UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

www.vscht.cz

Corrosion Engineering

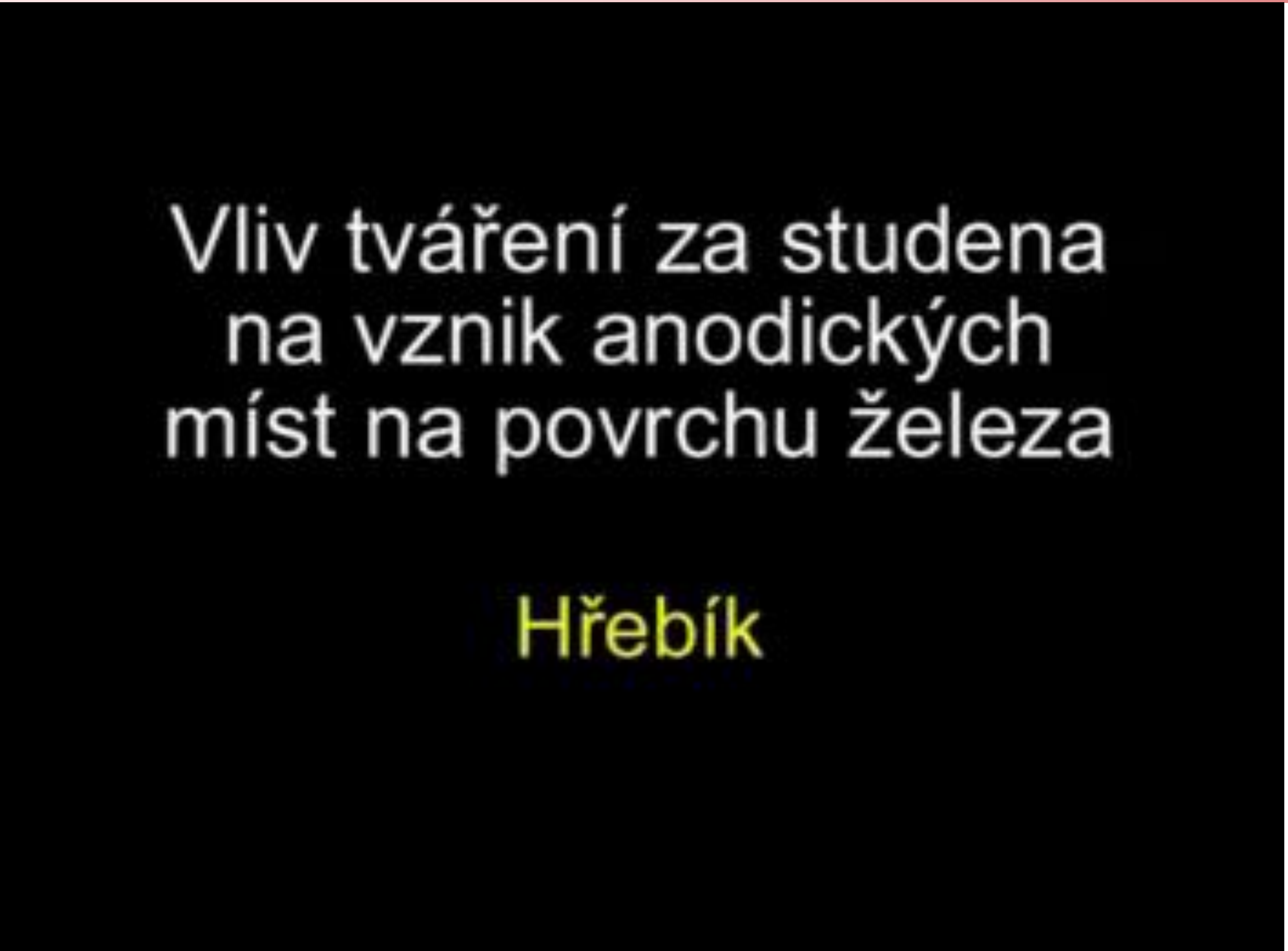
Tomáš Prošek

Corrosion of Materials I
Steel and Stainless Steel

Role of Metallurgical Parameters

- **Composition**: Nobility (standard potential series) and ability to passivate (E–pH diagrams), purity – alloys, phases, impurities, inclusions
- **Structure**: Lattice, grain size, grain boundaries, dislocations
- **Stress**: Tensile stress dangerous – cracking of passive films, adsorption of activators, environmentally assisted cracking
- **Surface state**: Smoothness, presence of impurities, contamination

Role of Forming



Water solution:

- 10 g/l NaCl
- 1 g/l $K_3[Fe(CN)_6]$
- Phenolphthalein

Blue color = presence of Fe^{2+} – Prussian blue (berlínská modř) $KFe[Fe(CN)_6]$ = anodic site

Red colour = pH > 8.2 = alkalization, cathodic site

Price of Basic Metals, Production

April 2017 (London Metal Exchange and other sources)

Metal	Price [CZK/kg]
Au	1 031 500
Pt	784 500
Pd	642 900
Ag	14 832
Ta	3 226
Co	1 411
Sn	507
Mo	384
Ti	257
Ni	253

Metal	Price [CZK/kg]
Cu	145
Cr [1]	87
SS 316 [2]	67
Zn	65
Pb	57
Mg	55
SS 304 [2]	52
Mn	49
Al	48
Steel [3]	11–20

Metal	Production [Mt]	Energy cost [GJ/t]
Steel	1440	25
Plastics	265	80
Al	41	175
SS	31	31
Cu	16	90

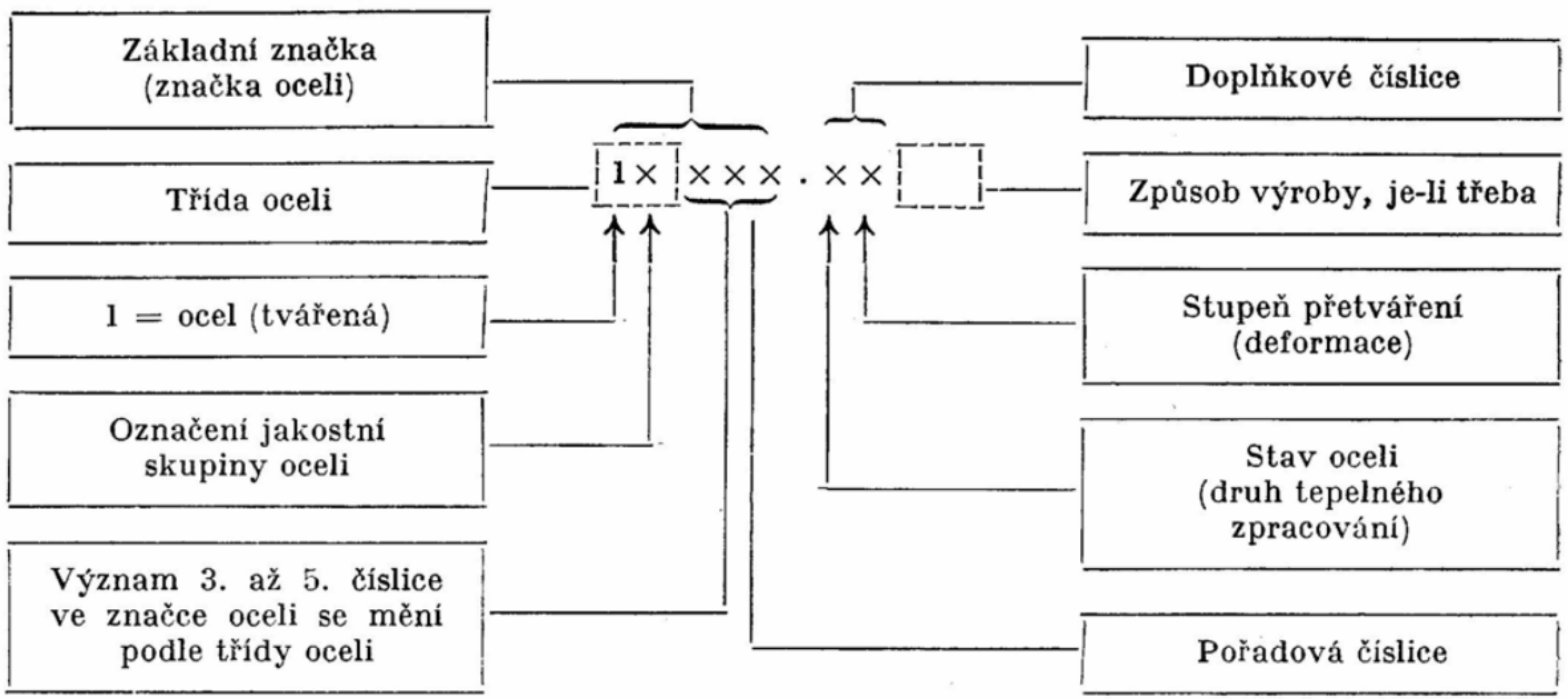
Data 2010

SS Stainless steel
[1] As ferrochromium
[2] Sheet
[3] Products (rebar, sheet, …)

Steel – Selected Application Types

- **Construction steels / *konstrukční***: non-alloyed, used for engineering and construction applications
- **Free cutting steels / *automatové:*** carbon steel with increased content of sulfur (about 0.3 %) and manganese (about 1 %); presence of MnS makes them well machinable (fragile chips)
- **Reinforcing steels / *betonářské***: reinforcing wires or bars for concrete; non-alloyed or low-alloyed
- **Spring steels / *pérová, pružinová***: good static and dynamic loading properties, high fatigue limits; elevated carbon or manganese, chromium and silicon contents
- **Hardening steels / *oceli pro kalení (precipitačně vytvrditelné)***: low carbon content ensures good mechanical properties after quenching
- **Electrical steel sheets / *ocel pro elektrotechnické plechy***: cores of transformers; good magnetic properties; containing 1 to 4.5 % silicon
- **Deep-drawing steels / *hlubokotažné***: good plastic deformation properties; low carbon and impurities content; micro-alloying with aluminum, titanium, vanadium, boron, zirconium and niobium; for car body
- **Heat-resistant steels / *žáruvzdorné a žárupevné***: medium content of alloying elements
- **Tool steels / *nástrojové***: higher carbon content; used for tools and molds
- **Weathering steels / *patinující***: addition of Cu, Ni, Si, Cr, P
- **High strength steels / *vysoko pevnostní***: yield strength >600 (usually 1000–2000) MPa; alloying with Mn, Si, Cr, Mo, Ti, …

