Corrosion Basics

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Definition of corrosion

Where is the corrosion damage?

- Corrosion is the chemical reaction or the physicochemical interaction between a material and its environment that causes the deterioration of the material itself or of its properties. Corrosion leads usually to the damage of the material, of the environment or of a technical device.
- Consequences of corrosion:
  - Injuries and loss of lives, e.g. by failure of technical devices or poisonous corrosion products
  - Damages to the environment and ecosystems, e.g. contamination and pollution
  - Economic cost, typically about 2-4 % of the GDP of a country, e.g. in Finland, 2023: ~5-11 G€
    - Capital cost, e.g. replacement of equipment, damages to products, loss of production or fines
    - Cost for corrosion control, repair and maintenance
    - Design cost, e.g. additional corrosion allowance and more expensive construction materials
    - Associated cost, e.g. insurance cost, technical support, training

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Corrosion of polymers

- Degradation mechanisms:
  - Disintegration of the polymer structure due to solvation or absorption and/or desorption e.g. by contact with organic solvents or pressurized gases
  - Hydrolysis, where ester, amide and carbamate linkages are broken, e.g. by hot water, acids or bases
  - Dehydration (rather uncommon), e.g. by contact with concentrated H_2SO_4
  - Oxidation of polymers e.g. by ozone
  - Radiation damage, e.g. by UV-light
  - Thermal degradation involving depolymerization and possibly repolymerization
- Possible consequences:
  - Softening, hardening, cracking, delamination, discoloration, dissolving, swelling, blistering, foaming and/or rupture

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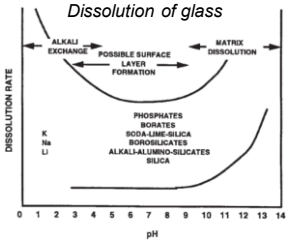
Corrosion of inorganic non-metals

- Ceramics:
  - Typically oxides, nitrides or carbides but silicides and borides, too
  - Often good heat-resistance and low solubility in water
  - Typical degradation mechanisms:
    - Dissolution in aqueous solutions
      - Especially at low or high pH value
      - Presence of complexing agents
      - Dissolution in organic solvents rare
    - Attack by molten glass, salt or metal
    - Chemical reaction with hot gases e.g. oxidation, nitridation, sulfidation, carburization, halogenes
- Glass:
  - Non-crystalline, inorganic materials
  - Increased dissolution into aggressive solutions, e.g. at low or high pH values
- Concrete:
  - Inorganic composite material consisting of cement and aggregate
  - Typical degradation mechanisms:
    - Alkali-aggregate reactions, sulphate attack and carbonation, degradation in seawater by reactions with carbon dioxide and magnesium, or dissolution by chemical reactions with aggressive chemicals like acids or bases



Source: R.A. McCauley, Corrosion of Ceramic and Composite Materials, Marcel Dekker, 2004

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Corrosion of metals

- Chemical reactions, electrochemical reactions and metallurgical changes

Uniform corrosion	Localized corrosion		Special forms of corrosion
	Macroscopic	Microscopic	
General corrosion	Galvanic corrosion	Intergranular corrosion	Atmospheric corrosion
High temperature corrosion	Erosion corrosion	Stress corrosion cracking	Microbially induced corrosion
Molten salt corrosion	Crevice corrosion	Corrosion fatigue	Under deposit corrosion
Liquid metal corrosion	Pitting corrosion	Hydrogen damage	Weld corrosion
	Filiform corrosion	Liquid metal embrittlement	and many more…
	Dealloying / selective corrosion		

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Chemical reactions

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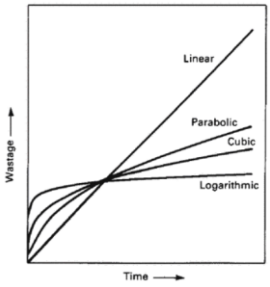
High temperature corrosion



Typical kinetics of high temperature corrosion reactions

- Chemical reactions between metals and hot gases can lead to the formation of corrosion products on or beneath the metal surface.
- Excessive formation of corrosion products results in material degradation.
  - Individual for each metal / hot gas combination – no influence of metal pairs

