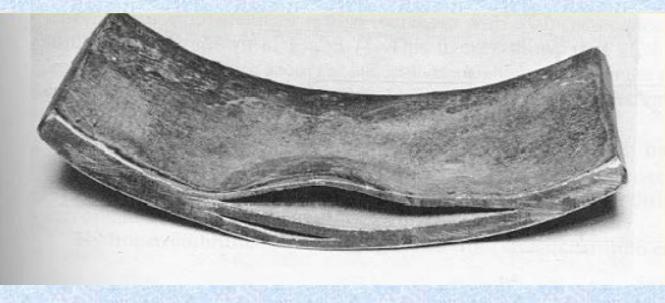
➢ Blistering

Hydrogen enters the lattice of a metal, diffuses to voids, creates high internal stresses → blisters . . .
Blistering may occur during exposure to:
• hydrocarbons;
• electroplating solutions;
• chemical process streams;
• pickling solutions;
• H-containing contaminants during welding;
• general corrosive environments.
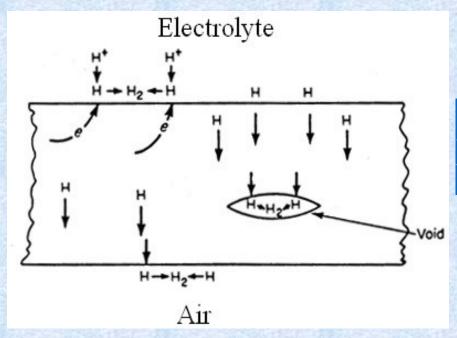
Cross section of a carbon steel plate removed from a petroleum process stream showing a large hydrogen blister. Exposure time: 2 years.

The mechanism of hydrogen uptake by metals must involve ATOMIC HYDROGEN - molecular hydrogen cannot diffuse through metal lattices. BUT . . . remember that molecular hydrogen may absorb and dissociate on metal surfaces.
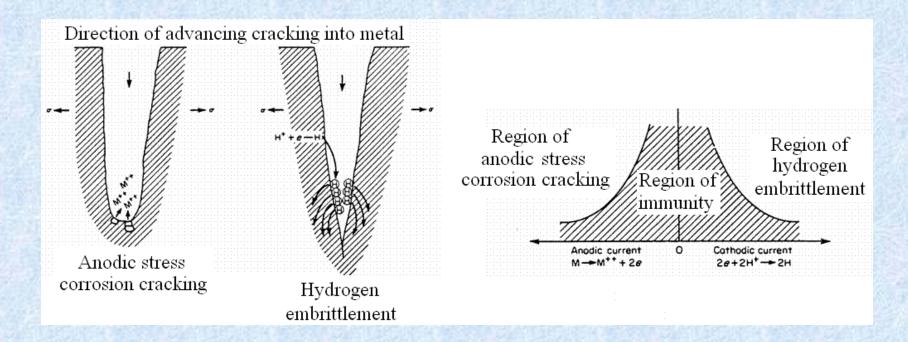
Schematic illustration showing the mechanism of hydrogen blistering.

Prevention of Blistering

► use steels with few or no voids; (Killed steel instead of rimmed)

► use coatings; (Metallic, inorganic and organic coatings , cladding , rubber and plastic coating and brick linings).

► use inhibitors

► remove poisons; (impurites that can promote hydrogen evolution . .S^{2-} (particularly bad), As compounds , CN^-, etc.

► use different materials (Ni-base alloys have low diffusion rates for hydrogen).

✡Hydrogen Embrittlements

Similar to blistering . . . hydrogen enters metal lattice . . . BUT . . .interaction with metal lattice different. High- strength (and more brittle) steels are susceptible. H- embrittlements different from SCC in nature of cracks . stress-corrosion cracks usually propagate anodically;

Direction of advancing cracking into metal

Anodic stress corrosion cracking

Hydrogen embrittlement

$H^+ + e \rightarrow H$

Region of anodic stress corrosion cracking

Region of immunity

Region of hydrogen embrittlement

Anodic current $M \rightarrow M^{++} + 2e$ 0   Cathodic current $2e + 2H^+ \rightarrow 2H$

Hydrogen embrittlement of austenite

Fe22Mn0.6C

Fe15Mn2Al0.7C

B. C. De Cooman, O. Kwon and K.-G. Chin,

Materials Science & Technology, 2012

Prevention of Embrittlement

☞   reduce corrosion rate (inhibitors, coatings, etc.).
☞   change electroplating process to minimize H effects
      (voltage, current density,bath composition, etc.).
☞   bake material to remove H; (200- 300 ^{o}F).
☞   minimize residual stresses;(annealing).
☞   use less susceptible material;(Alloying with Ni or Mb).
☞   maintain clean conditions during welding.(Dry condition).

✡Decarburization and Hydrogen Attack

High temperature process - C or carbide in steels can react with gaseous hydrogen

$$C \ + \ 2H_2 \ \rightarrow \ CH_4$$

Note that the reaction can occur with atomic H in the metal lattice . . .

$$C \ + \ 4H \ \rightarrow \ CH_4$$

May crack the steel from high internal pressure.
May cause loss of strength as C disappears.

CORROSION TESTING OF ENGINEERING MATERIALS AND DEVICES

CHAPTER 3

Corrosion Test

Methods used for corrosion testing.
1) **Wt. increase or decrease during corrosion.(measure the change in weight with time).**
2) **Electro-chemical method.**
   - ➢ **Measure current flow with time.**
   - ➢ **Measure change in potential with time.**

3)Electrical resistance measurements with time.

Purpose of corrosion tests:
   - ❖ **To evaluate the metals and alloys in given environments for the manufacture of equipment or for industrial plants.**
   - ❖ **To evaluate corrosion resistance of new alloys in various environments in order to specify their application .**
   - ❖ **For corrosion control , e.g. effect of various inhibitors**
   - ❖ **To study the corrosion mechanism.**

Tests are carried out at various levels for specific purposes.

i. **Laboratory tests . (100 – 150 hrs).**

ii. **Pilot plant tests**

iii. **Tests of Industrial equipments in operation.**   } **6 months**

iv. **Filed Tests , (3 – 20 yrs).**

Before start of test , these steps are necessary.

1 Materials and Specimens

�ख **Composition .**
�ख **Heat-treatment or % cold work.**
�ख **Fabrication method.**

2 Surface preparation

Polishing with No.120 abrasive cloth or paper

3 Measuring and Weighing

Surface area measurement

Weighing to nearest 0.1 mg

4 Exposure techniques

Corrosive should have easy access to specimen

Specimen should be electrically insulated (avoid galvanic effects)

Complete or partial or vapor phase immersion

For plant , specimen should be accessible

5 Duration

Planned Interval test

Weight change measurements :-

These are cyclic tests in a given environment and the gain or loss in wt. is measured at regular intervals .
e.g. every 50 hrs, of testing.

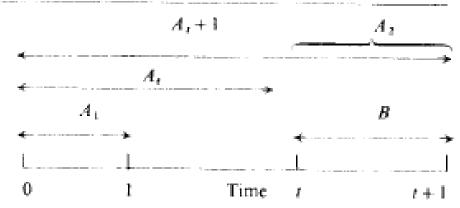$$2000/mpy = no. \ of \ hrs.$$

e.g. 2000/5 mpy = 400hrs.

Aeration (presence of oxygen)
In the corrosion system in most- cases corrosion rate increase with the presence of O_2 except that of Al – where it forms a protective oxide layer .

Planned Interval Test

Identical specimens placed in same corrosive fluid: imposed conditions of test constant for entire time $(t+1)$: A_1, A_t, A_t+1, B, represent corrosion damage experienced by each test specimen: A_2 is calculated by subtracting A_t from A_t+1.

Occurrences during corrosion test			
Liquid corrosiveness	Criteria	Metal corrodibility	Criteria
Unchanged	$A_1 = B$	Unchanged	$A_2 = B$
Decreased	$B < A_1$	Decreased	$A_2 < B$
Increased	$A_1 < B$	Increased	$B < A_2$

Combinations of situations		
Liquid corrosiveness	Metal corrodibility	Criteria
1. Unchanged	Unchanged	$A_1 = A_2 = B$
2. Unchanged	Decreased	$A_2 < A_1 = B$
3. Unchanged	Increased	$A_1 = B < A_2$
4. Decreased	Unchanged	$A_2 = B < A_1$
5. Decreased	Decreased	$A_2 < B < A_1$
6. Decreased	Increased	$A_1 > B < A_2$
7. Increased	Unchanged	$A_1 < A_2 = B$
8. Increased	Decreased	$A_1 < B > A_2$
9. Increased	Increased	$A_1 < B < A_2$

Planned Interval Test

	Interval, days	Weight loss, mg	Penetration, mils	Apparent corrosion rate, mpy
A_1	0–1	1080	1.69	620
A_t	0–3	1430	2.24	270
$A_t + 1$	0–4	1460	2.29	210
B	3–4	70	0.11	40
A_2	calc. 3–4	30	0.05	18

$$A_2 < B < A_1$$
$$0.05 < 0.11 < 1.69$$

*Conditions: Duplicate strips of low-carbon steel, $\frac{3}{4} \times 3$ in., immersed in 200 ml of 10% AlCl-90% SbCl misture through which dried HCl gas was slowly bubbled at atm pressure, 90°C. Liquid markedly decreased in corrosiveness during test, and formation of partially protective scale on the steel was indicated.

Standard Expression for Corrosion Rate

Corrosion Penetration Rate

mm / year ,most common method , K= 87

Mils per Year (MPY) 1 mil = 1/ 1000 in . K=534
Best – expresses penetration Without decimals or large numbers.

Corrosion Penetration Rate,   CPR = $\dfrac{KW}{\rho At}$

where W is the weight loss after exposure time t
ρ and A represent the density exposed specimen area

Standard Expression for Corrosion Rate

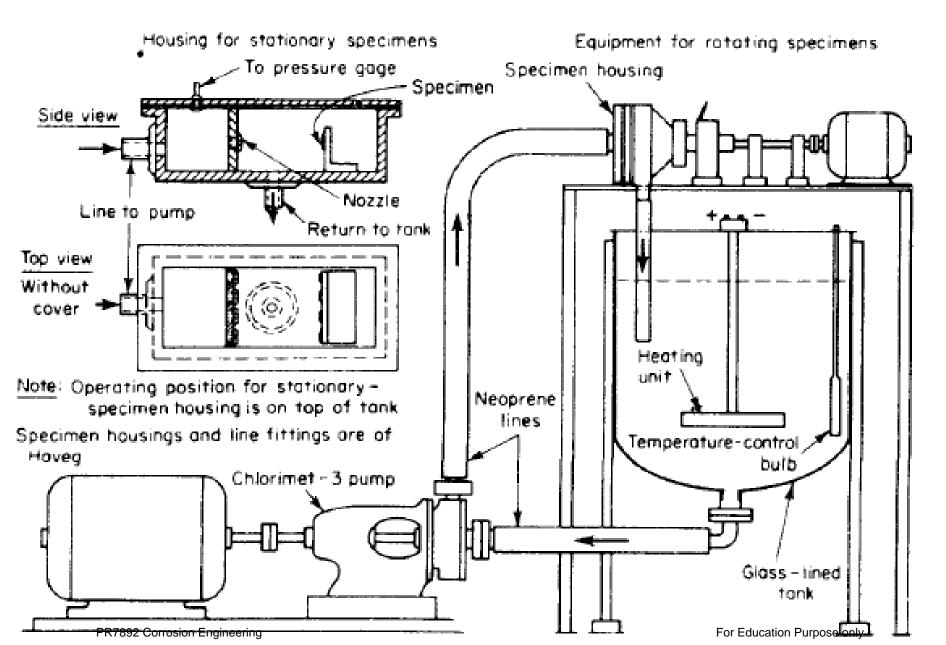## Table 4-5 Comparison of mils penetration per year (mpy) with equivalent metric-rate expressions

Relative corrosion resistance*	mpy	Approximate metric equivalent†			
		$\frac{mm}{yr}$	$\frac{\mu m}{yr}$	$\frac{nm}{hr}$	$\frac{pm}{sec}$
Outstanding	< 1	< 0.02	< 25	< 2	< 1
Excellent	1–5	0.02–0.1	25–100	2–10	1–5
Good	5–20	0.1–0.5	100–500	10–50	5–20
Fair	20–50	0.5–1	500–1000	50–150	20–50
Poor	50–200	1–5	1000–5000	150–500	50–200
Unacceptable	200 +	5 +	5000 +	500 +	200 +

*Based on typical ferrous- and nickel-based alloys. For more expensive alloys, rates greater than 5 to 20 mpy are usually excessive. Rates above 200 mpy are sometimes acceptable for cheap materials with thick cross sections (e.g., cast-iron pump body).
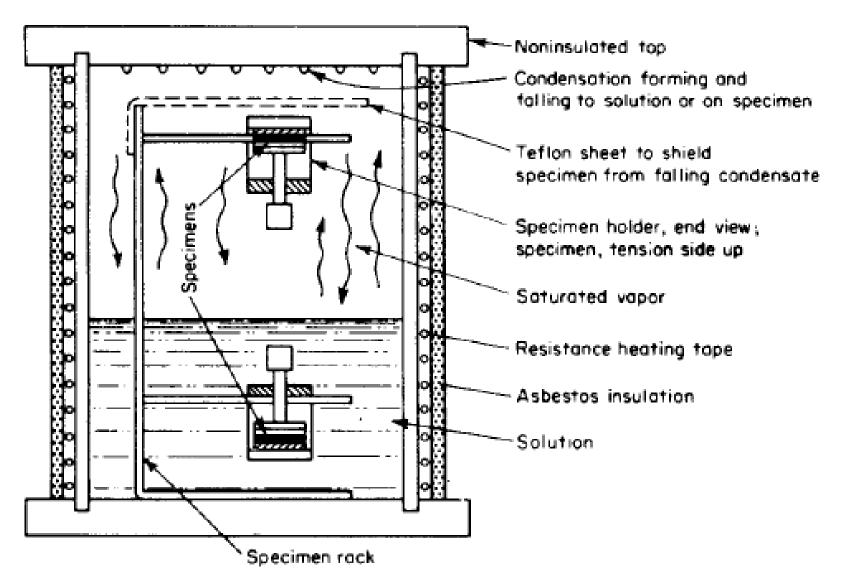
†Approximate values to simplify ranges.

$$1 \text{ mpy} = 0.0254 \frac{mm}{yr} = 25.4 \frac{\mu m}{yr} = 2.90 \frac{nm}{hr} = 0.805 \frac{pm}{sec}$$
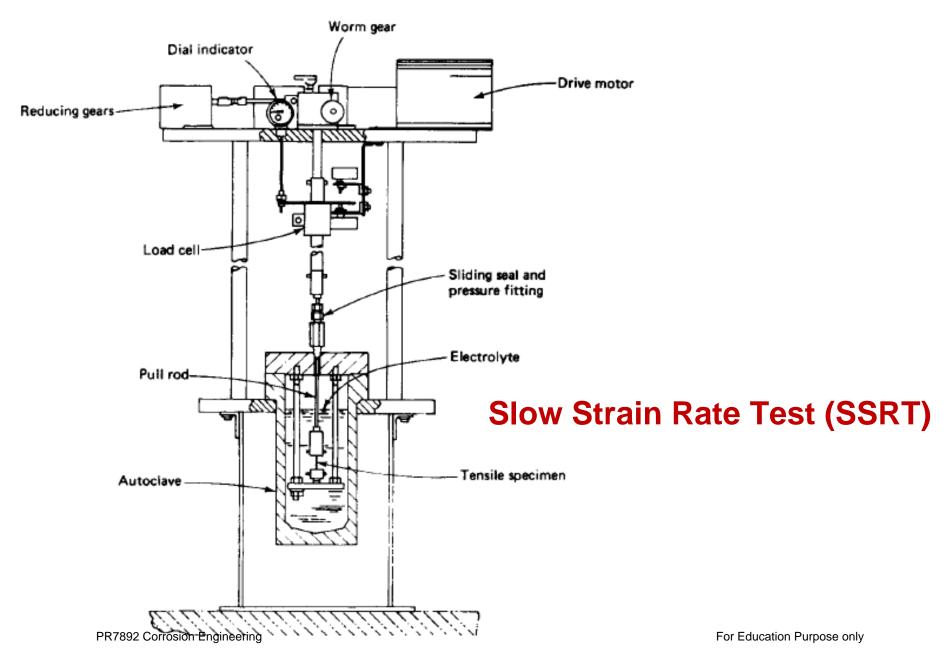
Test for Erosion Corrosion

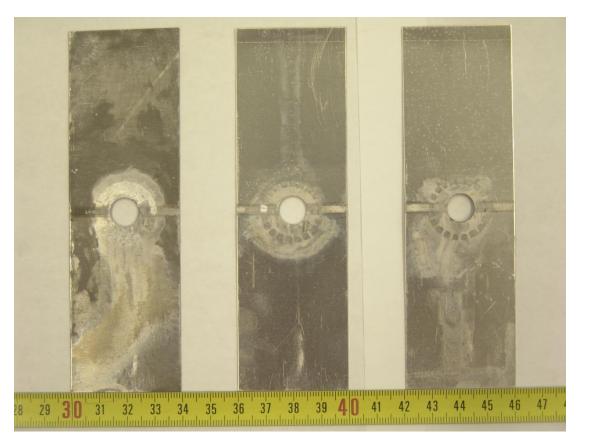# Test for Stress Corrosion Cracking

Test for Stress Corrosion Cracking

Slow Strain Rate Test (SSRT)
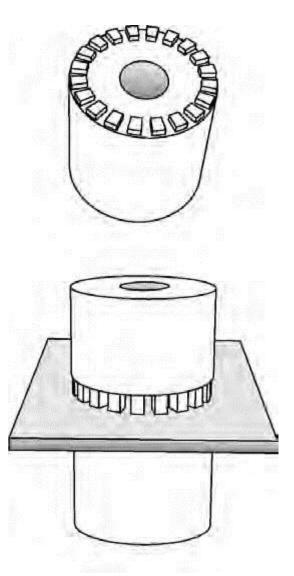
National Association of Corrosion Engineers (NACE)

TM-01-69	Laboratory Corrosion Testing of Metals for the Process Industries
TM-01-70	Visual Standard for Surfaces of New Steel Airblast Cleaned with Sand Abrasive
TM-02-70	Method of conducting Controlled Velocity Laboratory Corrosion Tests
TM-01-71	Autoclave Corrosion Testing of Metals in High Temperature Water
TM-01-72	Antirust Properties of Petroleum Products Pipeline Cargoes
TM-01-73	Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters
TM-01-74	Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service
TM-02-74	Dynamic Corrosion Testing of Metals in High Temperature Water
TM-03-74	Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution
TM-01-75	Visual Standard for Surfaces of New Steel Centrifugally Blast Cleaned with Steel Grit and Shot
TM-02-75	Performance Testing of Sucker Rods by the Mixed String, Alternate Rod Method
TM-03-75	Abrasion Resistance Testing of Thin Film Baked Coatings and Linings Using the Falling Sand Method
TM-01-77	Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures
TM-01-84	Accelerated Test Procedures for Screening Atmopsheric Surface Coating Systems for Offshore Platforms and Equipment

Crevice and Pitting Corrosion test

Sample is immersed in a FeCl3-solution at temperatures above room temperature

ASTM

Designation: A 262 – 98

Standard Practices for
Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels[1]

This standard is issued under the fixed designation A 262; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These practices cover the following five tests:

1.1.1 *Practice A*—Oxalic Acid Etch Test for Classification of Etch Structures of Austenitic Stainless Steels (Sections 3 to 7, inclusive),

1.1.2 *Practice B*—Ferric Sulfate-Sulfuric Acid Test for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels (Sections 8 to 14, inclusive),

1.1.3 *Practice C*—Nitric Acid Test for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels (Sections 15 to 21, inclusive),

1.1.4 *Practice E*—Copper-Copper Sulfate-Sulfuric Acid Test for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels (Sections 22 to 31, inclusive), and

1.1.5 *Practice F*—Copper-Copper Sulfate-50 % Sulfuric Acid Test for Detecting Susceptibility to Intergranular Attack in Molybdenum-Bearing Cast Austenitic Stainless Steels (Sections 32 to 38, inclusive).