Steel – Classes by ČSN 42 0002



Druh tepelného zpracování:
0 — tepelně nezpracováno
1 — normalizačně žíháno
2 — žíháno (uveden druh)
3 — žíháno na měkko
4 — kaleno a nízko popuštěno
5 — normalizačně žíháno a popuštěno
6 — zušlechtěno na dolní pevnost
7 — zušlechtěno na střední pevnost
8 — zušlechtěno na horní pevnost
9 — zvláštní stav tepelného zpracování (uvede se slovně za číslicí)

Způsob výroby:
T — Thomasův konvertor
M — Martinova pec
E — Elektrická pec
K — Kyslíkový konvertor

u — uklidněná
p — polouklidněná
n — neuklidněná

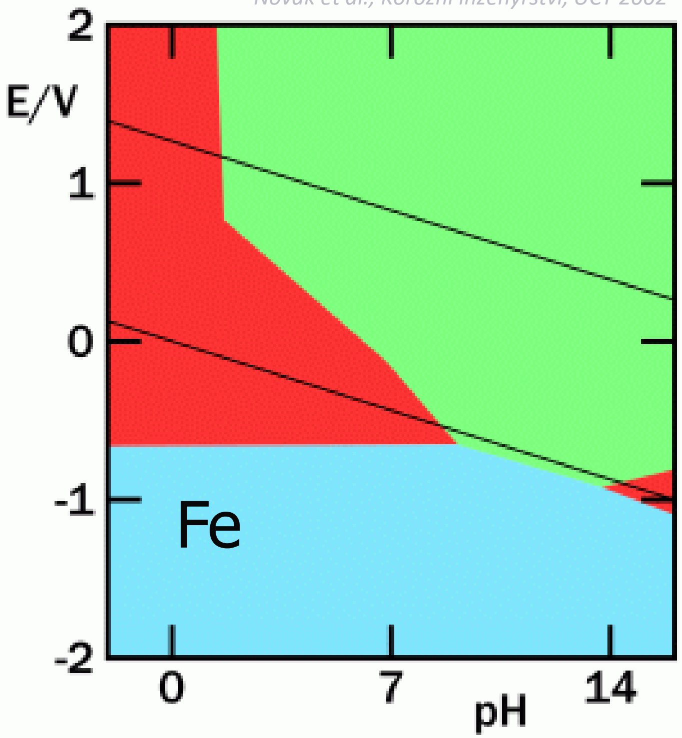
Stupeň přetváření:
0 — nepřeválcovaný
1 — lehce převálcovaný
2 — 1/4 tvrdý
3 — 1/2 tvrdý
4 — 3/4 tvrdý
5 — 4/4 tvrdý
6 — 5/4 tvrdý
7 — (neobsazeno)
8 — speciálně zpevněno
9 — podle zvláštního ujednání

Steel – Classes by ČSN 42 0002

- **CLASS 10**: cheap, low carbon content, purity and chemical composition not guaranteed; only minimal yield strength is given; good weldability and machinability; sheets, bars, wires, rails, tubes, fasteners
- **CLASS 11**: non-alloyed construction steels with guaranteed purity, content of phosphorus and sulfur, minimal yield strength and ductility; profiles, wires, sheets, tubes, deep drawing sheets, shafts, screws, cogged wheels; free cutting steels
- **CLASS 12–16**: low-alloyed construction steels for manufacturing of machine parts, engines and other car parts for hardening such as cogged wheels, springs, etc.
- **CLASS 17**: stainless steels for knives, surgery tools, industrial equipment and steels for permanent magnets
- **CLASS 19**: tool steels

Steel – Corrosion Resistance

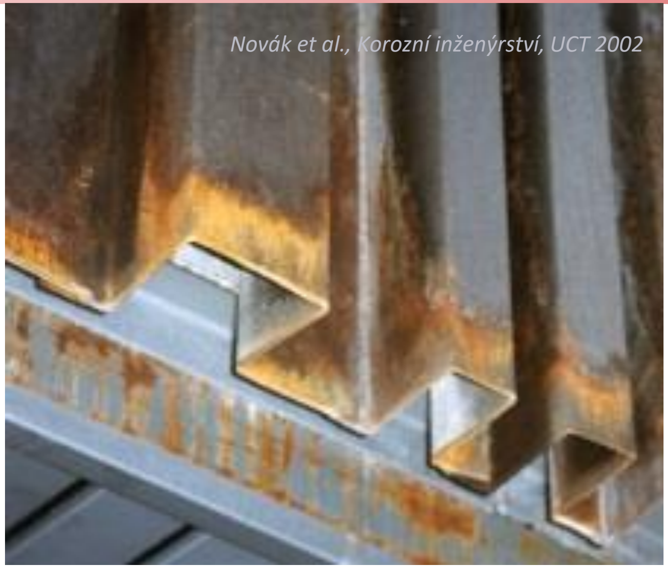
Novák et al., Korozní inženýrství, UCT 2002



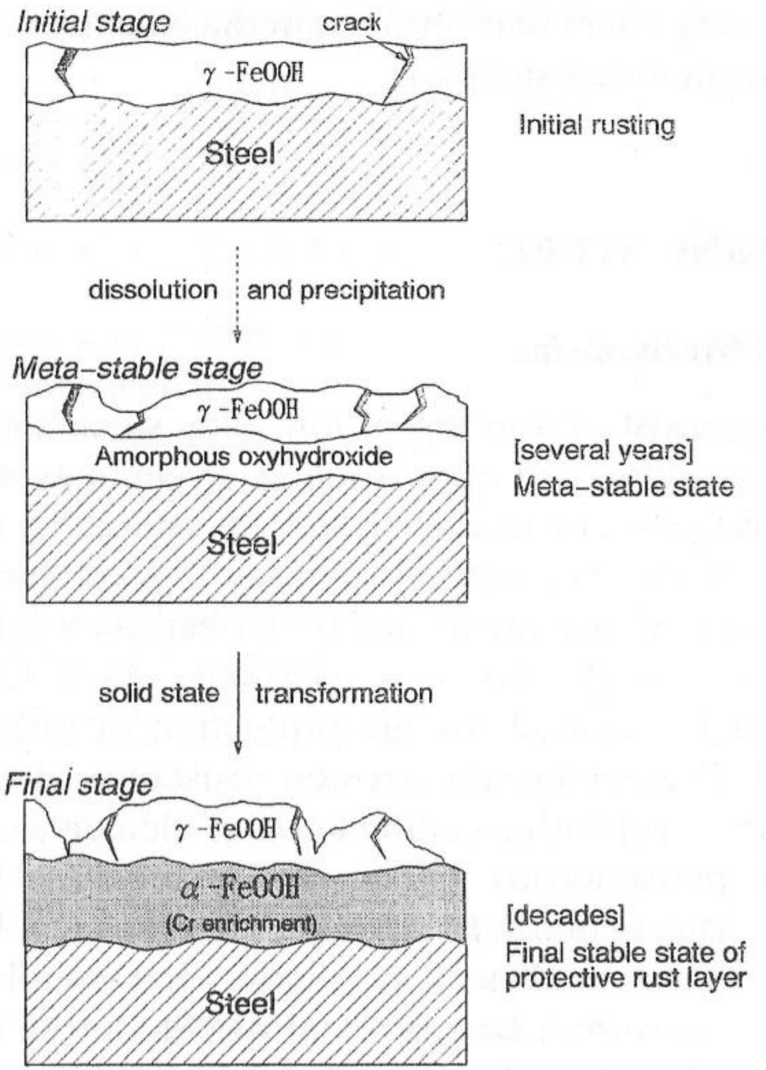
- Uniform corrosion with often unacceptable corrosion rate ⇨ protection necessary
- Worse stability especially under acidic conditions
- **Dry air**: Formation of protective oxide film
- **Outdoor atmosphere**: Corrosion rate in Central Europe 10–40 µm/year, marine and polluted industrial atmosphere up to hundreds of µm/year
- **Electrolytes**: Formation of FeOOH and Fe_2O_3 in different modifications, low protective ability (red rust)
- **Aqueous media**: 100–800 µm/year, access of O_2 critical, formation of deposits; protection necessary in most cases
- **Steam**: Formation of magnetite Fe_3O_4 with good protection ability
- **Soil**: Usually about 0.2, but up to 1–3 mm/year; protection (cathodic, coatings) necessary
- **Concrete**: Initially alkali, low corrosion rate under 0.1 µm/year, no protection required; 10–20 µm/year after carbonation
- **Non-uniform corrosion:** Hydrogen entry – **hydrogen embrittlement and blistering** (oil & gas); **stress corrosion cracking** in sodium hydroxide or HCO_3^-/CO_3^{2-} (soil)

Weathering Steel (Corten)

- Low-alloyed steel containing Cr, Ni, Cu (0.3–0.6 %), P, Si
- Compact and adherent layer of corrosion products
- Attractive to architects