Chemical reaction	Typical corrosion products	Typical properties
Oxidation	Oxide layers	Often protective
Sulfidation	Sulfide layers	Often low melting point
Carburization	Hard metal phases by alloying with the interstitial elements C or N	Mechanical stress in the metal surface
Nitridation		
Halogen gas corrosion	Halides and oxohalides	Often volatile compounds

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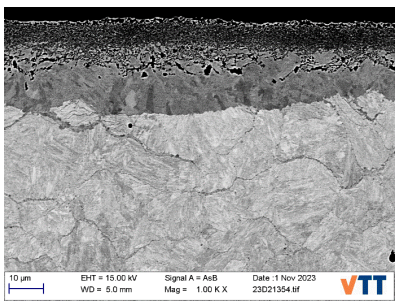
High temperature corrosion

Martensitic steel 34CrNiMo6 after 1000 h in 14% NH_3 in Ar at 500 °C (SEM, Sofia Ojasalo, VTT)



- When the corrosion products form a protective surface layer with good adhesion, the corrosion processes are slowed down.
- The breakdown of protective layers causes increased corrosion rates.

Breakdown cause	Result	Examples
Growth stress	Cracking & spalling	Thermal cycling of Fe-alloys in air
Reducing atmosphere	Chemical reduction	Hot H_2 reducing oxide layers
Liquid corrosion products	Fluxing off	Liquid Mo-oxides on steels
Volatile corrosion products	Evaporation	Volatile chloro-compounds

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Electrochemical reactions

Uniform corrosion

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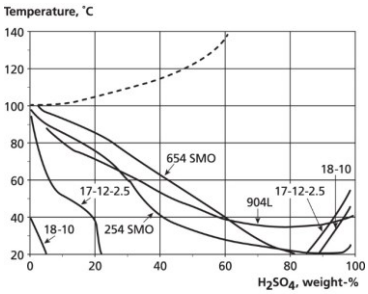
General corrosion

- The whole exposed surface corrodes leading to the uniform thinning of the metal in the active state.
  - A corrosion rate can be measured.
    - E.g. by weight loss measurements of coupons
    - Either as penetration rate, e.g. in mm/a, or as mass loss rate, e.g. in g/(m²·d).
    - Corrosion rates are usually higher at higher temperatures.
  - Corrosion rates can be used to predict the service lifetime of a component using data tables and iso-corrosion diagrams.
    - Corrosion rates < 0.1 mm/a are normally acceptable.
    - Corrosion rates < 1.0 mm/a may be manageable.
  - Soluble corrosion products: bright metallic surface
  - Insoluble corrosion products: surface layers, rust etc.

Iso-corrosion diagram of stainless steel in sulphuric acid



Isocorrosion diagram, 0.1 mm/year, for austenitic stainless steels in naturally aerated sulphuric acid of chemical purity. Broken-line curve represents the boiling point.

Source: Australian Stainless Steel Development Association (original from Avesta Corrosion Handbook)

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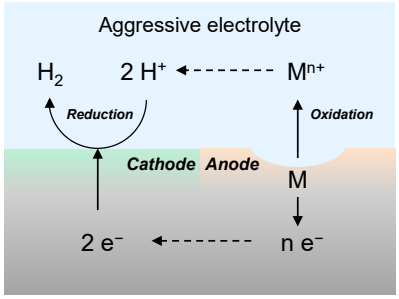
General corrosion

- Electrochemical reactions:
  - An electrolyte is necessary.
    - Examples: dissolved salts in H_2O or liquid NH_3
    - No electrolyte means no corrosion!
  - Anodic oxidation: metal dissolution
    - $M + n\ e^- \rightleftharpoons M^{n+}$
  - Cathodic reduction: supporting reaction
    - $2\ H^+ + 2\ e^- \rightleftharpoons H_2$ acidic solutions
      $H_2O + 2\ e^- \rightleftharpoons H_2 + 2\ OH^-$ alkaline solutions
    - $O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O$ acidic solutions
      $O_2 + 2\ H_2O + 4\ e^- \rightleftharpoons 4\ OH^-$ alkaline solutions
  - The anodic and cathodic areas may fluctuate over the metal surface leading to uniform material loss.



