

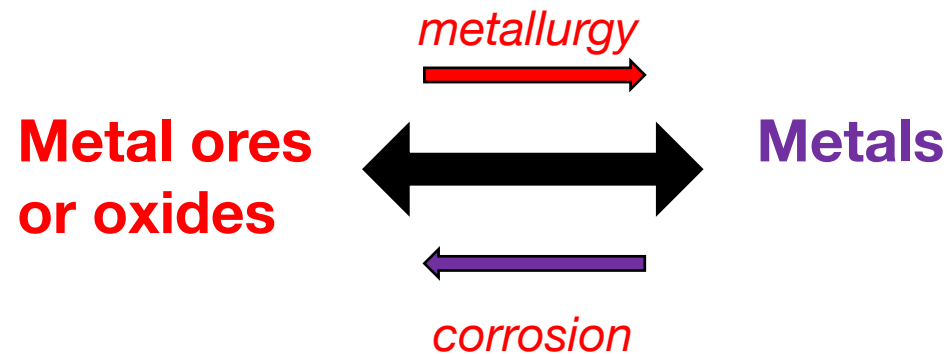
# MSc (Chemistry) II-Semester Physical Chemistry-II Unit-1 Corrosion and Electrochemistry



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# Corrosion

- ❖ **Definition:** Corrosion can be considered as a naturally occurring event which is the depreciation of a metal that results from a chemical or electrochemical reaction with its surroundings.
- ❖ Corrosion can also be considered as a reverse process of metallurgy where one extract the metal from its ores.



# Corrosion

A typical example of corrosion is rusting of iron that can be said to follow the following reaction:

