

Types of Metallic Corrosion and Anticorrosive Methods

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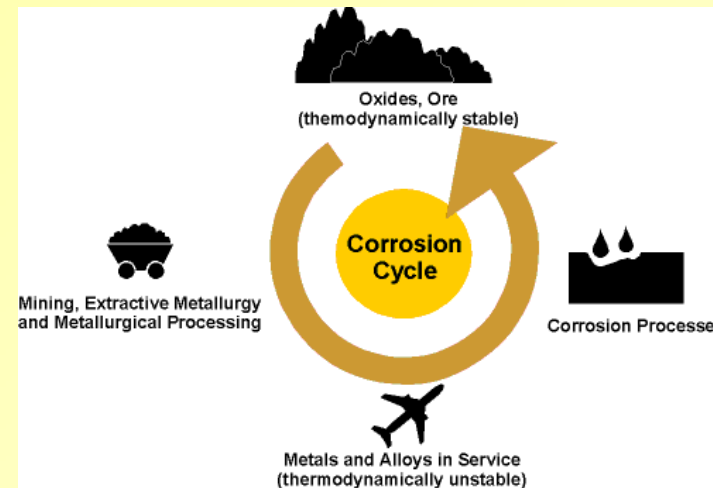
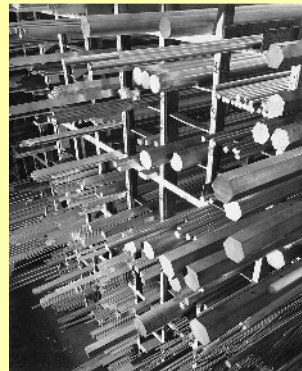
RECAPITULATION

What is corrosion?

Corrosion of metals x Degradation of materials

Economic impact of corrosion

Metallurgy vs corrosion



Thermodynamics and Kinetics

RECAPITULATION

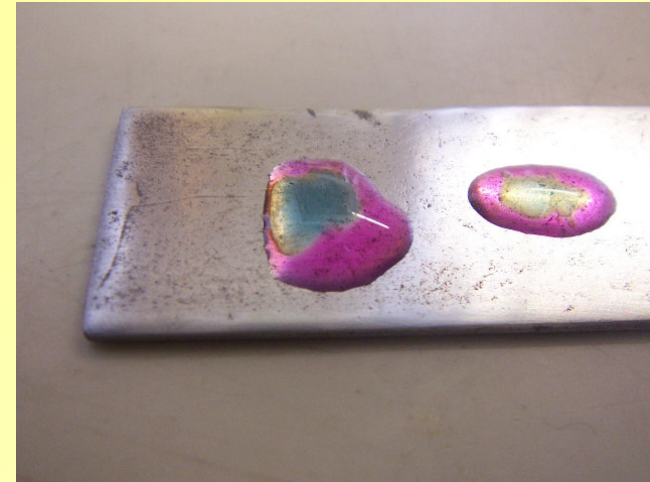
“Wet” corrosion

All metals can corrode

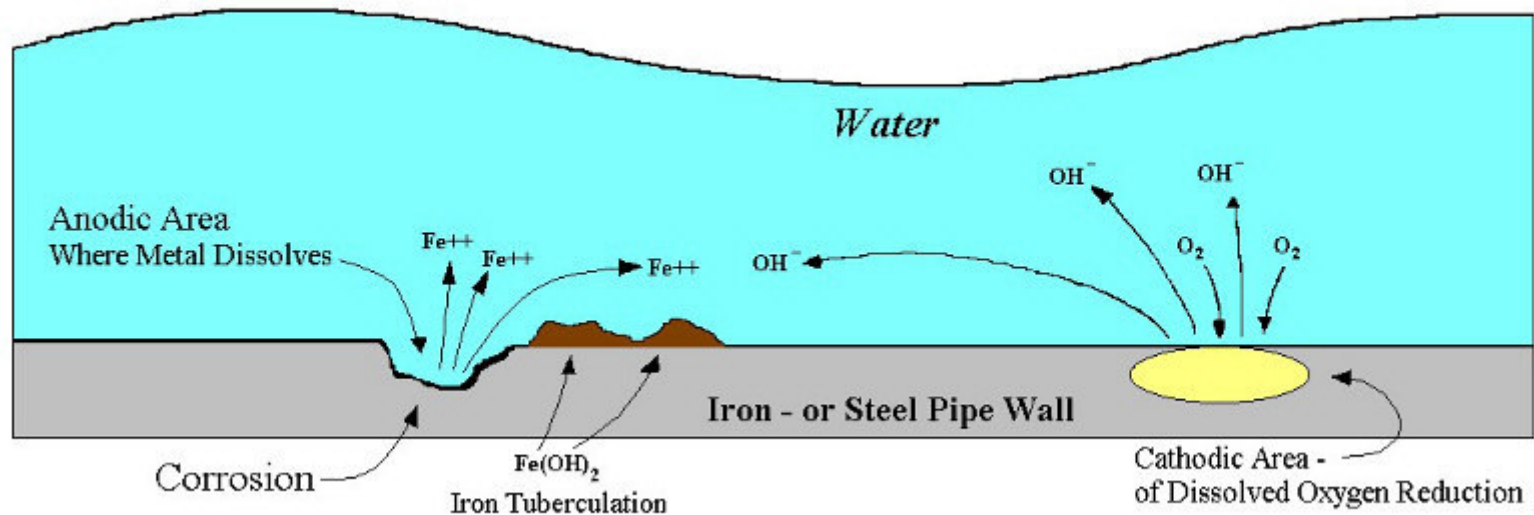
Processes are similar

Electrochemical mechanism of corrosion

2 half-reactions separated in space occurring simultaneously



The Corrosion Cell :



UNIFORM OR GENERALISED CORROSION



Attack takes place over the entire area or at a large fraction of it.

The attacked area is divided in minute anodic and cathodic regions, that switch place with time.

Accounts for the greatest tonnage of metal consumed.

Easy to detect, rarely leads to disastrous failures.

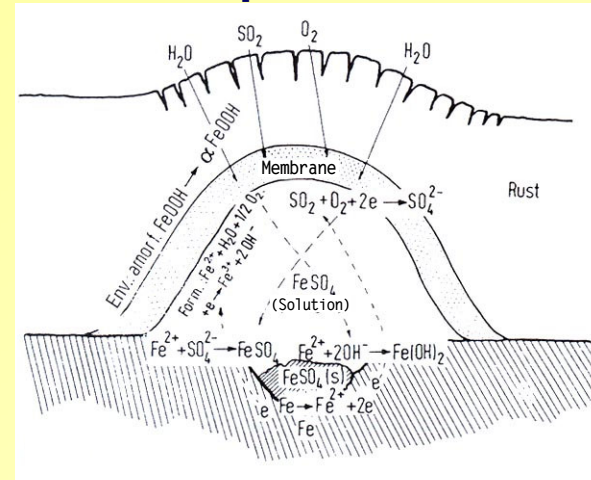
Usually, appearance is the main problem.

Typical examples:

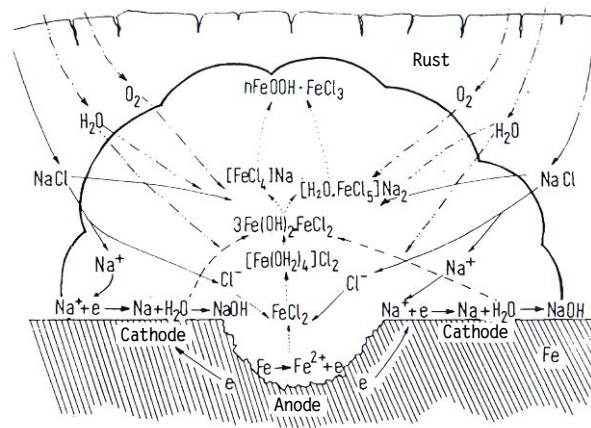
- atmospheric corrosion,
- steel corrosion in acid solution.



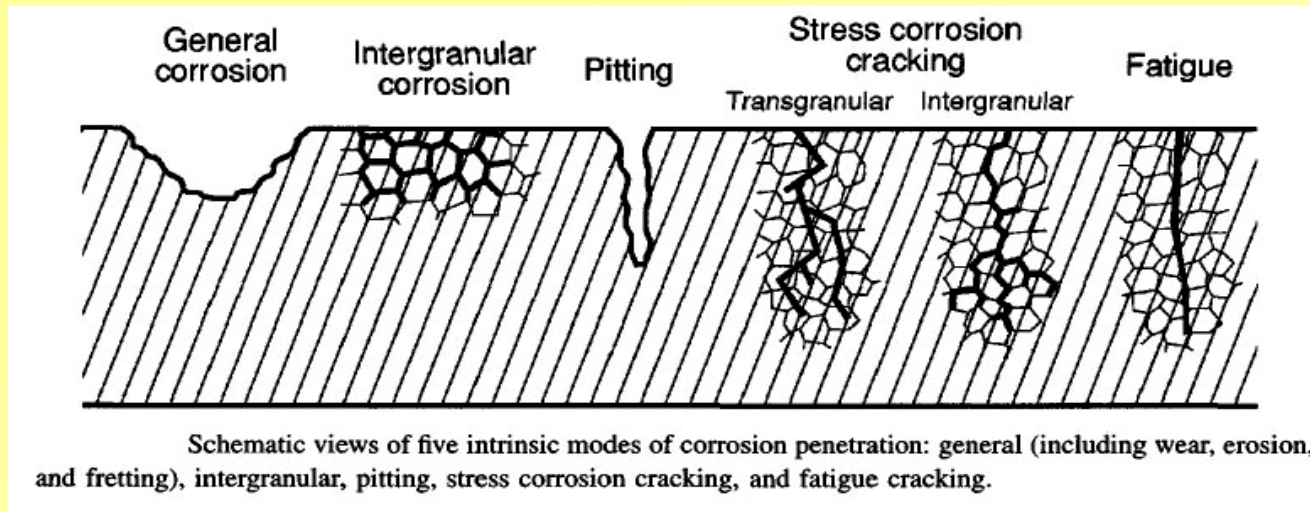
Sulphate nest



Chloride Agglomerate



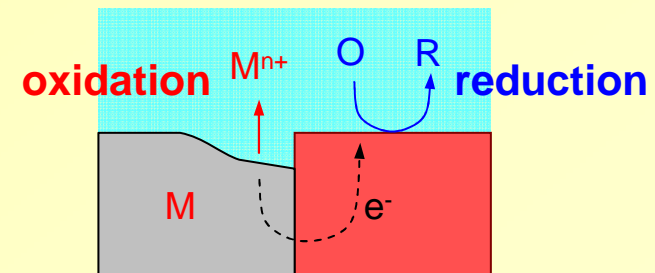
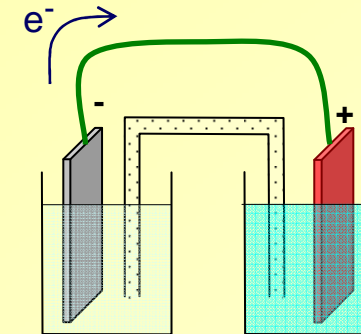
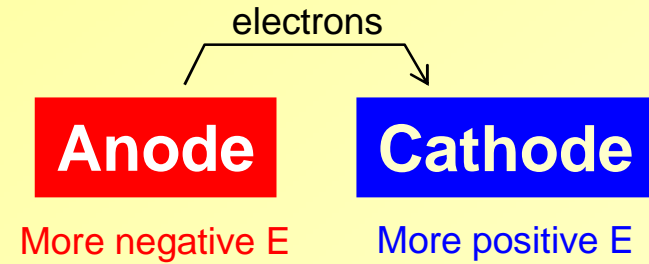
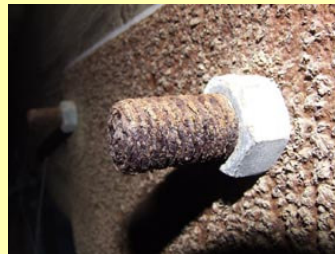
GENERALISED VS LOCALISED CORROSION