Novák et al., Korozní inženýrství, UCT 2002

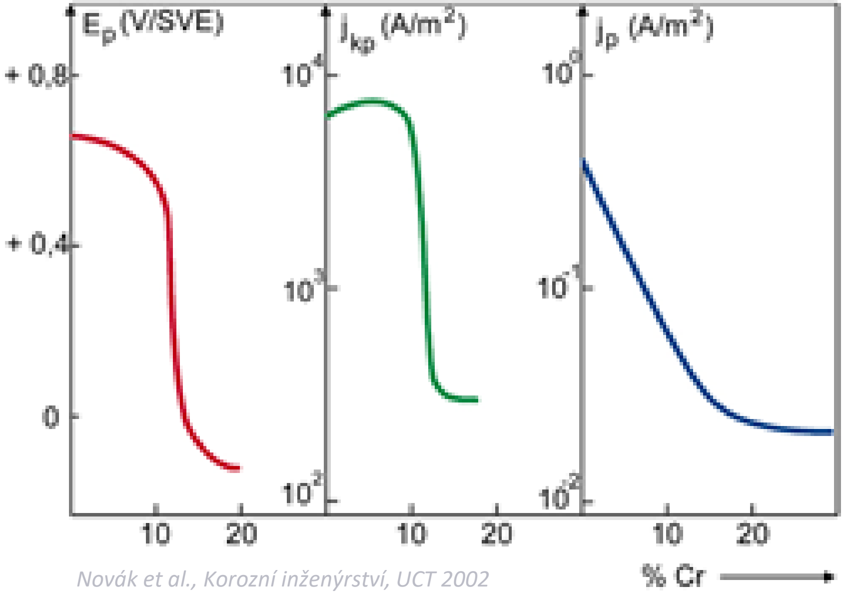


Novák et al., Korozní inženýrství, UCT 2002

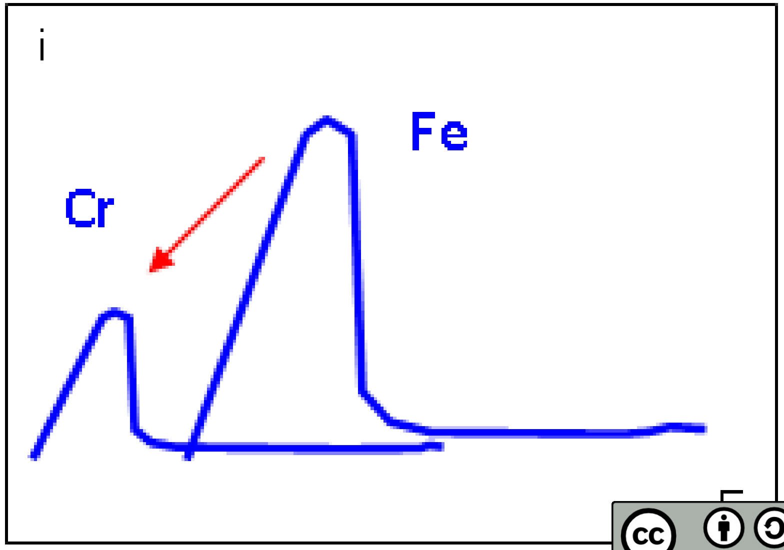
http://www.juluis.com/wp-content/uploads/2012/11/jl-Juluis-38.jpg

Stainless Steel

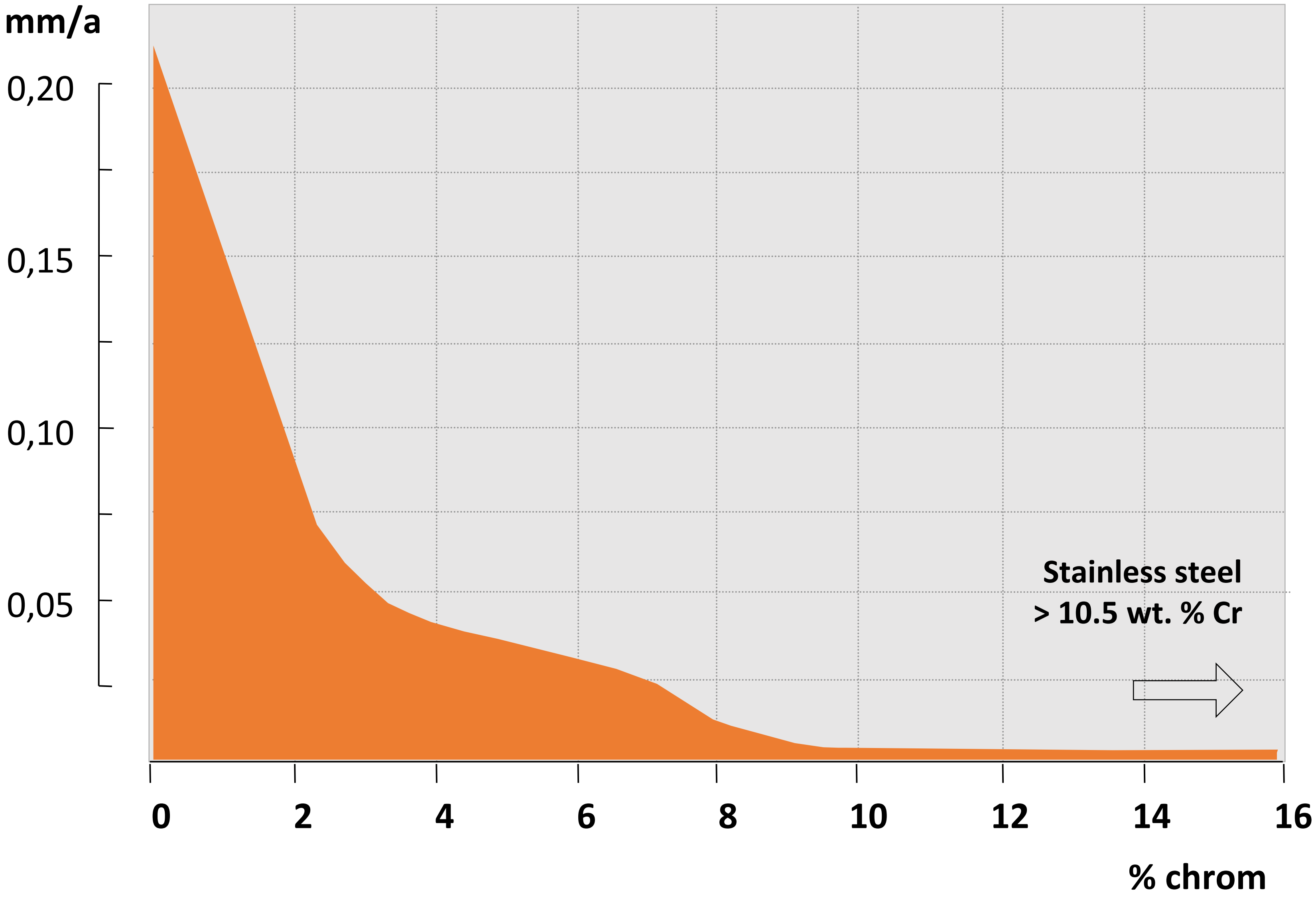
- One of several alloys developed due to corrosion resistance
- Combination of **Fe** (low corrosion resistance, high strength, cheap) and **Cr** (high corrosion resistance, brittle, expensive)
- Developed at beginning of 20th century simultaneously in the USA, France and Germany
- Passive film of Cr_2O_3 replaces fully Fe oxides at 10.5 wt. % Cr
- 12 wt. % practical limit, most stainless steels contain about 18 wt. % Cr, maximum 29 wt. % (poor mechanical properties above this level)