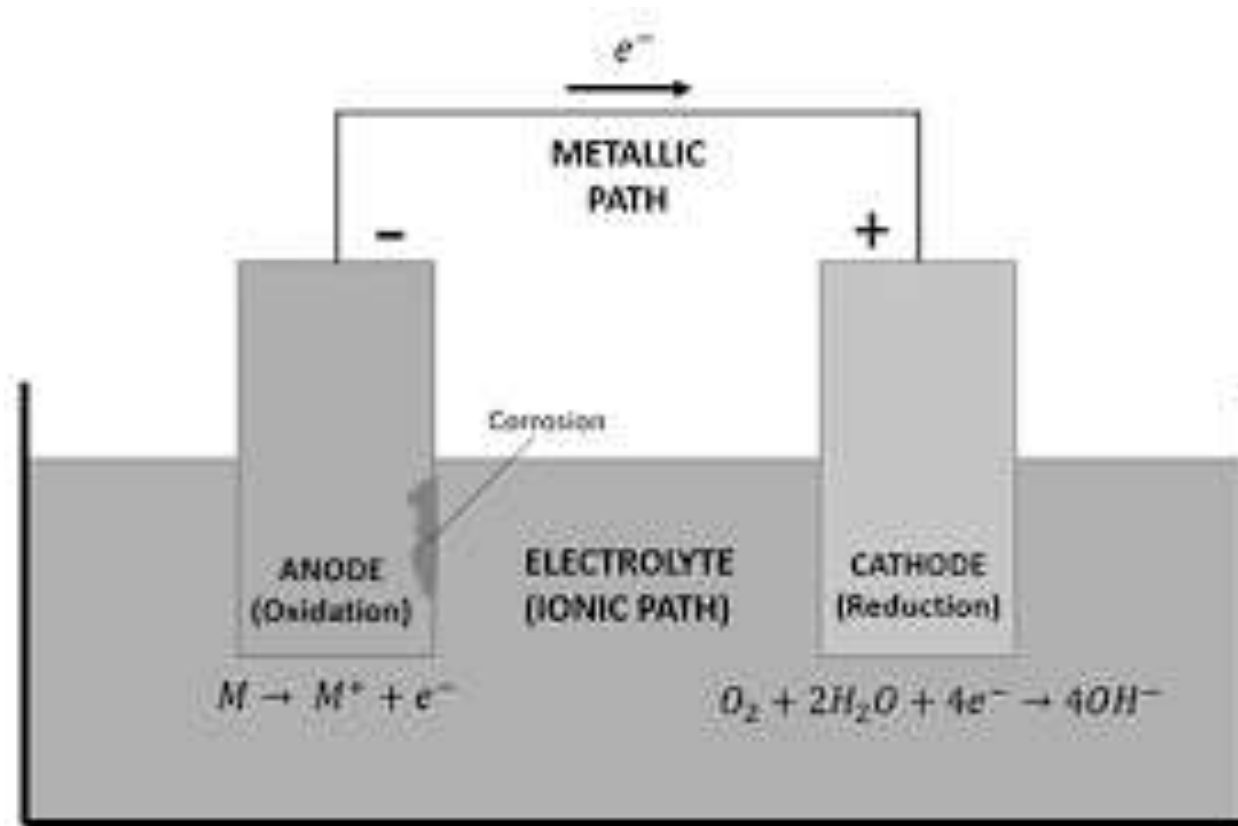


Some common problems associated due to the corrosion:

- (1) Damage or loss of the metal
- (2) Value of the goods is reduced
- (3) Contamination of water due to the water pipeline corrosion
- (4) Surface properties get affected

# Corrosion cell

**Corrosion cell:** Corrosion cell is a type of galvanic cell that is mainly considered as shown in below figure;



*Anode (corrosion):  $2Fe = Fe^{2+} + 2e$*

*Cathode (oxygen reduction):  $O_2 + 2H_2O + 4e = 4OH^-$*

# Corrosion

**Electrochemical theory of corrosion:** According to the electrochemical theory of

Corrosion, corrosion in a steel rod is considered to be of three main steps:

1- A large number of galvanic cells (corrosion cells) form on steel rod

2- Anode reaction starts on steel rod as following



3- Cathode reaction starts as following



3- Cathode reaction can occur in three different way depending on the surroundings



**Overall reaction:**



# Corrosion: Types

Types of common corrosions:

**Dry corrosion:** This type of corrosion takes place in the absence of moisture or liquid.

For example; oxidation of metal in the presence of air.

**Wet corrosion:** This type of corrosion takes place in the presence of moisture or liquid.

For example; water pipeline corrosion or corrosion in ocean going ships

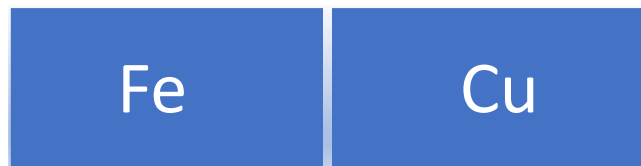


# Corrosion: Types

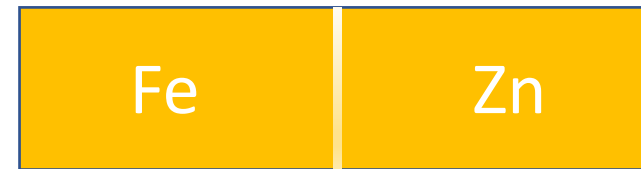
Common types of wet corrosion:

(1) Differential metal corrosion or dissimilar metal corrosion:

Galvanic series: This is a series where various metals and semimetals are listed based on their noble nature. At the top of the table, we have metals such as Au, Pt, Ag etc. Whereas at the bottom metals that can corrode very easily are kept. Generally in differential metal corrosion, the metals that are kept at the bottom undergo corrosion and they form anode of the galvanic cell.