1.2 The following factors govern the application of these practices:

1.2.1 Susceptibility to intergranular attack associated with the precipitation of chromium carbides is readily detected in all six tests.

1.2.2 Sigma phase in wrought chromium-nickel-molybdenum steels, which may or may not be visible in the microstructure, can result in high corrosion rates only in nitric acid.

1.2.3 Sigma phase in titanium or columbium stabilized alloys and cast molybdenum bearing stainless alloys, which may or may not be visible in the microstructure, can result in high corrosion rates in both the nitric acid and ferric sulfate-sulfuric acid solutions.

1.3 The oxalic acid etch test is a rapid method of identifying, by simple etching, those specimens of certain stainless steel grades which are essentially free of susceptibility to intergranular attack associated with chromium carbide precipitates. These specimens will have low corrosion rates in certain corrosion tests and therefore can be eliminated (screened) from testing as "acceptable."

1.4 The ferric sulfate-sulfuric acid test, the copper-copper sulfate-50 % sulfuric acid test, and the nitric acid test are based on weight loss determinations and, thus, provide a quantitative measure of the relative performance of specimens evaluated. In contrast, the copper-copper sulfate-16 % sulfuric acid test is based on visual examination of bend specimens and, therefore, classifies the specimens only as acceptable or non-acceptable.

1.5 In most cases either the 24-h copper-copper sulfate-16 % sulfuric acid test or the 120-h ferric sulfate-sulfuric acid test, combined with the oxalic acid etch test, will provide the required information in the shortest time. All stainless grades listed in the accompanying table may be evaluated in these combinations of screening and corrosion tests, except those specimens of molybdenum-bearing grades (for example 316, 316L, 317, and 317L), which represent steel intended for use in nitric acid environments.

1.6 The 240-h nitric acid test must be applied to stabilized and molybdenum-bearing grades intended for service in nitric acid and to all stainless steel grades which might be subject to end grain corrosion in nitric acid service.

1.7 Only those stainless steel grades are listed in Table 1 for which data on the application of the oxalic acid etch test and on their performance in various quantitative evaluation tests are available.

1.8 Extensive test results on various types of stainless steels evaluated by these practices have been published in Ref (**1**).[2]

1.9 The values stated in SI units are to be regarded as standard. The inch-pound equivalents are in parentheses and may be approximate.

1.10 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (Specific precautionary statements are given in 5.6, 11.1.1, 11.1.9, and 35.1.)

2. Referenced Documents

2.1 *ASTM Standards:*

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[1] These practices are under the jurisdiction of ASTM Committee A-1 on Steel, Stainless Steel and Related Alloysand are the direct responsibility of Subcommittee A01.14on Methods of Corrosion Testing.

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[2] The boldface numbers in parentheses refer to the list of references found at the end of these practices.

1

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TABLE 1 Application of Evaluation Tests for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels

NOTE 1—For each corrosion test, the types of susceptibility to intergranular attack detected are given along with the grades of stainless steels in which they may be found. These lists may contain grades of steels in addition to those given in the rectangles. In such cases, the acid corrosion test is applicable, but not the oxalic acid etch test.

NOTE 2—The oxalic acid etch test may be applied to the grades of stainless steels listed in the rectangles when used in connection with the test indicated by the arrow.

OXALIC ACID ETCH TEST
↓

↓	↓	↓	↓
AISI[A]: 304, 304L ACI[B]: CF-3, CF-8	AISI: 304, 304L, 316, 316L, 317, 317L ACI: CF-3, CF-8, CF-3M, CF-8M	AISI: 201, 202, 301, 304, 304L, 304H, 316, 316L, 316H, 317, 317L, 321, 347	ACI: CF-3M, CF-8M,

Nitric Acid Test[C] (240 h in boiling solution)	Ferric Sulfate-Sulfuric Acid Test (120 h in boiling solution)	Copper-Copper Sulfate-Sulfuric Acid Test (24 h in boiling solution)	Copper-Copper Sulfate-50 % Sulfuric Acid Testing Boiling Solution
Chromium carbide in: 304, 304L, CF-3, CF-8 Chromium carbide and sigma phase in:[D] 316, 316L, 317, 317L, 321, 347, CF-3M, CF-8M End-grain in: all grades	Chromium carbide in: 304, 304L, 316, 316L, 317, 317L, CF-3, CF-8 Chromium carbide and sigma phase in: 321, CF-3M, CF-8M[E]	Chromium carbide in: 201, 202, 301, 304, 304L, 316, 316L, 317, 317L, 321, 347	Chromium carbide in: CF-3M, CF-8M

[A] AISI: American Iron and Steel Institute designations for austenitic stainless steels.
[B] ACI: Alloy Casting Institute designations.
[C] The nitric acid test may be also applied to AISI 309, 310, 348, and AISI 410, 430, 446, and ACI CN-7M.
[D] Must be tested in nitric acid test when destined for service in nitric acid.
[E] To date, no data have been published on the effect of sigma phase on corrosion of AISI 347 in this test.

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PRACTICE A—OXALIC ACID ETCH TEST FOR CLASSIFICATION OF ETCH STRUCTURES OF AUSTENITIC STAINLESS STEELS (2)

3. Scope

3.1 The oxalic acid etch test is used for acceptance of material but not for rejection of material. This may be used in connection with other evaluation tests to provide a rapid method for identifying those specimens which are certain to be free of susceptibility to rapid intergranular attack in these other tests. Such specimens have low corrosion rates in the various hot acid tests, requiring from 4 to 240 h of exposure. These specimens are identified by means of their etch structures which are classified according to the following criteria:

3.2 The oxalic acid etch test may be used to screen specimens intended for testing in Practice B—Ferric Sulfate-Sulfuric Acid Test, Practice C—Nitric Acid Test, Practice

E—Copper-Copper Sulfate-16 % Sulfuric Acid Test, and Practice F—Copper-Copper Sulfate-50 % Sulfuric Acid Test.

3.2.1 Each practice contains a table showing which classifications of etch structures on a given stainless steel grade are equivalent to acceptable, or possibly nonacceptable performance in that particular test. Specimens having acceptable etch structures need not be subjected to the hot acid test. Specimens having nonacceptable etch structures must be tested in the specified hot acid solution.

3.3 The grades of stainless steels and the hot acid tests for which the oxalic acid etch test is applicable are listed in Table 2.

3.4 Extra low carbon grades, and stabilized grades, such as 304L, 316L, 317L, 321, and 347, are tested after sensitizing heat treatments at 650 to 675°C (1200 to 1250°F), which is the range of maximum carbide precipitation. These sensitizing treatments must be applied before the specimens are submitted to the oxalic acid etch test. The most commonly used sensitizing treatment is 1 h at 675°C (1250°F).

4. Apparatus

4.1 *Source of Direct Current*—Battery, generator, or rectifier capable of supplying about 15 V and 20 A.

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[3] *Annual Book of ASTM Standards*, Vol 01.03.

TABLE 2 Applicability of Etch Test

	AISI Grade No.	ACI Grade No.
Practice B—Ferric Sulfate-Sulfuric Acid Test	304, 304L, 316, 316L, 317, 317L	CF-3, CF-8, CF-3M,CF-8M
Practice C—Nitric Acid Test	304, 304L	CF-8, CF-3
Practice E—Copper-Copper Sulfate-16 % Sulfuric Acid Test	201, 202, 301, 304, 304L, 304H, 316, 316L, 316H, 317, 317L, 321, 347	...
Practice F—Copper-Copper Sulfate-50 % Sulfuric Acid Test	. . .	CF-8M, CF-3M

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4.2 *Ammeter*—Range 0 to 30 A (Note 1).

4.3 *Variable Resistance* (Note 1).

4.4 *Cathode*—A cylindrical piece of stainless steel or, preferably, a 1-qt (0.946-L) stainless steel beaker.

4.5 *Large Electric Clamp*—To hold specimen to be etched.

4.6 *Metallurgical Microscope*—For examination of etched microstructures at 250 to 500 diameters.

4.7 *Electrodes of the Etching Cell*—The specimen to be etched is made the anode, and a stainless steel beaker or a piece of stainless steel as large as the specimen to be etched is made the cathode.

4.8 *Electrolyte*——Oxalic acid, ($H_2C_2O_4 \cdot 2H_2O$), reagent grade, 10 weight % solution.

Note 1—The variable resistance and the ammeter are placed in the circuit to measure and control the current on the specimen to be etched.

5. Preparation of Test Specimens

5.1 *Cutting*—Sawing is preferred to shearing, especially on the extra-low carbon grades. Shearing cold works adjacent metal and affects the response to subsequent sensitization. Microscopical examination of an etch made on a specimen containing sheared edges, should be made on metal unaffected by shearing. A convenient specimen size is 25 by 25 mm (1 by 1 in.).

5.2 The intent is to test a specimen representing as nearly as possible the surface of the material as it will be used in service. Therefore the preferred sample is a cross section including the surface to be exposed in service. Only such surface finishing should be performed as is required to remove foreign material and obtain a standard, uniform finish as described in 5.3. For very heavy sections, specimens should be machined to represent the appropriate surface while maintaining reasonable specimen size for convenient testing. Ordinarily, removal of more material than necessary will have little influence on the test results. However, in the special case of surface carburization (sometimes encountered, for instance, in tubing or castings when lubricants or binders containing carbonaceous materials are employed) it may be possible by heavy grinding or machining to completely remove the carburized surface. Such treatment of test specimens is not permissible, except in tests undertaken to demonstrate such effects.

5.3 *Polishing*—On all types of materials, cross sectional surfaces should be polished for etching and microscopical examination. Specimens containing welds should include base plate, weld heat-affected zone, and weld metal. Scale should be removed from the area to be etched, by grinding to an 80 or 120-grit finish on a grinding belt or wheel without excessive heating, and then polishing on successively finer emery papers, No. 1, ½, ⅙, ⅖, and ⅜, or finer. This polishing operation can be carried out in a relatively short time since all large scratches need not be removed. Whenever practical, a polished area of 1 cm^2 or more is desirable. If any cross sectional dimension is less than 1 cm, a minimum length of 1 cm should be polished. When the available length is less than 1 cm, a full cross section should be used.

5.4 *Etching Solution*—The solution used for etching is prepared by adding 100 g of reagent grade oxalic acid crystals ($H_2C_2O_4 \cdot 2H_2O$) to 900 mL of distilled water and stirring until

all crystals are dissolved.

5.5 *Etching Conditions*—The polished specimen should be etched at 1 A/cm^2 for 1.5 min. To obtain the correct current density:

5.5.1 The total immersed area of the specimen to be etched should be measured in square centimetres, and

5.5.2 The variable resistance should be adjusted until the ammeter reading in amperes is equal to the total immersed area of the specimen in square centimetres.

5.6 *Etching Precautions*:

5.6.1 **Caution**—Etching should be carried out under a ventilated hood. Gas, which is rapidly evolved at the electrodes with some entrainment of oxalic acid, is poisonous and irritating to mucous membranes.

5.6.2 A yellow-green film is gradually formed on the cathode. This increases the resistance of the etching cell. When this occurs, the film should be removed by rinsing the inside of the stainless steel beaker (or the steel used as the cathode) with an acid such as 30 % HNO_3.

5.6.3 The temperature of the etching solution gradually increases during etching. The temperature should be kept below 50°C by alternating two beakers. One may be cooled in tap water while the other is used for etching. The rate of heating depends on the total current (ammeter reading) passing through the cell. Therefore, the area etched should be kept as small as possible while at the same time meeting the requirements of desirable minimum area to be etched.

5.6.4 Immersion of the clamp holding the specimen in the etching solution should be avoided.

5.7 *Rinsing*—Following etching, the specimen should be thoroughly rinsed in hot water and in acetone or alcohol to avoid crystallization of oxalic acid on the etched surface during drying.

5.8 On some specimens containing molybdenum (AISI 316, 316L, 317, 317L) which are free of chromium carbide sensitization, it may be difficult to reveal the presence of step structures by electrolytic etching with oxalic acid. In such cases, an electrolyte of a 10 % solution of ammonium persulfate, ($NH_4)_2S_2O_8$, may be used in place of oxalic acid. An etch of 5 or 10 min at 1 A/cm^2 in a solution at room temperature readily develops step structures on such specimens.

6. Classification of Etch Structures

6.1 The etched surface is examined on a metallurgical microscope at 250× to 500× for wrought steels and at about 250× for cast steels.

6.2 The etched cross-sectional areas should be thoroughly examined by complete traverse from inside to outside diameters of rods and tubes, from face to face on plates, and across all zones such as weld metal, weld-affected zones, and base plates on specimens containing welds.

6.3 The etch structures are classified into the following types (Note 2):

6.3.1 *Step Structure* (Fig. 1)—Steps only between grains, no ditches at grain boundaries.

6.3.2 *Dual Structure* (Fig. 2)—Some ditches at grain boundaries in addition to steps, but no single grain completely surrounded by ditches.
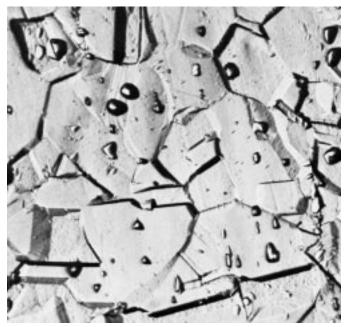
3

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FIG. 1 Step Structure (500×) (Steps between grains, no ditches at grain boundaries)

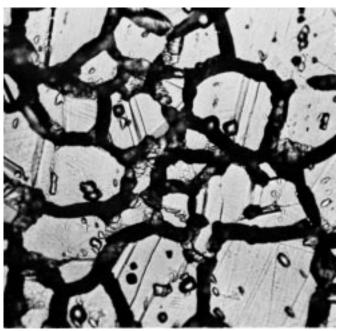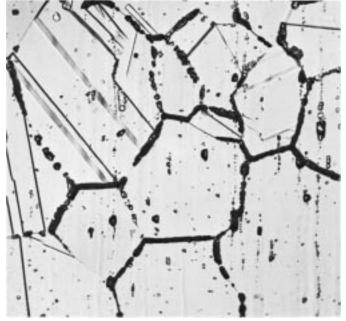**FIG. 3 Ditch Structure (500×) (One or more grains completely surrounded by ditches)**

FIG. 2 Dual Structure (250×) (Some ditches at grain boundaries in addition to steps, but no one grain completely surrounded)

FIG. 4 Isolated Ferrite Pools (250×) (Observed in castings and welds. Steps between austenite matrix and ferrite pools)

6.3.3 *Ditch Structure* (Fig. 3)—One or more grains completely surrounded by ditches.

6.3.4 *Isolated Ferrite* (Fig. 4)—Observed in castings and welds. Steps between austenite matrix and ferrite pools.

6.3.5 *Interdendritic Ditches* (Fig. 5)—Observed in castings and welds. Deep interconnected ditches.

6.3.6 *End-Grain Pitting I* (Fig. 6)—Structure contains a few deep end-grain pits along with some shallow etch pits at 500×. (Of importance only when nitric acid test is used.)

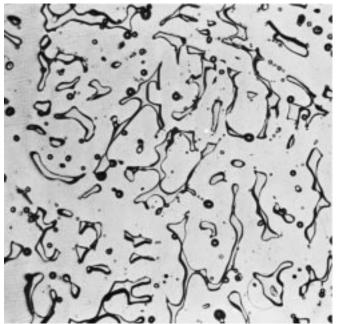6.3.7 *End-Grain Pitting II* (Fig. 7)—Structure contains numerous, deep end-grain pits at 500×. (Of importance only

when nitric acid test is used.)

NOTE 2—All photomicrographs were made with specimens that were etched under standard conditions: 10 % oxalic acid, room temperature, 1.5 min at 1 A/cm².

6.4 The evaluation of etch structures containing steps only and of those showing grains completely surrounded by ditches in every field can be carried out relatively rapidly. In cases that appear to be dual structures, more extensive examination is required to determine if there are any grains completely encircled. If an encircled grain is found, the steel should be
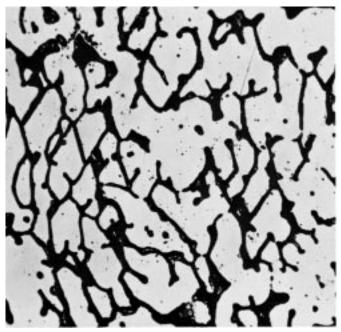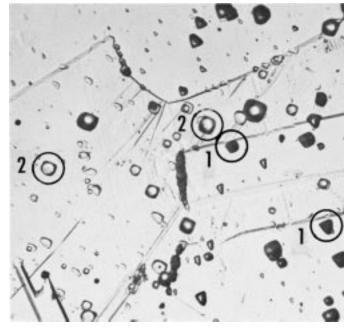
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FIG. 5 Interdendritic Ditches (250×) (Observed in castings and welds. Deep interconnected ditches)
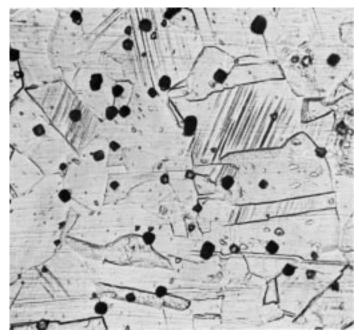

To differentiate between the types of pits, use a magnification of 500× and focus in the plane of etched surface. The pits which now appear completely black are end grain pits.

FIG. 6 End Grain Pitting I (500×) (A few deep end grain pits (see 1 in figure) and shallow etch pits (3))

This or a greater concentration of end grain pits at 500× (using standard etching conditions) indicates that the specimen must be tested when screening is for nitric acid test.

FIG. 7 End Grain Pitting II (500×)

may contain a random pattern of pits. If these pits are sharp and so deep that they appear black (Fig. 7) it is possible that the specimen may be susceptible to end grain attack in nitric acid only. Therefore, even though the grain boundaries all have step structures, specimens having as much or more end grain pitting than that shown in Fig. 7 cannot be safely assumed to have low nitric acid rates and should be subjected to the nitric acid test whenever it is specified. Such sharp, deep pits should not be confused with the shallow pits shown in Fig. 1 and Fig. 6.

