

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

Anticorrosion protection

- Coating material with polymer layer (paint, varnish) is a most common way to protect metal against the corrosion.
- Due to the metal object use and/or violation of its structure (through riveting, welding, etc.) it is often hard to avoid crevice corrosion. It is not always possible to evenly coat the whole construction/object with the protective layer (and the untight coating can be more dangerous to the object than lack of such coating). Thus, it is common to use electrochemical anticorrosion protection.

3

Electrochemical series

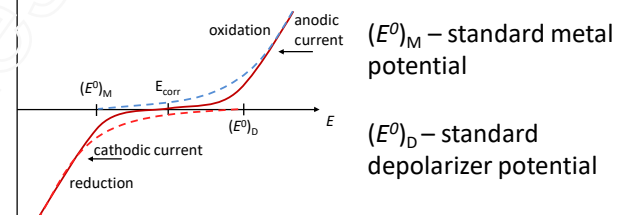
(standard half-cell potentials vs SHE)

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

2

Oxidation and reduction reactions

E_{corr} – mixed corrosion potential; it cannot be determined by the Nernst equation



In case of the corrosion the following relationship is always fulfilled: $(E^0)_M < E_{\text{corr}} < (E^0)_D$

4

Oxidation and reduction reactions

Half-reaction of metal oxidation:



Half-reaction of depolarizer reduction:



Oxidation rate and reduction rate are equal at the E_{corr} .

5

What is depolarizer?

Depolarizer can be any ion/molecule that can be reduced, such as H₃O⁺ or O₂.

Depending on the corrosion agent type, we call it corrosion with the:

- hydrogen depolarization, when
 $2H_3O^+ + 2e^{-} \rightarrow H_2 + 2H_2O$

It occurs when $E_{M^+/M} < E_{H_3O^+/H_2}$

- oxygen depolarization, when
 $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$

It occurs when $E_{M^+/M} < E_{O_2/OH^{-}}$

6

Pourbaix diagram

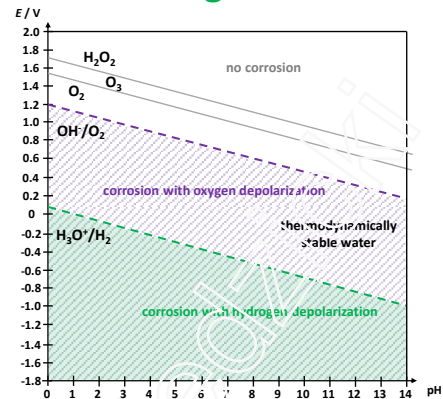
Pourbaix diagram is one of the most common tool for determining the most suitable anticorrosion protection.

Pourbaix diagram is a plot of reaction potentials against the pH of the reaction environment.

Thus, it is possible to determine, if metal in the given environment undergoes corrosion or if it will be protected with its own oxide layer (passivation).

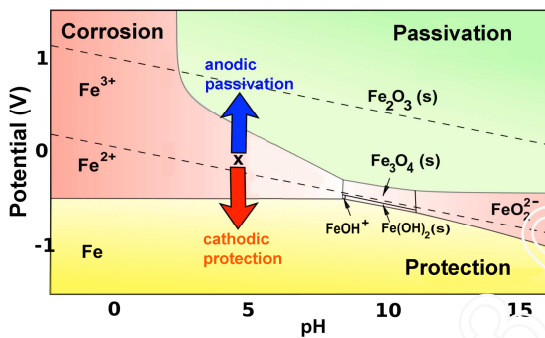
7

Pourbaix diagram for water



8

Pourbaix diagram for iron



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9

Pourbaix diagram - shortcomings

Pourbaix diagram provide a lot of useful information. However, they do not say anything about the rate of corrosion. The sole fact that process (corrosion) occurs does not always mean that it is very harmful. It is determined by the rate of it.

10

Anticorrosion protection

One of the possibilities is selection of such conditions (environment) so the metal coating (naturally occurring or formed at the given conditions) was in its stable state (for instance, in the area of insoluble oxide occurrence).