Novák et al., Korozní inženýrství, UCT 2002



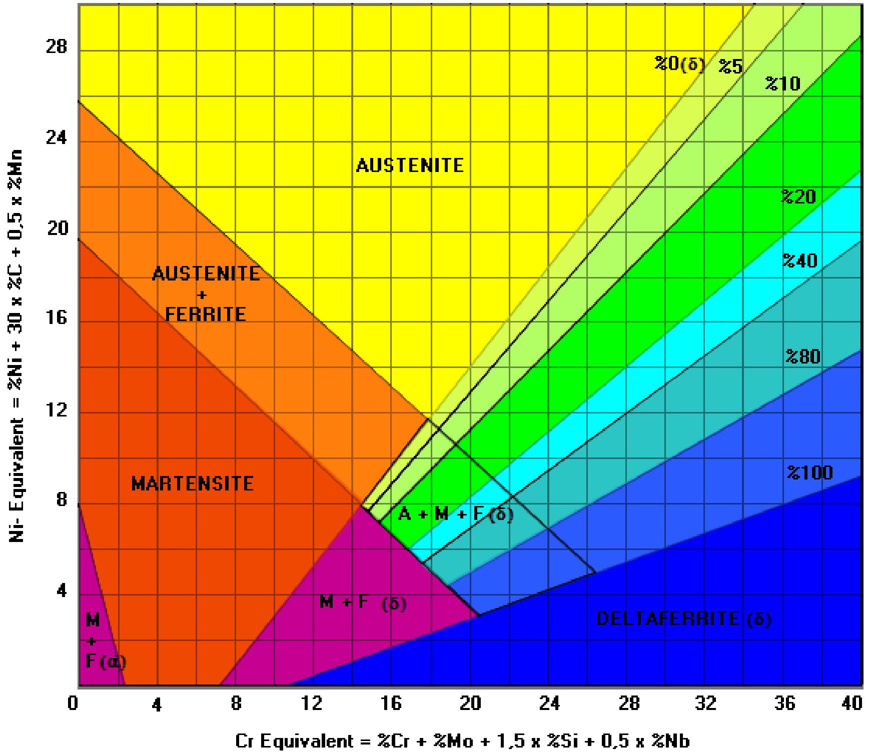
Stainless Steel



Corrosion Rate in Atmosphere

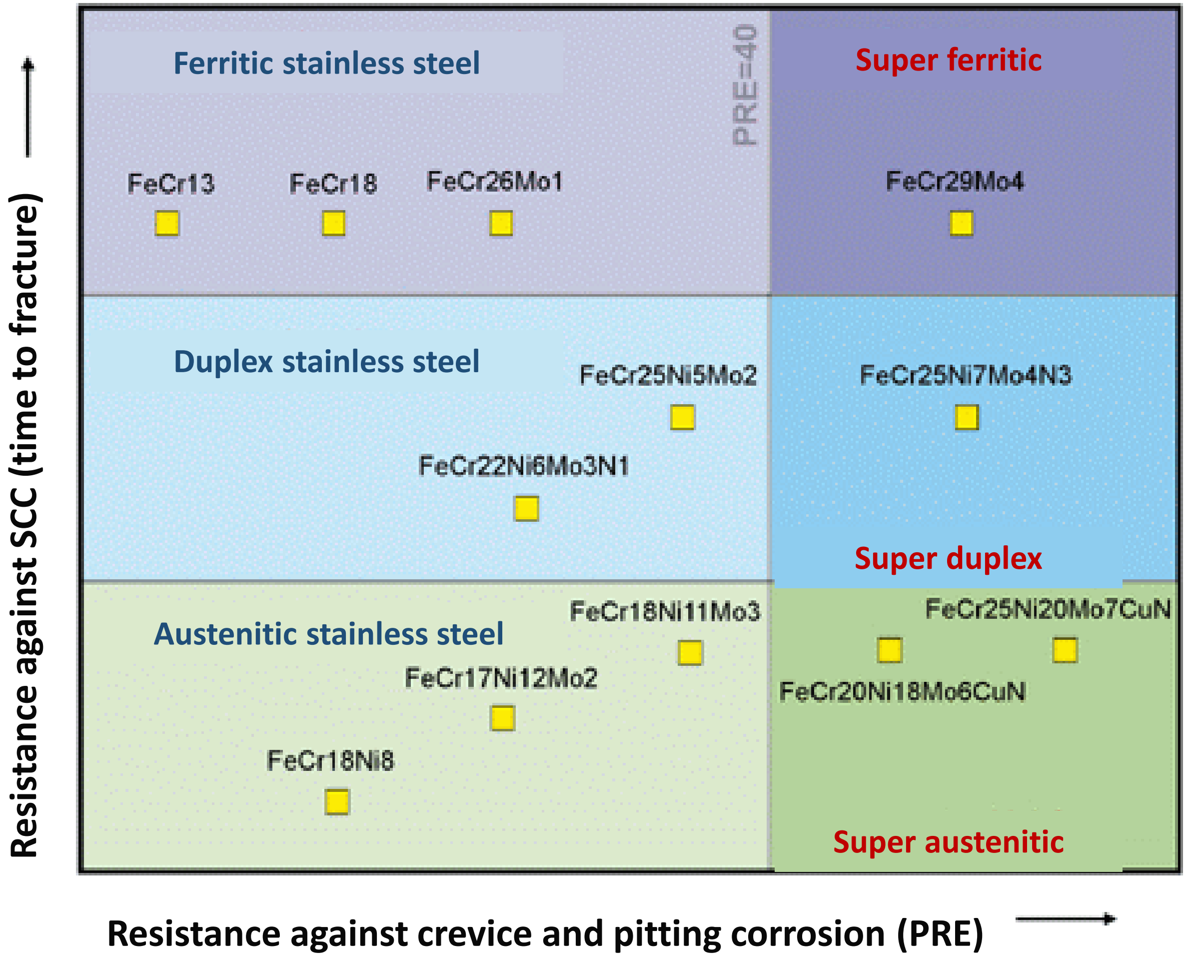
Stainless Steel – Groups

Group	Strength	Ductility	Magnetic	Weldable	Formable
Austenitic	●●	●●●	✗	✓	●●●
Duplex	●●●	●●	✓	✓	●●
Ferritic	●●	●●	✓	(✓)	●●



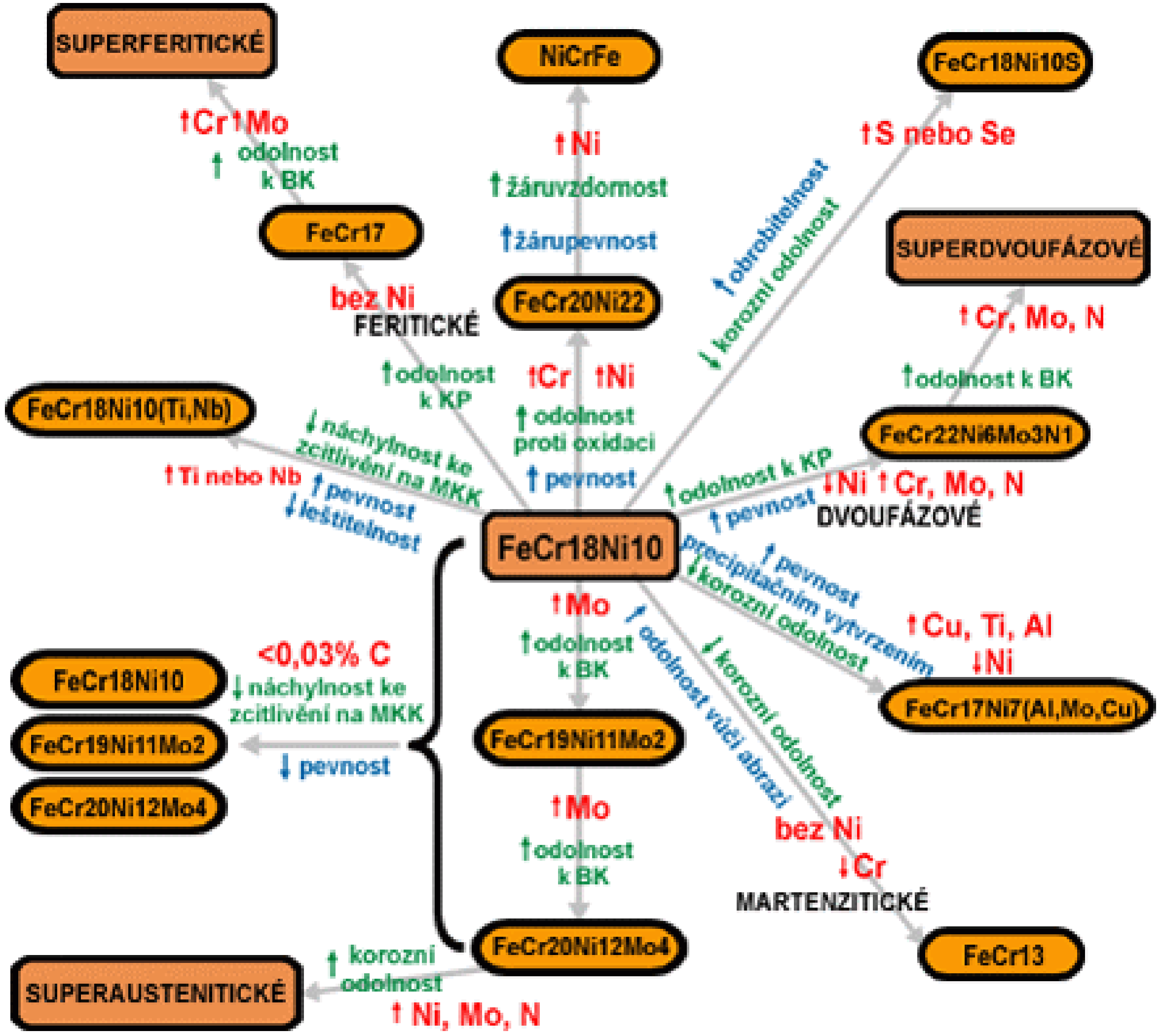
Schaefflerův diagram

Novák et al., Korozní inženýrství, UCT 2002

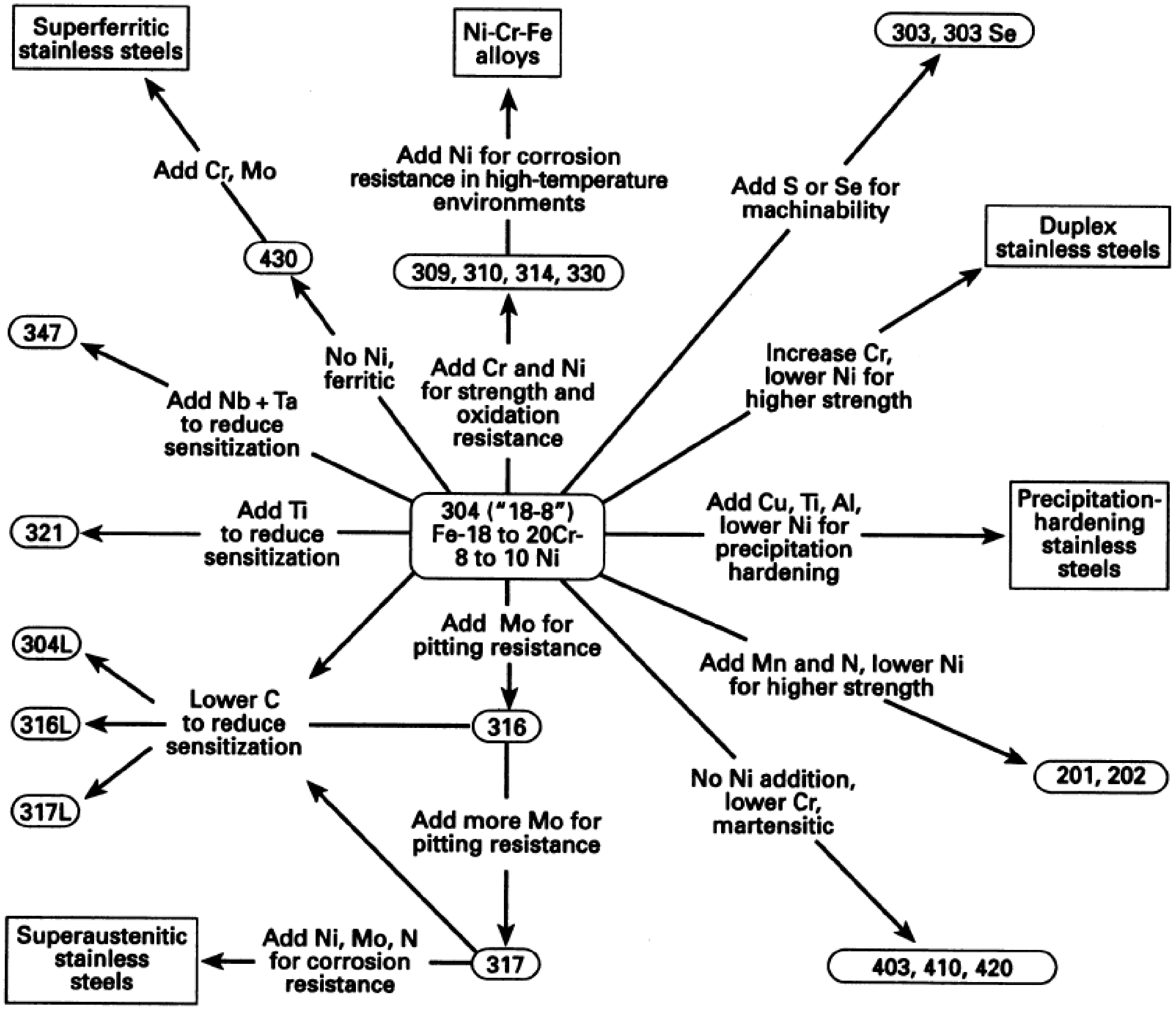


Limited application: Martensitic and precipitation hardening (PH)

Stainless Steel – Types (Grades)