7. Use of Etch Structure Classifications

7.1 The use of these classifications depends on the hot acid corrosion test for which stainless steel specimens are being screened by etching in oxalic acid and is described in each of the practices. Important characteristics of each of these tests are described below.

7.2 *Practice B—Ferric Sulfate-Sulfuric Acid Test* is a 120-h test in boiling 50 % solution that detects susceptibility to intergranular attack associated primarily with chromium carbide precipitate. It does not detect susceptibility associated with sigma phase in wrought chromium-nickel-molybdenum stainless steels (316, 316L, 317, 317L) which is known to lead to rapid intergranular attack only in certain nitric acid environments. It does not detect susceptibility to end grain attack which is also found only in certain nitric acid environments. The ferric sulfate-sulfuric acid test does reveal susceptibility associated with a sigma-like phase constituent in stabilized stainless steels, AISI 321, 347, and in cast chromium-nickel-molybdenum stainless steels (CF-8M, CF-3M, C6-8M, and CG-3M).

7.3 *Practice C—Nitric Acid Test* is a 240-h test in boiling, 65 % nitric acid which detects susceptibility to rapid intergranular attack associated with chromium carbide precipitate

evaluated as a ditch structure. Areas near surfaces should be examined for evidence of surface carburization.

6.4.1 On stainless steel castings (also on weld metal) the steps between grains formed by electrolytic oxalic acid etching tend to be less prominent than those on wrought materials, or are entirely absent. However, any susceptibility to intergranular attack is readily detected by pronounced ditches.

6.5 Some wrought specimens, especially from bar stock,

5

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and with sigma-like phase precipitate. The latter may be formed in molybdenum-bearing and in stabilized grades of austenitic stainless steels and may or may not be visible in the microstructure. This test also reveals susceptibility to end grain attack in all grades of stainless steels.

7.4 *Practice E—Copper-Copper Sulfate-16 % Sulfuric Acid Test* is a 24-h test in a boiling solution containing 16 % sulfuric acid and 6 % copper sulfate with the test specimen embedded in metallic copper shot or grindings, which detects susceptibility to intergranular attack associated with the precipitation of chromium-rich carbides. It does not detect susceptibility to intergranular attack associated with sigma phase, or end-grain corrosion, both of which have been observed to date only in certain nitric acid environments.

7.5 *Practice F—Copper-Copper Sulfate-50 % Sulfuric Acid Test* is a 120-h test in a boiling solution which contains 50 % sulfuric acid, copper sulfate, and metallic copper and which detects susceptibility to intergranular attack associated with the precipitation of chromium-rich carbides. It does not detect susceptibility to attack associated with sigma phase.

PRACTICE B—FERRIC SULFATE-SULFURIC ACID TEST FOR DETECTING SUSCEPTIBILITY TO INTERGRANULAR ATTACK IN AUSTENITIC STAINLESS STEELS (3)

8. Scope

8.1 This practice describes the procedure for conducting the boiling, 120-h ferric sulfate-50 % sulfuric acid test (Note 3) which measures the susceptibility of stainless steels to intergranular attack. The presence or absence of intergranular attack in this test is not necessarily a measure of the performance of the material in other corrosive environments. The test does not provide a basis for predicting resistance to forms of corrosion other than intergranular, such as general corrosion, pitting, or stress-corrosion cracking.

NOTE 3—See Practice A for information on the most appropriate of the several test methods available for the evaluation of specific grades of stainless steel.

8.1.1 The ferric sulfate-sulfuric acid test detects susceptibility to intergranular attack associated with the precipitation of chromium carbides in unstabilized austenitic stainless steels. It does not detect susceptibility to intergranular attack associated with sigma phase in wrought austenitic stainless steels containing molybdenum, such as Types 316, 316L, 317, and 317L. The ferric sulfate-sulfuric acid test will detect intergranular corrosion associated with sigma phase in the cast stainless steels CF-3M and CF-8M.

NOTE 4—To detect susceptibility to intergranular attack associated with sigma phase in austenitic stainless steels containing molybdenum, the nitric acid test, Practice C, should be used.

8.2 In stabilized stainless steel, Type 321 (and perhaps 347) and cast austenitic stainless steels containing molybdenum such as Types CF-8M, CF-3M, CG-8M, and CG-3M, the ferric sulfate-sulfuric acid test detects susceptibility associated with precipitated chromium carbides and with a sigma phase which may be invisible in the microstructure.

8.3 The ferric sulfate-sulfuric acid test may be used to evaluate the heat treatment accorded as-received material. It

may also be used to check the effectiveness of stabilizing columbium or titanium additions and of reductions in carbon content in preventing susceptibility to rapid intergranular attack. It may be applied to wrought products (including tubes), castings, and weld metal.

8.4 Specimens of extra low carbon and stabilized grades are tested after sensitizing heat treatments at 650 to 675°C (1200 to 1250°F), which is the range of maximum carbide precipitation. The length of time of heating used for this sensitizing treatment determines the maximum permissible corrosion rate for such grades in the ferric sulfate-sulfuric acid test. The most commonly used sensitizing treatment is 1 h at 675°C (1250°F).

9. Rapid Screening Test

9.1 Before testing in the ferric sulfate sulfuric acid test, specimens of certain grades of stainless steels (see Table 3) may be given a rapid screening test in accordance with procedures given in Practice A, Oxalic Acid Etch Test for Classification of Etch Structures of Austenitic Stainless Steels. Preparation, etching, and the classification of etch structures are described therein. The use of etch structure evaluations in connection with the ferric sulfate-sulfuric acid test is specified in Table 3.

9.1.1 Corrosion test specimens having acceptable etch structures in the oxalic acid etch test will be essentially free of intergranular attack in the ferric sulfate-sulfuric acid test. Such specimens are acceptable without testing in the ferric sulfate-sulfuric acid test. All specimens having nonacceptable etch structures must be tested in the ferric sulfate-sulfuric acid test.

10. Apparatus

10.1 The apparatus (Note 6) is illustrated in Fig. 8.

10.1.1 An Allihn or Soxhlet condenser with a minimum of four bulbs and with a 45/50 ground glass joint. Overall length: about 330 mm (13 in), condensing section, 9½in. (241 mm).

10.1.2 A 1-L Erlenmeyer flask with a 45/50 ground glass joint. The ground glass opening is somewhat over 38 mm (1½ in.) wide.

10.1.3 The glass cradle (Note 5) can be supplied by a glass-blowing shop. To pass through the ground glass joint on

TABLE 3 Use of Etch Structure Classifications from the Oxalic Acid Etch Test with Ferric Sulfate-Sulfuric Acid Test

NOTE 1—Grades AISI 321 and 347 cannot be screened because these grades may contain a type of sigma phase which is not visible in the etch structure but which may cause rapid corrosion in the ferric sulfate-sulfuric acid test.

Grade	Acceptable Etch Structures	Nonacceptable Etch Structures [A]
AISI 304	Step, Dual, End Grain, I & II	Ditch
AISI 304L	Step, Dual, End Grain, I & II	Ditch
AISI316	Step, Dual, End Grain, I & II	Ditch
AISI316L	Step, Dual, End Grain, I & II	Ditch
AISI 317	Step, Dual, End Grain, I & II	Ditch
AISI 317L	Step, Dual, End Grain, I & II	Ditch
AISI 321	None	...
ACI CF-3	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches
ACI CF-8	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches
ACI CF-3M	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches
ACI CF-8M	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches

[A] Specimens having these structures must be tested in the ferric sulfate-sulfuric acid test.
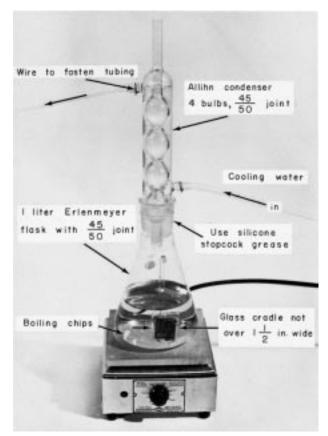
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FIG. 8 Apparatus for Ferric Sulfate-Sulfuric Acid Test

the Erlenmeyer flask, the width of the cradle should not exceed 38 mm (1½ in.), and the front-to-back distance must be such that the cradle will fit the 34-mm (1⅓-in.) diameter opening. It should have three or four holes to increase circulation of the testing solution around the specimen.

NOTE 5—Other equivalent means of specimen support, such as glass hooks or stirrups, may also be used.

10.1.4 Boiling chips must be used to prevent bumping.

10.1.5 A silicone grease[4] is recommended for the ground glass joint.

10.1.6 During testing, there is some deposition of iron oxides on the upper part of the Erlenmeyer flask. This can be readily removed, after test completion, by boiling a solution of 10 % hydrochloric acid in the flask.

10.1.7 A device such as an electrically heated hot plate which provides heat for continuous boiling of the solution.

10.1.8 An analytical balance capable of weighing to the nearest 0.001 g.

NOTE 6—No substitutions for this equipment may be used. The cold-finger type of condenser with standard Erlenmeyer flasks may not be used.

11. Ferric Sulfate-Sulfuric Acid Test Solution

11.1 Prepare 600 mL of 50 % (49.4 to 50.9 %) solution as follows:

11.1.1 **Caution**—Protect the eyes and use rubber gloves for handling acid. Place the test flask under a hood.

11.1.2 First, measure 400.0 mL of distilled water in a 500-mL graduate and pour into the Erlenmeyer flask.

11.1.3 Then measure 236.0 mL of reagent grade sulfuric acid of a concentration which must be in the range from 95.0 to 98.0 % by weight in a 250-mL graduate. Add the acid slowly to the water in the Erlenmeyer flask to avoid boiling by the heat evolved.

NOTE 7—Loss of vapor results in concentration of the acid.

11.1.4 Weigh 25 g of reagent grade ferric sulfate (contains about 75 % $Fe_2(SO_4)_3$) and add to the sulfuric acid solution. A trip balance may be used.

11.1.5 Drop boiling chips into the flask.

11.1.6 Lubricate ground glass joint with silicone grease.

11.1.7 Cover flask with condenser and circulate cooling water.

11.1.8 Boil solution until all ferric sulfate is dissolved (see Note 7).

11.1.9 **Caution**—It has been reported that violent boiling resulting in acid spills can occur. It is important to ensure that the concentration of acid does not become more concentrated and that an adequate number of boiling chips (which are resistant to attack by the test solution) are present.[5]

12. Preparation of Test Specimens

12.1 A specimen having a total surface area of 5 to 20 cm^2 is recommended. Specimens containing welds should be cut so that no more than 13-mm (½-in.) width of base metal is included on either side of the weld.

12.2 The intent is to test a specimen representing as nearly as possible the surface of the material as used in service. Only such surface finishing should be performed as is required to remove foreign material and obtain a standard, uniform finish as specified. For very heavy sections, specimens should be machined to represent the appropriate surface while maintaining reasonable specimen size for convenience in testing. Ordinarily, removal of more material than necessary will have little influence on the test results. However, in the special case of surface carburization (sometimes encountered, for instance, in tubing or castings when lubricants or binders containing carbonaceous materials are employed) it may be possible by heavy grinding or machining to remove the carburized surface completely. Such treatment of test specimens is not permissible, except in tests undertaken to demonstrate such surface effects.

12.3 When specimens are cut by shearing, the sheared edges should be refinished by machining or grinding prior to testing.

12.4 Any surfaces of the specimen, including sheared edges, that are to be refinished should be done by using No. 80 or 120 grit abrasive paper. If dry abrasive paper is used, polish slowly to avoid overheating. Sand blasting should not be used.

12.5 All traces of oxide scale formed during heat treatments must be thoroughly removed. Any scale which cannot be

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[4] Dow Corning Stopcock Grease has been found satisfactory for this purpose.

[5] Amphoteric alundum granules, Hengar Granules, from the Hengar Co., Philadelphia, PA have been found satisfactory for this purpose.

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removed by grinding, for example, in stamped numbers, must be removed by immersing the specimen in concentrated nitric acid at about 93°C (200°F). (Residual oxide scale causes galvanic action and consequent activation in the test solution.)

12.6 The specimen should be measured including the inner surfaces of any holes and the total exposed area calculated.

12.7 The specimen should then be degreased and dried using suitable nonchlorinated agents, such as soap and acetone, and then weighed to the nearest 0.001 g.

13. Procedure

13.1 Place specimen in glass cradle and immerse in boiling solution.

13.2 Mark liquid level on flask with wax crayon to provide a check on vapor loss which would result in concentration of the acid. If there is an appreciable change in the level, the test must be repeated with fresh solution and a reground specimen.

13.3 Continue immersion of the specimen for a total of 120 h, then remove specimen, rinse in water and acetone, and dry.

13.4 Weigh specimen and subtract weight from original weight.

13.5 No intermediate weighings are usually necessary. The tests can be run without interruption for 120 h. However, if preliminary results are desired, the specimen can be removed at any time for weighing.

13.6 No changes in solution are necessary during the 120-h test periods.

13.7 Additional ferric sulfate inhibitor may have to be added during the test if the corrosion rate is extraordinarily high as evidenced by a change in the color of the solution. More ferric sulfate must be added if the total weight loss of all specimens exceeds 2 g. (During the test, ferric sulfate is consumed at a rate of 10 g for each 1 g of dissolved stainless steel.)

13.8 Several specimens may be tested simultaneously. The number (3 or 4) is limited only by the number of glass cradles that can be fitted into the flask.

14. Calculation and Report

14.1 The effect of the acid solution on the material shall be measured by determining the loss of weight of the specimen. The corrosion rates should be reported as millimeters of penetration per month (Note 8), calculated as follows:

$$\text{Millimeter per month} = (7290 \times W)/(A \times t \times d) \qquad (1)$$

where:
t = time of exposure, h,
A = area, cm^2,
W = weight loss, g, and
d = density, g/cm^3
for chromium-nickel steels, d = 7.9 g/cm^3
for chromium-nickel-molybdenum steels, d = 8.00 g/cm^3

Note 8—Conversion factors to other commonly used units for corrosion rates are as follows:
Millimeters per month × 0.0^4= inches per month
Millimeters per month × 0.4^7= inches per year
Millimeters per month × 12 = millimeters per year
Millimeters per month × 472 = mils per year
Millimeters per month × density/3 = milligram per square decimeter per day

Millimeters per month × 1.39 × density = grams per square meter per hours

PRACTICE C—NITRIC ACID TEST FOR DETECTING SUSCEPTIBILITY TO INTERGRANULAR ATTACK IN AUSTENITIC STAINLESS STEELS

15. Scope

15.1 This practice describes the procedure for conducting the boiling nitric acid test (**4**) as employed to measure the relative susceptibility of austenitic stainless steels to intergranular attack. The presence or absence of intergranular attack in this test is not necessarily a measure of the performance of the material in other corrosive environments; in particular, it does not provide a basis for predicting resistance to forms of corrosion other than intergranular, such as general corrosion, pitting, or stress-corrosion cracking.

15.2 The boiling nitric acid test may be used to evaluate the heat treatment accorded "as-received" material. It is also sometimes used to check the effectiveness of stabilizing elements and of reductions in carbon content in preventing susceptibility to rapid intergranular attack.

Note 9—Intergranular attack in nitric acid is associated with one or more of the following: (*1*) intergranular precipitation of chromium carbides, (*2*) sigma or transition phases in molybdenum-bearing grades, and (*3*) sigma phase constituents in stabilized grades. The boiling nitric acid test should not be used for extra low carbon molybdenum-bearing grades unless the material tested is to be used in nitric acid service. See Practice A, Oxalic Acid Etching Test, for information on the most appropriate of the several test methods available for the evaluation of specific grades of stainless steel.

15.3 Specimens of extra low carbon and stabilized grades are tested after sensitizing heat treatments at 650 to 675°C (1200 to 1250°F), which is the range of maximum carbide precipitation. The length of time used for this sensitizing treatment determines the maximum permissible corrosion rate in the nitric acid test. The most commonly used sensitizing treatment is 1 h at 675°C (1250°F).

15.4 This practice may be applied to wrought products (including tubes), castings, and weld metal of the various grades of stainless steel (Note 9).

16. Rapid Screening Test

16.1 Before testing in the nitric acid test, specimens of certain grades of stainless steel as given in Table 1 may be given a rapid screening test in accordance with procedures given in Practice A, Oxalic Acid Etch Test for Classification of Etch Structures of Austenitic Stainless Steels. The use of the etch structure evaluations in connection with the nitric acid test is specified in Table 4.

16.1.1 Corrosion test specimens having acceptable etch structures in the oxalic acid etch test will be essentially free of intergranular attack in the nitric acid test; such specimens are acceptable without testing in the nitric acid test. All specimens having nonacceptable etch structures must be tested in the nitric acid test.

17. Apparatus

17.1 *Container*—A 1-L Erlenmeyer flask equipped with a

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NOTE 1—AISI 316, 316L, 317, 317L, 347, and 321 cannot be screened because these steels may contain sigma phase not visible in the etch structure. This may cause rapid intergranular attack in the nitric acid test.

Grade	Acceptable Etch Structures	Nonacceptable Etch Structures [A]
AISI 304	Step, Dual, End Grain I	Ditch, End Grain II
AISI 304L	Step, Dual, End Grain I	Ditch, End Grain II
ACI CF-8	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches
ACI CF-3	Step, Dual, Isolated Ferrite Pools	Ditch, Interdendritic Ditches

[A] Specimens having these structures must be tested in the nitric acid test.

cold finger-type condenser, as illustrated in Fig. 9, is recommended.

NOTE 10—Two other types of containers have been employed in the past and may be used if agreed upon between the supplier and purchaser. One of these consists of a 1-L Erlenmeyer flask with a ground glass joint and equipped with a 762-mm (30-in.) reflux condenser; it has been shown that results obtained with a reflux condenser tend to be somewhat higher than with the cold finger-type condenser due to greater vapor loss. The second type of container is the so called multi-sample testing apparatus **(5)** which was designed to permit the testing of a large number of specimens simultaneously by providing for replacement of the acid in contact with the specimens several times per hour with redistilled acid. Because of the lesser accumulation of corrosion products in the testing solution, the rates obtained with the multi-sample tester are consistently lower than those obtained with the conventional apparatus; the differences are small on properly annealed or stabilized material which will show low rates in both types of test but can be very large for sensitized specimens. For research purposes or where results are to be compared directly, it is essential that the same type of apparatus be used for all tests.

17.2 *Specimen Supports*—Glass hooks, stirrups, or cradles for supporting the specimens in the flask fully immersed at all times during the test and so designed that specimens tested in the same container do not come in contact with each other.

17.3 *Heater*—A means for heating the test solutions and of keeping them boiling throughout the test period. An electrically heated hot plate is satisfactory for this purpose.

17.4 *Balance*—An analytical balance capable of weighing to at least the nearest 0.001 g.