As environment (pH, ions present) usually cannot be chosen, one can select construction material resistant to the environment or the way to protect it against the corrosion.

11

Anticorrosion protection methods

1) Cathodic protection can be realized by:

- sacrificial anodes;
- external current source (cathodic stations);
- electric drainage.

2) Anodic protection can be realized by:

- sacrificial cathodes;
- external direct current source (potentiostats);

12

Cathodic protection in case of iron

It consists in potential reduction for this metal, until it is in the stable range. Due to the use of external current source, the potential of the protected object can be controlled precisely.

13

Iron protection – sacrificial anodes

Sacrificial anodes are made of metals with the lower electrochemical standard potential (than that of protected metal). That way the protected object becomes a cathode (thus the name – cathodic protection).

Iron is usually protected by sacrificial anodes made of zinc, magnesium or aluminum alloys.

14

Sacrificial anodes

Protection by sacrificial anodes does not require any electricity source, although it requires regular inspection of their state and exchange to new ones.



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Zinc sacrificial anodes

15

Anticorrosion protection

Small structures/objects are protected by coating with the protective metal (sacrificial material, anode), bigger ones, like ship hulls, are protected often by sacrificial anodes (and by other methods as well).

16

Anticorrosion protection

Active cathodic protection can be realized by connections between the protected object and the external direct current source and from the protected object to the non-corroding material (in the given environment) like graphite or platinum.

Providing electrons from outside hinders giving up electrons by metal atoms (constant metal reduction enforcement).

This way the pipelines and fuel tanks at gas stations are protected.

17

Stray currents

Stray currents formation is one of the electrochemical corrosion causes. They can be formed by welding, for instance. Stray currents are also produced by current leakage from the streetcar/railway electric traction. This type of the corrosion is harmful not only to the tractions themselves, but also to the underground structures nearby, like pipelines.

Protection against stray currents is realized through connection between rails (current source), and underground structure (like pipeline).

18

Anodic protection

In this type of protection passivation of metals is used. Protected metal (which is an anode) is connected to another metal with higher standard electrochemical potential.

Three conditions have to be fulfilled:

- there is potential range at which corrosion rate is negligible (and passivation occurs);
- environment is stable over time at the given potential (no changes in environment composition);
- lack of "aggressive" ions – destroying oxide layer on metal (thus forming different Pourbaix diagram).

19

Other anticorrosion protection methods

- protective coatings – paints, polymers, varnishes, *etc.* (work only when airtight);
- selection of protected object shape – turbulent flow/stirring increase corrosion risk/rate (mechanical blows of liquid to object, blows of mechanical impurities in liquid, cavitation related effects);
- modification of environment – use of corrosion inhibitors; solution deoxidation;
- Alloying/alloy additive use for protected object metal material.

20

Paint coatings, polymeric coatings

Their main aim is to physically separate protected object from the environment. It is crucial that coating has to perfectly adhere to the protected surface and to be airtight. Unfortunately, if the coating should be even slightly damaged, risk of crevice corrosion increases. Upon damage, coating detaches from the metal surface.

Some coatings can be not resistant to high (melting, decomposition) or very low (cracking) temperatures.

21

Paint coatings

In case of paint protection the surface usually is protected with a number of layers:

a) **primer** – has to adhere well to the surface to ensure the following properties:

- isolating – mechanically and electrochemically (resins containing pigments like oxides of iron, zinc and titanium);
- passivating – passivation of metal substrate underneath (as a pigment, *e.g.* Pb_3O_4);
- protective – isolating but electrochemically protective as well (corrosion-inhibiting pigment: Zn or Al dust);

22

Paint coatings

ad a)

- reactive – reacting with corrosion products, thus it is possible to paint corroded surface – thus obtaining tight, well adhering layers.

b) **undercoat paint** – its aim is to tighten the paint layer, decrease permeability and obtain required thickness of the layer.

c) **topcoat paint** – its aim is to provide the resulting coating additional properties such as: increased abrasion/wear resistance, inhibition of algae growth, increased high temperature resistance.

23