Novák et al., Korozní inženýrství, UCT 2002



Stainless Steel – Labeling

Labeling of Stainless Steels

According to (ČSN) EN 10088:
- EN 1.4301
- X5CrNi18-10

Older Czech system:
- ČSN 17240
- AKV 7

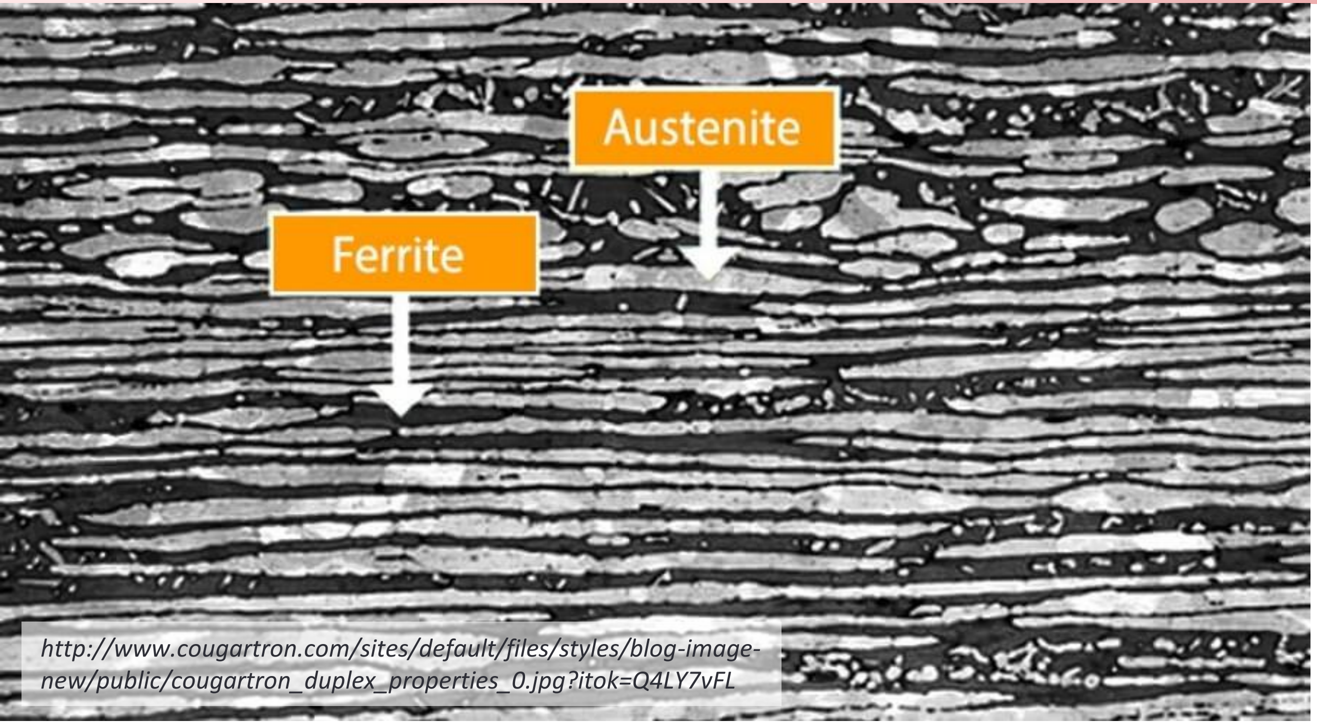
Further standards/systems:
- AISI / ASTM 304 (USA)
- BS 304S31 (British Standard)
- UNS S30400 (Unified Numbering System)

(ČSN) EN 10088 :

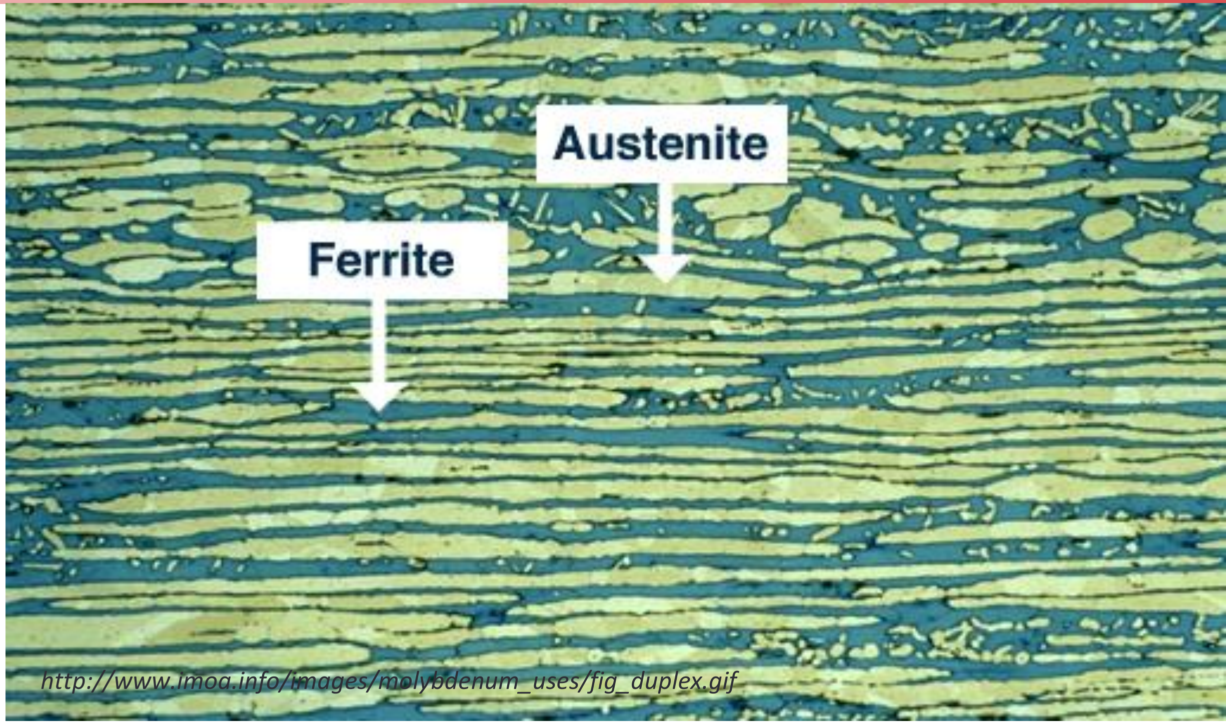
1.	43	01
Steel	Group of stainless steels	Type

Groups defined in ČSN EN 10027-2:
- 1.40XX: SS with Ni < 2.5 %, no Mo, Nb, Ti
- 1.41XX: SS with Ni < 2.5 % and Mo, no Nb, Ti
- 1.43XX: SS with Ni ≥ 2.5 %, no Mo, Nb, Ti
- 1.44XX: SS with Ni ≥ 2.5 % and Mo, no Nb, Ti
- 1.45XX: SS with special alloying elements
- 1.46XX: chemically resistant SS and high temperature SS

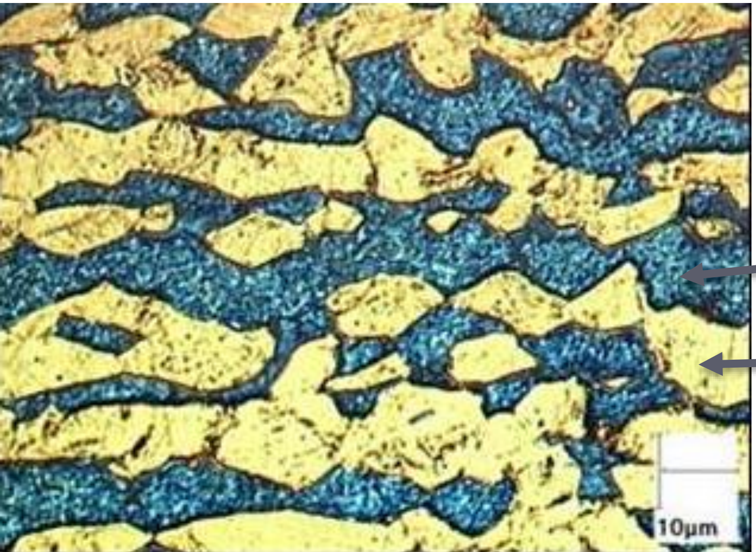
Duplex Stainless Steel



http://www.cougartron.com/sites/default/files/styles/blog-image-new/public/cougartron_duplex_properties_0.jpg?itok=Q4LY7vFL



http://www.imoa.info/images/molybdenum_uses/fig_duplex.gif



Ferrite

Austenite

Stainless steel type	Labeling / Grade			wt. %				
	General	UNS	EN	Cr	Mo	Ni	N	PRE
I. generation	329	S32900	1.4460	25.5	1.5	3.5		30
II. generation	2304	S32304	1.4362	23.0	0.8	4.2	0.1	27
	2205	S31803	1.4462	22.0	3.0	5.5	0.1	34
	2205	S32205	1.4462	22.5	3.2	5.5	0.2	36
Super duplex	2507	S32750	1.4410	25.0	4.0	7.0	0.3	43

$PRE\ [\%] = w(Cr) + 3.3 \times w(Mo) + 16 \times w(N)$

Novák et al., Korozní inžen...

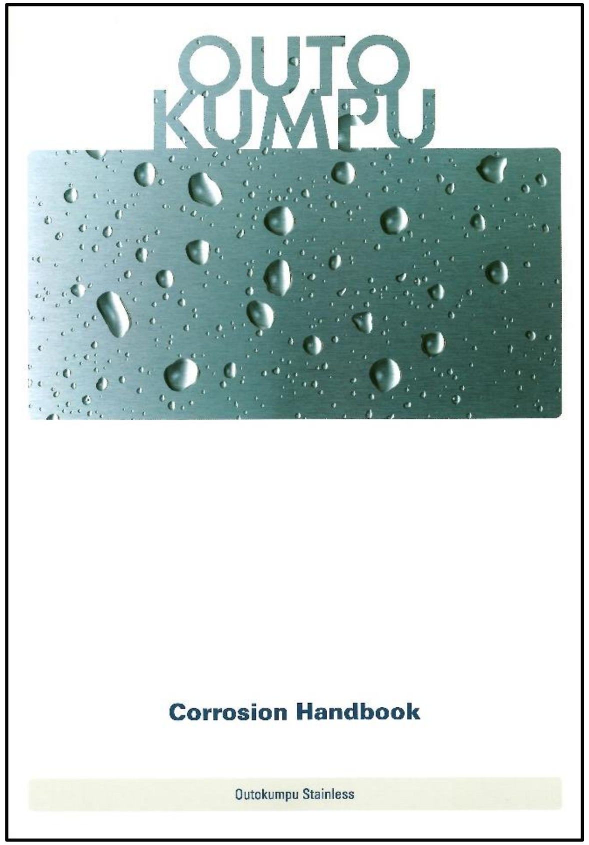
http://cemam.grenoble-inp.fr/servlet/com.univ.collaboratif.utils.LectureFichiergw?ID_FICHIER=1341223229722&ID_FICHE=49067

Stainless Steel – Type Selection

- Grade selection: sufficient corrosion resistance at the lowest possible cost is required
- For most aqueous environments, data available