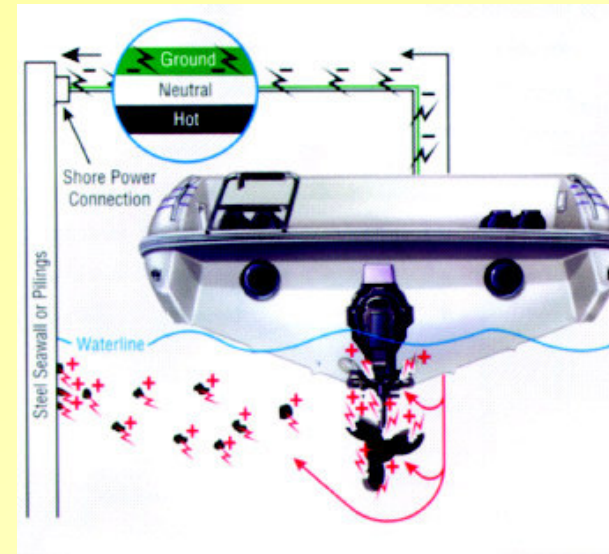
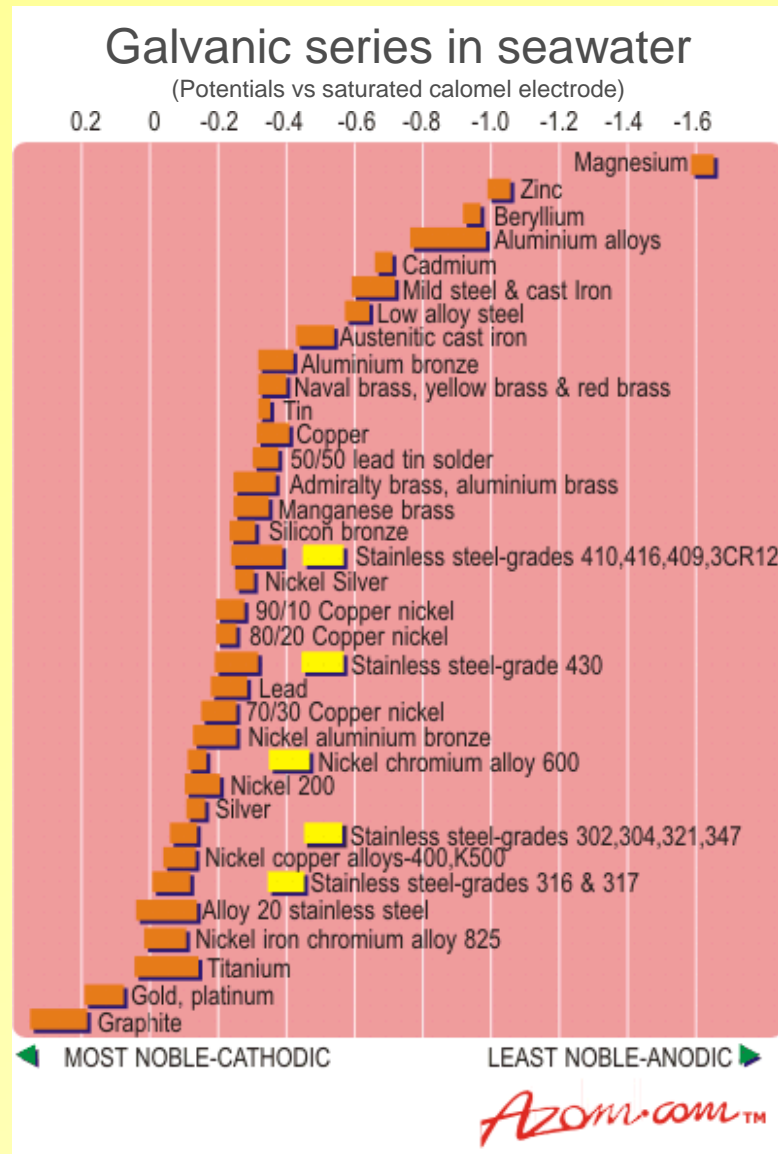
Uniform Corrosion	Localised corrosion
All over the surface	Metal oxidation occurs in localised points usually with high current densities
Easy to detect, measure, predict and control	Difficult to detect, measure, predict and control
Loss of appearance is the main problem Rarely leads to disastrous failures	Failure is often unpredictable leading to disastrous failures
Large loss of material	Small loss of material
	Much more dangerous!

GALVANIC CORROSION

A metal is electrically connected to a different metal (or other conductive material) in a corrosive environment.



GALVANIC CORROSION



SELECTIVE CORROSION

(dealloying, selective leaching)

Removal of a metal from an alloy by galvanic interaction with a more “noble” metal in the same alloy.



Dezincification (ex: Cu-Zn alloys with Zn > 15%)

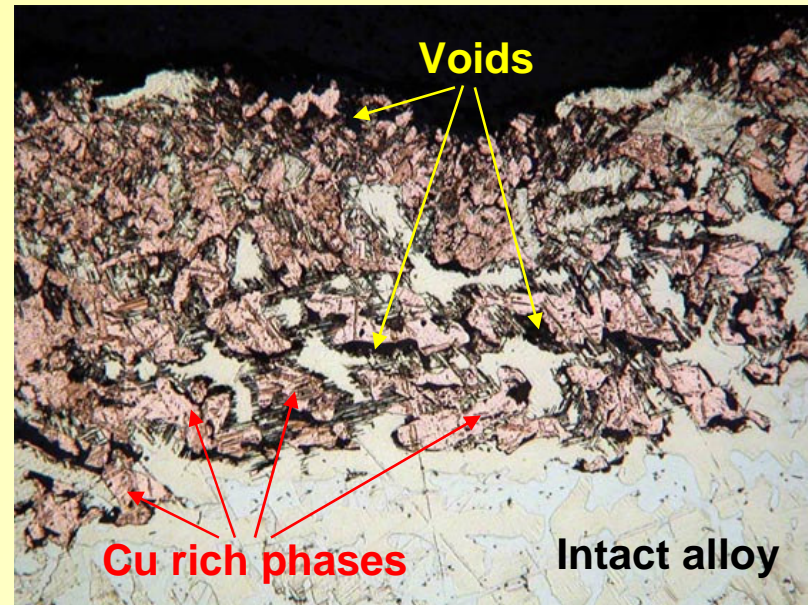
Decobaltification

Denickelification

Dealuminization (Dealuminification)

Graphitic corrosion (ex: gray cast iron)

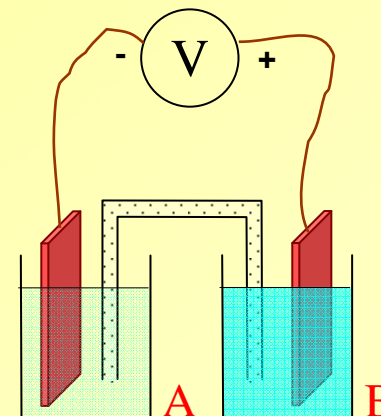
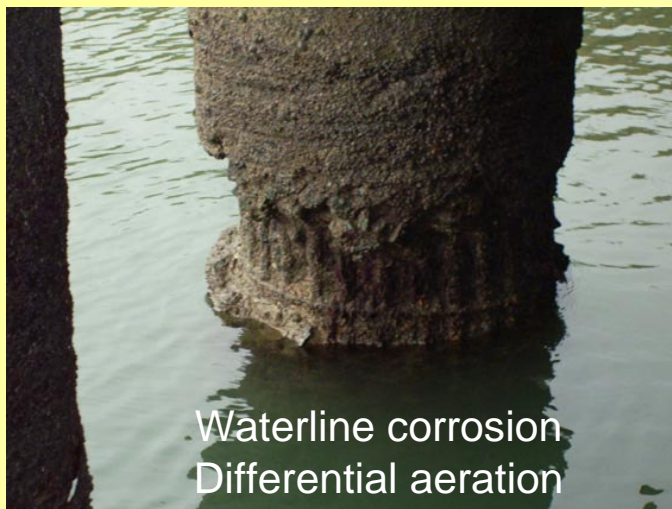
Decarburization



CONCENTRATION CELLS

- Salt concentration cells
- Differential aeration cells
- Differential temperature cells

$$\Delta E = (E_A^\circ - E_B^\circ) + \frac{RT}{nF} \ln \frac{a_A}{a_B}$$



Differential temperature cells

Heat exchangers, boilers, immersion heaters, etc

Cu: hot electrode is cathode; cold is anode.

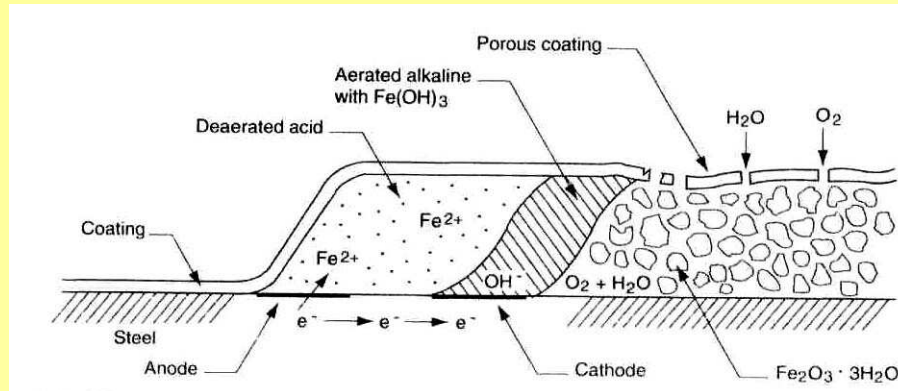
Copper dissolves in the cold electrode and deposits on the hot electrode. **Pb** is similar but **Ag** is reversed.

Fe in NaCl: hot is anodic to cold electrode, but after several hours the polarity may reverse, depending on aeration, stirring rate and whether the two electrodes are short-circuited.



CONCENTRATION CELLS

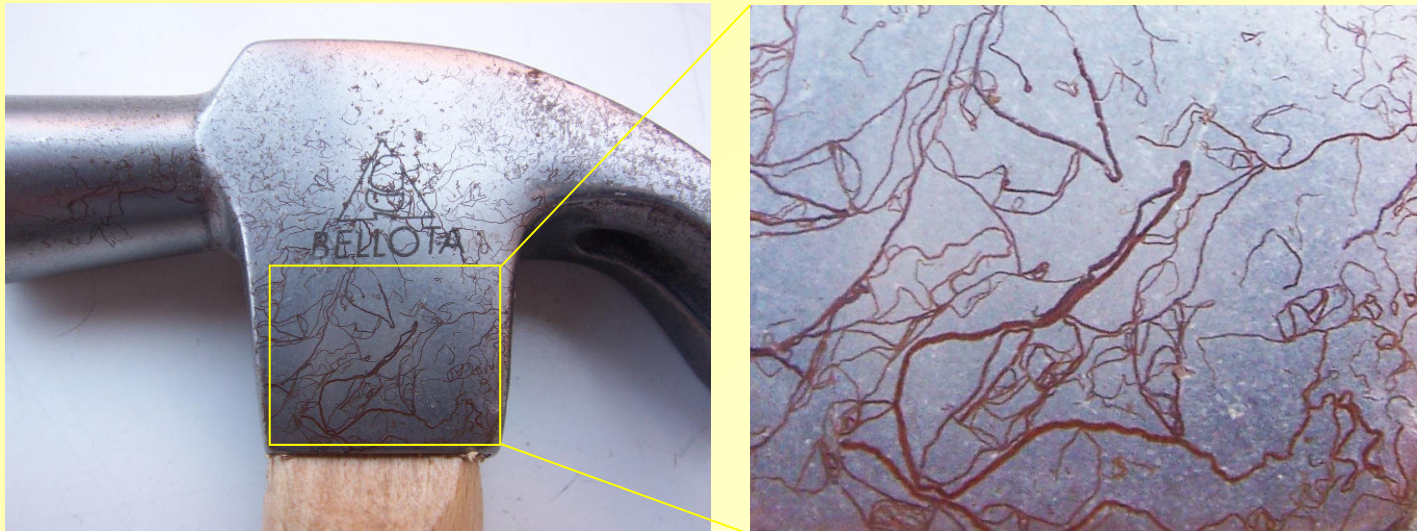
FILIFORM CORROSION



A special form of O_2 concentration cell which occurs on metals covered by an organic coating.

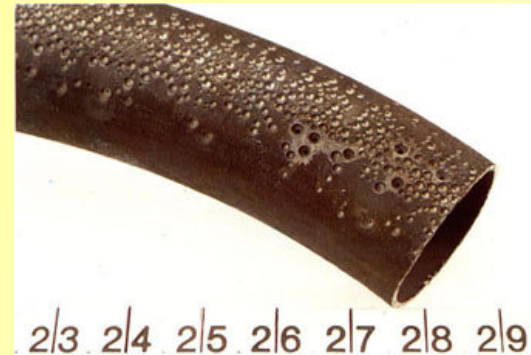
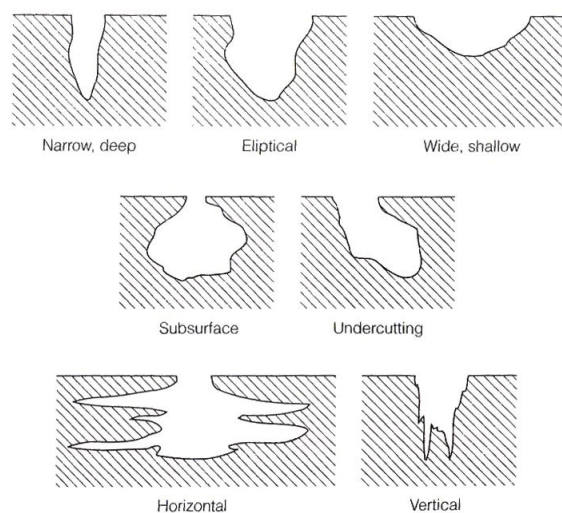
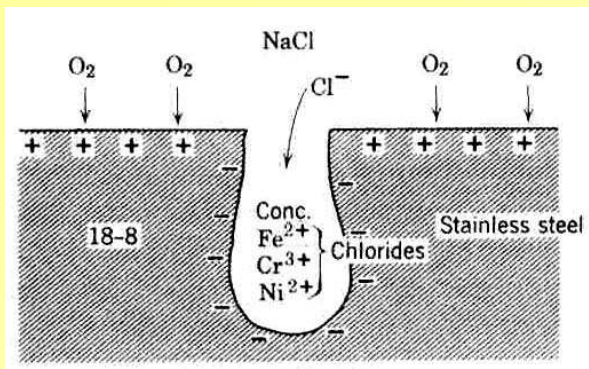
Recognized by its characteristic worm like trace beneath the paint film.