Schematic representation of a corrosion cell

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General corrosion

- Electrochemical reactions:
  - An electrolyte is necessary.
    - Examples: dissolved salts in H_2O or liquid NH_3
    - No electrolyte means no corrosion!
  - Anodic oxidation: metal dissolution = low potential
    - $M + n\ e^- \rightleftharpoons M^{n+}$
  - Cathodic reduction: supporting reaction = high potential
    - $2\ H^+ + 2\ e^- \rightleftharpoons H_2$ acidic solutions
      $H_2O + 2\ e^- \rightleftharpoons H_2 + 2\ OH^-$ alkaline solutions
    - $O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O$ acidic solutions
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Galvanic series, examples

Redox pair	Oxidized form		Reduced form	Standard potential
Gold (Au)	Au^{3+}	$+ 3\ e^- \rightleftharpoons$	Au	+1,50 V
Chlorine (Cl)	$Cl_{2\,(aq)}$	$+ 2\ e^- \rightleftharpoons$	$2\ Cl^-$	+1,40 V
Oxygen (O) / pH 0	**$O_2 + 4\ H^+$**	**$+ 4\ e^- \rightleftharpoons$**	**$2\ H_2O$**	**+1,23 V**
Platinum (Pt)	Pt^{2+}	$+ 2\ e^- \rightleftharpoons$	Pt	+1,18 V
Silver (Ag)	Ag^+	$+ e^- \rightleftharpoons$	Ag	+0,80 V
Iron (Fe(II)/(III))	Fe^{3+}	$+ e^- \rightleftharpoons$	Fe^{2+}	+0,77 V
Copper (Cu(I))	Cu^+	$+ e^- \rightleftharpoons$	Cu	+0,52 V
Oxygen (O) / pH 14	**$O_2 + 2\ H_2O$**	**$+ 4\ e^- \rightleftharpoons$**	**$4\ OH^-$**	**+0,40 V**
Copper (Cu(I)/(II))	Cu^{2+}	$+ 2\ e^- \rightleftharpoons$	Cu	+0,34 V
Copper (Cu(II))	Cu^{2+}	$+ e^- \rightleftharpoons$	Cu^+	+0,16 V
Hydrogen (H) / pH 0	**$2\ H^+$**	**$+ 2\ e^- \rightleftharpoons$**	**H_2**	**0 V**
Lead (Pb)	Pb^{2+}	$+ 2\ e^- \rightleftharpoons$	Pb	−0,13 V
Tin (Sn)	Sn^{2+}	$+ 2\ e^- \rightleftharpoons$	Sn	−0,14 V
Iron (Fe)	Fe^{2+}	$+ 2\ e^- \rightleftharpoons$	Fe	−0,41 V
Sulphur (S)	S	$+ 2\ e^- \rightleftharpoons$	S^{2-}	−0,48 V
Zinc (Zn)	Zn^{2+}	$+ 2\ e^- \rightleftharpoons$	Zn	−0,76 V
Hydrogen (H) / pH 14	**$2\ H_2O$**	**$+ 2\ e^- \rightleftharpoons$**	**$H_2 + 2\ OH^-$**	**−0,83 V**
Titanium (Ti)	Ti^{2+}	$+ 2\ e^- \rightleftharpoons$	Ti	−1,63 V
Aluminium (Al)	Al^{3+}	$+ 3\ e^- \rightleftharpoons$	Al	−1,68 V
Magnesium (Mg)	Mg^{2+}	$+ 2\ e^- \rightleftharpoons$	Mg	−2,36 V

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Electrochemical reactions

Localized corrosion

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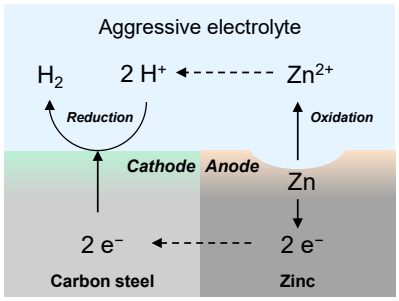
Galvanic corrosion

Galvanised steel fasteners on mirror-polished stainless steel

- Prerequisites:
  - Two different metals are in electrical contact with each other.
  - At least one of the two metals can corrode in the environment.
  - A sufficiently conductive aggressive electrolyte
- The less noble metal can become the anode and may corrode.
  - The other metal of the pair is the cathode and is protected from corrosion.