18. Nitric Acid Test Solution

18.1 The test solution shall be 65 ± 0.2 weight % as nitric acid determined by analysis. This solution may be prepared by
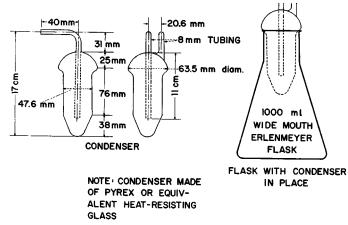
adding distilled water to concentrated nitric acid (reagent grade HNO_3, sp gr 1.42) (Note 11) at the rate of 108 mL of distilled water per litre of concentrated nitric acid.

NOTE 11—The nitric acid used should conform to the recommended specifications for analytical reagent chemicals of the American Chemical Society **(6)** as follows:

Nonvolatile matter, max, %	0.0005
Sulfate (SO_4), max, %	0.0002
Arsenic, max, %	0.000003
Chlorine, max, % about	0.00007
Heavy metals, max, % about lead	0.0005
and iron	0.0001

In addition, the fluorine content shall not exceed 0.0001 % and phosphate (PO_4) shall not exceed 0.00002 %.

19. Preparation of Test Specimens

19.1 The size and shape of the specimen must be considered with respect to available facilities for accurate weighing and the volume of test solution to be used. Normally, the maximum convenient weight of specimen is about 100 g. Specimens containing welds should be cut so that no more than 13 mm (½ in.) width of base metal is included on either side of the weld. Furthermore, in the case of bar, wire, and tubular products, the proportion of the total area represented by the exposed cross section may influence the results. Cross-sectional areas in these products may be subject to end grain attack in nitric acid. The proportion of end grain in the specimen should therefore be kept low unless such surface is actually to be exposed in service involving nitric acid. When specimens of such products are being tested in research investigations, the ratio of the cross-sectional area exposed to the total area should be kept constant from test to test. For inspection tests, specimens cut from bars, wires, or tubes should be proportioned so that the areas of the exposed cross sections shall not exceed half the total exposed area of the specimen.

19.2 Special heat treatment of specimens prior to testing or the use of specimens which contain a weld may be specified.

19.3 The intent is to test a specimen representing as nearly as possible the surface of the material as used in service. Only such surface finishing should be performed as is required to remove foreign material and obtain a standard uniform finish as specified. For very heavy sections, specimens should be machined to represent the appropriate surface while maintaining reasonable specimen size for convenience in testing. Ordinarily, removal of more material than necessary will have little influence on the test results. However, in the special case of surface carburization (sometimes encountered, for instance, in tubing or castings when lubricants or binders containing carbonaceous materials are employed), it may be possible by heavy grinding or machining to remove the carburized surface completely. Such treatment of test specimens is not permissible except in tests undertaken to demonstrate such surface effects.

19.4 When specimens are cut by shearing, the sheared edges should be refinished by machining or grinding prior to testing.

19.5 Any surfaces of the specimen, including sheared edges, that are to be refinished should be done by using No. 80 or 120 grit abrasive paper. If dry abrasive paper is used, polish slowly to avoid overheating. Sandblasting should not be used.

19.6 The specimen should be measured including the inner surfaces of any holes and the total exposed area calculated.

NOTE: CONDENSER MADE OF PYREX OR EQUIV-ALENT HEAT-RESISTING GLASS

FIG. 9 Flask and Condenser for Nitric Acid Test

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19.7 The specimen should then be degreased and dried using suitable nonchlorinated agents, such as soap and acetone (Note 12), and then weighed to the nearest 0.001 g (see 17.4).

NOTE 12—The cleaning treatment described may be supplemented by immersing the specimen in nitric acid (for example, 20 weight % at 49 to 60°C (120 to 140°F) for 20 min, followed by rinsing, drying, and weighing. In the case of small-diameter tubular specimens which cannot be conveniently resurfaced on the inside, it is desirable to include in the preparation an immersion in boiling nitric acid (65 %) for 2 to 4 h using the same apparatus as for the actual test. The purpose of these treatments is to remove any surface contamination that may not be accomplished by the regular cleaning method and which may increase the apparent weight loss of the specimen during the early part of the test.

19.8 It is common practice to test only one specimen of each material or lot of material, as defined by those using the test for specification purposes. However, the use of at least two specimens for check purposes is recommended.

20. Procedure

20.1 Use a sufficient quantity of the nitric acid test solution to cover the specimens and to provide a volume of at least 20 mL/cm^2 (125 mL/in.^{2}) of specimen surface. Normally, a volume of about 600 cm^3 is used.

20.2 The best practice is to use a separate container for each test specimen.

NOTE 13—For routine evaluations, it is acceptable to test as many as three specimens in the same container provided that they all are of the same grade and all show satisfactory resistance to corrosion. If more than one of the specimens tested in the same container fail to pass the test, it is necessary to retest all specimens in separate containers, since excessive corrosion of one specimen may result in accelerated corrosion of the other specimens tested with it. Excessive corrosion may often be detected by changes in the color of the test solution, and it may be appropriate to provide separate containers for such specimens without waiting until the end of the test period. A record should be made showing which specimens were tested together.

NOTE 14—If the multi-sample testing apparatus (see Note 10) is employed, a large number of specimens may be tested in the large container provided.

20.3 After the specimens have been placed in the acid in the container, pass cooling water through the condenser and bring the acid to a boil on the hot plate and then keep boiling throughout the test period (Note 15). After each test period, rinse the specimens with water and treat by scrubbing with rubber or a nylon brush under running water to remove any adhering corrosion products, after which they should be dried and weighed. Drying may be facilitated, if desired, by dipping the specimens in acetone after they are scrubbed.

NOTE 15—Care should be taken to prevent contamination of the testing solution, especially by fluorides, either before or during the test. Experience has shown that the presence of even small amounts of hydrofluoric acid will increase the corrosion rate in the nitric acid test. It is not permissible, for example, to conduct nitric-hydrofluoric acid tests in the same hood with nitric acid tests.

20.4 For most consistent results, the test should consist of five boiling periods of 48 h each (Note 16) with a fresh test solution being used in each period.

NOTE 16—For specification purposes, those experienced in the use of the test may, by mutual agreement, shorten the standard test to three 48-h boiling periods. However, if with this shorter test procedure the rate of

attack in the third period should exceed that in either the first or second periods to some previously agreed-upon extent, then the test should be continued for a total of five periods. As an alternative, when the test is being used for inspection prior to approval of steel for shipment, a procedure may be agreed upon by the purchaser and the manufacturer whereby the material will be released for shipment following satisfactory performance in three 48-h boiling periods with final acceptance being dependent upon satisfactory performance in the longer test of five 48-h boiling periods. Also, by mutual agreement, a combination of one 48-h period and two 96-h periods (not necessarily in that order) instead of five 48-h test periods may be acceptable for routine evaluations.

21. Calculation and Report

21.1 *Calculation*—The effect of the acid on the material shall be measured by determining the loss of weight of the specimen after each test period and for the total of the test periods. Such weight-loss determinations should be made with the accuracy prescribed in 17.4. The corrosion rates are usually reported as millimeters per month (Note 17), calculated in the following rate of corrosion equation:

$$\text{Millimeters per month} = (7290 \times W)/(A \times d \times t) \qquad (2)$$

where:
t = time of exposure, h,
A = total surface area, cm^2,
W = weight loss, g, and
d = density of the sample, g/cm^3.

NOTE 17—Conversion factors to other commonly used units for corrosion rates are as follows:
Millimeters per month $\times$ 0.04 = inches per month
Millimeters per month $\times$ 0.47 = inches per year
Millimeters per month $\times$ 12 = millimeters per year
Millimeters per month $\times$ 472 = mils per year
Millimeters per month $\times$ density/3 = milligram per square decimeter per day
Millimeters per month $\times$ 1.39 $\times$ density = grams per square meter per hours

21.2 *Report*—Results should be reported for the individual periods, as well as the average for the three or five test periods.

PRACTICE E—COPPER-COPPER SULFATE-16 % SULFURIC ACID TEST FOR DETECTING SUSCEPTIBILITY TO INTERGRANULAR ATTACK IN AUSTENITIC STAINLESS STEELS (7) (8)

22. Scope

22.1 This practice describes the procedure by which the copper-copper sulfate-16 % sulfuric acid test is conducted to determine the susceptibility of austenitic stainless steels to intergranular attack. The presence or absence of intergranular corrosion in this test is not necessarily a measure of the performance of the material in other corrosive media. The test does not provide a basis for predicting resistance to other forms of corrosion, such as general corrosion, pitting, or stress-corrosion cracking.

22.2 The copper-copper sulfate-16 % sulfuric acid test indicates susceptibility to intergranular attack associated with the precipitation of chromium-rich carbides. It does not detect susceptibility associated with sigma phase. This test may be used to evaluate the heat treatment accorded as-received material. It may also be used to evaluate the effectiveness of

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stabilizing element additions (Cb, Ti, and so forth) and reductions in carbon content to aid in resisting intergranular attack.

22.3 All wrought products and weld material of austenitic stainless steels can be evaluated by this test.

23. Rapid Screening Test

23.1 Before testing in the copper-copper sulfate-16 % sulfuric acid test, specimens of certain grades of stainless steel (see Table 5) may be given a rapid screening test in accordance with the procedures given in Practice A (Sections 3 through 7). Preparation, etching, and the classification of etch structures are described therein. The use of etch-structure evaluations in connection with the copper-copper sulfate-16 % sulfuric acid test is specified in Table 5.

23.1.1 Corrosion test specimens having acceptable etch structures in the oxalic acid etch test will be essentially free of intergranular attack in the copper-copper sulfate-16 % sulfuric acid test. Such specimens are acceptable without testing in the copper-copper sulfate-16 % sulfuric acid test. All specimens having nonacceptable etch structures must be tested in the copper-copper sulfate-16 % sulfuric acid test.

24. Summary of Practice

24.1 A suitable sample of an austenitic stainless steel, embedded in copper shot or grindings, is exposed to boiling acidified copper sulfate solution for 24 h. After exposure in the boiling solution, the specimen is bent. Intergranular cracking or crazing is evidence of susceptibility.

25. Apparatus

25.1 A 1-L glass Erlenmeyer flask with a ground 45/50 glass joint and four-bulb (minimum) Allihn condenser with 45/50 ground glass joint (as in 10.1.1 and 10.1.2 and Fig. 8) are required. A silicone grease is recommended for the ground glass joint.

25.2 *Specimen Supports*—An open glass cradle capable of supporting the specimens and copper shot or grindings in the flask is recommended.

NOTE 18—It may be necessary to embed large specimens, such as from heavy bar stock, in copper shot on the bottom of the test flask. A copper cradle may also be used.

TABLE 5   Use of Etch Structure Classifications from the Oxalic Acid Etch Test with the Copper-Copper Sulfate-16 % Sulfuric Acid Test

Grade	Acceptable Etch Structures	Nonacceptable Etch Structures [A]
AISI 201	Step, Dual, End Grain I and II	Ditch
AISI 202	Step, Dual, End Grain I and II	Ditch
AISI 301	Step, Dual, End Grain I and II	Ditch
AISI 304	Step, Dual, End Grain I and II	Ditch
AISI 304L	Step, Dual, End Grain I and II	Ditch
AISI 304H	Step, Dual, End Grain I and II	Ditch
AISI 316	Step, Dual, End Grain I and II	Ditch
AISI 316L	Step, Dual, End Grain I and II	Ditch
AISI 316H	Step, Dual, End Grain I and II	Ditch
AISI 317	Step, Dual, End Grain I and II	Ditch
AISI 317L	Step, Dual, End Grain I and II	Ditch
AISI 321	Step, Dual, End Grain I and II	Ditch
AISI 347	Step, Dual, End Grain I and II	Ditch

[A] Specimens having these structures must be tested in the copper-copper sulfate-16 % sulfuric acid test.

25.3 *Heat Source*—Any gas or electrically heated hot plate may be utilized for heating the test solution and keeping it boiling throughout the test period.

26. Acidified Copper Sulfate Test Solution

26.1 Dissolve 100 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 700 mL of distilled water, add 100 mL of sulfuric acid (H_2SO_4, cp, sp gr 1.84), and dilute to 1000 mL with distilled water.

NOTE 19—The solution will contain approximately 6 weight % of anhydrous $CuSO_4$ and 16 weight % of H_2SO_4.

27. Copper Addition

27.1 Electrolytic grade copper shot or grindings may be used. Shot is preferred for its ease of handling before and after the test.

27.2 A sufficient quantity of copper shot or grindings is to be used to cover all surfaces of the specimen whether it is in a vented glass cradle or embedded in a layer of copper shot on the bottom of the test flask.

27.3 The amount of copper used, assuming an excess of metallic copper is present, is not critical. The effective galvanic coupling between copper and the test specimen may have importance **(9)**.

27.4 The copper shot or grindings may be reused if they are cleaned in warm tap water after each test.

28. Specimen Preparation

28.1 The size of the sample submitted for test and the area from which it is to be taken (end or middle of coil, midway surface and center, and so forth) is generally specified in the agreement between the purchaser and the seller. The testing apparatus dictates the final size and shape of the test specimen. The specimen configuration should permit easy entrance and removal through the neck of the test container.

28.1.1 Table 6 may be used as a guide to determine acceptable specimen sizes. There may be restrictions placed on specimen size by the testing apparatus.

28.1.2 Specimens obtained by shearing should have the sheared edges machined or ground off prior to testing. Care should be taken when grinding to avoid overheating or "burning." A "squared" edge is desirable.

28.2 Any scale on the specimens should be removed mechanically unless a particular surface finish is to be evaluated. Chemical removal of scale is permissible when this is the case. Mechanical removal of scale should be accomplished with 120-grit iron-free aluminum oxide abrasive.

28.2.1 Each specimen should be degreased using a cleaning solvent such as acetone, alcohol, ether, or a vapor degreaser prior to being tested.

28.3 All austenitic material in the "as-received" (mill-annealed) condition should be capable of meeting this test.

28.3.1 Specimens of extra low carbon and stabilized grades are tested after sensitizing heat treatments at 650 to 675°C (1200 to 1250°F), which is the range of maximum carbide precipitation. The most commonly used sensitizing treatment is 1 h at 675°C. Care should be taken to avoid carburizing or nitriding the specimens. The heat treating is best carried out in air or neutral salt.

NOTE 20—The sensitizing treatment 675°C is performed to check the

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TABLE 6 Sizes of Test Specimens

Type of Material	Size of Test Specimen
Wrought wire or rod:	
Up to 6 mm (¼ in.) in diameter, incl	Full diameter by 75 mm (3 in.) (min) long
Over 6 mm (¼ in.) in diameter	Cylindrical segment 6 mm (¼ in.) thick by 25 mm (1 in.) (max) wide by 75 to 125 mm (3 to 5 in.) long [A]
Wrought sheet, strip, plates, or flat rolled products:	
Up to 5 mm (³⁄₁₆ in.) thick, incl	Full thickness by 9 to 25 mm (⅜ to 1 in.) wide by 75 mm (3 in.) (min) long
Over 5 mm (³⁄₁₆ in.) thick	5 to 13 mm (³⁄₁₆ to ½ in.) thick by 9 to 25 mm (⅜ to 1 in.) wide by 75 mm (3 in.) (min) long [B]
Tubing:	
Up to 38 mm (1½ in.) in diameter, incl	Full ring, 25 mm (1 in.) wide [C]
Over 38 mm (1½ in.) in diameter	A circumferential segment 75 mm (3 in.) (min) long cut from a 25 mm (1-in.) wide ring [D]

[A] When bending such specimens, the curved surface shall be on the outside of the bend.

[B] One surface shall be an original surface of the material under test and it shall be on the outside of the bend. Cold-rolled strip or sheets may be tested in the thickness supplied.

[C] Ring sections are not flattened or subjected to any mechanical work before they are subjected to the test solution.

[D] Specimens from welded tubes over 38 mm (1½ in.) in diameter shall be taken with the weld on the axis of the bend.

effectiveness of stabilized and 0.03 % maximum carbon materials in resisting carbide precipitation, hence, intergranular attack.

29. Test Conditions

29.1 The volume of acidified copper sulfate test solution used should be sufficient to completely immerse the specimens and provide a minimum of 8 mL/cm^2 (50 mL/in.^{2}) of specimen surface area.

29.1.1 As many as three specimens can be tested in the same container. It is ideal to have all the specimens in one flask to be of the same grade, but it is not absolutely necessary. The solution volume-to-sample area ratio is to be maintained.

29.1.2 The test specimen(s) should be immersed in ambient test solution which is then brought to a boil and maintained boiling throughout the test period. Begin timing the test period when the solution reaches the boiling point.

NOTE 21—Measures should be taken to minimize bumping of the solution when glass cradles are used to support specimens. A small amount of copper shot (8 to 10 pieces) on the bottom of the flask will conveniently serve this purpose.

29.1.3 The time of the test shall be a minimum of 24 h unless a longer time is agreed upon between the purchaser and the producer. If not 24 h, the test time shall be specified on the test report. Fresh test solution would not be needed if the test were to run 48 or even 72 h. (If any adherent copper remains on the specimen, it may be removed by a brief immersion in concentrated nitric acid at room temperature.)

NOTE 22—Results in the literature indicate that this test is more sensitive if it is run for longer times **(10), (11).**

30. Bend Test

30.1 The test specimen shall be bent through 180° and over a diameter equal to the thickness of the specimen being bent (see Fig. 10). In no case shall the specimen be bent over a

FIG. 10 A Bent Copper-Copper Sulfate-Sulfuric Acid Test Specimen

smaller radius or through a greater angle than that specified in the product specification. In cases of material having low ductility, such as severely cold worked material, a 180° bend may prove impractical. Determine the maximum angle of bend without causing cracks in such material by bending an untested specimen of the same configuration as the specimen to be tested.

30.1.1 Duplicate specimens shall be obtained from sheet material so that both sides of the rolled samples may be bent through a 180° bend. This will assure detection of intergranular attack resulting from carburization of one surface of sheet material during the final stages of rolling.

NOTE 23—Identify the duplicate specimen in such a manner as to ensure both surfaces of the sheet material being tested are subjected to the tension side of the 180° bends.

30.1.2 Samples machined from round sections or cast material shall have the curved or original surface on the outside of the bend.

30.1.3 The specimens are generally bent by holding in a vise and starting the bend with a hammer. It is generally completed by bringing the two ends together in the vise. Heavy specimens may require bending in a fixture of suitable design. An air or hydraulic press may also be used for bending the specimens.

30.1.4 Tubular products should be flattened in accordance with the flattening test, prescribed in Test Methods and Definitions A 370.

30.1.5 When agreed upon between the purchaser and the producer, the following shall apply to austenitic stainless steel plates 4.76 mm (0.1875 in.) and thicker:

30.1.5.1 Samples shall be prepared according to Table 7.

30.1.5.2 The radius of bend shall be two times the sample thickness, and the bend axis shall be perpendicular to the direction of rolling.

