

Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester
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Corrosion

Electrochemical series

(standard half-cell potentials vs SHE)

Li ⁺ /Li	-3.045 V	AgCl/Ag	+0.222 V
Ca ²⁺ /Ca	-2.864 V	Hg ₂ Cl ₂ /2Hg	+0.268 V
Na ⁺ /Na	-2.711 V	Cu ²⁺ /Cu	+0.338 V
Mg ²⁺ /Mg	-2.370 V	I ₂ /2I ⁻	+0.536 V
Al ³⁺ /Al	-1.700 V	MnO ₄ ⁻ /MnO ₄ ²⁻	+0.558 V
SO ₄ ²⁻ /SO ₃ ²⁻	-0.932 V	Fe ³⁺ /Fe ²⁺	+0.771 V
Zn ²⁺ /Zn	-0.763 V	Ag ⁺ /Ag	+0.799 V
Cr ³⁺ /Cr	-0.744 V	Pt ²⁺ /Pt	+0.963 V
Fe ²⁺ /Fe	-0.441 V	Cl ₂ /Cl ⁻	+1.358 V
Ni ²⁺ /Ni	-0.234 V	Au ³⁺ /Au	+1.498 V
Pb ²⁺ /Pb	-0.126 V	MnO ₄ ⁻ /Mn ²⁺	+1.531 V
H ₃ O ⁺ /H ₂	0.000 V	F ₂ /F ⁻	+2.866 V

Corrosion

- **Corrosion** is a general name for chemical and/or electrochemical processes that damage materials (usually metallic ones) as a result of contact with the surrounding environment (spontaneously).
- Corrosion takes place due to material contact with moist air, water (particularly salty one), moist soil or certain microorganisms. Corrosion can also occur due to contact with certain gases (particularly moist ones) or due to high temperatures (particularly frequently changing ones).

Corrosion

- Corrosion is a process in which metal (iron for instance) has a contact with water and forms a half-cell (Fe/Fe²⁺) as a result. As water always contains some H₃O⁺ ions, it forms H₃O⁺/H₂ half-cell, so metal starts to oxidize and its cations are dissolving in electrolyte.
- All metals with standard half-cell potential below 0 V vs SHE will corrode in water. The more acidic solution is (or it contains more chlorides or fluorides), the higher rate of the corrosion is.
- Corrosion can occur also in basic environment (through reaction with oxygen: O₂/OH⁻).

How corrosion occurs

Corrosion occurs in different ways: metal ions that are already formed at the metal surface can flow away (diffuse away) out of the surface vicinity, they can also react with ions available on site, like OH⁻, forming hydroxides/oxides; with sulfides, sulfates, chlorides, etc.
 Rust is a type of such metal behavior.

How corrosion occurs

Metals such as aluminum, copper or nickel also react with water or air, but their reaction product (oxide) is forming tight and homogeneous layer at the metal surface which is not permeable for water or oxygen (so the reaction stops quickly due to the lack of substrate). Such behavior is called **passivation** of metal and as a result of it metal is not corroding further (apart for the passive layer on the surface and as long as no other corrosion factor is introduced to the solution).

How corrosion occurs

Common example of corrosion resulting from chlorides presence is *aqua regia* dissolving gold – hydrochloric acid is providing chloride ions and nitric acid provides oxidizing and acidic environment. Gold chlorides that are formed are soluble in water, thus the gold is dissolving (in pure/acidic water gold is reacting to hydroxides and oxides that form thin passive layer on the surface).

- Patina is another example – copper usually passivates, however in the presence of sulfates (acid rains) forms complex salts containing sulfur that build on the copper surface and are permeable to more ions and water, thus enabling further corrosion.

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Corrosion types

Corrosion consequences are not only dissolution or metal transformation to salt, but also:

- Weakening of the material structure (salt brittleness);
- Volume (density) change resulting in change of stresses and/or cracking of object or exfoliation of the coating on the metal surface.

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Corrosion types

- uniform corrosion;
- pitting corrosion;
- crevice corrosion;
- stress corrosion (cracking);
- intercrystalline corrosion;
- selective corrosion;
- fatigue corrosion;
- hydrogen embrittlement.

Uniform corrosion

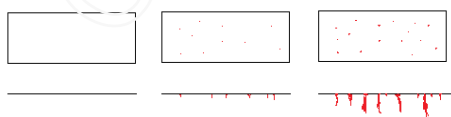
it occurs uniformly on the whole surface. It is assumed that it is homogeneous and small inhomogeneities of the surface are neglected. This type of corrosion often occurs in the acidic environment, where the oxide (or hydroxide) protective layers formation on the surface of the metal is hindered.