Anode



Anode

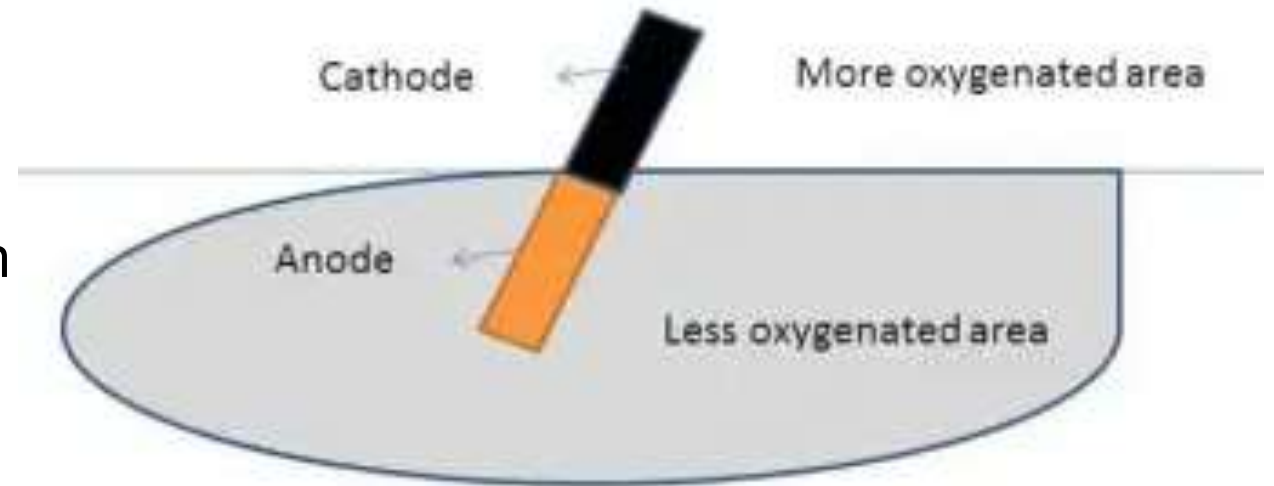


# Corrosion: Types

## (2) Differential aeration corrosion:

Differential aeration corrosion occurs when there is a difference in the amount of oxygen supply to different regions on the metal.

The region that has more oxygen supply becomes cathode and therefore, the region with limited supply of oxygen becomes anode and gets corroded.



At the anode, Less oxygenated area



At the cathode, more oxygenated area



# Corrosion: Types

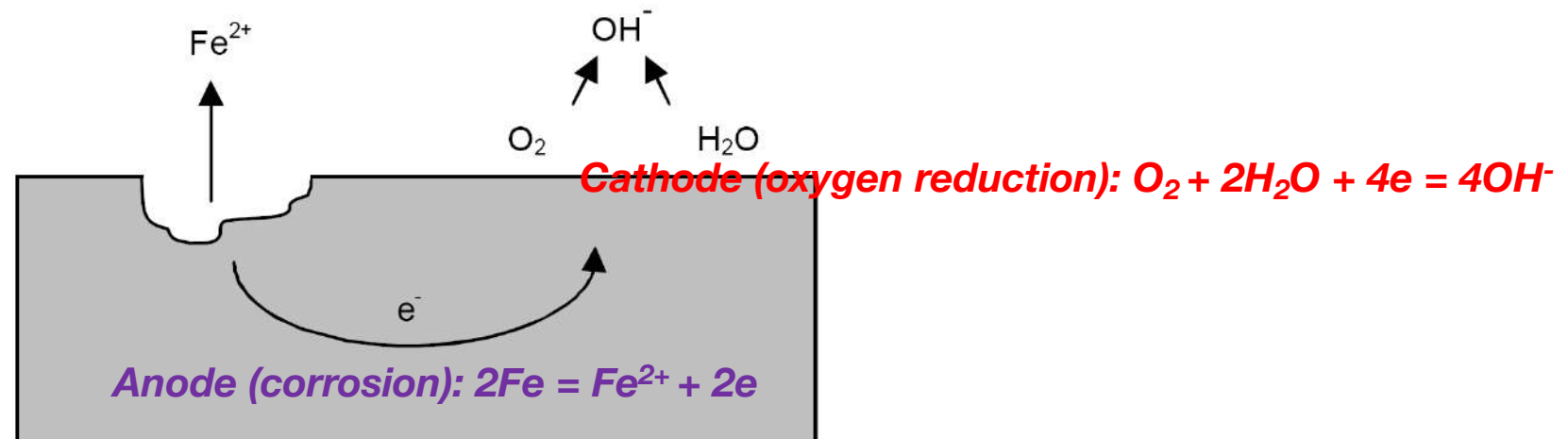
## (3) Crevice corrosion:

This type of corrosion is industrially very damaging and thus important to study. This corrosion occurs when a small volume of stagnant solution gets stuck in the crevices of machine parts e.g., nuts, bolts, screws, etc. A lower supply of oxygen in the crevices causes the crevice to get corroded with time.