TABLE 7 Use of Etch Structure Classifications from the Oxalic Acid Etch Test With the Copper-Copper Sulfate-50 % Sulfuric Acid Test

Grade	Acceptable Etch Structures	Non-acceptable Etch Structures
CF-3M	Step, Dual, Isolated Ferrite	Ditch, Interdendritic Ditches
CF-8M	Step, Dual, Isolated Ferrite	Ditch, Interdendritic Ditches

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30.1.5.3 Welds on material 4.76 mm (0.1875 in.) and thicker shall have the above bend radius, and the weld-base metal interface shall be located approximately in the centerline of the bend.

30.1.5.4 Face, root, or side bend tests may be performed, and the type of bend test shall be agreed upon between the purchaser and the producer. The bend radius shall not be less than that required for mechanical testing in the appropriate material specification (for base metal) or in ASME Code Section IX (for welds).

31. Evaluation

31.1 The bent specimen shall be examined under low (5 to 20×) magnification (see Fig. 11). The appearance of fissures or cracks indicates the presence of intergranular attack (see Fig. 12).

31.1.1 When an evaluation is questionable (see Fig. 13), the presence or absence of intergranular attack shall be determined by the metallographic examination of the outer radius of a longitudinal section of the bend specimen at a magnification of 100 to 250×.

NOTE 24—Cracking that originates at the edge of the specimen should be disregarded. The appearance of deformation lines, wrinkles, or "orange peel" on the surface, without accompanying cracks or fissures, should be disregarded also.

NOTE 25—Cracks suspected as arising through poor ductility may be investigated by bending a similar specimen which was not exposed to the boiling test solution. A visual comparison between these specimens should assist in interpretation.

PRACTICE F—COPPER-COPPER SULFATE-50 % SULFURIC ACID TEST FOR DETERMINING SUSCEPTIBILITY TO INTERGRANULAR ATTACK IN AUSTENITIC STAINLESS STEELS

32. Scope

32.1 This practice describes the procedure for conducting the boiling copper-copper sulfate-50 % sulfuric acid test which measures the susceptibility of stainless steels to intergranular attack. The presence or absence of intergranular attack in this test is not necessarily a measure of the performance of the material in other corrosive environments. The test does not provide a basis for predicting resistance to forms of corrosion other than intergranular, such as general corrosion, pitting, or stress-corrosion cracking.

32.2 This test may be used to evaluate the susceptibility of as received material to intergranular corrosion caused by chromium carbide precipitation. It may also be used to evaluate the resistance of extra-low carbon grades to sensitization to intergranular attack caused by welding or heat treatments.

32.3 This test should not be used to detect susceptibility to intergranular attack resulting from the formation of sigma phase. For detecting susceptibility to environments known to cause intergranular attack due to sigma use Practices B or C.

33. Rapid Screening Test

33.1 Before testing in copper-copper sulfate-50 % sulfuric acid test, specimens of certain grades of stainless steels (see Table 1) may be given a rapid screening test in accordance with procedures given in Practice A, oxalic acid etch test for
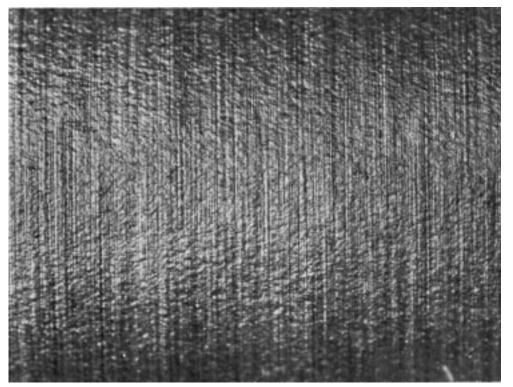

FIG. 11 Passing Test Specimen—View of the Bent Area (20× magnification before reproduction)
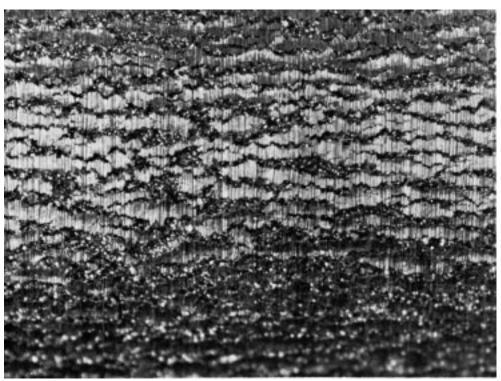
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FIG. 12 Failing Test Specimen (Note the many intergranular fissures. Bent area at 20× magnification before reproduction.)
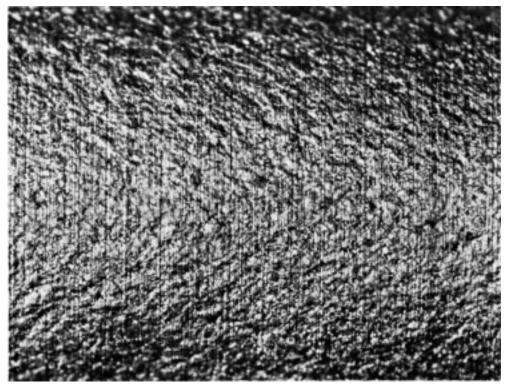

FIG. 13 Doubtful Test Result (Note the traces of intergranular fissures and "orange-peel" surface. Bent area at 20× magnification before reproduction.)

classification of etch structures of austenitic stainless steels. Preparation, etching, and the classification of etch structures are described therein. The use of etch structure evaluations in connection with the copper-copper sulfate-50 % sulfuric acid test is specified in Table 7.

33.1.1 Corrosion test specimens having acceptable etch structures in the oxalic acid etch test will be essentially free of intergranular attack in the copper-copper sulfate-50 % sulfuric acid test. Such specimens are acceptable without testing in the copper-copper sulfate-50 % sulfuric acid test. All specimens

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having nonacceptable etch structures must be tested in the copper-copper sulfate-50 % sulfuric acid test.

34. Apparatus

34.1 The basic apparatus is described in Section 10. Also needed are the following:

34.1.1 For weight loss determination, an analytical balance capable of weighing to the nearest 0.001 g.

34.1.2 A piece of copper metal about 3.2 by 19 by 38 mm (⅛ by ¾ by 1½ in.) with a bright, clean finish. An equivalent area of copper shot or chips may be used. The copper should be washed and degreased before use. A rinse in 5 % H_2SO_4 will clean corrosion products from the copper.

35. Copper-Copper Sulfate-50 % Sulfuric Acid Test Solution

35.1 Prepare 600 mL of test solution as follows. **Caution**—Protect the eyes and face by face shield and use rubber gloves and apron when handling acid. Place flask under hood.

35.1.1 First, measure 400.0 mL of distilled water in a 500-mL graduate and pour into the Erlenmeyer flask.

35.1.2 Then measure 236.0 mL of reagent grade sulfuric acid of a concentration that must be in the range from 95.0 to 98.0 weight % in a 250 mL graduate. Add the acid slowly to the water in the Erlenmeyer flask to avoid boiling by the heat received.

35.1.3 Weigh 72 g of reagent grade copper sulfate (CuSO$_4$·5 H$_2$O) and add to the sulfuric acid solution. A trip balance may be used.

35.1.4 Place the copper piece into one glass cradle and put it into the flask.

35.1.5 Drop boiling chips into the flask.[5]

35.1.6 Lubricate the ground-glass joint with silicone grease.

35.1.7 Cover the flask with the condenser and circulate cooling water.

35.1.8 Heat the solution slowly until all of the copper sulfate is dissolved.

36. Preparation of Test Specimens

36.1 Prepare test specimens as described in Section 12.

36.2 Specimens of extra-low carbon and stabilized grades are tested after sensitizing heat treatments at 650 to 675°C (1200 to 1250°F) which is the range of maximum carbide

precipitation. The length of time of heating used for this sensitizing treatment determines the maximum permissible corrosion rate for such grades in the copper-copper sulfate-50 % sulfuric acid test. The most commonly used sensitizing treatment is 1 h at 675°C.

37. Procedure

37.1 Place the specimen in another glass cradle and immerse in boiling solution.

37.2 Mark the liquid level on the flask with wax crayon to provide a check on vapor loss which would result in concentration of the acid. If there is an appreciable change in the level, repeat the test with fresh solution and a reground specimen.

37.3 Continue immersion of the specimen for 120 h, then remove the specimen, rinse in water and acetone, and dry. If any adherent copper remains on the specimen, it may be removed by a brief immersion in concentrated nitric acid at room temperature.

37.4 For weight loss determination, weigh the specimen and subtract the weight from the original weight.

37.5 No intermediate weighings are usually necessary. The tests can be run without interruption. However, if preliminary results are desired, the specimen can be removed at any time for weighing.

37.6 No changes in solution are necessary during the test.

38. Calculation and Report

38.1 The effect of the acid solution on the material shall be measured by determining the loss of weight of the specimen. The corrosion rate should be reported as millimeters of penetration per month (Note 8) calculated as follows:

$$\text{Millimeters per month} = (7290 \times w)/(A \times t \times d) \qquad (3)$$

where:
t = time or exposure, h,
A = area, cm^2,
w = weight loss, g, and
d = density, g/cm^3.
For chromium-nickel-molybdenum steels, $d = 8.00$ g/cm^3.

39. Keywords

39.1 austenitic stainless steel; copper sulfate; corrosion testing; etch structures; ferric sulfate; intergranular corrosion; nitric acid; oxalic acid

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(**4**) For original descriptions of the boiling nitric acid test, see Huey, W. R., "Corrosion Test for Research and Inspection of Alloys," *Transactions, American Society of Steel Treating,* Vol 18, 1930, p. 1126; also, "Report of Subcommittee IV on Methods of Corrosion Testing," *Proceedings,* ASTM, Vol 33, Part I, 1933, p. 187.

(**5**) For details, see DeLong, W. B., "Testing Multiple Specimens of Stainless Steels in a Modified Boiling Nitric Acid Test Apparatus," *Symposium on Evaluation Tests for Stainless Steels, ASTM STP 93,* ASTM, 1950, p. 211.

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(**7**) The use of copper to accelerate the intergranular corrosion of sensitized austenitic stainless steels in copper sulfate-sulfuric acid was first described by H. J. Rocha in the discussion of a paper by Brauns, E., and Pier, G., *Stahl und Eisen,* Vol 75, 1955, p. 579.

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(**10**) Streicher, M. A., "Theory and Application of Evaluation Tests for Detecting Susceptibility to Intergranular Attack in Stainless Steels and Related Alloys-Problems and Opportunities," *Intergranular Corrosion of Stainless Alloys, ASTM STP 656*, R. F. Steigerwald ed., ASTM, 1978, pp. 3–84.

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Designation: G46 – 94 (Reapproved 2018)

Standard Guide for
Examination and Evaluation of Pitting Corrosion[1]

1. Scope

1.1 This guide covers the selection of procedures that can be used in the identification and examination of pits and in the evaluation of pitting (See Terminology G15) corrosion to determine the extent of its effect.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
E3 Guide for Preparation of Metallographic Specimens
G1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens
G15 Terminology Relating to Corrosion and Corrosion Testing (Withdrawn 2010)[3]
G16 Guide for Applying Statistics to Analysis of Corrosion Data

2.2 *National Association of Corrosion Engineers Standard:*
NACE RP-01-73 Collection and Identification of Corrosion Products[4]

3. Significance and Use

3.1 It is important to be able to determine the extent of pitting, either in a service application where it is necessary to predict the remaining life in a metal structure, or in laboratory test programs that are used to select the most pitting-resistant materials for service.

4. Identification and Examination of Pits

4.1 *Visual Inspection*—A visual examination of the corroded metal surface is usually beneficial, and this is done under ordinary light, with or without the use of a low-power magnifying glass, to determine the extent of corrosion and the apparent location of pits. It is often advisable to photograph the corroded surface at this point so that it can be compared with the clean surface after the removal of corrosion products.

4.1.1 If the metal specimen has been exposed to an unknown environment, the composition of the corrosion products may be of value in determining the cause of corrosion. Follow recommended procedures in the removal of particulate corrosion products and reserve them for future identification (see NACE RP-01-73).

4.1.2 To expose the pits fully, use recommended cleaning procedures to remove the corrosion products and avoid solutions that attack the base metal excessively (see Practice G1). It may be advisable during cleaning to probe the pits with a pointed tool to determine the extent of undercutting or subsurface corrosion (Fig. 1). However, scrubbing with a stiff bristle brush will often enlarge the pit openings sufficiently by removal of corrosion products, or undercut metal to make the pits easier to evaluate.

4.1.3 Examine the cleaned metal surface under ordinary light to determine the approximate size and distribution of pits. Follow this procedure by a more detailed examination through a microscope using low magnification (20×).

4.1.4 Determine the size, shape, and density of pits.

4.1.4.1 Pits may have various sizes and shapes. A visual examination of the metal surface may show a round, elongated, or irregular opening, but it seldom provides an accurate indication of corrosion beneath the surface. Thus, it is often necessary to cross section the pit to see its actual shape and to determine its true depth. Several variations in the cross-sectioned shape of pits are shown in Fig. 1.

4.1.4.2 It is a tedious job to determine pit density by counting pits through a microscope eyepiece, but the task can

FIG. 1 Variations in the Cross-Sectional Shape of Pits

be made easier by the use of a plastic grid. Place the grid, containing 3 to 6-mm squares, on the metal surface. Count and record the number of pits in each square, and move across the grid in a systematic manner until all the surface has been covered. This approach minimizes eyestrain because the eyes can be taken from the field of view without fear of losing the area of interest.

4.1.5 *Metallographic Examination*—Select and cut out a representative portion of the metal surface containing the pits and prepare a metallographic specimen in accordance with the recommended procedures given in Methods E3. Examine microscopically to determine whether there is a relation between pits and inclusions or microstructure, or whether the cavities are true pits or might have resulted from metal dropout caused by intergranular corrosion, dealloying, and so forth.

4.2 *Nondestructive Inspection*—A number of techniques have been developed to assist in the detection of cracks or cavities in a metal surface without destroying the material (**1**).[5] These methods are less effective for locating and defining the shape of pits than some of those previously discussed, but they merit consideration because they are often used in situ, and thus are more applicable to field applications.

4.2.1 *Radiographic*—Radiation, such as X rays, are passed through the object. The intensity of the emergent rays varies with the thickness of the material. Imperfections may be detected if they cause a change in the absorption of X rays. Detectors or films are used to provide an image of interior imperfections. The metal thickness that can be inspected is dependent on the available energy output. Pores or pits must be as large as $\frac{1}{2}$ % of the metal thickness to be detected. This technique has only slight application to pitting detection, but it

might be a useful means to compare specimens before and after corrosion to determine whether pitting has occurred and whether it is associated with previous porosity. It may also be useful to determine the extent of subsurface and undercutting pitting (Fig. 1).
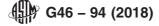
4.2.2 *Electromagnetic:*

4.2.2.1 Eddy currents can be used to detect defects or irregularities in the structure of electrically conducting materials. When a specimen is exposed to a varying magnetic field, produced by connecting an alternating current to a coil, eddy currents are induced in the specimen, and they in turn produce a magnetic field of their own. Materials with defects will produce a magnetic field that is different from that of a reference material without defects, and an appropriate detection instrument is required to determine these differences.

4.2.2.2 The induction of a magnetic field in ferromagnetic materials is another approach that is used. Discontinuities that are transverse to the direction of the magnetic field cause a leakage field to form above the surface of the part. Ferromagnetic particles are placed on the surface to detect the leakage field and to outline the size and shape of the discontinuities. Rather small imperfections can be detected by this method. However, the method is limited by the required directionality of defects to the magnetic field, by the possible need for demagnetization of the material, and by the limited shape of parts that can be examined.

4.2.3 *Sonics:*

4.2.3.1 In the use of ultrasonics, pulses of sound energy are transmitted through a couplant, such as oil or water, onto the metal surface where waves are generated. The reflected echoes are converted to electrical signals that can be interpreted to show the location of flaws or pits. Both contact and immersion methods are used. The test has good sensitivity and provides instantaneous information about the size and location of flaws.

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[5] The boldface numbers in parentheses refer to the list of references at the end of this practice.

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However, reference standards are required for comparison, and training is needed to interpret the results properly.

4.2.3.2 An alternative approach is to use acoustic emissions in detecting flaws in metals. Imperfections, such as pits, generate high-frequency emissions under thermal or mechanical stress. The frequency of emission and the number of occurrences per unit time determine the presence of defects.

4.2.4 *Penetrants*—Defects opening to the surface can be detected by the application of a penetrating liquid that subsequently exudes from the surface after the excess penetrant has been removed. Defects are located by spraying the surface with a developer that reacts with a dye in the penetrant, or the penetrant may contain a fluorescent material that is viewed under black light. The size of the defect is shown by the intensity of the color and the rate of bleed-out. This technique provides only an approximation of the depth and size of pits.

4.2.5 None of these nondestructive test methods provide satisfactory detailed information about pitting. They can be used to locate pits and to provide some information about the size of pits, but they generally are not able to detect small pits, and confusion may arise in attempting to differentiate between pits and other surface blemishes. Most of these methods were developed to detect cracks or flaws in metals, but with more refined development they may become more applicable to pitting measurements.

5. Extent of Pitting

5.1 *Mass Loss*—Metal mass loss is not ordinarily recommended for use as a measure of the extent of pitting unless general corrosion is slight and pitting is fairly severe. If uniform corrosion is significant, the contribution of pitting to total metal loss is small, and pitting damage cannot be determined accurately from mass loss. In any case, mass loss can only provide information about total metal loss due to pitting but nothing about depth of penetration. However, mass loss should not be neglected in every case because it may be of value; for example, mass loss along with a visual comparison of pitted surfaces may be adequate to evaluate the pitting resistance of alloys in laboratory tests.

5.2 *Pit Depth Measurement:*

5.2.1 *Metallographic*—Pit depth can be determined by sectioning vertically through a pre-selected pit, mounting the cross-sectioned pit metallographically, and polishing the surface. The depth of the pit is measured on the flat, polished surface by the use of a microscope with a calibrated eyepiece. The method is very accurate, but it requires good judgment in the selection of the pit and good technique in cutting through the pit. Its limitations are that it is time consuming, the deepest pit may not have been selected, and the pit may not have been sectioned at the deepest point of penetration.

5.2.2 *Machining* (**2, 3**):

5.2.2.1 This method requires a sample that is fairly regular in shape, and it involves the destruction of the specimen. Measure the thickness of the specimen between two areas that have not been affected by general corrosion. Select a portion of the surface on one side of the specimen that is relatively unaffected; then machine the opposite surface where the pits are located on a precision lathe, grinder, or mill until all signs

of corrosion have disappeared. (Some difficulty from galling and smearing may be encountered with soft metals, and pits may be obliterated.) Measure the thickness of the specimen between the unaffected surface and subtract from the original thickness to give the maximum depth of pitting. Repeat this procedure on the unmachined surface unless the thickness has been reduced by 50 % or more during the machining of the first side.

5.2.2.2 This method is equally suitable for determining the number of pits with specific depths. Count the visible pits; then machine away the surface of the metal in measured stages and count the number of visible pits remaining at each stage. Subtract the number of pits at each stage from the count at the previous stage to obtain the number of pits at each depth of cut.