Common in steel and Al alloys.



PITTING

Typical of passive metals (stainless steels, Al and Ni alloys) in the presence of chlorides.
Starts with depassivation in localized points which become anodic while the remaining area acts as cathode.
High current densities lead to rapid localised loss of material.



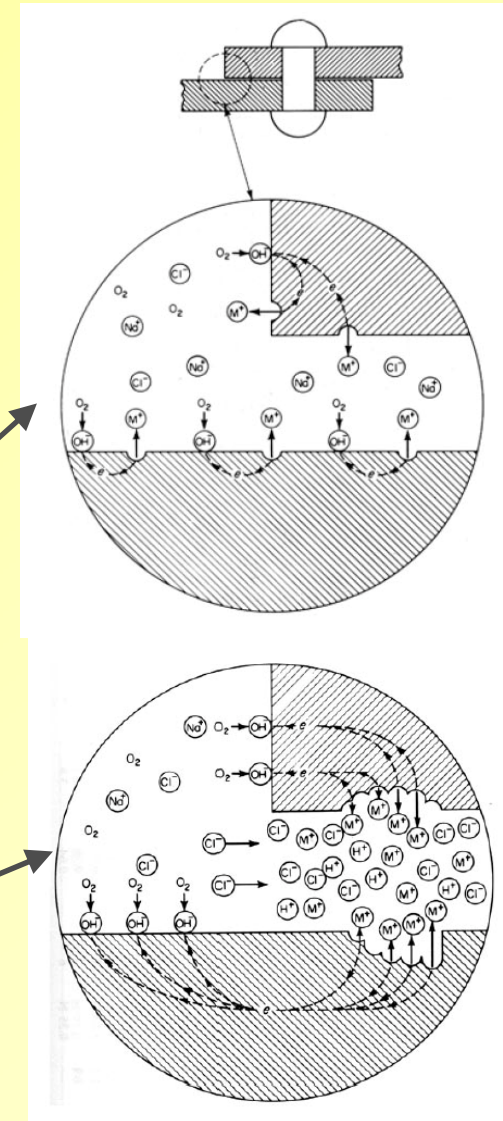
CREVICE CORROSION

Occurs at crevices in passive metals

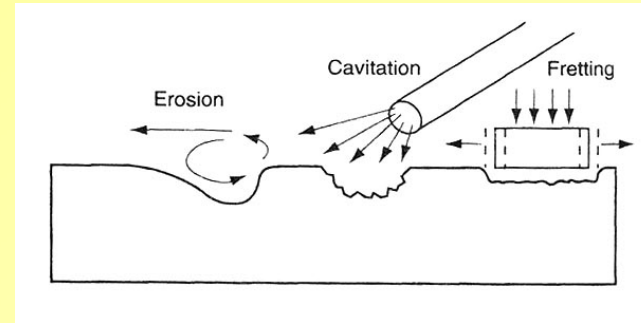


Starts like a differential aeration cell

Continues following pitting mechanism



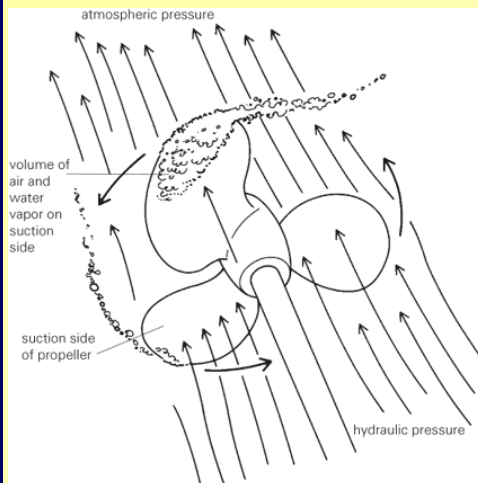
CORROSION + MECHANICAL ATTACK AT THE SURFACE (Removal of protective film)



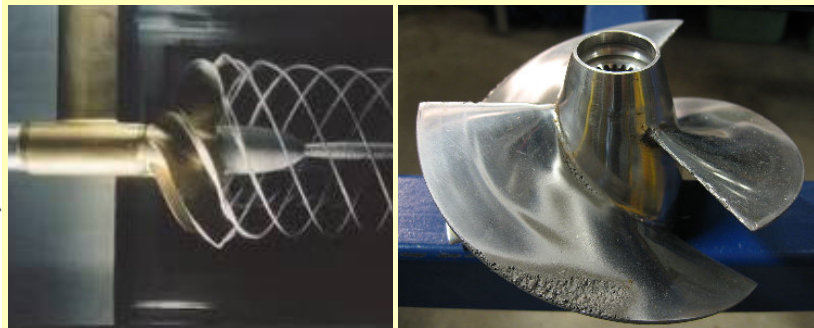
FRETTING



Surface against surface, often from vibration.

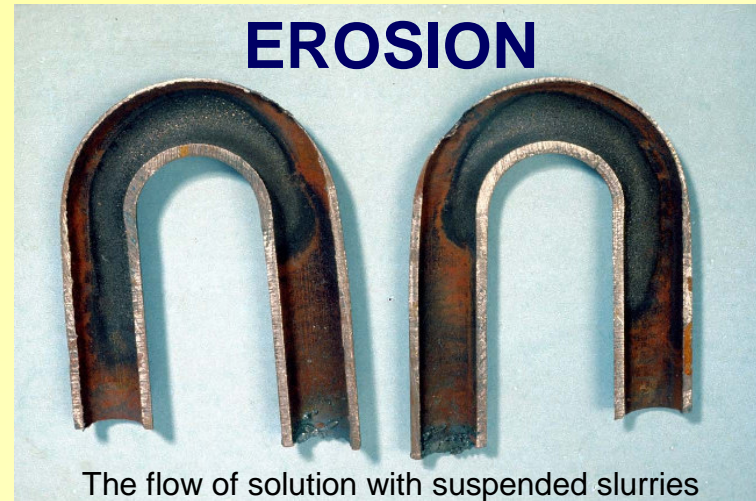


CAVITATION



The fluid high velocity flow originates pressure reductions that lead to vapour bubbles which implode on the surface disrupting the protective film.

EROSION

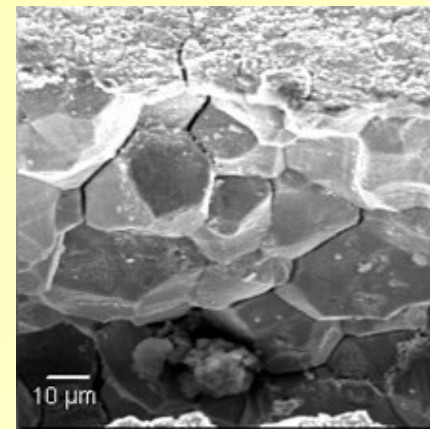
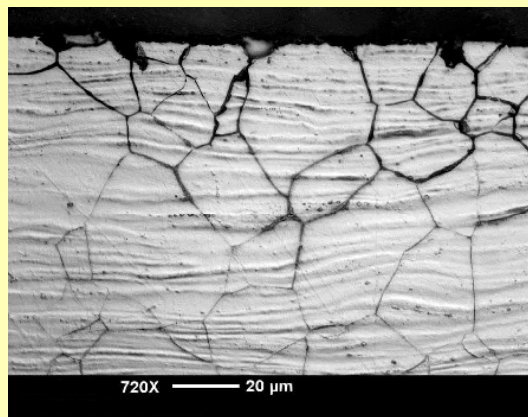
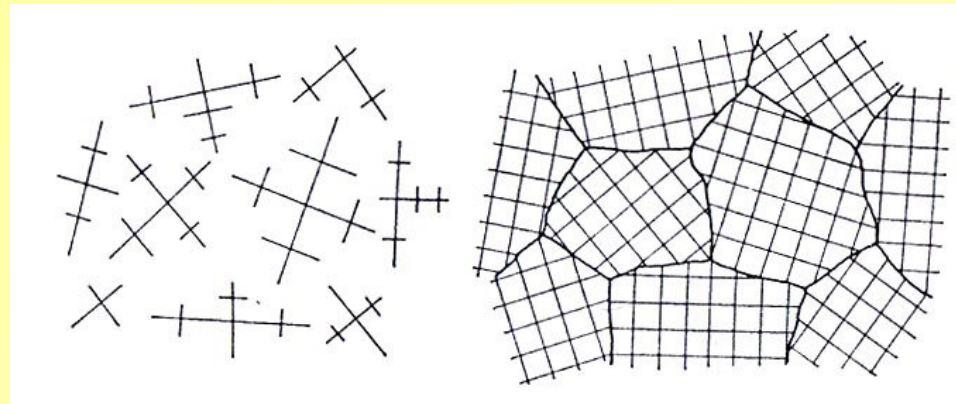


The flow of solution with suspended slurries removes the surface film.

INTERGRANULAR CORROSION

Selective attack of a metal at or adjacent to grain boundaries.

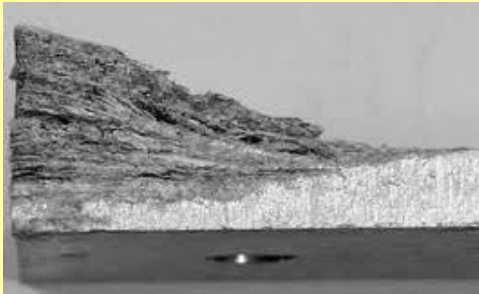
- Grain boundaries have higher energy (are more disorder) than the interior.
- Impurities tend to concentrate in the grain boundaries.
- Local depletion of an alloying element (e.g. by heat treatment, sensitization).



INTERGRANULAR CORROSION

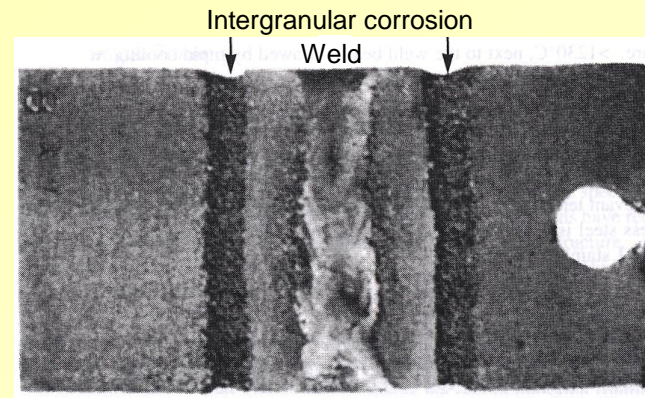
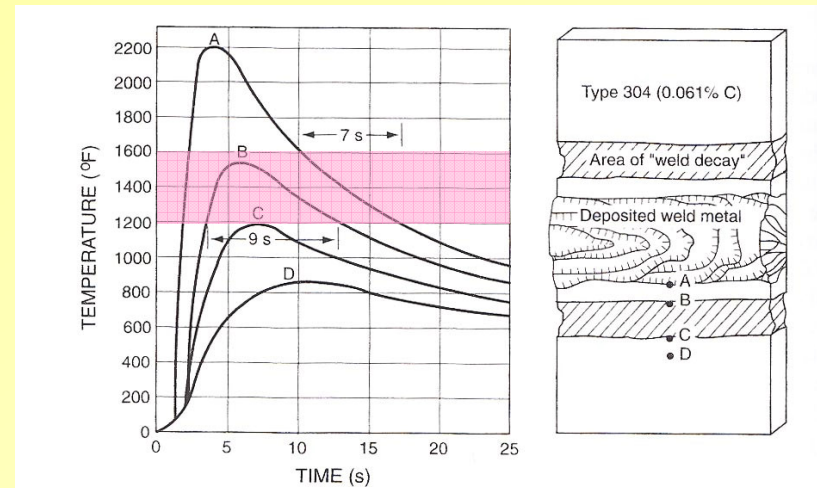
EXFOLIATION CORROSION

is characterized by the lifting up of the surface grains by the expanding force of corrosion products produced at the grain boundaries just below.