Schematic representation of the galvanic corrosion of zinc in contact with carbon steel as example

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Galvanic corrosion

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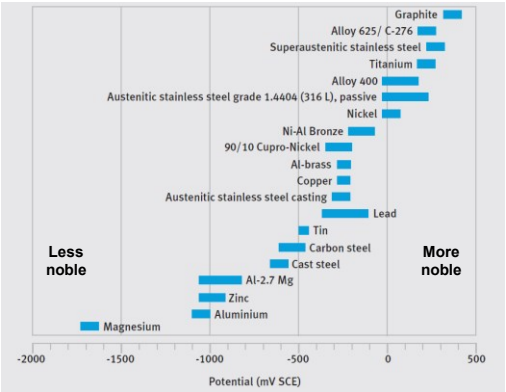
- The less noble metal can become the anode and may corrode.
  - The other metal of the pair is the cathode and is protected from corrosion.
  - Galvanic series help to predict which metals is likely to be the corroding anode.
  - Application: galvanic corrosion protection

Galvanic series of engineering metals in seawater at 10 °C



Source: Euro-Inox

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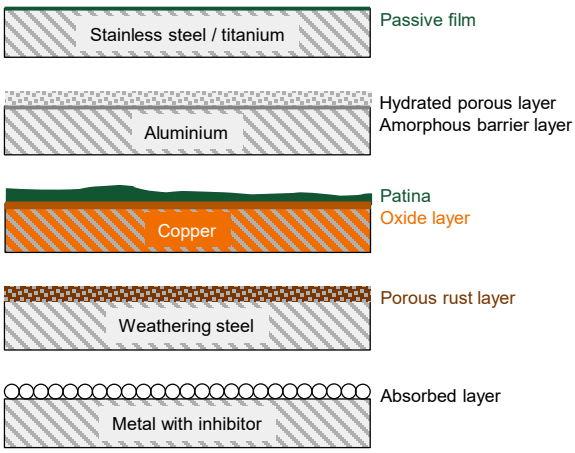
Influence of surface layers on corrosion processes

- Passivation
  - Formation of protective surface layers on metals that slow down the kinetic of the corrosion reactions.
- Porous corrosion product layers
  - Example: corrosion resistance of weathering steels
- Absorbed, often organic chemicals
  - Corrosion inhibitors
- Other porous surface depoits
  - Examples: corrosion products, limestone
  - May reduce or increase corrosion risks



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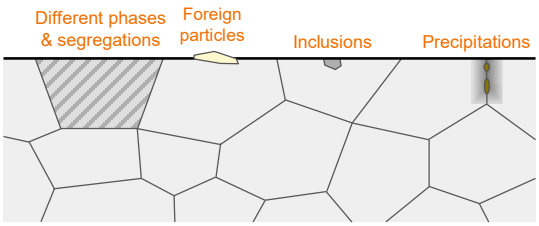
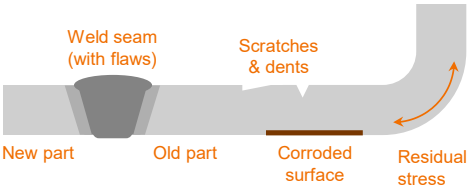
Influence of surface inhomogeneities on corrosion processes

- Corrosion starts preferably at inhomogeneities in the metal surface.
  - Microscopic level:



  - Macroscopic level:



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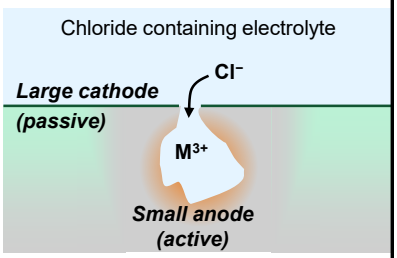
Pitting corrosion

Corrosion pit (hot water) in a copper pipe

- Mechanism:
  - Local breakdown of the protective passive layer on passive metals, e.g. aluminium, titanium and stainless steel, due to the attack of aggressive anions, e.g. Cl^-, Br^- or $S_2O_3^{2-}$.
    - Influence of the concentration of the aggressive ions, pH, temperature and redox potential of the environment
  - The damaged area becomes active and acts as small anode. The undamaged area remains passive and becomes cathodic.
  - High currents at the anode cause locally fast anodic dissolution.
- Severe conditions in the corrosion pit:
  - Limited diffusion due to the geometry of the pit.
  - Low pH value in the pit, because transition metal cations can act like an acid: $M^{3+} + H_2O \rightleftharpoons M(OH)^{2+} + H^+$
  - Enrichment of Cl^- in the pit makes the attack stronger.
  - Trapped solution with low O_2 content prevents re-passivation.