# Corrosion: Types

- (4) **Pitting corrosion:** Pitting corrosion occurs when a small portion of metal is defective with cracks/pits. The accumulation of solution in pits then causes it to become anode and get corroded. This is also very dangerous type of corrosion as it may cause the whole industrial structure to collapse. It is also difficult to detect as the pits are often get covered with the rust.



# Corrosion: Types

**(5) Stress-corrosion cracking:** This type of corrosion is defined as a brittle fracture that is caused by the combined action of tensile strength and corrosive environment.

Some examples are corrosion cause by residual stress and hot/cold environment

**(6) Microbial corrosion:** Microbial corrosion occurs when degradation in the materials structure is caused by the microbes such as bacteria, fungi, etc. Certain types of bacteria can consume oxygen and deplete that region with oxygen. The depletion of oxygen then causes the differential aeration corrosion in the metal.

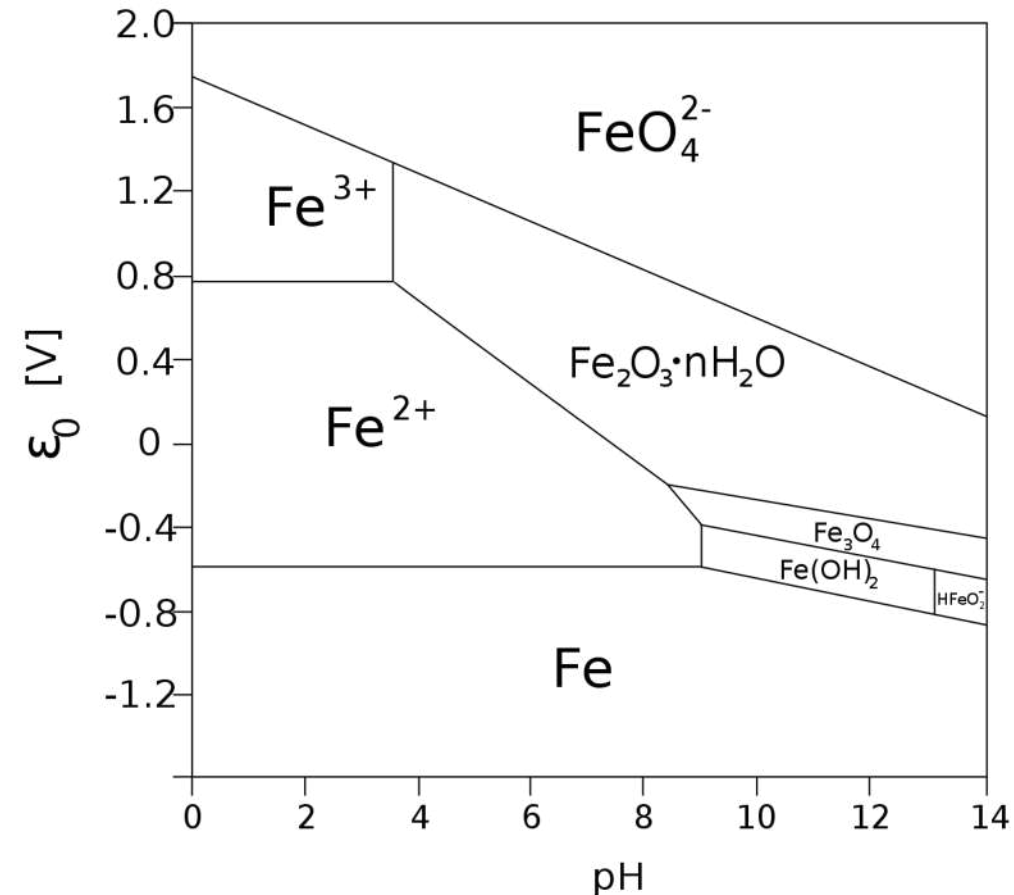
# Thermodynamics of Corrosion (Pourbaix plot)

## Pourbaix plot (Potential-pH plot):

Pourbaix plot for a metal shows that what metal species are stable under a given potential and pH conditions. A plot for Fe is shown here.