WELD DECAY in 304 stainless steel.

The heat generated during welding produces chromium carbides $(Fe,Cr)_{23}C_6$. This reduces the content in Cr and in these regions the alloy is not passive.



CORROSION + EXTERNAL FORCES

Static tensile stress

**STRESS CORROSION CRACKING
(SCC)**

Cyclic stress

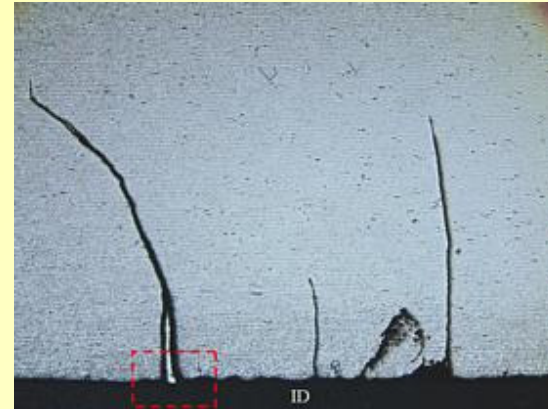
CORROSION FATIGUE

Both SCC and fatigue nucleate at pits

SCC cracks are highly branched



**Fatigue cracks have
little branches**



HYDROGEN DAMAGE

Hydrogen is produced in many electrochemical processes: corrosion, electroplating, cathodic protection, metal pickling (cleaning), phosphating. It is also present in the petroleum industry, in storage tanks and refining processes.

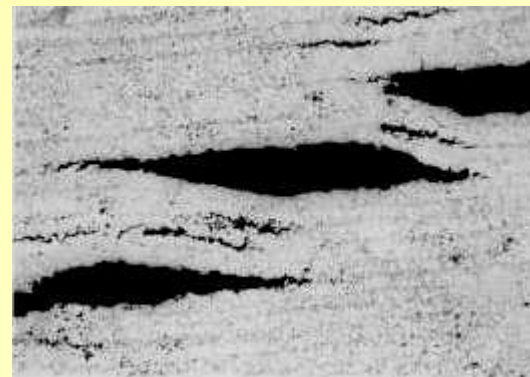
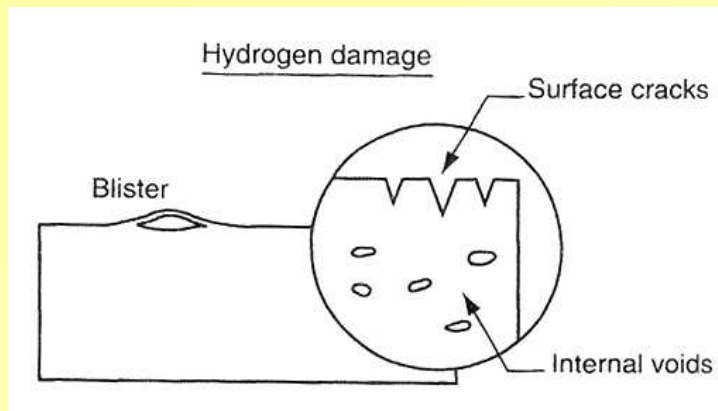
Atomic hydrogen diffuses readily through many metals. Molecular hydrogen does not.

Hydrogen blistering

Atomic H occupies voids inside the metal where it combines to molecular H_2 . The concentration and internal pressure increase with time, ultimately resulting in cracking.

Hydrogen embrittlement

Not so well understood. Once inside the metal, H forms brittle hydrides leading to cracking. This is proved for Ti, Zr, V, but still unclear for iron and steel.



At high temperatures

Hydrogen can remove carbon from steel (**decarburization**) or interact with other elements from the alloy (**hydrogen attack**), leading to reduction of tensile strength, increase in ductility and creep rate.

SUMMARY

D.A. Jones, Principles and Prevention of Corrosion 2nd Ed
Prentice Hall, 1996

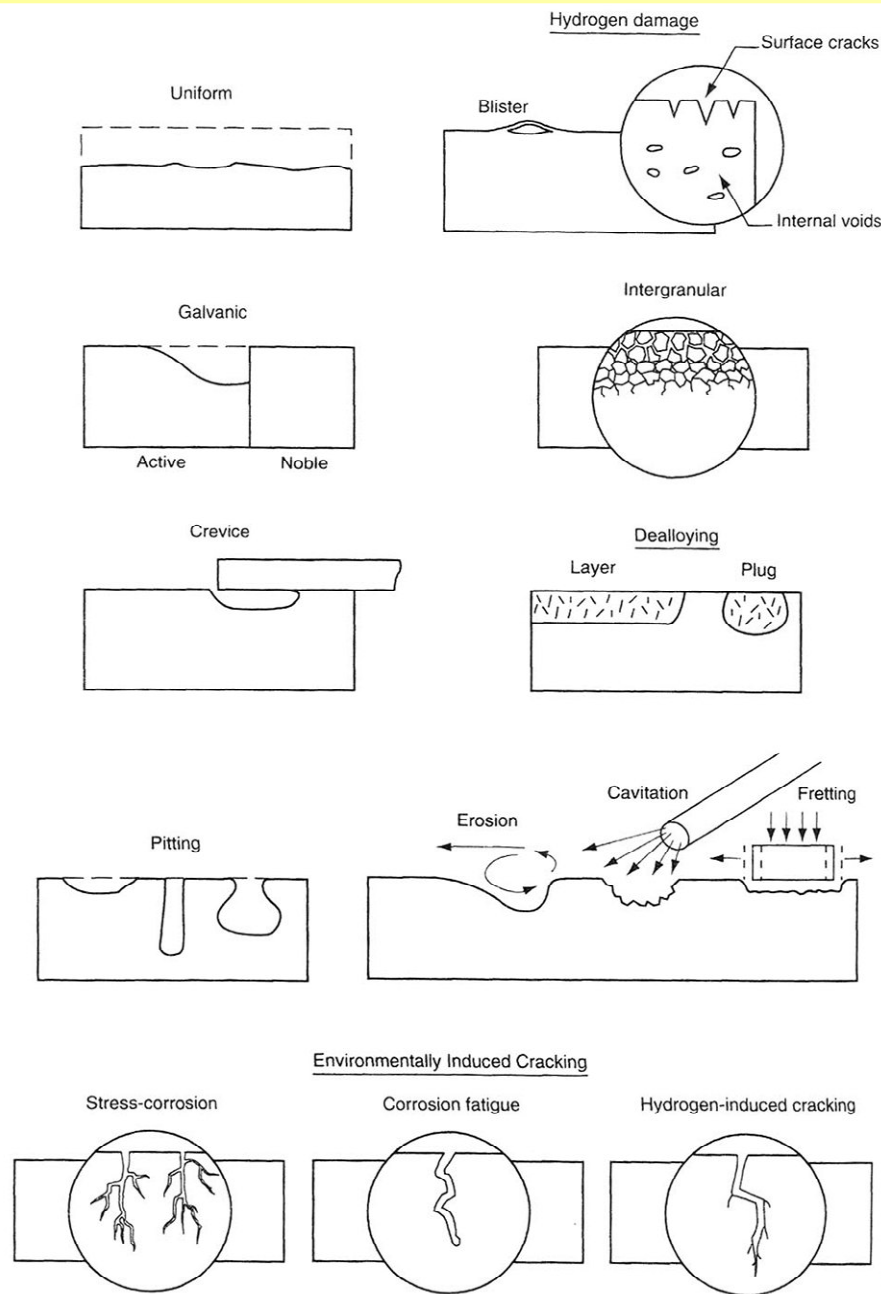


FIGURE 1.4 Schematic summary of the various forms of corrosion.

MICROBIOLOGICAL CORROSION

The presence of microbial colonies on a metal surface can promote corrosion in many ways and lead to several types of corrosion.

Aerobic colonies consume oxygen and originate differential aeration cells.

Sulfate-reducing bacteria operate in anaerobic conditions. Reduce sulfate to sulfides which react with the metal.

Acid-producing bacteria

Produce acids that dissolve the passive film (oxide) and accelerate the cathodic reaction rate.

Hydrogen-producing bacteria

Can be a source of hydrogen damage.

Iron bacteria

Oxidize Fe^{2+} to Fe^{3+} . The ferric iron attracts chloride ions and produces highly corrosive FeCl_3 deposits.



The sunken **Titanic** is covered by rusticles, 'rust flows' and 'rust flakes', which are a mixture of goethite and lepidocrocite, both polymorphs of the iron oxyhydroxide, respectively $\alpha\text{-FeO(OH)}$ and $\gamma\text{-FeO(OH)}$. Due to the very low O_2 content, corrosion is mainly due to sulfate-reducing bacteria that grow rapidly under anaerobic conditions.

Biofouling or biological fouling is the undesirable accumulation of microorganisms, plants, algae, and animals on immersed structures, especially ships' hulls. These lead to differential aeration cells.

CORROSION IN CONCRETE

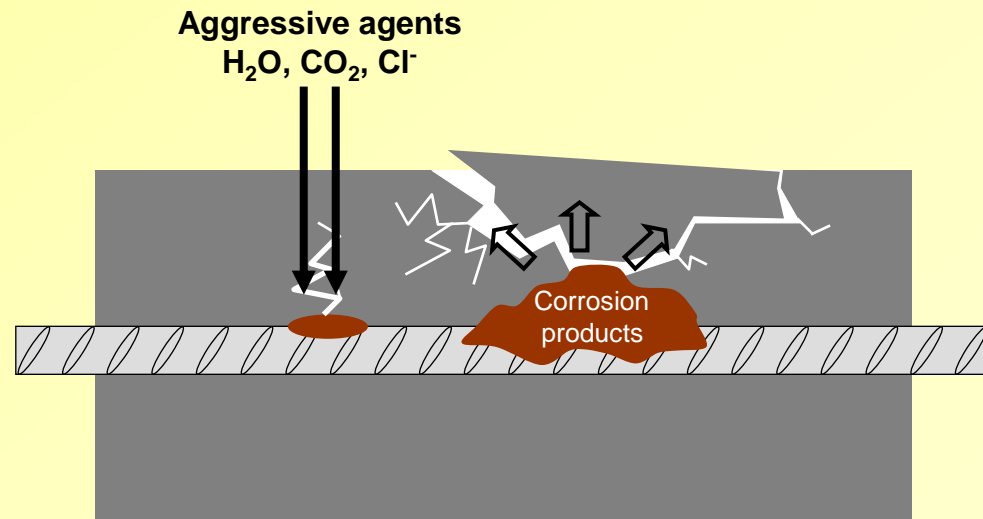
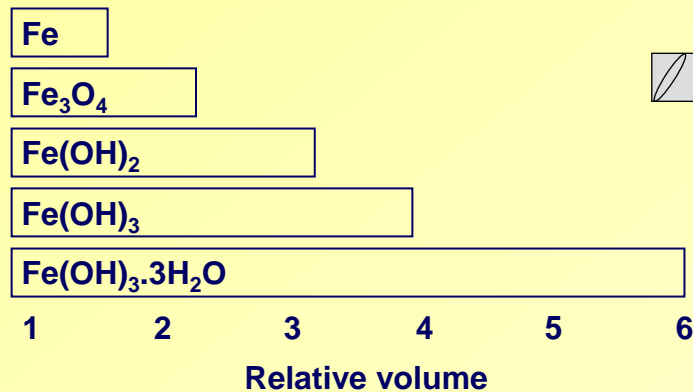


Originally steel in concrete is in passive state (pH inside concrete pores is around 13, $\text{Ca}(\text{OH})_2$).

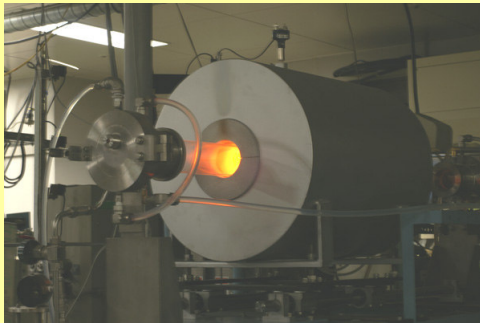
With time, H_2O and CO_2 ingress leads to carbonation of concrete and lowering of pH.

At a certain point corrosion starts. This is accelerated in the presence of chlorides (e.g. marine environment).

Accumulation of corrosion products generates internal stresses that lead to cracking and delamination of concrete.