Uniform corrosion in the hole but no corrosion outside the pit

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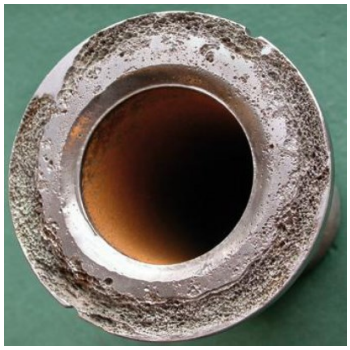
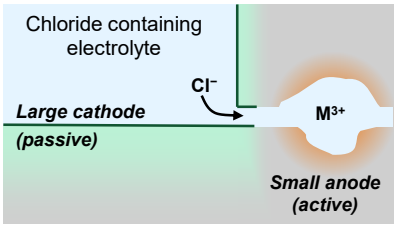
Crevice corrosion

- Properties:
  - The passive film breaks down easier in a crevice, e.g. in a joint, than on a bare metal surface.
  - Crevice corrosion starts under less severe condition than pitting corrosion.
  - The crevice geometry has a strong influence on the corrosion processes – which is difficult to predict!
  - Crevice corrosion is often hidden in the crevice.
- Mechanism:
  - Principally the same as pitting corrosion
  - Difference: the bad geometry, i.e. the hole, is already there – it's the crevice!
  - Trapped solution with low oxygen content and enrichment of Cl^- right from the beginning.

Corroded flange





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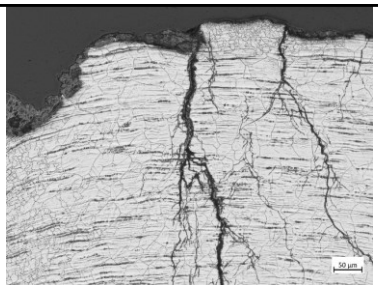
Stress corrosion cracking

- Passive metals under tensile load may crack easier in a corrosive environment than they would break in dry air.
  - Tensile stress in the surface is needed to enable stress corrosion cracking.
  - Leads often to catastrophic failure.
  - Many engineering metals can be affected.
- Two common cracking modes:
  - Transgranular or intergranular depending on the metal or after improper heat treatments
  - Depending on the metal, its metallurgical state and the aggressive environment



Transgranular Cl^- induced stress corrosion cracks in austenitic stainless steel

Metal	Critical environments
Carbon steels	NO_3^-, OH^-, and HCO_3^- / CO_3^{2-} solutions, high purity steam, anhydrous NH_3
Stainless steels	Hot concentrated Cl^- and OH^- solutions
High Ni alloys	Hot high-purity water and steam, wet HF
Cu alloys, e.g. α-brass	NH_3 and NO_2^- solutions, moist air containing SO_2
Al alloys	Cl^-, Br^- and I^- solutions (often IGSCC)
Ti and its alloys	Cl^-, Br^- and I^- solutions, anhydrous MeOH, anhydrous N_2O_4, fuming HNO_3

Cracking in sour H_2S containing environments is often related to hydrogen embrittlement.

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Metallurgical changes

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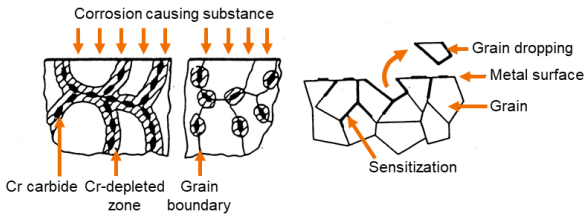
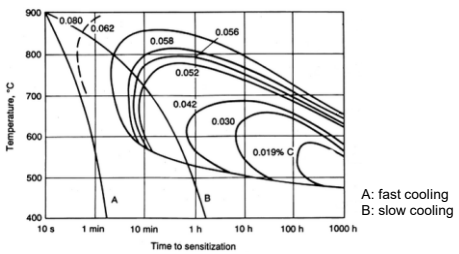
Intergranular corrosion