5.2.3 *Micrometer or Depth Gage:*

5.2.3.1 This method is based on the use of a pointed needle attached to a micrometer or calibrated depth gage to penetrate the pit cavity. Zero the instrument on an unaffected area at the lip of the pit. Insert the needle in the pit until it reaches the base where a new measurement is taken. The distance traveled by the needle is the depth of the pit. It is best to use constant-tension instruments to minimize metal penetration at the base of the pit. It can be advantageous to use a stereomicroscope in conjunction with this technique so that the pit can be magnified to ensure that the needle point is at the bottom of the pit. The method is limited to pits that have a sufficiently large opening to accommodate the needle without obstruction; this eliminates those pits where undercutting or directional orientation has occurred.
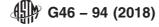
5.2.3.2 In a variation of this method, attach the probe to a spherometer and connect through a microammeter and battery to the specimen (**3, 4**). When the probe touches the bottom of the pit, it completes the electrical circuit, and the probe movement is a measurement of pit depth. This method is limited to very regularly shaped pits because contact with the side of the pit would give a false reading.

5.2.4 *Microscopical*—This method is particularly valuable when pits are too narrow or difficult to penetrate with a probe type of instrument. The method is amenable to use as long as light can be focused on the base of the pit, which would not be possible in the case of example (*e*) in Fig. 1.

5.2.4.1 Use a metallurgical microscope with a magnification range from 50 to 500× and a calibrated fine-focus knob (for example, 1 division = 0.001 mm). If the latter is not available, a dial micrometer can be attached to the microscope in such a way that it will show movement of the stage relative to the microscope body.

5.2.4.2 Locate a single pit on the metal surface and center under the objective lens of the microscope at low magnification (for example, 50×). Increase the objective lens magnification until the pit area covers most of the field under view. Focus the specimen surface at the lip of the pit, using first the coarse and then the fine-focusing knobs of the microscope. Record the initial reading from the fine-focusing knob. Refocus on the bottom of the pit with the fine-focusing knob and record the reading. The difference between the initial and the final readings on the fine-focusing knob is the pit depth.

5.2.4.3 Repeat the steps in 5.2.4.2 to obtain additional measurements or until satisfactory duplication has been obtained. The repeatability of pit depth measurements on a single pit at four magnifications is shown in Annex A1.

5.2.4.4 A variation of the microscopical technique employs the use of an interference microscope. A beam of light is split, and one portion is projected on the specimen and the other on a reference mirror surface. The reflected light from these two surfaces is recombined, and interference fringes are formed that provide a topographical map of the specimen surface. These fringes can be used to measure vertical deviations on the metal surface. However, the method is limited to the shallower pits, that is, less than 25 µm, because the number of fringes increases to the point where they are difficult to count.
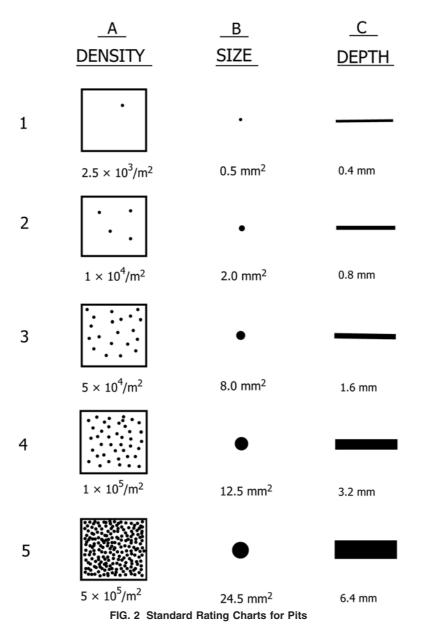
6. Evaluation of Pitting

6.1 There are several ways in which pitting can be described, given a quantitative expression to indicate its

significance, or used to predict the life of a material. Some of the more commonly used methods are described in this section, although it is often found that no single method is sufficient by itself.

6.2 *Standard Charts* (3):

6.2.1 Rate the pits in terms of density, size, and depth on the basis of standard charts, such as those shown in Fig. 2. Columns A and B relate to the extent of pitting at the surface of the metal (that is, Column A is a means for rating the number of sites per unit area and Column B a means for showing the average size of these sites). Column C rates the intensity or average depth of attack. A typical rating might be A-3, B-2, C-3, representing a density of 5×10^4 pits/m^2, an average pit opening of 2.0 mm^2, and an average pit depth of 1.6 mm.

6.2.2 This method offers an effective means of communication between those who are familiar with the charts, and it is a simple means for storing data for comparison with other test

	A DENSITY	B SIZE	C DEPTH
1	2.5×10^3/m^2	0.5 mm^2	0.4 mm
2	1×10^4/m^2	2.0 mm^2	0.8 mm
3	5×10^4/m^2	8.0 mm^2	1.6 mm
4	1×10^5/m^2	12.5 mm^2	3.2 mm
5	5×10^5/m^2	24.5 mm^2	6.4 mm

FIG. 2 Standard Rating Charts for Pits

results. However, it is tedious and time consuming to measure all pits, and the time is usually not justified because maximum values (for example, pit depths) usually have more significance than average values.

6.3 *Metal Penetration:*

6.3.1 Measure the deepest pits and express metal penetration in terms of the maximum pit depth or the average of the ten deepest pits, preferably both. This type of measurement is particularly significant when the metal is associated with an enclosure for a gas or liquid, and a hole could lead to a loss of fluid.

6.3.2 Metal penetration can also be expressed in terms of a pitting factor. This is the ratio of the deepest metal penetration to the average metal penetration, determined from weight loss, as shown in the following relationship:

$$\text{Pitting Factor} = \frac{\text{deepest metal penetration}}{\text{average metal penetration}} \qquad (1)$$

A pitting factor of one represents uniform corrosion; the larger the number, the greater the depth of penetration. The factor does not apply in those cases where pitting or general corrosion is very small because values of zero or infinity can readily be obtained when dealing with a ratio.

6.4 *Statistical:*

6.4.1 The application of statistics to the analysis of corrosion data is covered in detail in Guide G16. The subject is discussed briefly in this standard to show that statistics have a bearing on the evaluation of pitting data; more detailed information can be obtained from other publications.

6.4.2 The probability that pits will initiate on a metal surface is dependent on a number of factors, such as the pitting tendency of the metal, the corrosivity of the solution, the specimen area, and the time of exposure. A pitting probability test can be conducted to determine the susceptibility of metals to pitting, but it will not provide information about the rate of propagation, and the results are only applicable to the conditions of exposure. The pitting probability (P) in % after the exposure of a number of specimens to a particular set of conditions can be expressed as follows (5, 6):

$$P = \frac{N_p}{N} \times 100 \qquad (2)$$

where:

N_p = number of specimens that pit, and
N = total number of specimens.

6.4.3 The relationship between pit depth and area or time of exposure may vary with the environment, the metal exposed, and other variables. The relationships cited in 6.4.3.1 and 6.4.3.2 are examples that have been found to apply under certain exposure conditions.

6.4.3.1 The following relationship was found between the maximum pit depth (D) and the area (A) of a pipeline exposed to soil (7, 8, 9):

$$D = bA^a \qquad (3)$$

where ^{a} and $b > 0$, and ^{a} and b are constants that were derived from the slope and the y-intercept of a straight line curve obtained when the logarithms of the mean pit depth for successively increasing areas on the pipe were plotted against the logarithms of the corresponding areas. The dependence on area is attributed to the increased chance for the deepest pit to be found when the size of the sample of pits is increased through an increased area of corroded surface.

6.4.3.2 The maximum pit depth (D) of aluminum exposed to various waters was found to vary as the cube root of time (t), as shown in the following relationship (5, 10):

$$D = Kt^{1/3} \qquad (4)$$

K is a constant that is a function of the composition of the water and alloy. This relationship has been found to apply to several aluminum alloys exposed to different waters.

6.4.4 Extreme value probability statistics (11, 12) have been applied successfully to maximum pit depth data to estimate the maximum pit depth of a large area of material on the basis of examination of a small portion of that area (3, 5, 10). The procedure is to measure maximum pit depths on several replicate specimens that have pitted, and then arrange the pit depth values in order of increasing rank. A plotting position for each order of ranking is obtained by substituting in the relation, $M/(n+1)$, where M = order of ranking, and n = total number of specimens or values. For example, the plotting position for the second value out of 10 would be $2/(10+1) = 0.1818$. These values are plotted on the ordinate of extreme value probability paper versus their respective maximum pit depths. If a straight line is obtained, it shows that extreme value statistics apply. Extrapolation of the straight line can be used to determine the probability that a specific depth will occur or the number of observations that must be made to find a particular pit depth.

6.5 *Loss in Mechanical Properties*—If pitting is the predominant form of corrosion and the density of pitting is relatively high, the change in a mechanical property may be used advantageously to evaluate the degree of pitting. Typical properties that are considered for this purpose are tensile strength, elongation, fatigue strength, impact resistance, and burst pressure (13, 14).

6.5.1 The precautions that must be taken in the application of these mechanical test procedures are covered in most standard methods, but it must be stressed that it is important to use as nearly replicate specimens as possible for both the exposed and unexposed specimens. Thus, consideration should be given to edge effects, direction of rolling, surface conditions, and so forth.

6.5.2 Representative specimens of the metal are exposed to the same conditions except for the corrosive environment. The mechanical properties of the exposed and unexposed specimens are measured after the exposure; the difference between the two results is attributed to corrosion.

6.5.3 Some of these methods are more properly suited to the evaluation of other forms of localized corrosion, such as intergranular or stress corrosion, so their limitations must be considered. The often erratic nature of pitting and the location of pits on the specimen can affect results. In some cases the change in mechanical properties due to pitting may be too small to provide meaningful results. Probably one of the most difficult problems is to separate the effects due to pitting from those caused by some other form of corrosion.

7. Report

7.1 The report should include as much detailed information as possible, such as the following:

7.1.1 Metallurgical treatment of the metal, surface preparation, and final surface finish before exposure to test,

7.1.2 Environmental conditions and duration of exposure,

7.1.3 Appearance of the corroded surface before and after cleaning,

7.1.4 Identification of corrosion products,

7.1.5 Characterization of pits to include: size, shape, density, uniformity of distribution, depth (average and maximum), and location of pits with reference to microstructure, face, edge, crevice, and so forth,

7.1.6 Change in mechanical properties as the result of corrosion, and the method by which determined, and

7.1.7 Statistical information.

8. Keywords

8.1 metallographic inspection; pit density; pit depth; pit morphology; pitting corrosion; visual inspection

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ANNEX

(Mandatory Information)

A1. REPEATABILITY OF MICROSCOPICAL PIT DEPTH MEASUREMENTS

A1.1 Repeatability of pit depth measurements on a single pit at four magnifications is shown in Table A1.1.

A1.2 The data in Table A1.1 indicate that as the magnification was increased (that is, from 65 to 370×), the average pit depth that was measured decreased from 0.174 mm to 0.151 mm. Repeatability of measurement improved with magnification, and, as will be shown in A1.3, accuracy also showed marked improvement.

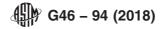A1.3 The pit used for the measurements in Table A1.1 was cross sectioned and photographed at 100× through a micro-scope with a micrometer reticle. As shown in Fig. A1.1, the depth measured in cross section is 0.152 mm. This result is in excellent agreement with that found under high magnification, and shown in Table A1.1.
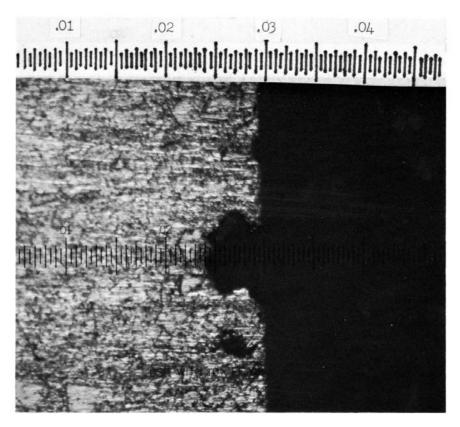
A1.4 Pit depth measurements have been made over the range from 0.04 to 0.34 mm. The only limitation to this method is that associated with the range of movement of the calibrated focusing knob on the microscope.

TABLE A1.1 Microscopical Pit Depth Measurements

Magnification	Pit Depth, mm
65	0.183
	0.159
	0.179
	0.174avg
132	0.159
	0.160
	0.155
	0.159
	0.159avg
200	0.149
	0.157
	0.150
	0.153
	0.152avg
370	0.151
	0.151
	0.152
	0.151avg

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NOTE 1—Use with 10× F.F. Objective.
FIG. A1.1 Cross Section of Pit Used for Depth Measurements in Table A1 (Each Scale Division Equals 0.0005 in. (13 μm))
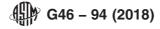
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8

EFFECTS OF CORROSIVE ENVIRONMENTS AND AGEING STUDIES OF ENGINEERING MATERIALS AND DEVICES

CHAPTER 4

Environments

❖ **Atmosphere**
❖ **Sea water**
❖ **Fresh water**
❖ **Soil**

Atmospheric corrosion

Classification

- **Dry**
- **Damp**
- **Wet**

Rural This type of atmosphere is generally the least corrosive and normally does not contain chemical pollutants, but does contain organic and inorganic particulates. The principal corrodents are moisture, oxygen, and carbon dioxide. Arid and tropical types are special extreme cases in the rural category.
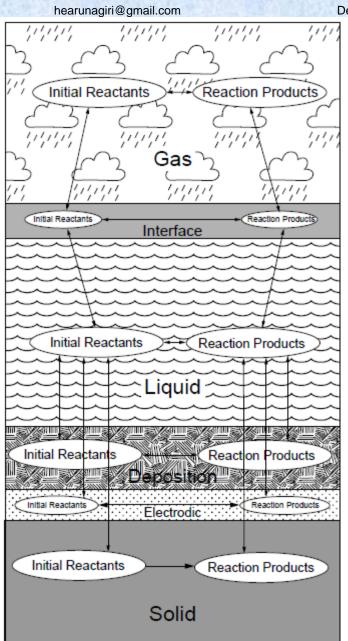
Urban This type of atmosphere is similar to the rural type in that there is little industrial activity. Additional contaminants are of the SO_x and NO_x variety, from motor vehicle and domestic fuel emissions.

Industrial These atmospheres are associated with heavy industrial processing facilities and can contain concentrations of sulfur dioxide, chlorides, phosphates, and nitrates.

Marine. Fine windswept chloride particles that get deposited on surfaces characterize this type of atmosphere. Marine atmospheres are usually highly corrosive, and the corrosivity tends to be significantly dependent on wind direction, wind speed, and distance from the coast. It should be noted that an equivalently corrosive environment is created by the use of deicing salts on the roads of many cold regions of the planet.

Figure 2.5 A framework describing the six regimes of atmospheric corrosion.

The regimes in this so-called GILDES-type model are the gaseous region (G), the gas-to-liquid interface (I), the surface liquid (L), the deposition layer (D), the electrodic layer (E), and the corroding solid (S).

	Common Species	Rarer Species
Al	$Al(OH)_3$ Al_2O_3, $Al_2O_3.3H_2O$	$AlOOH$, $Al_x(OH)_y(SO_4)_z$, $AlCl(OH)_2.4H_2O$
Fe	Fe_2O_3, $FeOOH$, $FeSO_4.4H_2O$	$Fe_x(OH)_yCl_z$, $FeCO_3$
Cu	Cu_2O, $Cu_4SO_4(OH)_6$, $Cu_4SO_4(OH)_6.2H_2O$, $Cu_3SO_4(OH)_4$	$Cu_2Cl(OH)_3$, $Cu_2CO_3(OH)_2$, $Cu_2NO_3(OH)_3$
Zn	ZnO, $Zn_5(OH)_6(CO_3)_2$, $ZnCO_3$	$Zn(OH)_2$, $ZnSO_4$, $Zn_5Cl_2(OH)_8.H_2O$

Figure 2.6 Nature of corrosion products formed on four metals.

Atmospheric corrosion
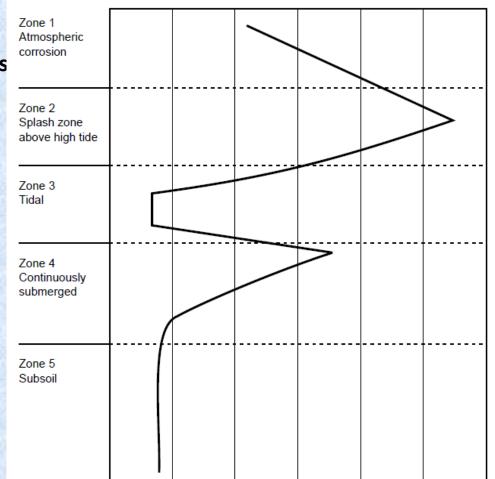
TABLE 2.5   ISO 9223 Corrosion Rates after One Year of Exposure Predicted for Different Corrosivity Classes

Corrosion category	Steel, $g/m^2 \cdot year$	Copper, $g/m^2 \cdot year$	Aluminum, $g/m^2 \cdot year$	Zinc, $g/m^2 \cdot year$
C_1	≤ 10	≤ 0.9	Negligible	≤ 0.7
C_2	11–200	0.9–5	≤ 0.6	0.7–5
C_3	201–400	5–12	0.6–2	5–15
C_4	401–650	12–25	2–5	15–30
C_5	651–1500	25–50	5–10	30–60

Corrosion by Sea Water

Seawater systems are used by many industries, such as shipping, offshore oil and gas production, power plants, and coastal industrial plants. The main use of seawater is for cooling purposes, but it is also used for fire fighting, oilfield water injection, and desalination plants.

- **Salinity**
- **Other ions**
- **Precipitation of inorganic compounds**
- **Oxygen**
- **Organic compounds**

Zone 1 Atmospheric corrosion

Zone 2 Splash zone above high tide

Zone 3 Tidal

Zone 4 Continuously submerged

Zone 5 Subsoil

Relative loss in metal thickness

Corrosion by Sea Water

Component	Low-cost system	Low-maintenance system
Pipe	Galvanized steel	90/10 cupronickel
Flanges	Steel	Cast or forged 90/10 cupronickel Steel welded overlayed with cupronickel Gunmetal 6% Mo austenitic high duplex
Tube plates	60/40 brass/naval brass	Nickel aluminum bronze 90/10 cupronickel 6% Mo austenitic high duplex
Tubes	Aluminum brass	70/30 cupronickel (particularly 2% Fe + 2% Mn) 90/10 cupronickel
Pump casing	Cast iron or leaded gunmetal	Cast cupronickel Nickel aluminum bronze Admiralty gunmetal Ni-resist type D2
Pump impeller	Gunmetal	Monel alloy 410 Alloy 20 (CN7M) Stainless steel (CF3 and CF8) Nickel aluminum bronze
Pump shaft	Naval brass	Monel alloy 400 or 500 Nickel aluminum bronze Ni-resist iron type D2 Nickel aluminum 6% Mo austenitic high duplex UNS 31600 stainless steel
Strainer body	Cast iron	Cast cupronickel Gunmetal 6% Mo austenitic high duplex
Strainer	Galvanized iron	Monel alloy 400 6% Mo austenitic high duplex
Plate	Munz metal	6% Mo austenitic high duplex

Corrosion by Sea Water

TABLE 2.23   Effect of Velocity on the Corrosion of Metals in Seawater

Alloy	Deepest pit, mm	Average corrosion rate, $mm \cdot y^{-1}$		
			Flowing seawater	
	Quiet seawater		$8.2\ m \cdot s^{-1}$	$35\text{–}42\ m \cdot s^{-1}$
Carbon steel	2.0	0.075	—	4.5
Grey cast iron (graphitized)	4.9	0.55	4.4	13.2
Admiralty gunmetal	0.25	0.027	0.9	1.07
85/5/5/5 Cu/Zn/Pb/Zn	0.32	0.017	1.8	1.32
Ni resist cast iron type 1B	Nil	0.02	0.2	0.97
Ni Al bronze	1.12	0.055	0.22	0.97
70/30 Cu/Ni + Fe	0.25	<0.02	0.12	1.47
Type 316 stainless steel	1.8	0.02	<0.02	<0.01
6% Mo stainless steel	Nil	0.01	<0.02	<0.01
Ni-Cu alloy 40	1.3	0.02	<0.01	0.01

Corrosion by Fresh Water

Enormous quantities are required for cooling of products and equipment, for process needs, for boiler feed, and for sanitary and potable water.