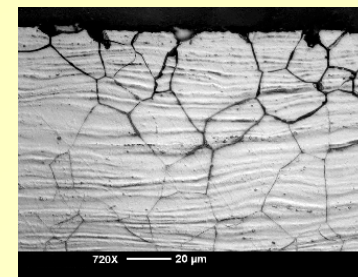
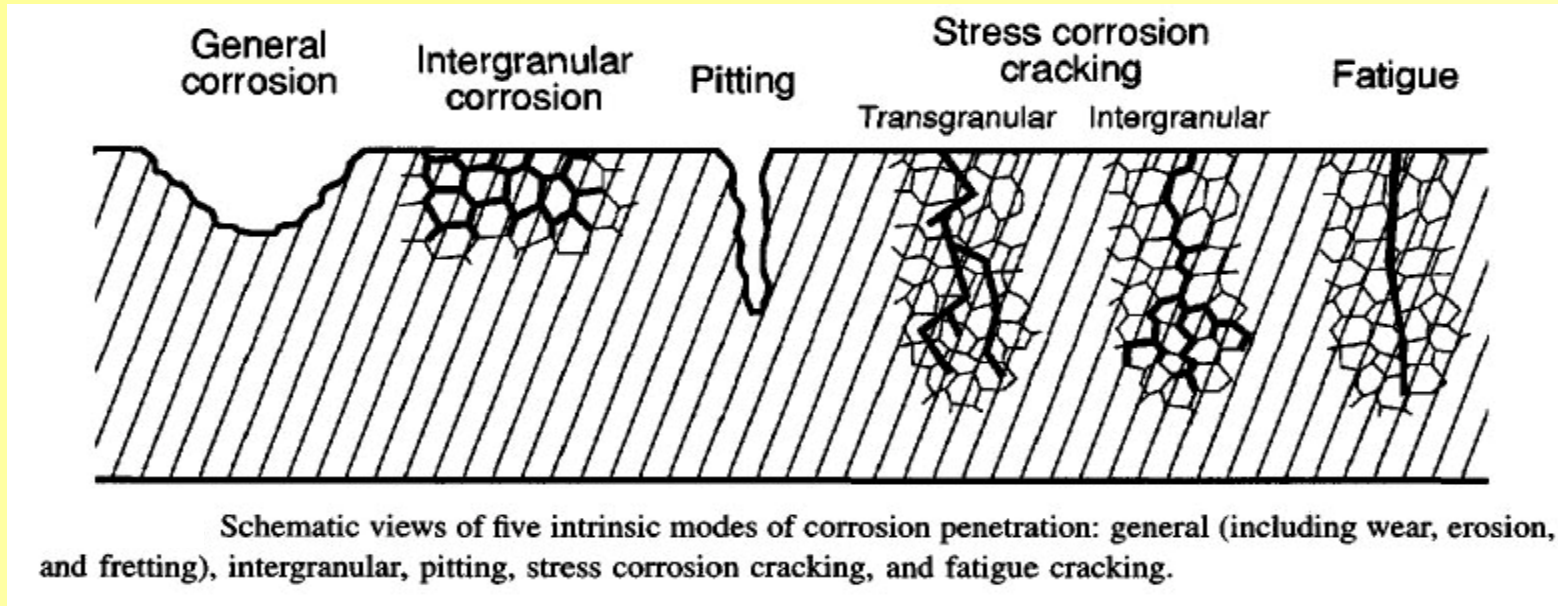


HIGH TEMPERATURE CORROSION



RECAPITULATION

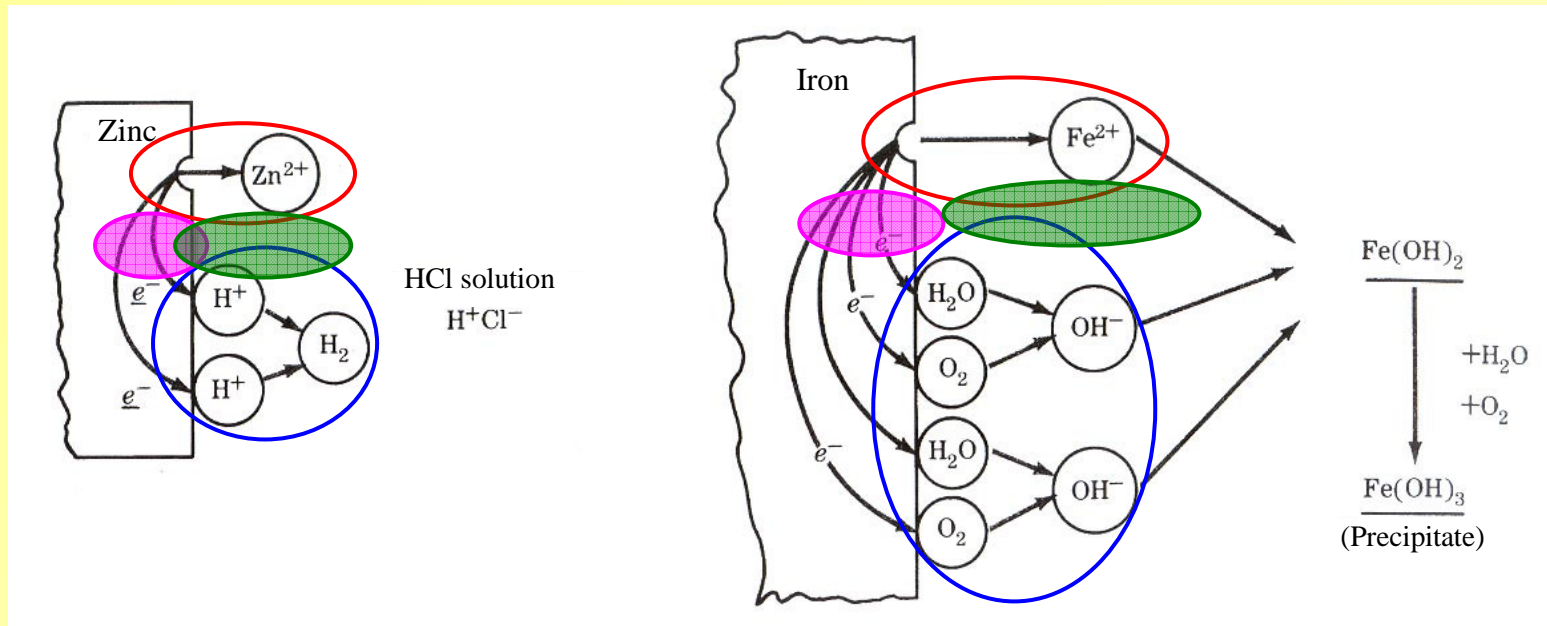
Forms of corrosion



2/3 2/4 2/5 2/6 2/7 2/8 2/9

ANTICORROSIVE PROTECTION

RECALL THE CORROSION MECHANISM

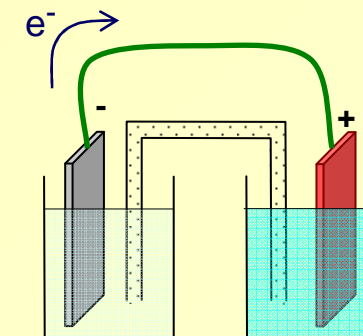


Anodic reaction

Cathodic reaction (amount of oxidizer)

Electronic path (internal resistance)

Ionic path (external resistance; solution conductivity)



ANTICORROSIVE PROTECTION

- Selection of materials
- Design of structures
- Location / placement of structures
- Modification of environment {
 - controlling humidity
 - removing O₂
- Corrosion Inhibitors
- Cathodic protection
- Anodic protection
- Coatings {
 - metallic
 - inorganic (CCC, phosphate, anodized)
 - organic (paints and varnishes)

SELECTION OF MATERIALS

Corrosion Data

Chemicals	Aluminum	Brass	Carbon Steel	Ductile Iron/Cast Iron	316 Stainless Steel	17-4PH	Alloy 20	Monel	Hastelloy C	Buna-N (Nitrile)	Delrin	EPDM/EPR	Viton	Flexible Graphite	Teflon-Reinforced/ or NRG
Acetaldehyde	B	C	C	C	A		A	A	A	D	A	B	C		A
Acetamide	B	B	B	B	B					A	A				A
Acetate Solvents	A	B	A	B	A			A	A	D	D		D	C	A
Acetic Acid, aerated	B	D	D	D	A			A	A	C					A
Acetic Acid, Air Free	B	B	D	D	A	A	A	A	A	C	D		D	A	A
Acetic Acid, crude	C	C	C	C	A	A	A	B	A	D	D		D	A	A
Acetic Acid, glacial						A			A	D		B	C	A	A
Acetic Acid, pure	C	C	D	D	A	A	A	D	A	D	D		D	A	A
Acetic Acid, 10%	C	C	C	C	A	A	A	A	A	D	B	B	D	A	A
Acetic Acid, 80%	C	C	C	C	A	A	A	B	A	D	D	C	D	A	A
Acetic Acid Vapors	B	D			D	D	B	C	A	D				A	A
Acetic Anhydride	B	D	D	D	B	B	B	B	A	D	C	C	D	A	A
Acetone	A	A	A	A	A	A	A	A	A	D	A	A	D	A	A
Other Ketones	A	A	A	A	A	A	A	A	A	D	A	D	D	A	A
Acetyl Chloride	D	A		D	C			B	A	D	D	D	D		A
Acetylene	A	B	A	A	A	A	A	A	A	B	A	A	A		A
Acid Fumes	B	D	D	D	B		B			C	D				A
Acrylonitrile	B	A	A	C	A		B	A	A	D	D	D	C		A
Air	A	A	A	A	A		A	A	A	A	A	A	A		A
Alcohol, Amyl	B	B	B	C	A		B	B	B	C	A	A	B	A	A
Alcohol, Butyl	B	B	B	C	A		A	A	A	B	A	C	A	A	A
Alcohol, Diaacetone	A	A	A	A	A		A	B	A	D	A	B	D	A	A
Alcohol, Ethyl	B	B	B	B	B		A	B	A	A	A	A	A	A	A
Alcohol, Fatty	B	B	B	B	A		A	A	A	B	A	A	A	A	A
Alcohol, Isopropyl	B	B	B	B	B		A	B	B	C	A	A	A	A	A
Alcohol, Methyl	B	B	B	B	A		A	A	A	B	A	A	C	A	A
Alcohol, Propyl	A	A	B	B	A		A	A	A	B	A	A	A	A	A
Alumina	A	A							A	A	A	A	A		A
Aluminum Acetate	C	D		D	A	B	D	C	B	D	D	A	D	A	A
Aluminum Chloride dry	B	B	C	D	C		B	B	B	B	A	A	A	A	A
Aluminum Chloride Solution	C				D	C	B	B	A	B	D		A	A	A
Aluminum Fluoride	C		D	D	C		B	B	A	A	C	A	A		A
Aluminum Hydroxide	A	A	D	D	A	B	B	B	B	A	C	A	A		A
Aluminum Nitrate	D	D		D	C		B	C	B	B	D	B	D		A
Aluminum Oxalate	B						A	B	A						A
Alum (Aluminum Potassium Sulfate)	D	D		D	B	C	B	C	A	B	D		B	A	A
Alum (Aluminum Sulfate)	C	C	D	D	B	A	B	C	A	A	D	C	A	A	A
Amines	B	B	B	C	A	A	A	B	B	D	C	C	D		A
Ammonia, Alum	C				A	A	A		A	B	C			A	A
Ammonia, Anhydrous Liquid	A	D	A	B	A	A	A	B	A	B	D	B	D	A	A
Ammonia, Aqueous	B	D	A	A	A		A	B	B	B	D		A	A	A
Ammonia, Gas, hot	A	D		B	A		A	B	B	C	D	A	D	A	A
Ammonia Liquor					A		A		B					A	A
Ammonia Solutions	C	D	B	B	A		A	B	B	B	D	B	D	A	A
Ammonium Acetate	B	D		B	B		A	B	B	B	D	A	D		A
Ammonium Bicarbonate	B	B	C	B	B		B	B		B	A	A	A		A
Ammonium Bromide 5%	D				B		B	B		A					A
Ammonium Carbonate	B	B	B	B	B		B	B		C	D	A	B		A
Ammonium Chloride	D	D	D	D	C	C	B	B	B	B	C	A	A		A
Ammonium Hydroxide 28%	C	D	C	C	B	A	A	D	B	B	D	B	A	A	A

Ratings: A - Excellent B - Good C - Poor D - Do not use Blank - No Information

C-2

Tables with the susceptibility of each alloy to different environments and applications.