SULPHURIC ACID
H_2SO_4

Conc, % Temp. °C	0.1 100 =BP	0.5 20	0.5 50	0.5 100 =BP	1 20	1 50	1 70	1 85	1 100 =BP	2 20	2 50	2 60	3 20	3 35	3 50
Carbon steel	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
13% Cr-steel	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
18-2	2	0	2	2	0	2	2	2	2	0	2	2	0	2	2
18-10	2	0	1	2	0	1	1	2	2	0	1	1	0	1	1
17-12-2.5	1	0	0	1	0	0	0	1	1	0	0	0	0	0	0
18-13-3	1	0	0	1	0	0	0	1	1	0	0	0	0	0	0
17-14-4	1	0	0	1	0	0	0	0	1	0	0	0	0	0	0
904L	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0
Sanicro 28		0	0	0	0	0	0	0	0	0	0	0	0	0	0
254 SMO		0	0		0	0	0	0	1	0	0	0	0	0	0
654 SMO		0	0		0	0	0	0	0	0	0	0	0	0	0
SAF 2304	1	0	0		0	0	0	0	1	0	0	0	0	0	0
2205		0	0	1	0	0	0	0		0	0	0	0	0	0
SAF 2507		0	0		0	0	0	0	0	0	0	0	0	0	0
Ti	1	0	0	1	0	0	1	1	1	0	0	1	0	0	1



0: v_{corr} <0.1 mm/year
1: v_{corr} 0.1–1 mm/year
2: v_{corr} >1 mm/year

Stainless Steel – Type Selection

Atmospheric conditions:

- Standard (ČSN) EN 1993-1-4/A1 (Eurocode) defines Corrosion Resistance Factor (CRF) for any environment

CRF = F1 + F2 + F3

- F1 = Risk of exposure to chlorides from salt water or de-icing salts
- F2 = Risk of exposure to SO_2
- F3 = Cleaning regime or exposure to washing by rain

Swimming pool halls and ferritic stainless steels not included

F_1 Risk of exposure to chlorides from salt water or de-icing salts		
NOTE M is distance from the sea and S is distance from roads with de-icing salts.		
1	Internally controlled environment	
0	Low risk of exposure	M > 10 km or S > 0,1 km
-3	Medium risk of exposure	1 km < M ≤ 10 km or 0,01 km < S ≤ 0,1 km
-7	High risk of exposure	0,25 km < M ≤ 1 km or S ≤ 0,01 km
-10	Very high risk of exposure	Road tunnels where de-icing salt is used or where vehicles might carry de-icing salt into the tunnel
-10	Very high risk of exposure	M ≤ 0,25 km
		North Sea coast of Germany and Baltic coastal areas
-15	Very high risk of exposure	M ≤ 0,25 km
		Atlantic and Mediterranean coast line

F_2 Risk of exposure to sulphur dioxide		
0	Low risk of exposure	<10 μg/m³ average gas concentration
-5	Medium risk of exposure	10 - 90 μg/m³ average gas concentration
-10	High risk of exposure	90 - 250 μg/m³ average gas concentration

F_3 Cleaning regime or exposure to washing by rain (if $F_1 + F_2 \geq 0$, then F_3=0)	
0	Fully exposed to washing by rain
-2	Specified cleaning regime
-7	No washing by rain or no specified cleaning

Stainless Steel – Type Selection

Atmospheric conditions:

- Corrosion Resistance Class (CRC) established from CRF

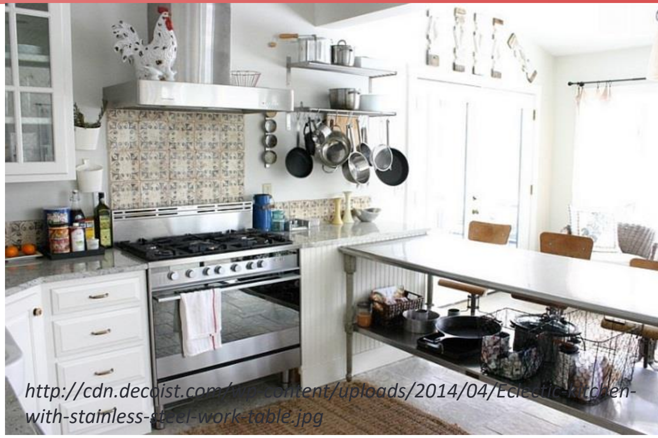
CRF	CRC
CRF = 1	I
0 ≥ CRF > -7	II
-7 ≥ CRF > -15	III
-15 ≥ CRF ≥ -20	IV
CRF < -20	V

Corrosion resistance class CRC				
I	II	III	IV	V
1.4003	1.4301	1.4401	1.4439	1.4565
1.4016	1.4307	1.4404	1.4462	1.4529
1.4512	1.4311	1.4435	1.4539	1.4547
	1.4541	1.4571		1.4410
	1.4318	1.4429		1.4501
	1.4306	1.4432		1.4507
	1.4567	1.4162		
	1.4482	1.4662		
		1.4362		
		1.4062		
		1.4578		

Stainless Steel – Applications

http://www.steritool.com/images/product/IMG_0246.jpg


http://ecx.images-amazon.com/images/I/71ckpcd510L._SL1500_.jpg


http://cdn.decoist.com/wp-content/uploads/2014/04/Eclectic-kitchen-with-stainless-steel-work-table.jpg

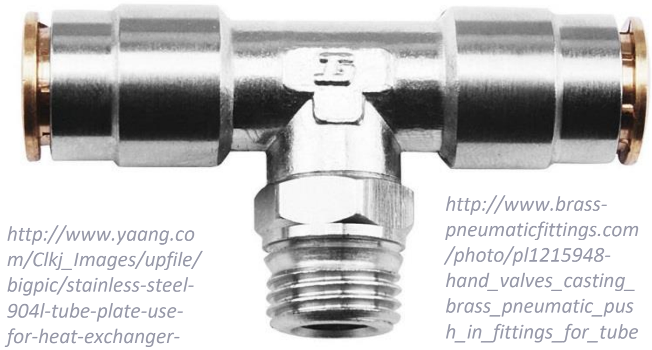
https://s3.amazonaws.com/lumberjocks.com/ngacpo8.jpg

http://img.archiexpo.com/images_ae/photo-g/62102-5160933.jpg

http://image.made-in-china.com/43f34j00UjOtkoeckvbS/Home-Use-Stainless-Steel-Dish-Washer-6-9-12-14-Sets.jpg

https://s-media-cache-ak0.pinimg.com/736x/65/f1/8d/65f18d6da4de0f78410a2354367e02f0.jpg

http://www.yaang.com/Clkj_Images/upfile/bigpic/stainless-steel-904l-tube-plate-use-for-heat-exchanger-01.jpg



http://www.brass-pneumaticfittings.com/photo/pl1215948-hand_valves_casting_brass_pneumatic_push_in_fittings_for_tube_aisi_301.jpg

http://www.meadmetals.com/images/sstcoils.jpg

Copyright & Contact

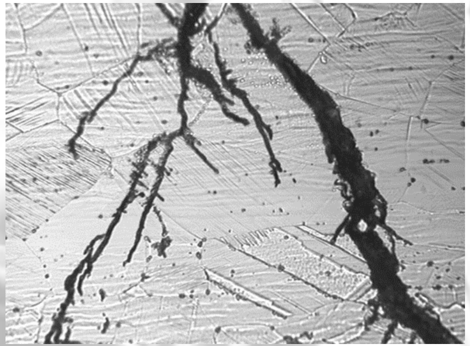
Tomáš Prošek, Ph.D.

University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS



www.vscht.cz

Corrosion Engineering

Tomáš Prošek

Corrosion of Materials II
Non-Ferrous Metals

Price of Basic Metals, Production

April 2017 (London Metal Exchange and other sources)

Metal	Price [CZK/kg]
Au	1 031 500
Pt	784 500
Pd	642 900
Ag	14 832
Ta	3 226
Co	1 411
Sn	507
Mo	384
Ti	257
Ni	253

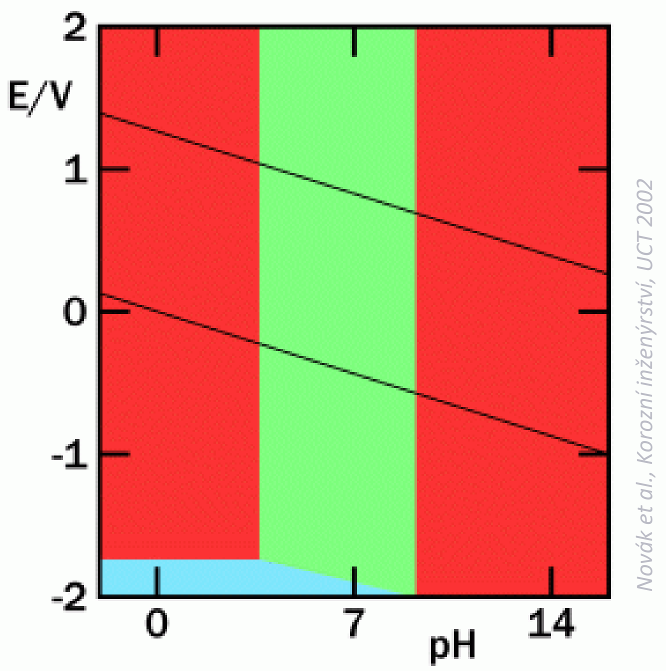
Metal	Price [CZK/kg]
Cu	145
Cr [1]	87
SS 316 [2]	67
Zn	65
Pb	57
Mg	55
SS 304 [2]	52
Mn	49
Al	48
Steel [3]	11–20

Metal	Production [Mt]	Energy cost [GJ/t]
Steel	1440	25
Plastics	265	80
Al	41	175
SS	31	31
Cu	16	90

Data 2010

SS Stainless steel
[1] As ferrochromium
[2] Sheet
[3] Products (rebar, sheet, …)

Aluminum and Alloys



- Active metal; applicability due to presence of stable passive film
- Amphoteric, maximal stability at neutral pH (4–8.5)

- Light; high strength to mass ratio (in particular for alloys)
- Corrosion resistance maximal for pure Al; alloys often require additional protection
- Atmosphere: Low uniform corr. rates:
  - Rural: 0–0.1 μm·year^{-1}
  - Urban: up to 1 μm·year^{-1}
  - Marine: 0.4–0.6 μm·year^{-1}
- Risk of pitting and crevice corrosion (chlorides; atmosphere without SO_2), galvanic corrosion (e.g., Cu)