- Grain boundaries of the crystallites in a metal can become more prone to corrosion due to metallurgical changes in the metal.
  - Inappropriate heat-treatments can cause the depletion of alloying elements near the grain boundaries leading to sensitization for intergranular corrosion.
    - Temperature and time dependent
  - Preferred corrosion attack at the weakened grain boundaries causes grain dropping (e.g. in stainless steels) or exfoliation in extruded metals (e.g. in aluminium alloys).
    - Suitable corrosive environments required

Cr-depletion at the grain boundaries of stainless steel caused by Cr carbide formation leading to grain dropping



Time-sensitization diagram for different carbon contents in a standard austenitic stainless steel



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Special forms of corrosion

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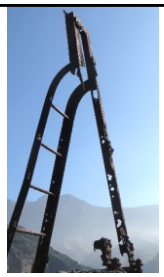
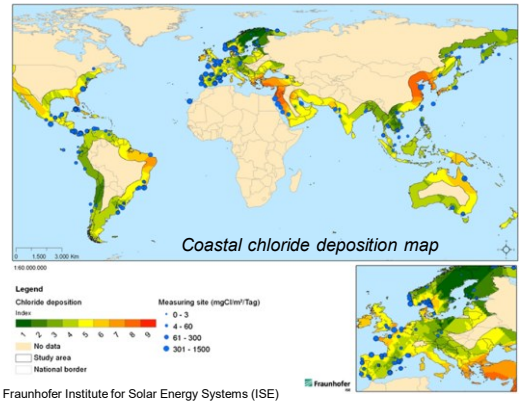
Special forms of corrosion

- Corrosion modes may be categorized and named also by the environment or the conditions under which they occur.
  - Resulting in different corrosion forms depending on the environment.
- Atmospheric corrosion:
  - Uniform, pitting / crevice corrosion or even SCC in wet or dry, indoor or outdoor atmospheres
    - Formation of patina possible depending on metal
  - Definition of corrosion classes for carbon steel, aluminium and zinc
    - Prediction of corrosion rates
      - Based on Cl^-, SO_2 and time of wetness
    - Material selection guidelines for stainless steels
  - Concerns also organic and metallic coatings on metals, e.g. painted galvanised steel



Atmospheric corrosion of carbon steel



Coastal chloride deposition map

Source: Fraunhofer Institute for Solar Energy Systems (ISE)

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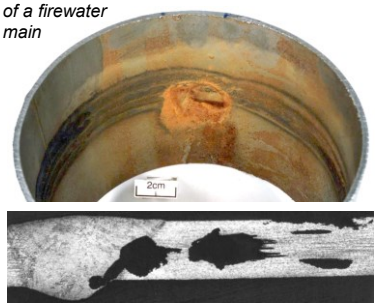
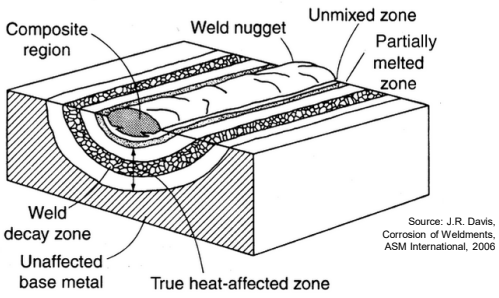
Special forms of corrosion

- Weld corrosion
  - Different (= better or worse) corrosion resistance of weld joints due to chemical composition and metallurgical structure of the weld nugget and metallurgical changes in the heat affected zone.
    - Galvanic corrosion commonly only when two different metals had been welded to each other.
  - Oxide scale and weld defects can reduce locally corrosion resistance in the welded area.
    - Proper welding practices and weld cleaning are important.
    - Typical are pitting corrosion, microbially induced corrosion, stress corrosion cracking and inter-granular corrosion in the heat affected zone

Pitting at a weld of a firewater main





Source: J.R. Davis, Corrosion of Weldments, ASM International, 2006

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Summary

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Summary

- The knowledge and understanding of corrosion processes is important for the development of strategies to avoid costly and dangerous corrosion damages.
- Typical corrosion protection measures:
  - Selection of the most suitable material for the environmental conditions in the application
    - Other material properties need to be considered, including price!
  - Adjustment of the conditions in the application to the corrosion resistance of the material
    - Only rarely possible in process environments
  - Additional corrosion protection measures
    - For example, corrosion resistant surface coatings or sacrificial anodes for metals
- Knowledge on corrosion was needed, is needed and will be needed in the future.
  - That's why we are here today. That's what we do.

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beyond the obvious

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