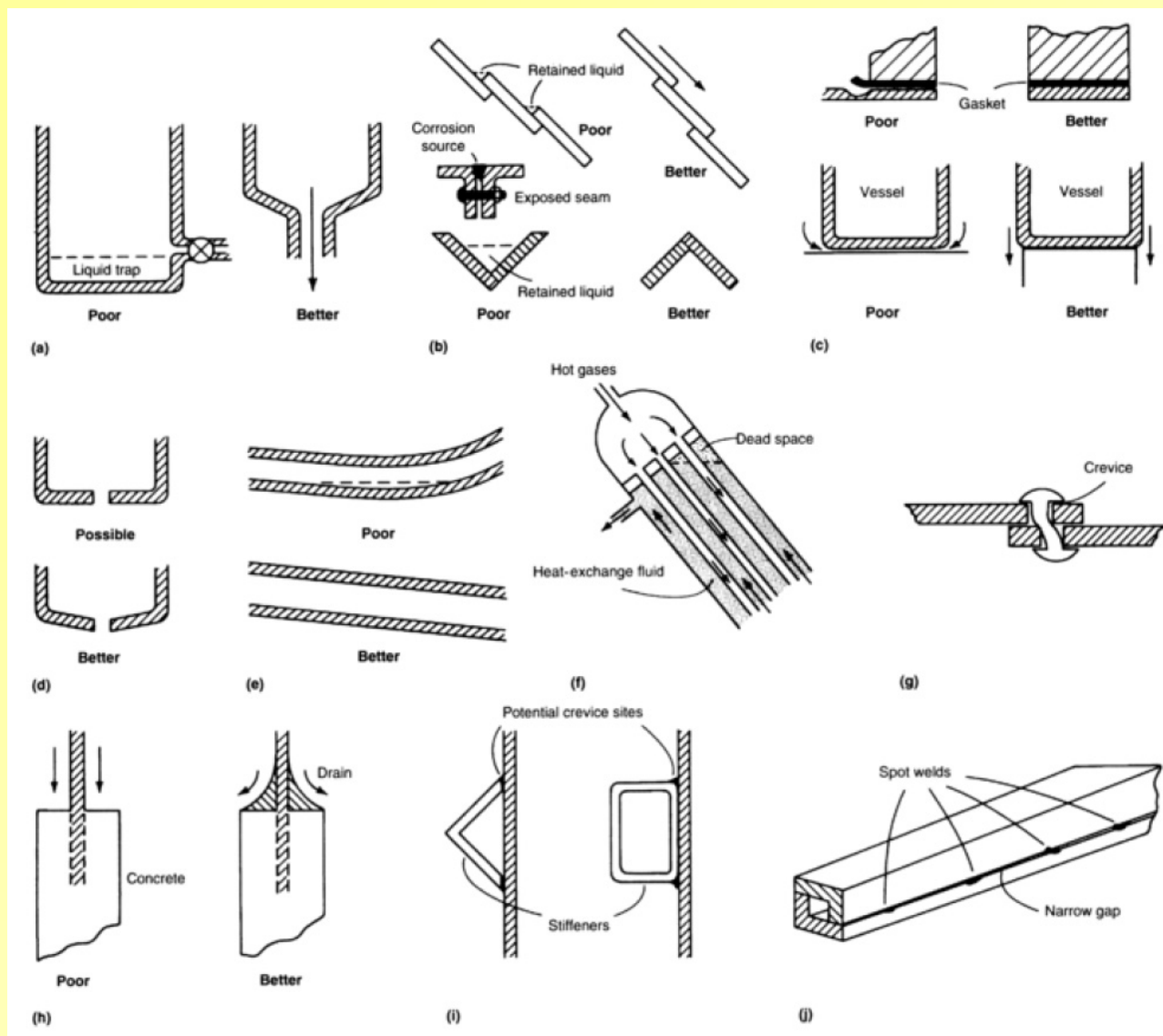
Most of the corrosion cases can be prevented by choosing a proper alloy.

Consider using non metallic materials: wood, ceramics, polymers, etc.

The best solution is a cost - benefit compromise.

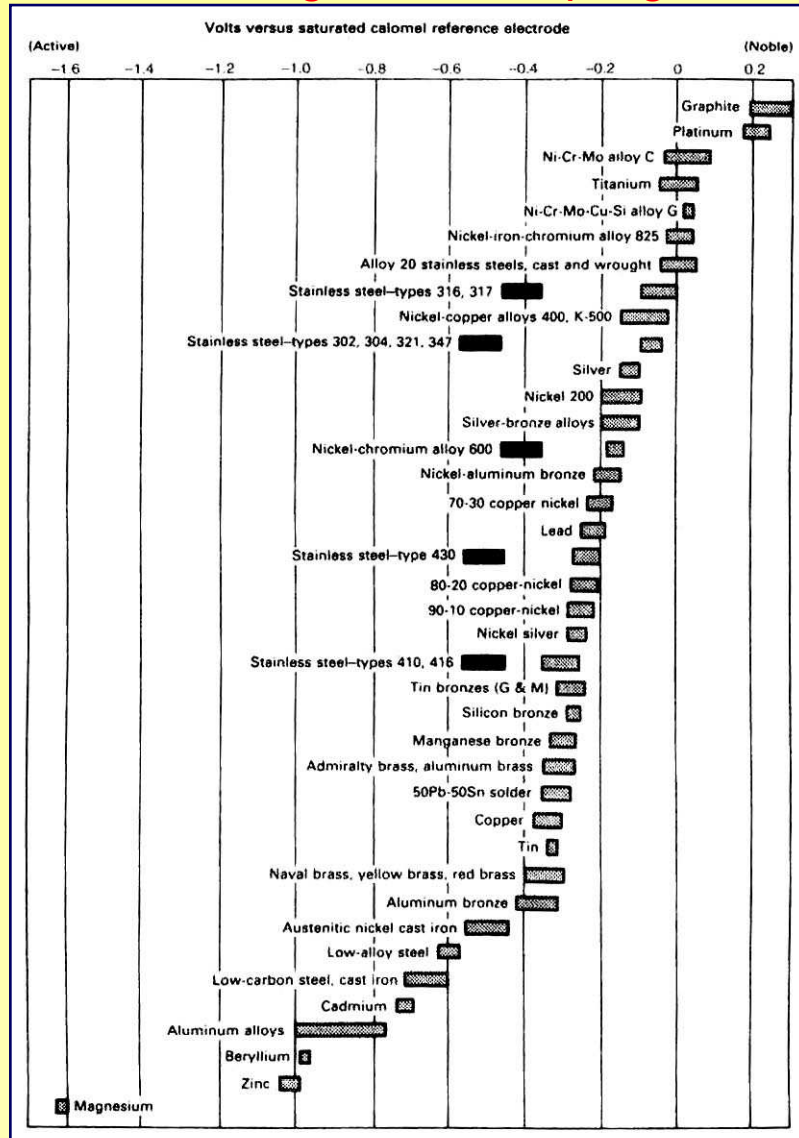
DESIGN OF STRUCTURES

Avoid water accumulation.

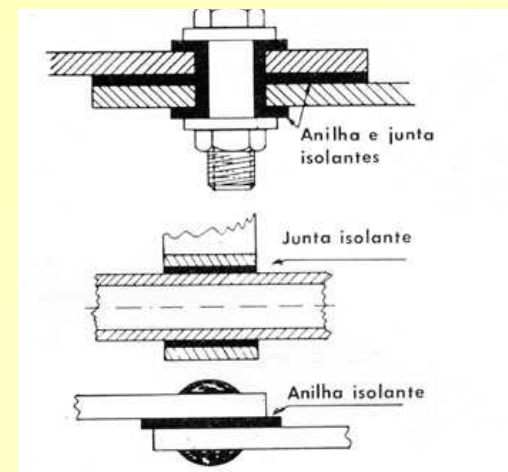


DESIGN OF STRUCTURES

Avoid galvanic coupling.



Usually galvanic coupling becomes a problem for potential differences higher than 50 mV!



LOCATION OF STRUCTURES

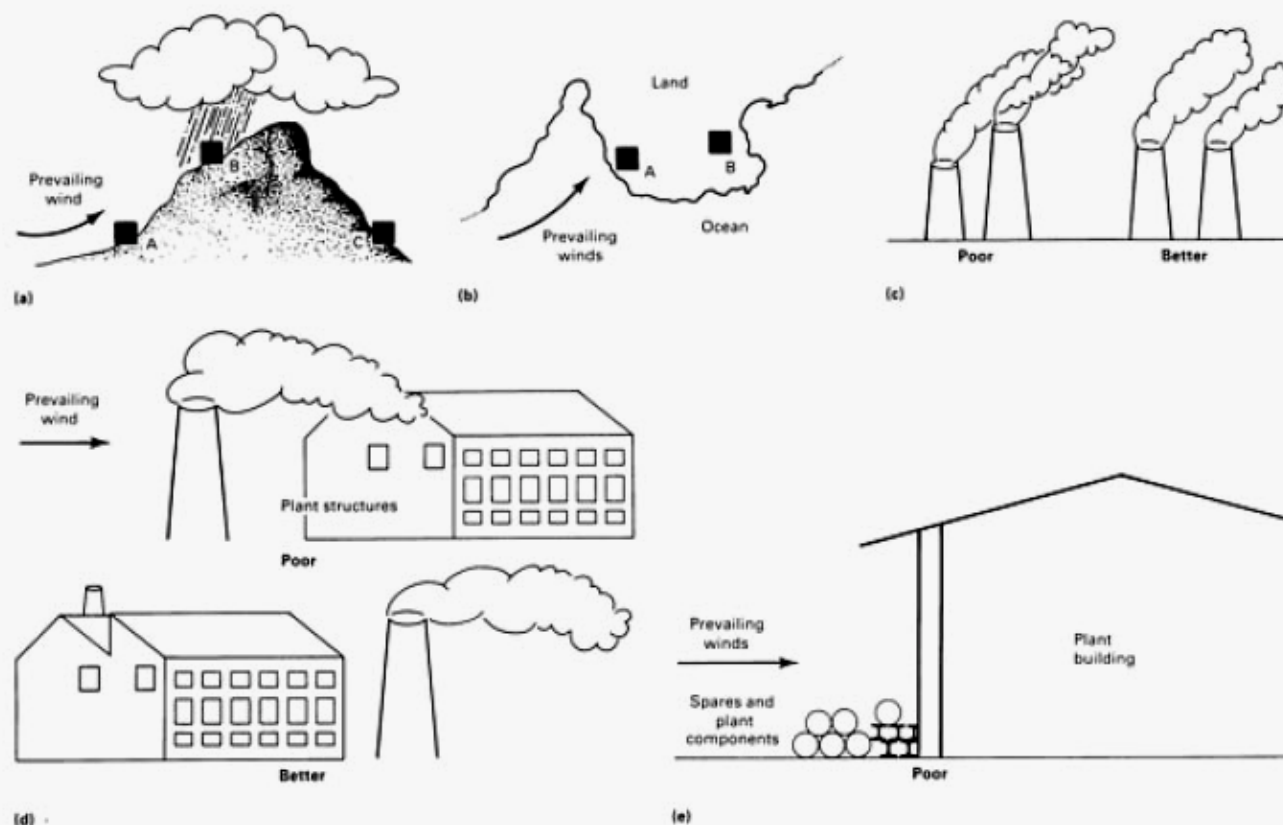
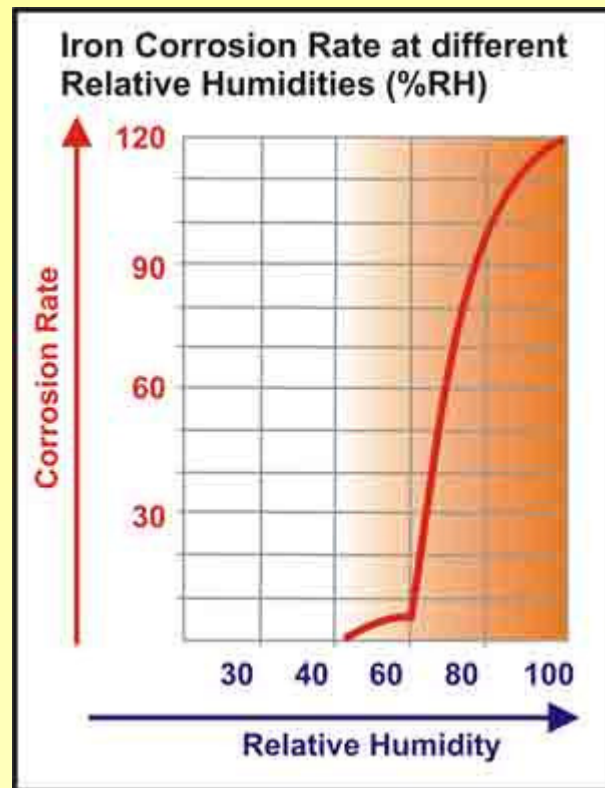


Fig. 5 Site location as a design consideration. (a) Topographic features must be considered in choosing a site. Location C would be the preferred site. (b) In marine atmospheres, prevailing winds should be taken into account; location B is the preferred site. (c) Local industry can affect corrosion of chimney stacks and similar structures. "Lick-over" of gases, which relates to stack height, location, and prevailing winds, should be avoided. (d) Plant structures should be located upwind from stacks. (e) spares and components should be stored away from the prevailing wind.