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Pitting corrosion

Pitting corrosion is one of the most important and dangerous types of corrosion.

Metal surface apparently looks good, however in the bulk of metal corrosion progress can be significant. Thus, it can seriously affect materials strength, for instance.



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Pitting corrosion

In case of this type of corrosion it is very hard to evaluate metal state, *i.e.* how long it can be still used until corrosion products will be visible on the other side of the metal plate (until it will break or be in danger of that). It is particularly important in case of systems in which state of metal is determining leakproofness of the reactor, pipe, ship, *etc.* All types of the industrial metals are susceptible to it (carbon/common steel, chromium steel, aluminum, titanium and their alloys). It results from the metal/alloy microstructure and its processing or its surface finish. Particularly, if its protective layer was compromised even slightly or it was not there.

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Crevice corrosion

It occurs everywhere the oxygen access is hindered. Most frequently it occurs at the elements links/joints: binders/filler metals, screws, washers, bolts, *etc.* It can also occur under the metal coatings, plastic coatings or paint coatings (commonly found). Particularly the non-tight coatings of metals (coatings usually should protect against corrosion) can cause the crevice corrosion.

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Crevice corrosion

Sometimes pollutants drifting onto the surface, like sand, corrosion products or other solid objects can cause this type of corrosion.

Non-uniform oxygen access can cause metal corrosion in the crevice (metal dissolves). Corrosion products are showing up on the surface at the mouth of the crevice where oxygen is available. Thus, the whole liquid environment in the crevice is acidified.

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Crevice corrosion – special case

So-called filiform corrosion is the special case of the crevice corrosion.

It can occur due to the local damage of the paint coating on steel, aluminum or magnesium.



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Stress corrosion cracking

it can be observed when two factors affect metal: continuous stress (usually the tensile one) and corrosion factors. Metal starts to crack in the place of the highest stress. Stresses can be a result not of the present stress only, but also of the inner stresses caused by the previous metalworking (treatment/processing).

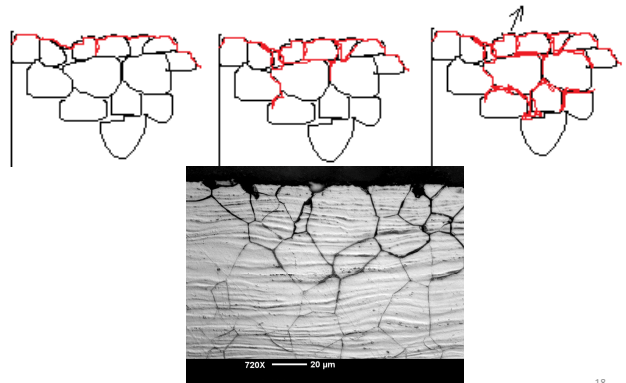
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Intercrystalline corrosion

It occurs in materials (particularly alloys), which contain grains of various metals. Regions with chemical constitution different than that of the grain bulk form at the grain boundaries. Corrosive environment attacks particularly that region of the alloy resulting in its destruction. If metal that is an object of this corrosion type sounds dully, it might be the result of huge structural damage inside (different phonon propagation than that of the non-corroded material).

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Intercrystalline corrosion



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Selective corrosion

It occurs in alloys in which one of the constituents is corroding much faster than others in a given environment. This type of corrosion is very common in austenitic-ferritic steels, two-phase brasses, cast iron and certain composite materials (e.g. nickel-tungsten fibers). Material with the lower potential becomes anode (dissolves), as always.

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Selective corrosion

Often it is acidity of the environment that has big influence on which metal will dissolve. For instance in nickel-tungsten composite:

- In acidic environment nickel will dissolve;
- In alkaline environment with oxidative additives tungsten will dissolve.

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Fatigue corrosion

This type of corrosion occurs in metals that are under variable stress in the corrosive environment.

Steps of the crack formation:

- slip bands formation; formation of intrusions/exclusions;
- cracking nuclei formation with 10 μm length;
- cracking nuclei growth;
- cracks formation and growth.

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Hydrogen embrittlement

It occurs as a result of the hydrogen presence in metal. Hydrogen penetrates metal at high temperatures and high pressures or during electrochemical processes that result in hydrogen evolution.

Hydrogen accumulation in intercrystalline spaces leads to the formation of hydrogen bubbles/gas cavities. These negatively affect metal mechanical properties (thus the name – hydrogen embrittlement, plasticity drop, delayed cracking).

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