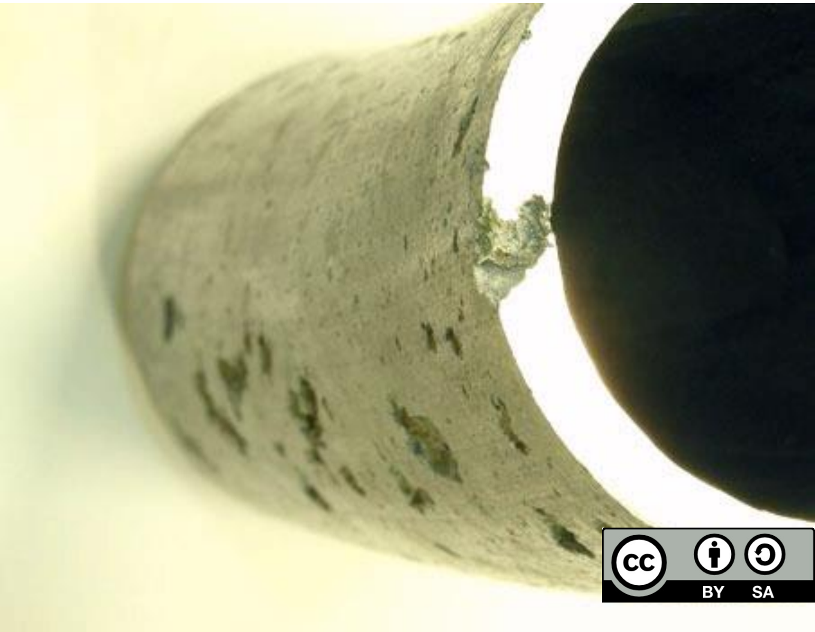
Aluminum and Alloys – Products

- Al oxide/hydroxide, Al_2O_3 (initial), later e.g. boehmite γ-AlOOH, bayerite $Al_2(OH)_3$

Substance[a]	Hey index no.[b]	Crystal system	Formula	K_{sp}[c]
Oxides and hydroxides				
Aluminum oxide		Cub.	γ-Al_2O_3	
Akdalaite	7.6.8	Hex.	$Al_2O_3 \cdot {}^1/_4H_2O$	4.8×10^{-13}
Boehmite	7.6.3	Orth.	γ-AlOOH	
Gibbsite	7.6.4	Mon.	$Al(OH)_3$	3.7×10^{-15}
Bayerite	7.6.5	Mon.	$Al(OH)_3$	1.5×10^{-14}
Tucanite		Amor.	$Al(OH)_3 \cdot {}^1/_2H_2O$	
Sulfates				
Aluminum sulfate hydrate		Amor.	$Al_x(SO_4)_y \cdot (H_2O)_2$	
Jurbanite			$Al(SO_4)(OH) \cdot 5H_2O$	1.6×10^{-18}
Aluminite	25.6.5	Mon.	$A1_2(SO_4)(OH)_4 \cdot 7H_2O$	
Chlorides				
Aluminum chloride		Mon.	$AlCl_3$	
Cadwaladerite	8.6.17	Amor.	$AlCl(OH)_2 \cdot 4H_2O$	

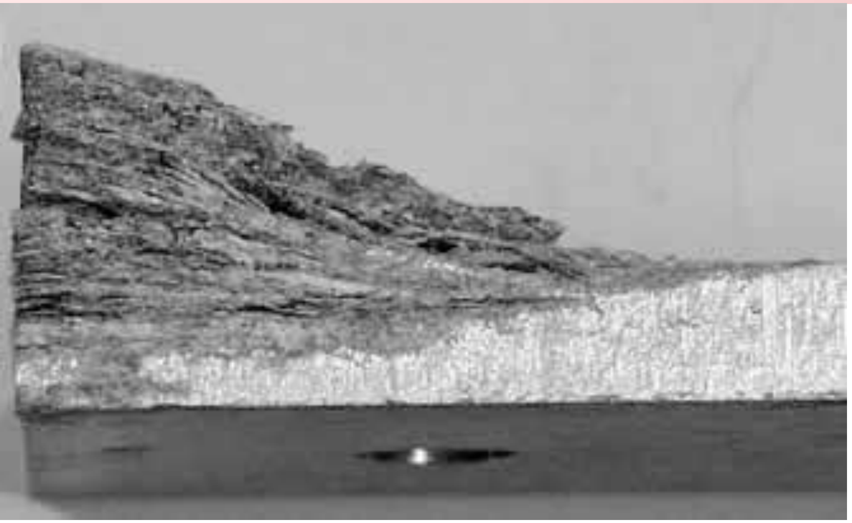
Aluminum and Alloys – Pitting

Novák et al., Korozní inženýrství, UCT 2002

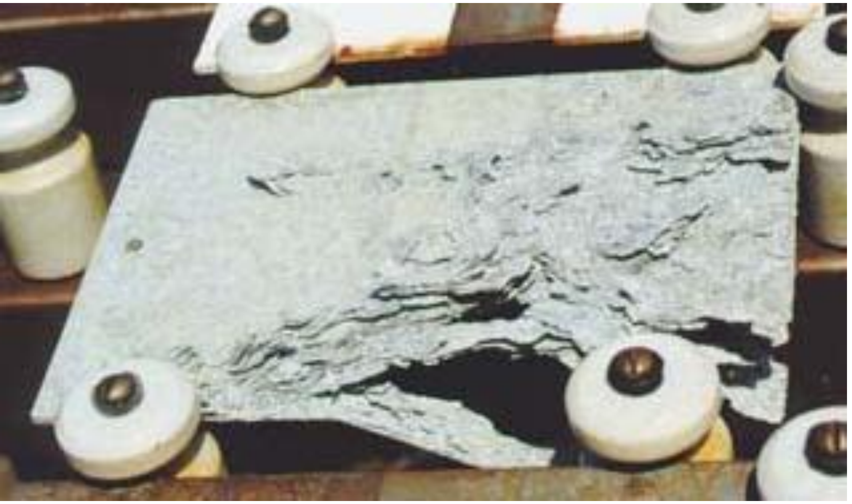


Aluminum in water containing chloride, before and after removal of corrosion products

Aluminum and Alloys – Exfoliation



https://www.nde-ed.org/EducationResources/CommunityCollege/Materials/Graphics/PhysicalProperties/ExfoliationCorrosion1.jpg



http://corrosion.ksc.nasa.gov/images/p15.jpg

http://www.amteccorrosion.co.uk/Aluminium%20Pics/End%20grain%20DSCN1992.jpg

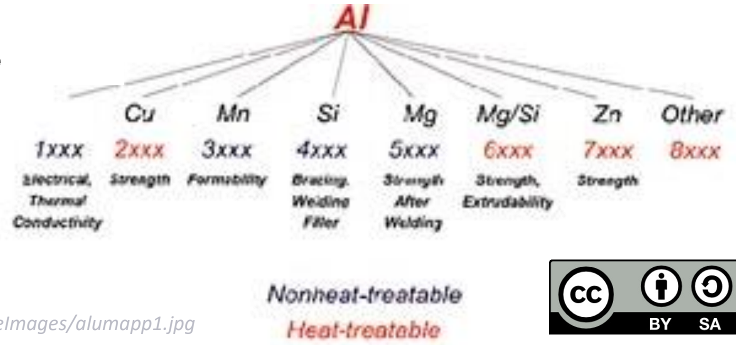
Aluminum Alloys

Alloy Class	Typical Temper*	Alloying Elements	Corrosion Resistance** General	Pitting	Exfoliation	SCC	
1xxx	All	Natural impurities in refinery Al	E	E	E	I	Limited commercial use
2xxx	T3,T4,	Cu	F	P	P	VS	Airframes
	T8		F	P	F	R	
3xxx	All	Mn; Mn + Mg	E	E	E	I	Kitchenware, food processing, construction
4xxx	All	Si	F	G	G	G	Welding wires
5xxx	Most	Mn, Mg, Cr	E	G	G	I-R	Train frames, ships
6xxx	All	Mg, Si	E	G	E	I	Automotive
7xxx	T6,	Zn, Mg, Mn, Cu	F	F	F-P	S-VS	Maximal strength; aeronautics, automotive (replacement of 2xxx)
	T73		F	F	G	R	

* T3, T4, T6: age hardened; T8, T73: overaged.

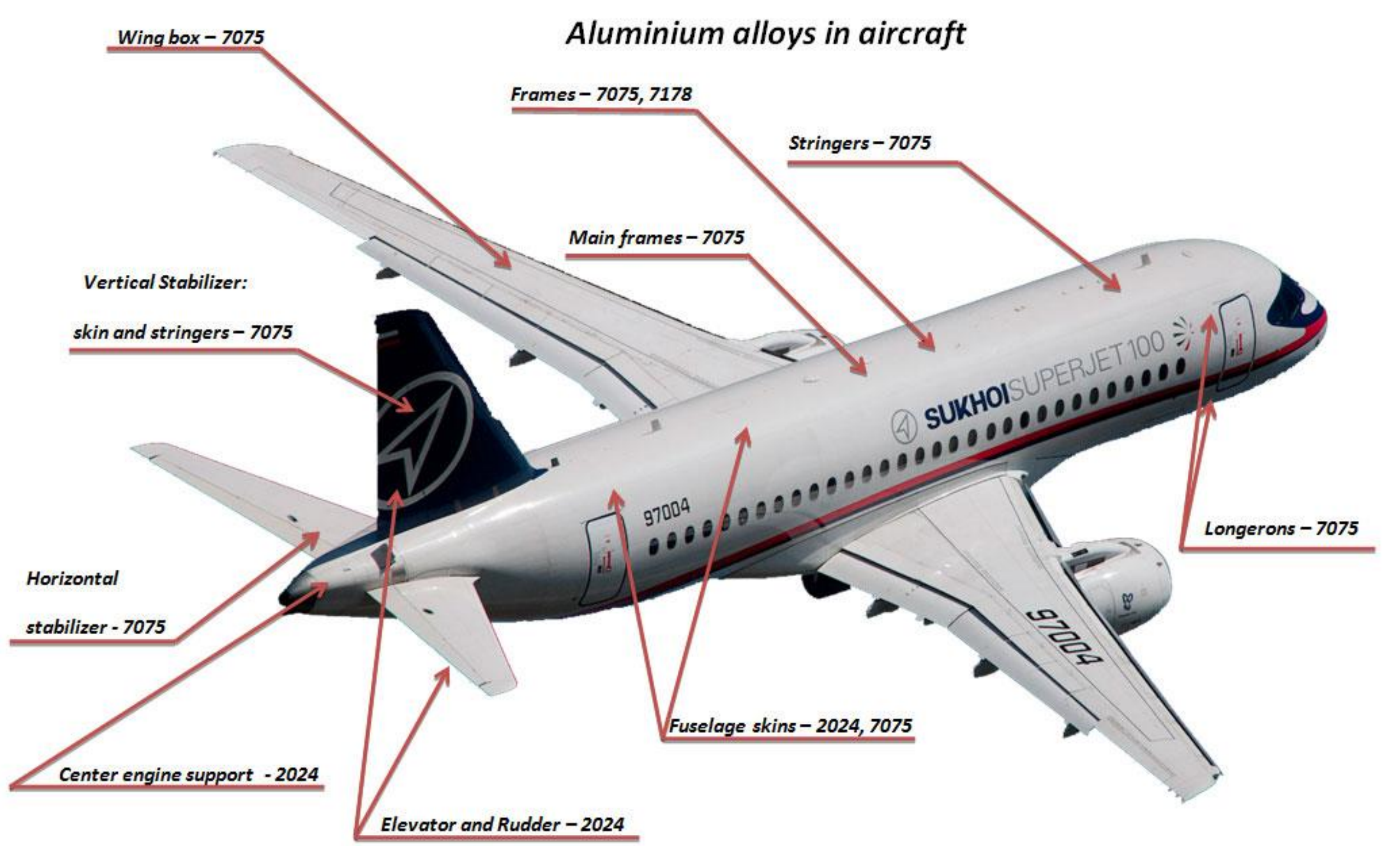
** E-excellent, G-good, F-fair, P-poor. I-immune, R-resistant, S-susceptible, VS-very susceptible.