MODIFICATION OF ENVIRONMENT

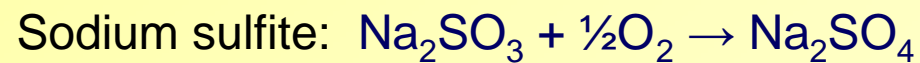
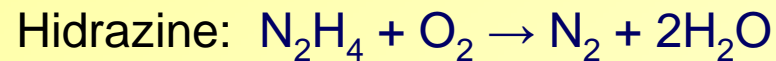
Controlling humidity



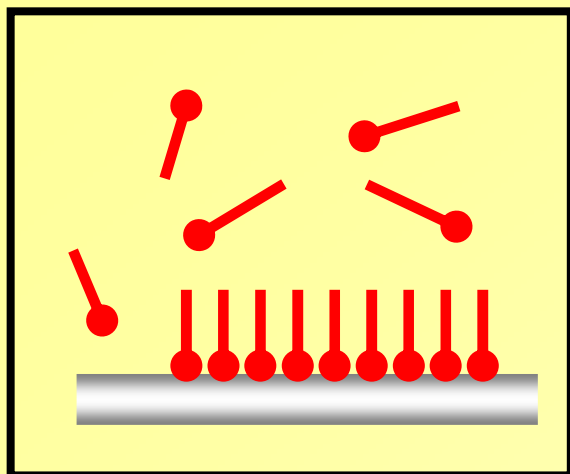
MODIFICATION OF ENVIRONMENT

Removing dissolved O₂

- Bubbling inert gasses
- Oxygen scavengers



CORROSION INHIBITORS



Passivating
films

adsorption

adherent, non porous,
insoluble precipitates

Inhibitors

anodic

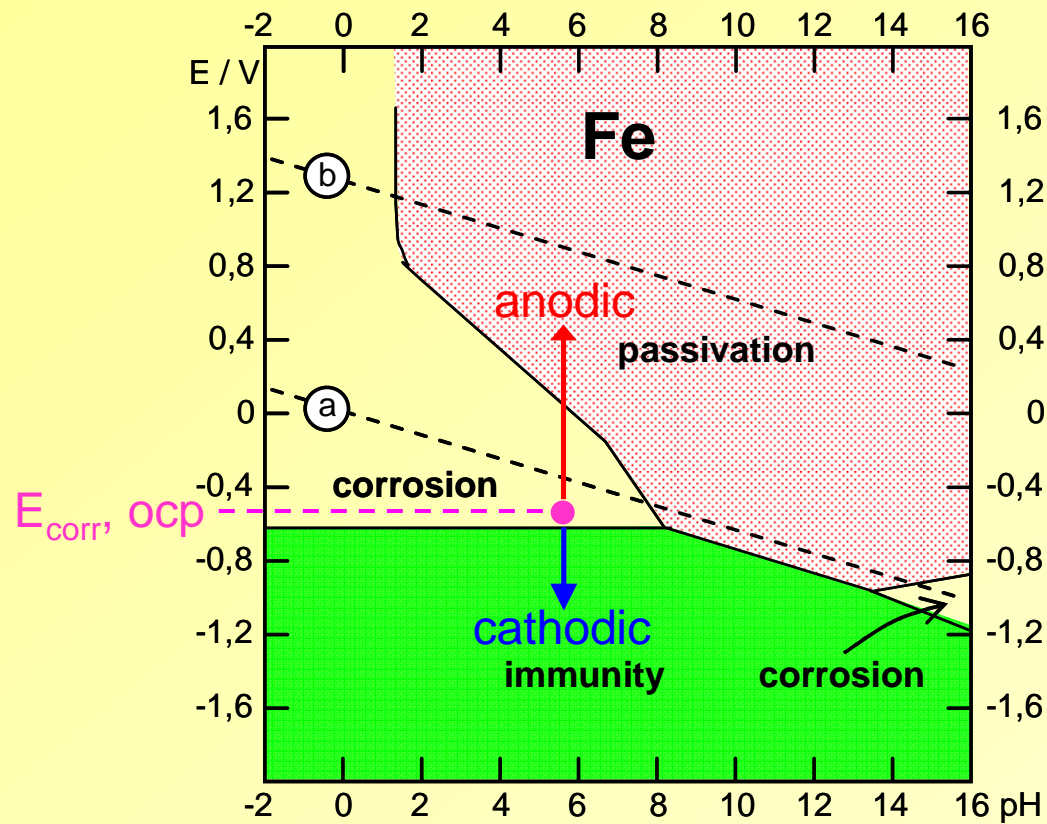
cathodic

mixed

TABLE 10.1 Some Corrosive Systems and the Inhibitors Used to Protect Them

System	Inhibitor	Metals	Concentration
Acids			
HCl	Ethylaniline	Fe	0.5%
	MBT*	..	1%
	Pyridine + phenylhydrazine	..	0.5% + 0.5%
	Rosin amine + ethylene oxide	..	0.2%
H ₂ SO ₄	Phenylacridine	..	0.5%
H ₃ PO ₄	NaI	..	200 ppm
Others	Thiourea	..	1%
	Sulfonated castor oil	..	0.5–1.0%
	As ₂ O ₃	..	0.5%
	Na ₃ AsO ₄	..	0.5%
Water			
Potable	Ca(HCO ₃) ₂	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5–10 ppm
	Ca(OH) ₂	Fe, Zn, Cu	10 ppm
	Na ₂ SiO ₃	..	10–20 ppm
Cooling	Ca(HCO ₃) ₂	Steel, cast iron	10 ppm
	Na ₂ CrO ₄	Fe, Zn, Cu	0.1%
	NaNO ₂	Fe	0.05%
	NaH ₂ PO ₄	..	1%
	Morpholine	..	0.2%
Boilers	NaH ₂ PO ₄	Fe, Zn, Cu	10 ppm
	Polyphosphate	..	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	..	O ₂ scavenger
	Ammonia	..	Neutralizer
	Octadecylamine	..	Variable
Engine coolants	Na ₂ CrO ₄	Fe, Pb, Cu, Zn	0.1–1%
	NaNO ₂	Fe	0.1–1%
	Borax	..	1%
Glycol/water	Borax + MBT*	All	1% + 0.1%
Oil field brines	Na ₂ SiO ₃	Fe	0.01%
	Quaternaries	..	10–25 ppm
	Imidazoline	..	10–25 ppm
Seawater	Na ₂ SiO ₃	Zn	10 ppm
	NaNO ₂	Fe	0.5%
	Ca(HCO ₃) ₂	All	pH dependent
	NaH ₂ PO ₄ + NaNO ₂	Fe	10 ppm + 0.5%

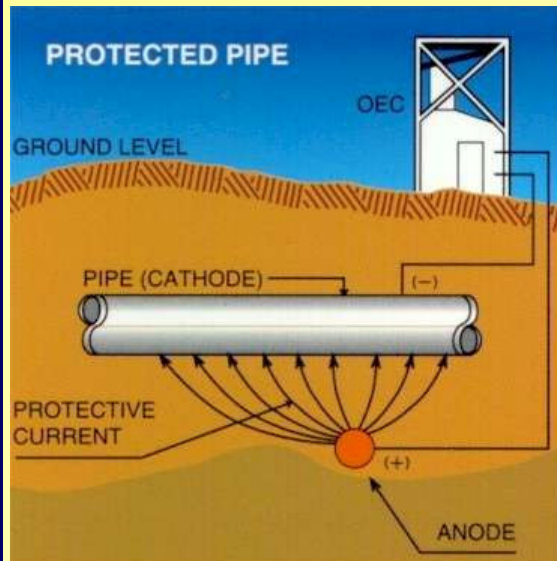
ANODIC AND CATHODIC PROTECTION



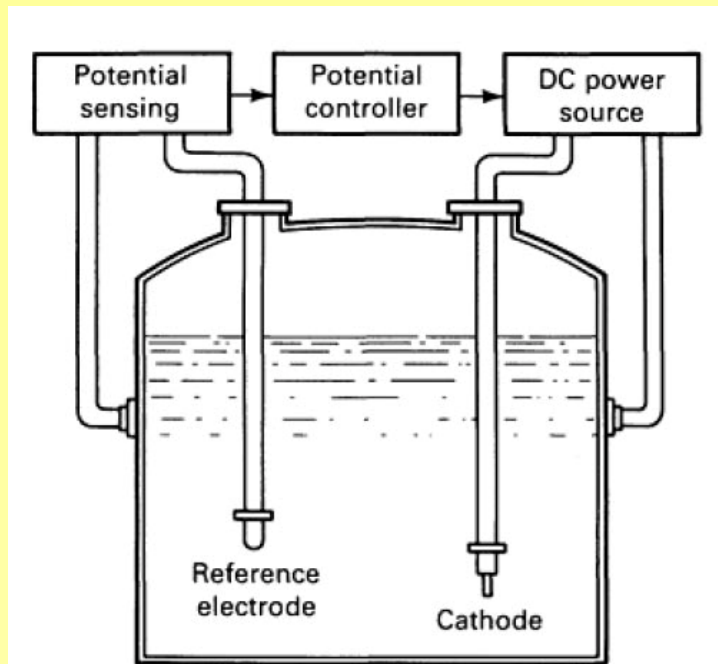
CATHODIC PROTECTION

Widely used in pipelines, storage tanks, bridges, naval ships, off shore structures, etc.

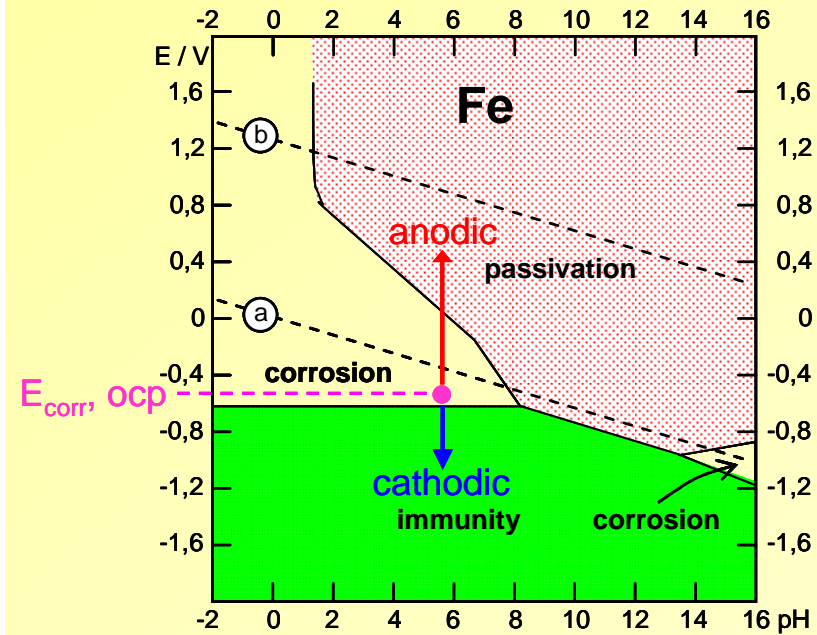
2 ways: sacrificial anodes; imposed currents



ANODIC PROTECTION



ASM Handbook, Vol. 13A, Corrosion, ASM International, 2003



Anodic inhibitors

Oxidant environments

STAINLESS STEELS

100 Series - austenitic chromium-nickel-manganese alloys

Type 101 - austenitic that is hardenable through cold working for furniture

Type 102 - austenitic general purpose stainless steel working for furniture

200 Series - austenitic chromium-nickel-manganese alloys

Type 201 - austenitic that is hardenable through cold working

Type 202 - austenitic general purpose stainless steel

300 Series - austenitic chromium-nickel alloys

Type 301 - highly ductile, for formed products. Good weldability. Better wear resistance and fatigue strength than 304.

Type 302 - same corrosion resistance as 304, with slightly higher strength due to additional carbon.

Type 303 - free machining version of 304 via addition of sulfur and phosphorus.

Type 304 - the most common grade; the classic 18/8 stainless steel.

Type 304L - same as the 304 grade but contains less carbon to increase weldability. Is slightly weaker than 304.

Type 304LN - same as 304L, but also nitrogen is added to obtain a much higher yield and tensile strength than 304L.

Type 308 - used as the filler metal when welding 304

Type 309 - better temperature resistance than 304, also sometimes used as filler metal when welding dissimilar steels.

Type 316 - the second most common grade (after 304). For food and surgical uses. Also known as marine grade stainless steel.

Type 321 - similar to 304 but lower risk of weld decay due to addition of Ti. See also 347 with Nb for desensitization during welding.

400 Series - ferritic and martensitic chromium alloys

Type 405 - ferritic for welding applications

Type 408 - heat-resistant; poor corrosion resistance; 11% chromium, 8% nickel.

Type 409 - cheapest type; used for automobile exhausts; ferritic (iron/chromium only).

Type 410 - martensitic (high-strength iron/chromium). Wear-resistant, but less corrosion-resistant.

Type 416 - easy to machine due to additional sulfur

Type 420 - Cutlery Grade martensitic; similar to the Brearley's original rustless steel. Excellent polishability.

Type 430 - decorative, e.g., for automotive trim; ferritic. Good formability, but with reduced temperature and corrosion resistance.