Lines and regions in the Pourbaix diagrams:

- (1) Horizontal lines: pure redox reactions
- (2) Vertical lines: pure acid-base reactions
- (3) Sloppy lines: combination of redox and acid-base reactions



# Corrosion measurements

**Weight loss method:** Corrosion rate is measured as following;

$$\Delta m / \Delta t \text{ or } \Delta x / \Delta t$$

$\Delta m = \text{weight change}$   
 $\Delta x = \text{thickness change}$

This method has advantages as this is a simple method with no significant instrumentations are required. However as the corrosion is often very slow therefore, this method is very time consuming and may take several days or even months.

**Open circuit potential (OCP) method:** Open circuit potential is also termed as the corrosion potential and it is measured in a sample when no external current is applied to the system and we only try to measure the naturally occurring potential. In a typical case a steel rod in the solution of HCl will

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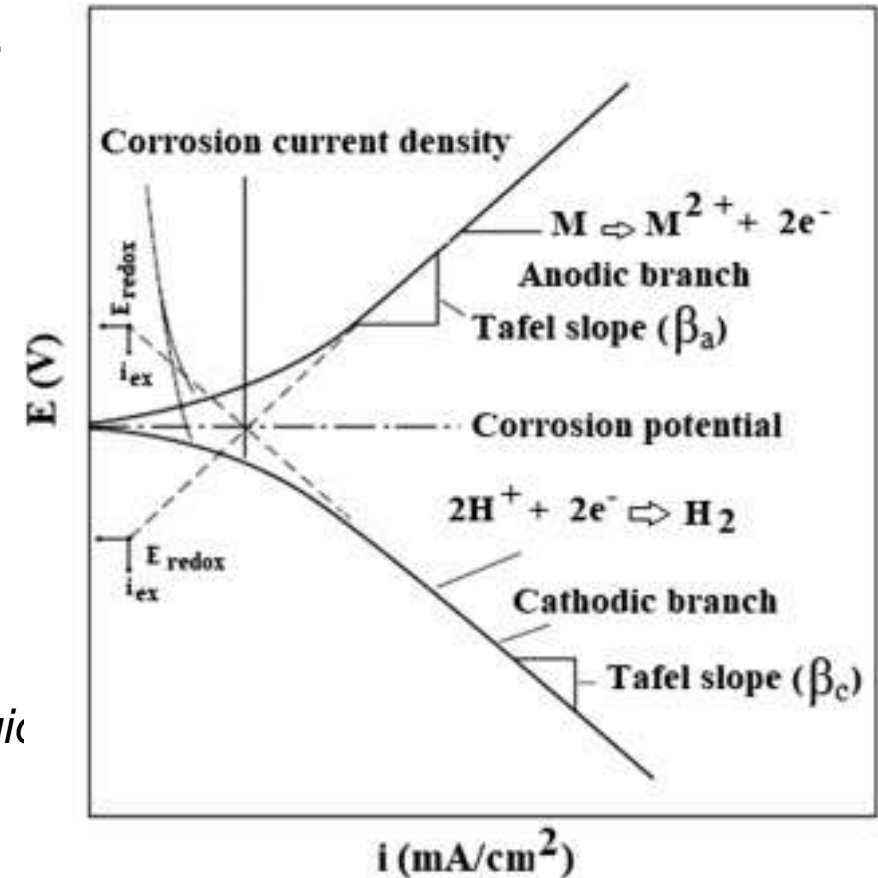
# Corrosion measurements

corrode because Fe can easily get oxidized to Fe ions in HCl .

When we try to measure the value of potential then we get a value of  $E_{cor}$  and this is known as the corrosion potential. A high  $E_{cor}$  value signifies a better corrosion resistance.