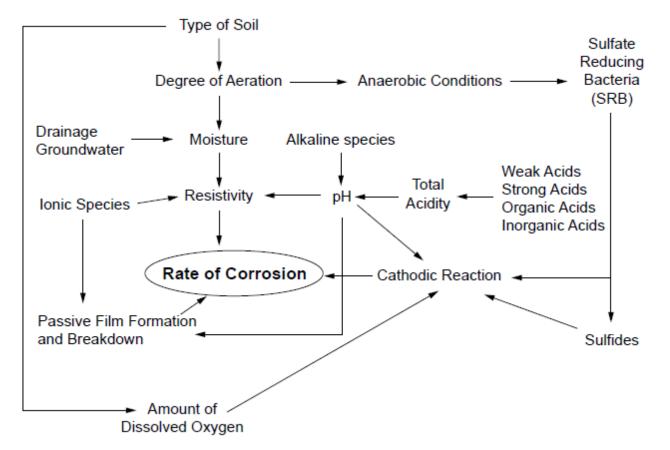- **Carbon dioxide and calcium carbonate**
- **Dissolved mineral salts**
- **Hardness**
- **pH of water**
- **Priority pollutants**
    - **Heavy metals (total and dissolved)**
    - **Pesticides**
    - **Polycyclic aromatic hydrocarbons (PAHs)**
    - **Polychlorinated biphenyls (PCBs)**

- **Organic matter**
    - **Biochemical oxygen demand**
    - **Nutrients**
    - **Organic carbon**
    - **Oil and grease**

Corrosion by Fresh Water

Constituent	Chemical formula	Difficulties caused	Means of treatment
Turbidity	None–expressed in analysis as units	Imparts unsightly appearance to water. Deposits in water lines, process equipment, etc. Interferes with most process uses	Coagulation, settling, and filtration
Hardness	Calcium and magnesium salts expressed as $CaCO_3$	Chief source of scale in heat-exchange equipment, boilers, pipelines, etc. Forms curds with soap, interferes with dyeing, etc.	Softening; demineralization; internal boiler water treatment; surface active agents
Alkalinity	Bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), expressed as $CaCO_3$	Foaming and carryover of solids with steam. Embrittlement of boiler steel. Bicarbonate and carbonate produce CO_2 in steam, a source of corrosion in condensate lines	Lime and lime soda softening; acid treatment; hydrogen zeolite softening; demineralization; dealkalization by anion exchange
Free mineral acid	H_2SO_4, HCl. expressed as $CaCO_3$	Corrosion	Neutralization with alkalies
Carbon dioxide	CO_2	Corrosion in water lines and particularly steam and condensate lines	Aeration; deaeration; neutralization with alkalies
pH	(H^+)	pH varies according to acidic or alkaline solids in water. Most natural waters have a pH of 6.0–8.0	pH can be increased by alkalies and decreased by acids
Sulfate	(SO_4^{2-})	Adds to solids content of water, but in itself is not usually significant. Combines with calcium to form calcium sulfate scale	Demineralization
Chloride	Cl^-	Adds to solids content and increases corrosive character of water	Demineralization
Oxygen	O_2	Corrosion of water lines, heat-exchange equipment, boilers, return lines, etc.	Deaeration; sodium sulfite; corrosion inhibitors

Corrosion by Soil

Soil is an aggregate of minerals, organic matter, water, and gases (mostly air). It is formed by the combined weathering action of wind and water, and also organic decay. The proportions of the basic constituents vary greatly in different soil types.

Examples of soil corrosion are related to oil, gas, and water pipelines; buried storage tanks (a vast number are used by gas stations); electrical communication cables and conduits; anchoring systems; and well and shaft casings. Such systems are expected to function reliably and continuously over several decades.

Corrosion by Soil

TABLE 2.28   Point System for Predicting Soil Corrosivity According to the AWWA C-105 Standard

Soil parameter	Assigned points
Resistivity, $\Omega \cdot cm$	
< 700	10
700–1000	8
1000–1200	5
1200–1500	2
1500–2000	1
> 2000	0
pH	
0–2	5
2–4	3
4–6.5	0
6.5–7.5	0
7.5–8.5	0
> 8.5	3
Redox potential, mV	
> 100	0
50–100	3.5
0–50	4
< 0	5
Sulfides	
Positive	3.5
Trace	2
Negative	0
Moisture	
Poor drainage, continuously wet	2
Fair drainage, generally moist	1
Good drainage, generally dry	0

American Water Works Association
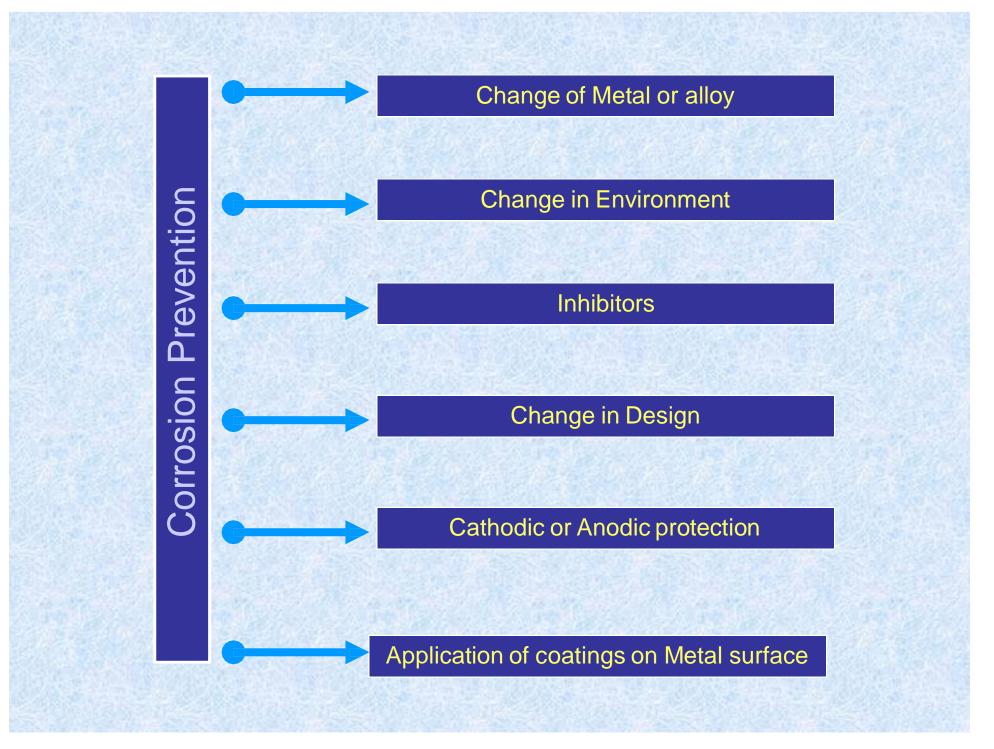
Corrosion on other Environments

- Aerospace
- Automobile
- Electronic equipment
- Nuclear Power Plants
- Thermal Power Plants
- Solar Power Plants

MODERN APPROACHES FOR CORROSION PREVENTION

CHAPTER 5

Corrosion Prevention

- Change of Metal or alloy
- Change in Environment
- Inhibitors
- Change in Design
- Cathodic or Anodic protection
- Application of coatings on Metal surface

1)Material selection

Metals and alloys The most common method of preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service.

Mediums and corrosion Resistant Metals

1)Very Oxidizing Medium   nitric acid, (St. Steels).

2) Caustic Solutions , (Ni & Ni-alloys).

3) HCl , (Monel alloy).

4) Hot HCl , (Hastelloys –chlorimets).

5) Dilute H_2SO_4, (lead).

6) Oxidizing mediums , (Al-alloy).

7) Distilled water , (Tin).

8) Hot strong oxidizing solutions , (Ti).

9)For all conditions except for HF , (Ta).

10)Concentrated H_2SO_4, (carbon steel).

Metal purification :The corrosion resistance of a pure metal is usually better than of one containing impurities or small amounts of other elements .However , pure metals are usually expensive and are relatively soft and weak.

Nonmetallics:-

Solid nonmetallic construction and sheet linings or coverings of substantial thickness (to differentiate from paint coatings) .They are

1- rubbers ,   2- plastics ,   3- ceramics ,   4- carbon and graphite , 5- wood.

Rubbers & plastics are weaker , softer , and more resistant to chloride ions and hydrochloric acid than metals and alloys , but less resistant to sulfuric acid and oxidizing acids (e.g. nitric acid) , less resistance to solvents , low temp. limitations.

Ceramics possess excellent corrosion and high temp. resistance. but brittle and low tensile strength .

Carbons shows good corrosion resistance , electrical and heat conductivity , but they are fragile.

Wood is attacked by aggressive environments.

2)Alteration of environment

changing mediums :-

1   lowering temperature :In most cases the corrosion rate will be less or stop.But in some cases by reducing the Temp. the corrosive will be faster ,e.g. fresh water or seawater are less corrosive at high temp. because oxygen is removed from the water.

2   Decreasing velocity : Excepts for pitting and erosion corrosion all the other types of corrosion rate is reduced by reducing in velocity .SCC stop with increasing medium velocity because pitting is stopped.

3   Removing oxygen or oxidizer from the system :- For most metals except for St.Steels and Al alloys corrosion would stop by removing oxygen. (Stainless steel and Al have protected oxide layer) .

4   Reduction in concentration :- In all cases except in two cases (H_2SO_4 and H_3PO_4) the reduction in conc. Reduces the corrosion rate .They passivated the surface of metal in concentrated form .

3) Inhibitors :-

An inhibitor is a substance which , when added in small concentrations to an environment , decreases the corrosion rate .There are numerous inhibitor types and compositions. Inhibitors can be classify according to their mechanism and composition .

1) **Adsorption – type inhibitors :-** these represent the largest class of inhibiting substances .these are organic compounds which adsorb on metal surface and suppress metal dissolution and reduction reactions. Such as Organic amines.

2) **Hydrogen – evolution poisons :-** such as arsenic and antimony ions , specifically retard the hydrogen – evolution reaction . (acidic solutions).

3) **Scavengers :-** These substances act by removing corrosive reagents from solution. Such as sodium sulfite and hydrazine , which remove dissolved oxygen from aqueous solutions .

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$
$$Na_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

Oxygen reduction is controlling cathodic reaction , it is not effective in strong acid solutions.

4) **Oxidizers :-** Such substances as chromate , nitrate , ferric salts ,they are primarily used to inhibit the corrosion of metals and alloys which demonstrate active – passive transitions , such as iron and its alloys and stainless steels.

5) **Vapor – Phase Inhibitors :-** These are very similar to the organic adsorption – type inhibitors and possess a very high vapor pressure. As a consequence , these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with metal surface. The vapor-phase inhibitors are usually only effective if used in closed spaces such as inside packages or on the interior of machinery during shipment.

4) Design :

In designing a structure in a corrosive environments the following considerations are essential :-

i) Weld rather than rivet tanks and other containers. Riveted joints provide sites for crevice corrosion.

ii) Design tanks and other containers for easy draining and easy cleaning. Tank bottoms should be sloped toward drain holes so that liquids cannot collect after the tank is emptied.

iii) Design systems for the easy replacement of components that are expected to fail rapidly in service. Frequently, pumps in chemical plants are designed so that they can be readily removed from a piping system, since they fail frequently

iv) There should be uniform stress distribution in the structure , otherwise SCC or accelerated corrosion of higher stressed parts would occur.

v) Two – metal contacts should be avoided , otherwise there would be Galvanic Corrosion at the joints.

vi) A void sharp bends in the structure , otherwise there would be accelerated Erosion Corrosion.

vii) There should be uniforms distribution of air or oxygen in the system , otherwise Galvanic effect would happen .

viii) A void hot spots during heat –transfer operations. And a void heterogeneity ,Dissimilar metals , vapor spaces , uneven heat and stress distributions.
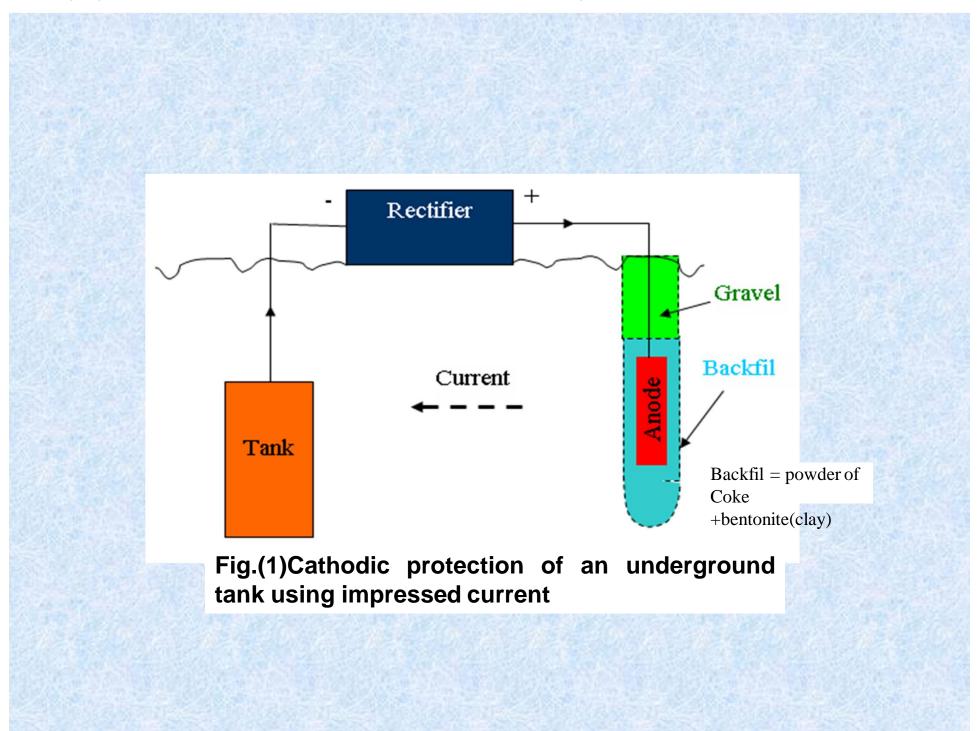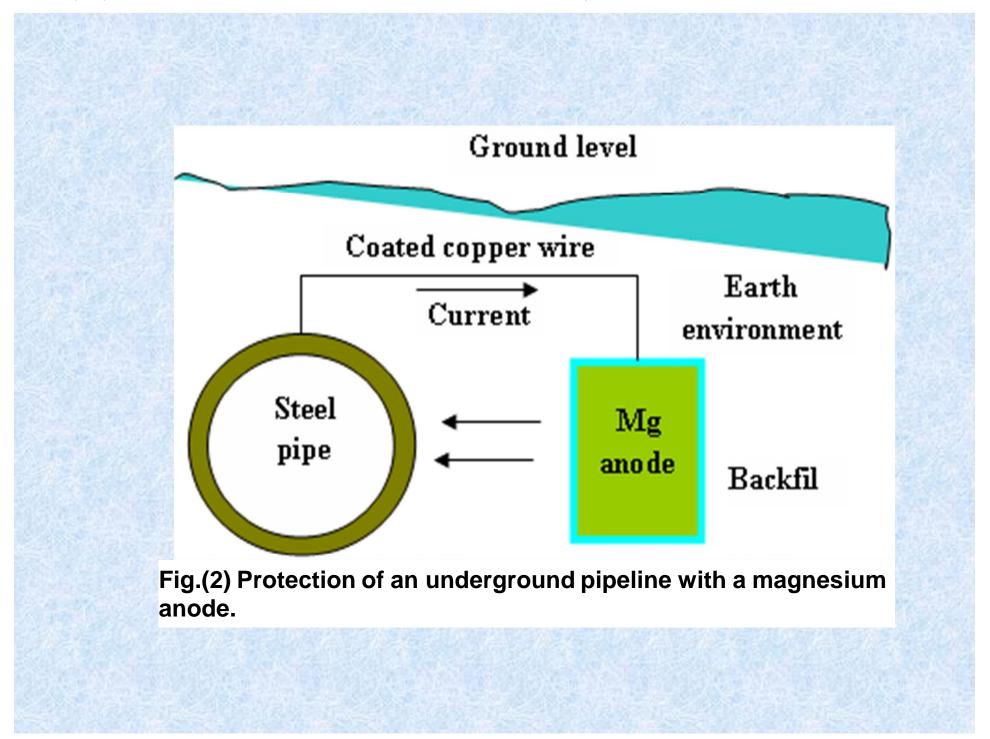
5) Cathodic and Anodic Protection

(I)Cathodic protection : The principles of Cathodic protection may be explained by considering the corrosion of a typical metal M in an acid environment.