Type 440 - a higher grade of cutlery steel also known as razor blade steel. Used on display-only and replica swords or knives.

Type 446 - For elevated temperature service

500 Series - heat-resisting chromium alloys

600 Series - martensitic precipitation hardening alloys

601 through 604: Martensitic low-alloy steels.

610 through 613: Martensitic secondary hardening steels.

614 through 619: Martensitic chromium steels.

630 through 635: Semiaustenitic and martensitic precipitation-hardening stainless steels.

650 through 653: Austenitic steels strengthened by hot/cold work.

660 through 665: Austenitic superalloys; all grades except alloy 661 are strengthened by second-phase precipitation.

Type 2205 - the most widely used duplex (ferritic/austenitic) stainless steel grade. Excellent corrosion resistance and high strength.

METALLIC COATINGS

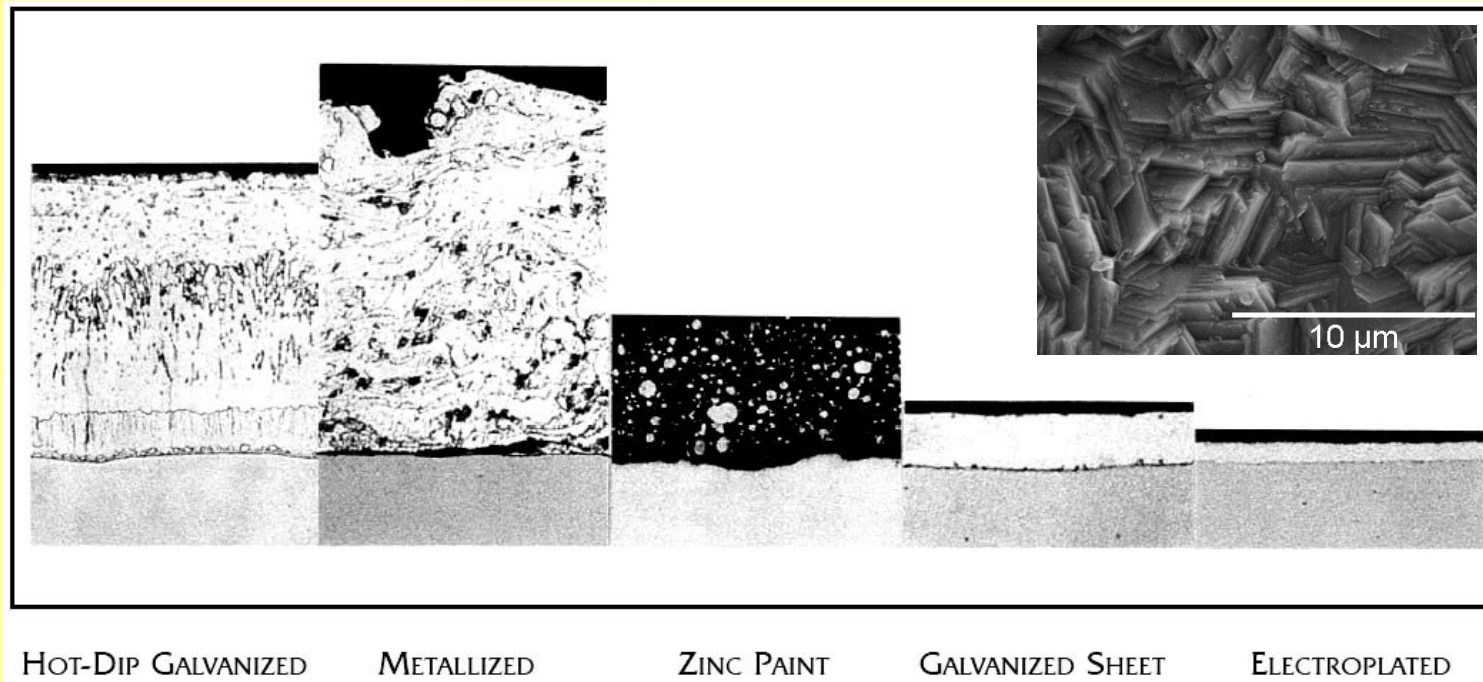
- Electrodeposition (electroplating)
- Hot dipping (Molten metal bath)
- Diffusion
- Spraying
- Chemical reduction, “*electroless*” deposition
- Vacuum evaporation
- Chemical vapour deposition (CVD)
- Physical vapour deposition (PVD)
- Ionic implantation
- Plasma deposition

Some of these processes lead to very thin films. Many times the objective is not anticorrosive protection, rather the modification of surface properties: hardness, wear resistance, colour, brightness, electrical or thermal conductivity, etc.

It is possible to co-deposit various metals or non metallic elements.

METALLIC COATINGS

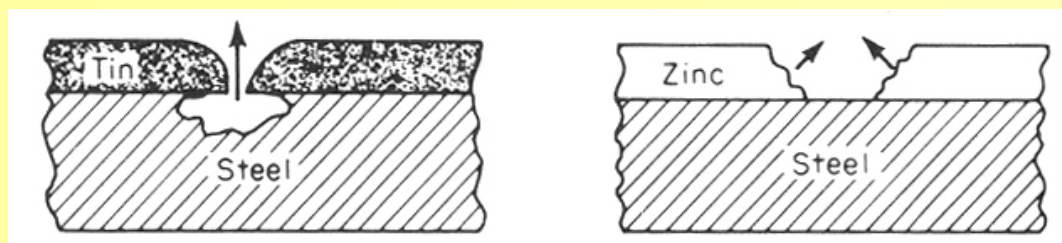
Example for zinc



- **GALVALUME** (55% Zn, 43,5% Al, 1,5% Si)
- **GALFAN** (95% Zn, 5% Al)
- **GALVANNEALED** (HDG followed by thermal treatment)
- **Co-deposition:** Zn-Fe, Zn-Ni, Zn-Co, Sn-Zn.

METALLIC COATINGS

Steel pipe protected with a metallic coating

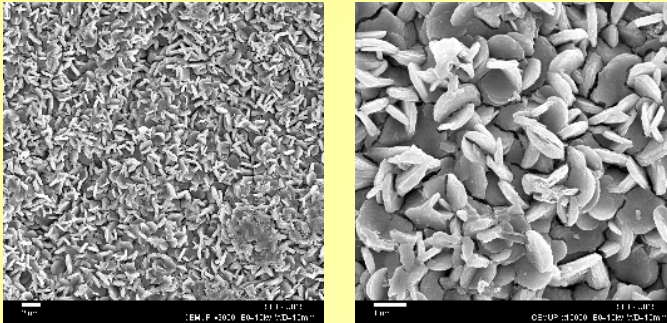


Standard electrode potentials		Galvanic potentials in 3% NaCl	
Sn ²⁺ /Sn	– 0,136 V	Cr	+ 0,23 V
Fe ²⁺ /Fe	– 0,440 V	Sn	– 0,25 V
Cr ³⁺ /Cr	– 0,74 V	Fe	– 0,50 V
Zn ²⁺ /Zn	– 0,763 V	Zn	– 0,83 V

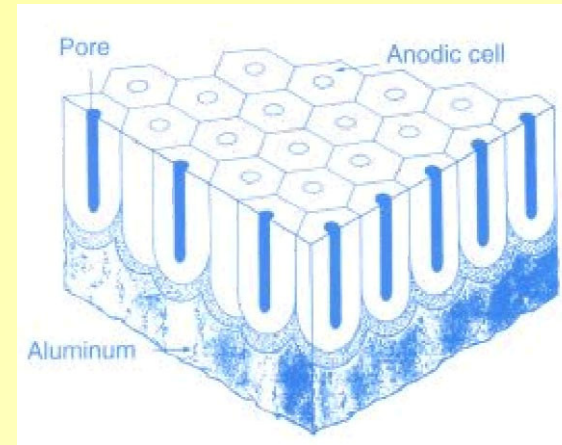
The electrochemical series suggests that chromium protects cathodically iron, which actually is not true. For corrosion problems the galvanic series are safer.

INORGANIC COATINGS

Phosphate coatings



Anodizing



Chromate Conversion Coatings



Silanes

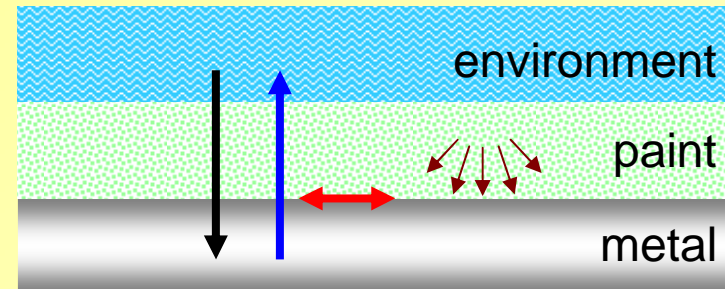
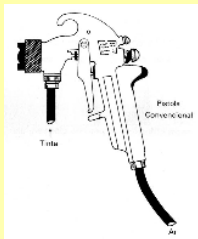
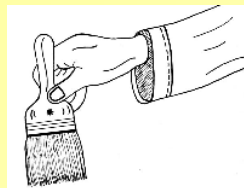
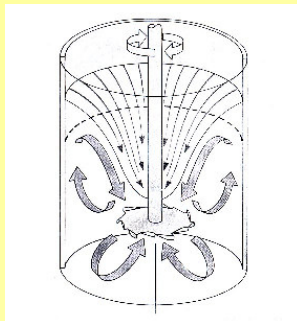
Sol-gel

Hybrids...

ORGANIC COATINGS (PAINTS)

Widely used, low-price, versatile.

Binder (first natural oils, now synthetic resins)
 Pigments (and fillers)
 Solvents
 Additives (defoamers, dispersants, thickeners...)

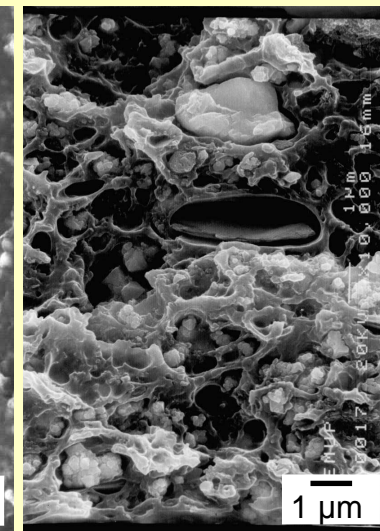
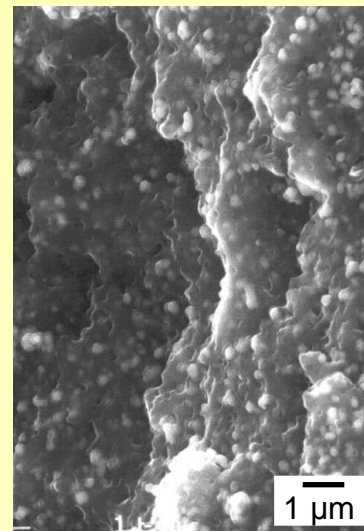


Barrier effect
 (water, gases, ions)

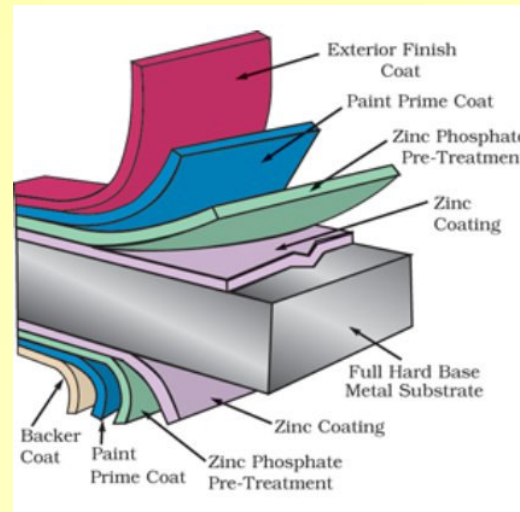
Barrier effect
 (corrosion products)

Adhesion
 (high R between anode and cathode)

Anticorrosive pigments



Anticorrosive protection of a car



Types of Corrosion and Anticorrosive Methods



Objectives:

- Costs and impact of corrosion
- Metallurgy vs corrosion
- Thermodynamics and Kinetics
- Corrosion (activity), passivity, immunity
- Types and forms of corrosion
- Anticorrosive measures and methods

For further reading...

Websites

<http://www.corrosion-doctors.org>

<http://www.efcweb.org>

<http://www.nace.org>

<http://corrosion.ksc.nasa.gov>

Books

D.A.Jones, Principles and Prevention of Corrosion 2nd Ed, Prentice Hall, 1996

M.G.Fontana, Corrosion Engineering 3rd Ed, McGraw-Hill, 1987

R.W.Revie, H.H.Uhlig, Corrosion and Corrosion Control 4th Ed, Wiley, 2008

H.Kaesche, Corrosion of Metals, Springer, 2003