**Electrochemical Method:** Using the electrochemical method, we can quickly determine the Corrosion potential ( $E_{cor}$ ) and corrosion current ( $i_{cor}$ ). This method typically calculate the corrosion rates from the Tafel plots that is log I vs E plots.

Here  $E_{cor}$  and  $i_{cor}$  can be calculated by extrapolating the linear region of the Tafel plots where the two lines intersect.



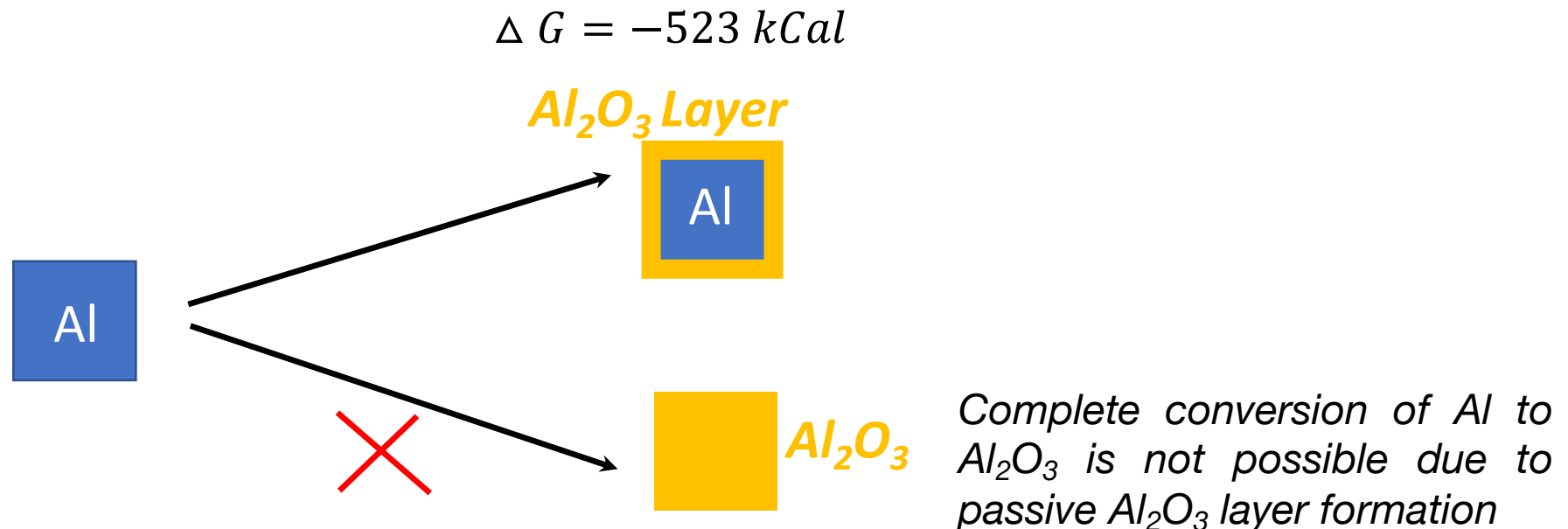
# Corrosion protection

**Passivity:** It is defined as the reduction in the chemical and electrochemical activity of a metal due to the formation of a thin film of passive protecting metal oxide on metal surface.

For example: formation of Al oxide layers on Aluminium.



The free energy for this reaction is highly negative and thus the reaction is feasible





# Corrosion protection

**Cathodic protection of metals:** It is defined as the combination of a metal with another metal that is more anodic in nature than the metal itself (i.e., a metal that is kept at lower place in the galvanic series than the metal that needs protection).

For example keeping Fe with Zn will make Zn to become more anodic and thus Zn get corroded and Fe is saved from corrosion. Here Zn acts as a sacrificial metal.

**Anodic protection of metals:** It is an electrochemical corrosion protection method wherein we control the corrosion of a metal surface by making it the anode of an electrochemical cell and we maintain the electrode potential in the region where the metal is passive. However, for this method to be successful, we need equipment such as potentiostat.

# References

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3. *National Association of corrosion engineers (NACE) portal* / [www.nace.org](http://www.nace.org)
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