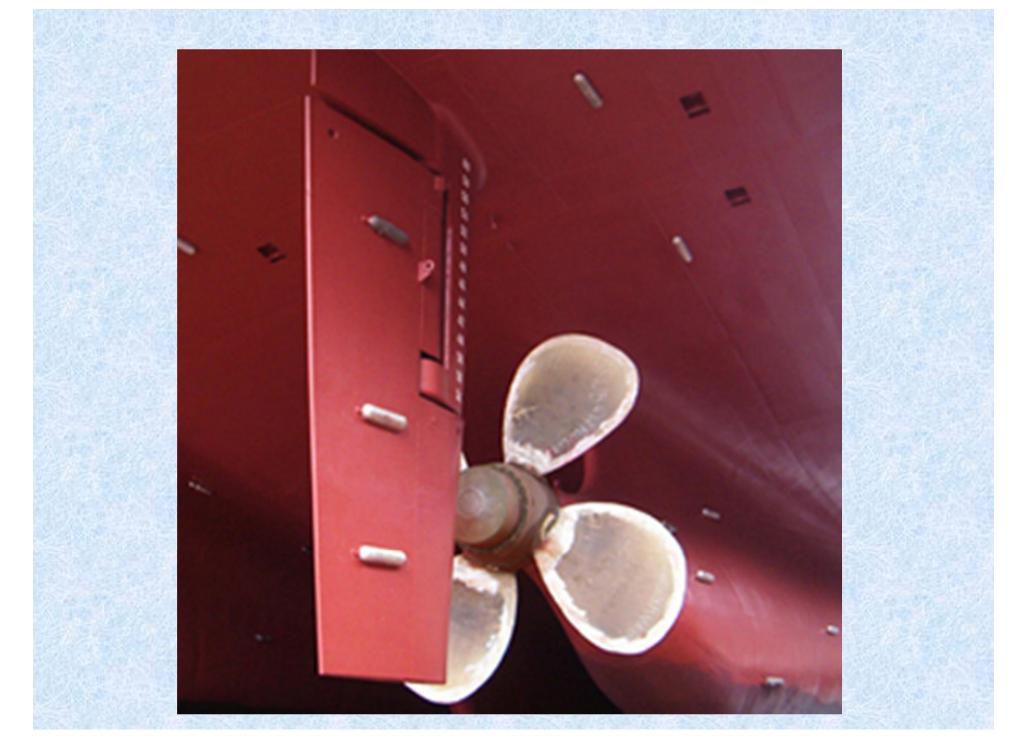$$M \rightarrow M^{+n} + ne$$

$$2H^+ + 2e \rightarrow H_2$$

Cathodic protection is achieved by supplying electrons to the metal structure to be protected. If current is considered to flow from (+) to (-) , as in conventional electrical theory , then a structure is protected if current enters it from the electrolyte. Conversely , accelerated corrosion occurs if current passes from the metal to the electrolyte. There are two ways to cathodically protect a structure :

(1) by an external power supply or , (2) by appropriate galvanic coupling .
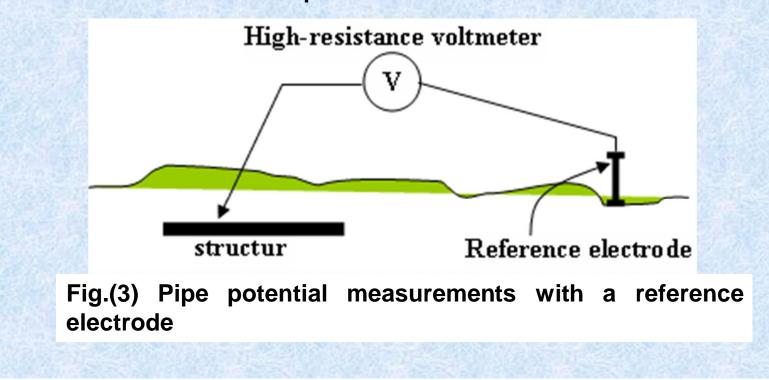
Fig.(1)Cathodic protection of an underground tank using impressed current

Fig.(2) Protection of an underground pipeline with a magnesium anode.

18.4 Standard Electrode Potential

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		(V)	
Stronger oxidizing agent ↑	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	Stronger reducing agent ↓
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Steel structures exposed to soils , fresh and brackish waters and sea water are protected if they are polarized to a potential of (-o.85 volt) versus copper/copper sulfate electrode. The potential of a structure is determined with a high-resistance voltmeter , during this measurement , the reference electrode is placed in ground or on sponge soaked in brine to make electric contact .The Cathodic current density necessary to polarize the pipe to (-0.85 volt) can be readily determined . In case of sacrificial anodes (e.g. Mg , Zn) are used , this same measurement is used to indicate the number and size of anodes needed for full protection.

High-resistance voltmeter

V

structur

Reference electrode

Fig.(3) Pipe potential measurements with a reference electrode

Anode selection for Cathodic protection is based on engineering and economic considerations. Table 1 compares several types of sacrificial and impressed-current anodes.

Table(1) comparisons of sacrificial and impressed-current anodes for Cathodic protection.

Sacrificial Anodes			
	Magnesium	**Zinc**	**Aluminum-Tin**
Theoretical consumption ,Lb/amp-year	9	23	6.5
Actual consumption, Lb/amp-year	18	25	16-20
Potential vs. Cu / CuSO4	-1.7	-1.15	-1.3

Stray – current effects are often encountered in Cathodic-protection systems. Stray current means extra current which is present in the soil near the industrial area , power a metallic object is placed in a strong current field , a potential difference develops across it and accelerated corrosion occurs at points where current leaves the object and enters the soil.
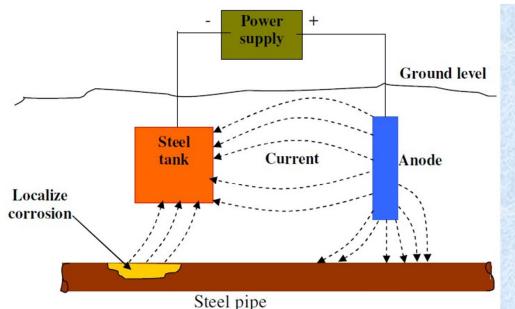
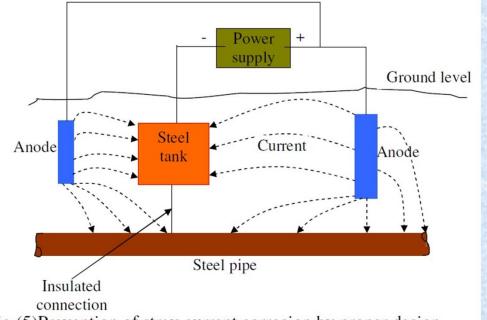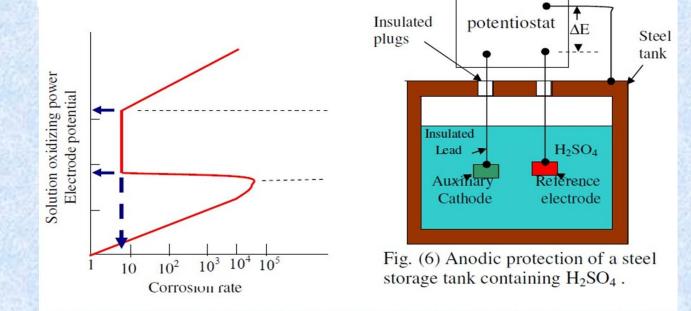Fig (4)Stray current resulting from Cathodic protection.

Fig.(5)Prevention of stray-current corrosion by proper design.

Fig.(4) illustrates stray currents resulting from a Cathodic-protection system. The buried tank catholically protected ,the pipe line Nearby will failed rapidly due to the stray-current filed. It is possible to applies Cathodic protection to prevent stray current attack , but it will produce stray current attack of the buried tank.

The solution to this problem is by electrically connecting the tank and pipe by a buss connector and rearranging anodes as shown in fig(5).In this system of protection a constant current is maintained or applied in order to maintain a constant potential difference.

(II) Anodic protection **:-** In contrast to Cathodic protection, anodic protection is relatively new. Anodic protection is based on the formation of a protective film on metals by externally applied anodic currents . Metals with active-passive transitions such as Nickel , Iron , Chromium , Titanium , and their alloys. If carefully controlled anodic currents are applied to these materials , they are passivated and the rate of metal dissolution is decreased. To anodically protect a structure , a device called a potentiostat is required. As indicted in fig. (6) . In operation, potentiostat maintains a constant potential between the tank and the reference electrode. The optimum potential for protection is determined by electrochemical measurements.

Fig. (6) Anodic protection of a steel storage tank containing H_2SO_4 .

Table (2) Anodic protection of Austenitic Stainless Steel at 30°C. (protected at 0.5 volts vs. Saturated Calomel Electrode)

| Alloy type | Environment (air exposed) | Corrosion rate, mpy | |
		Unprotected	Anodically protected
304 (19Cr-9Ni)	N H_2SO_4 + 10^{-5} M NaCl	14	0.025
	N H_2SO_4 + 10^{-3} M NaCl	2.9	0.045
	N H_2SO_4 + 10^{-1} M NaCl	3.2	0.20
	10N H_2SO_4 + 10^{-5} M NaCl	1930	0.016
	10N H_2SO_4 + 10^{-3} M NaCl	1125	0.04
	10N H_2SO_4 + 10^{-1} M NaCl	77	0.21

Anodic protection can decrease corrosion rate substantially. (Table 2) lists the corrosion rates of austenitic stainless steel in sulfuric acid solutions containing chloride ions with and without anodic protection. Although anodic protection is limited to passive metals and alloys, most structural materials of modern technology contain these elements. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements.

Comparison of Anodic and Cathodic Protection:

	Anodic protection	Cathodic protection
Applicability Metals	Active-passive metals only	All metals
Corrosion Relative cost	Weak to aggressive	Weak to moderate
Installation	High	Low
Operation	Very low	Medium to high
Throwing power	Very high	Low
Signification of applied	Often a direct measure of protected corrosion rate	Complex-dose not indicate corrosion rate

6) Coatings

Corrosion protection of over-ground and underground structures by protective coatings is one of the most proven methods. Coatings must have the following characteristics for good corrosion resistance:
  (a) a high degree of adhesion to the substrate .
  (b) minimum discontinuity in coating (porosity)
  (c) a high resistance to the flow of electrons.
  (d) a sufficient thickness (the greater the thickness , the more the resistance).
  (e) a low diffusion rate for ions such as Cl$^-$ and for H$_2$O.

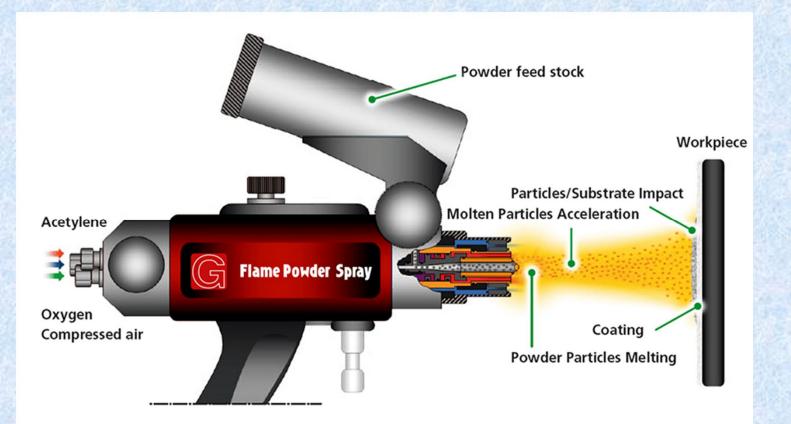## I) Metallic and Other Inorganic Coatings :-

Relatively thin coatings of metallic and inorganic materials can provide a satisfactory barrier between metal and its environment (sacrificial Zn coating) .

Metal coating are applied by electro deposition , flame spraying , cladding , hot dipping , and vapor deposition .

Inorganics are applied or formed by spraying , diffusion , or chemical conversion .

In both cases a complete barrier must be provided. Any porosity or other defects will accelerated localized attack . Examples of metal – coated galvanized steel, glassed steel tanks represents ceramic coating , also anodized aluminum and chromized steel .
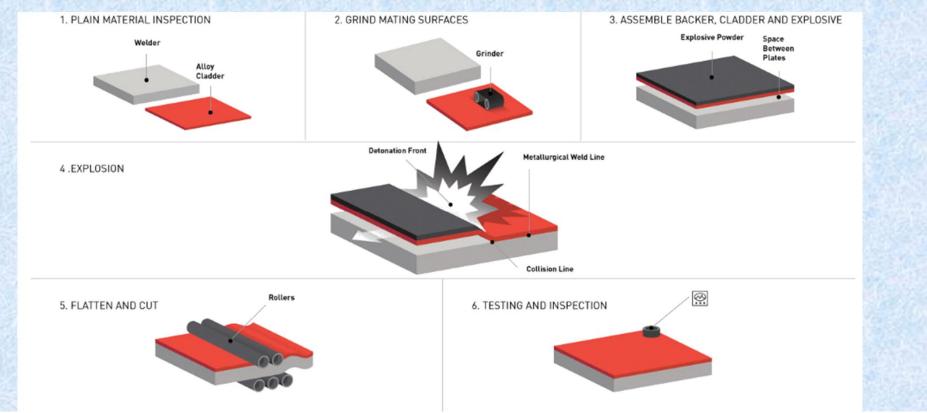
1-_Electro-deposition_ :-This process also called electro-plating , consists of immersing a part to be coated in a solution of the metal to be plated and passing a direct current between the part and another electrode. The character of the deposit depends on many factors including temperature , current density , time , and composition of the bath. For example an automobile bumper has an inner flash plate of copper (for good adhesion), an intermediate layer of nickel (for corrosion protection), and a thin top layer of chromium(primarily for appearance).

2)Flame Spraying :- This process , also called metallizing , consists of feeding a metal wire or powder through a melting flame

so the metal , in finely divided liquid particles , is blown on to the surface to be protected .High melting metals may be deposited by plasma- jet spraying .The coatings are usually porous and not protective under severe wet corrosive conditions.

3) *Cladding :-* This involves a surface layer of sheet metal usually put on by rolling two sheets of metal together. For example 0.25mm of nickel hot tolled with 3 mm of steel to produce a composite sheet. Cladding present a great economic advantage in that the corrosion barrier on expansive material is relatively thin and is backed up by inexpensive steel.
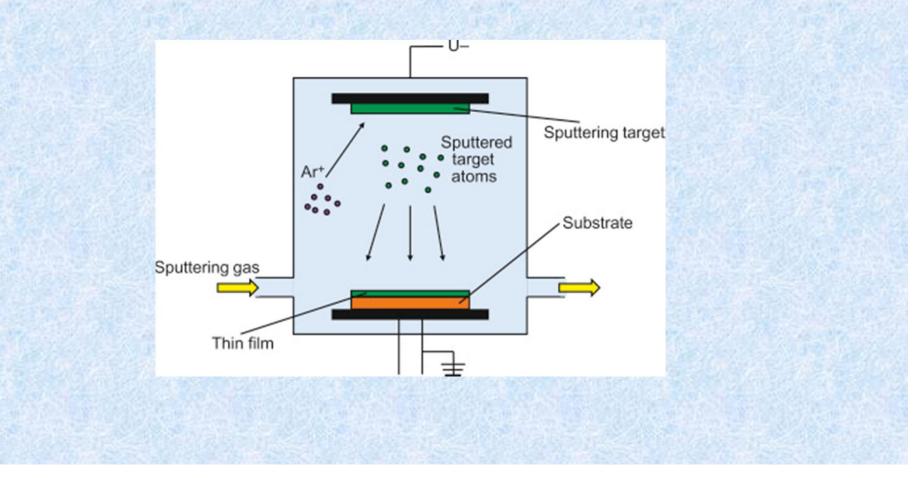

1. PLAIN MATERIAL INSPECTION
Welder
Alloy Cladder

2. GRIND MATING SURFACES
Grinder

3. ASSEMBLE BACKER, CLADDER AND EXPLOSIVE
Explosive Powder
Space Between Plates

4. EXPLOSION
Detonation Front
Metallurgical Weld Line
Collision Line

5. FLATTEN AND CUT
Rollers

6. TESTING AND INSPECTION
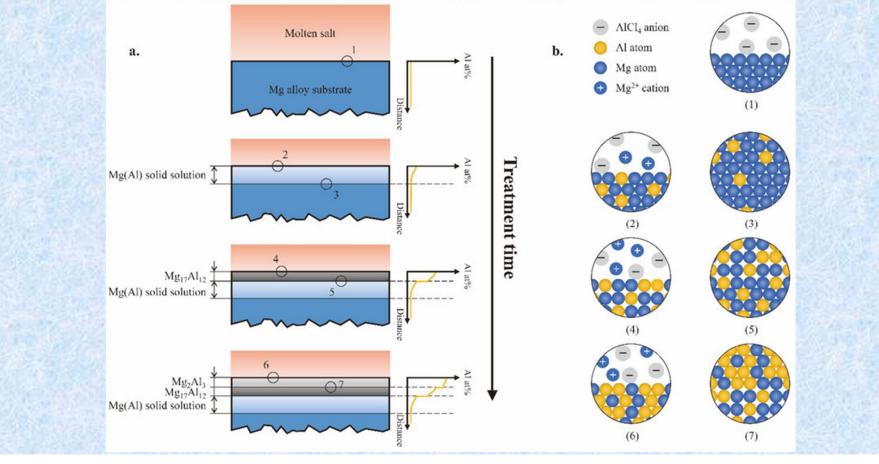
4)*Hot dipping :-* Hot dipping coating are applied to metals by immersing them in a molten metal bath of low melting point metals, chiefly Zinc , Tin , Lead , and Aluminum. Galvanized steel is a popular example. Thickness of coating is much greater than electro-plating.

5) *Vapor deposition :-* **This is accomplished in a high vacuum chamber. The coating metal is vaporized by heating electrically ,and the vapor deposits on the parts to be coated. This method is more expensive than others and generally limited to critical parts . For example high – strength parts for missiles and rockets.**

6) Diffusion :- Diffusion coatings involve heat treatment to cause alloy formation by diffusion of one metal into the other. This process is also termed **(surface alloying).** Parts to be coated are packed in solid materials or exposed to gaseous environments Which contain the metal that forms the coating. **Sherardizing** (zinc coating) , **Chromizing** (chromium) , and **Calorizing** (aluminum) are examples. In case of calorizing, the surface is oxidized to form a protective layer of (Al_2O_3). Calorizing and chromizing are utilized mainly for resistance to high – temperature oxidation.

7) *__Chemical conversion :-__* **Coating from chemical conversion are produced by "corroding" the metal surface to form an adherent and protective corrosion product.** *Anodizing* **consists of anodic oxidation in acid bath to build up an oxide layer. The surface layer is porous and provides good adherence for paints. The anodized surface can be "sealed" by exposing to boiling water. Additional examples are Bonderizing and Parkerizing (** *phosphatizing* **in a phosphoric acid bath) ,** *chromatizing* **(exposure to chromic acid and dichromates), and** *oxide* **or heat coatings for steel. Automobile bodies are the best known example of phosphatizing .**

❖*Glassed Steel* **or glass-lined , e.g., hot water tanks. The smooth surface is an advantage when ease of cleaning is requirement or sticky materials such as latex, are being handled**
❖*Concrete* **is utilized for many corrosion applications. Examples are encasing structural steel , concrete –lined pipe , and concrete vessels.**

II) *Organic   Coatings :-* **These involve a relatively thin barrier between substrate material and the environment. Paints , Varnishes , Lacquers , and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion. There are three main factors to consider for organic coating**

1) **Surface Preparation .**
2) **Selection of Primer or priming coat . And**
3) **Selection of top coat or coats .**

   Top coat is an organic coat and the Fe- phosphate is the primer(prime coating) it has Two purposes :-

1) **Acts as an inhibitor if the top layer is damaged.**
2) **Provides bounding medium between the metal and top layer.**

Surface   preparation **involves   surface   roughening   to   obtain mechanical bonding as well as removal of dirt , rust , mill scale , oil , grease , welding flux , crayon marks , wax and other impurities.**