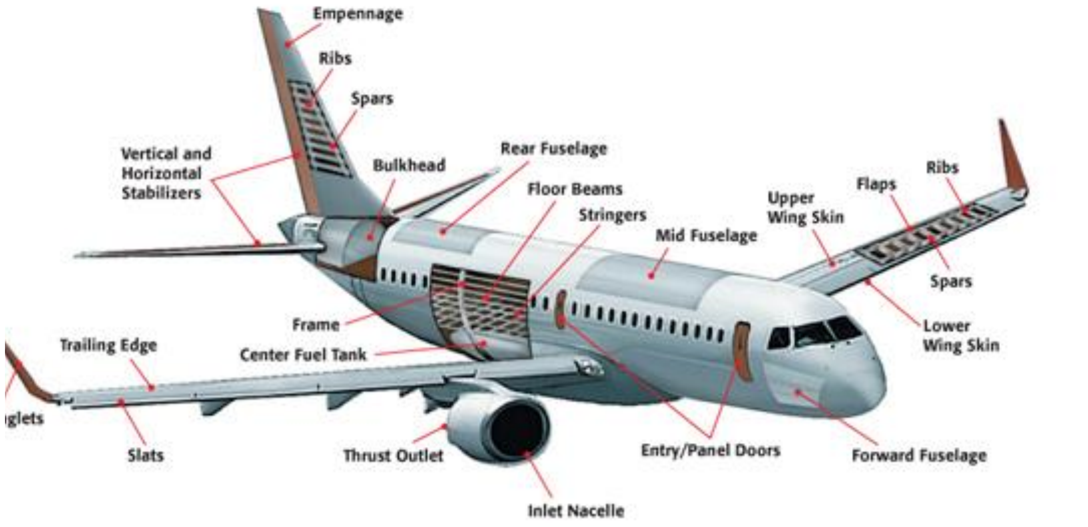
D. A. Jones, Principles and prevention of corrosion, Prentice Hall, 1996



http://www.lincolnelectric.com/en-us/education-center/PublishingImages/ArticleImages/alumapp1.jpg

Aluminum and Alloys – Application





http://www.kaiseraluminum.com/wp-content/uploads/2007/03/cutaway-3.jpg?phpMyAdmin=42e3cc806abc544588f44458e84ca981

http://aluminium.matter.org.uk/content/media/images/airbusA340.jpg

http://www.alcoa.com/mill_products/europe/en/images/nautical_rotating_image5.jpg

http://www.futuna-yachts.com/yachtnews/wp-content/uploads/2012/01/aluminum-hull.jpg

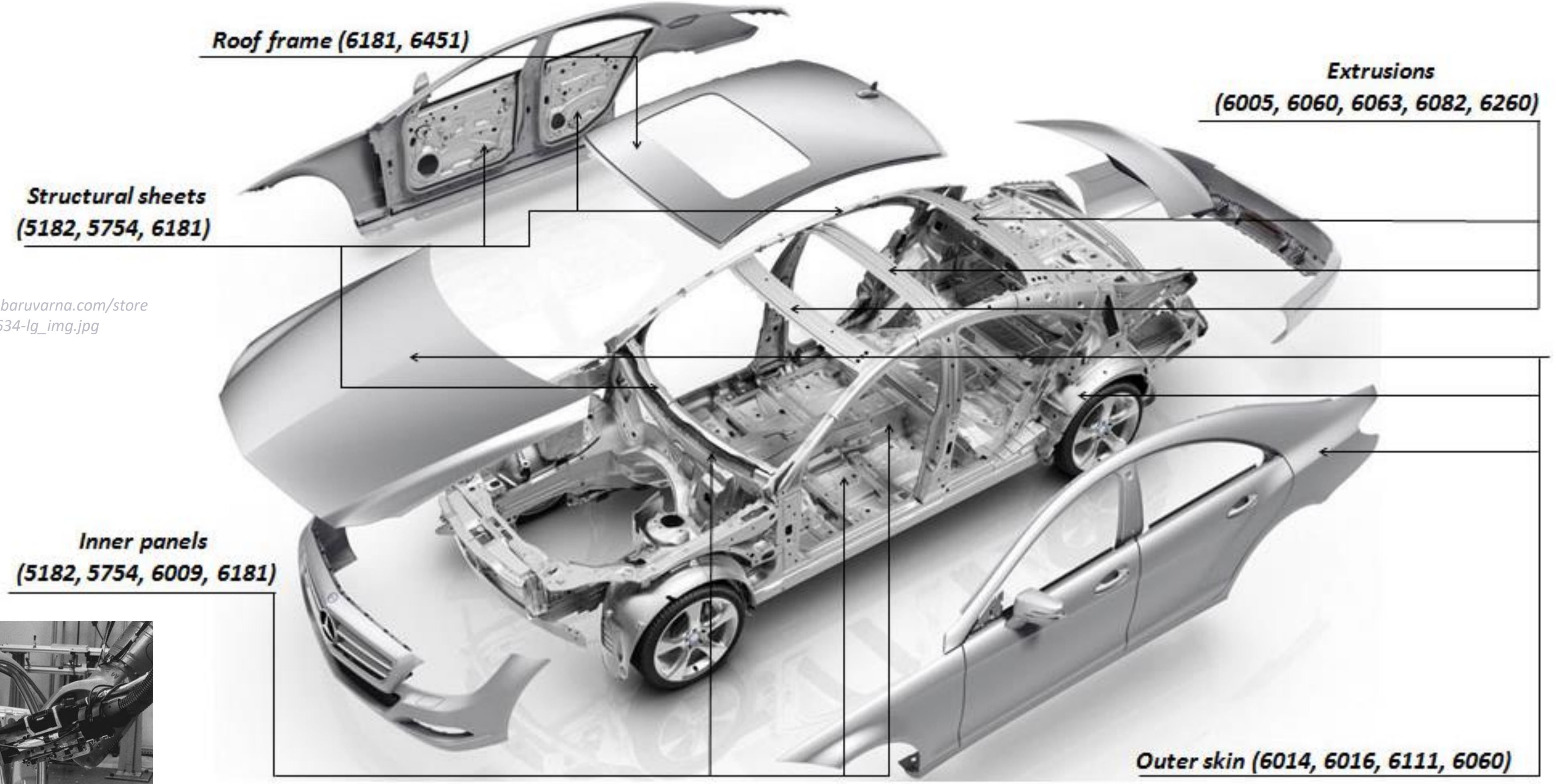
http://www.futuna-yachts.com/explorer54/images-exploration-yacht/expedition-yacht-11.jpg

Aluminum and Alloys – Application

http://www.subaruvarna.com/store/images/e001634-lg_img.jpg

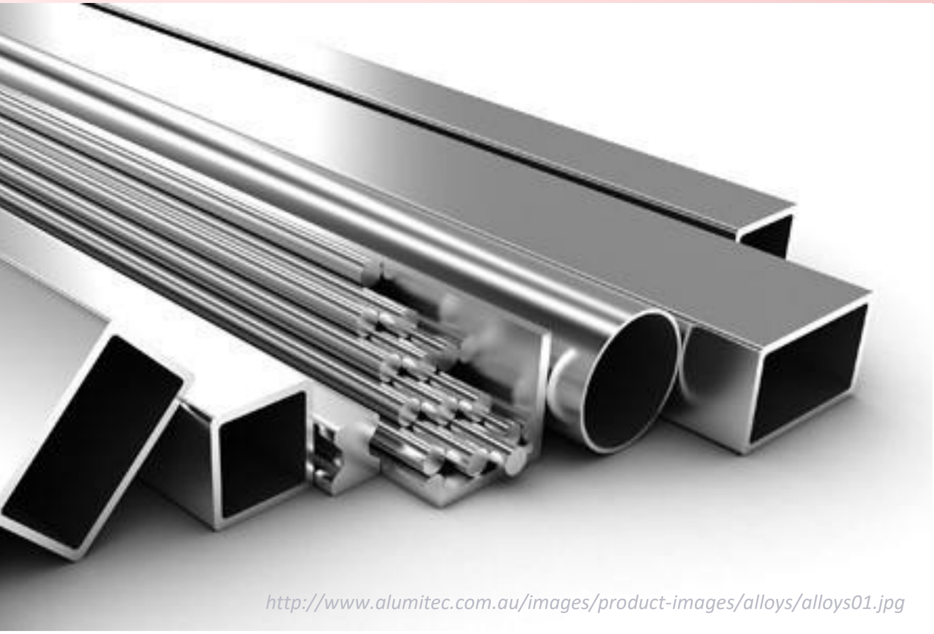
http://altmob.com/images/Pictures/2012/Q3/audi_a2_body.jpg

http://www.impol-servis.com/en/imagelib/source/default/fotografije/izdelki/avtomobilska-industrija-2.jpg



http://www.unimetllc.ru/images/photos/articles/overview6k/overview12.jpg

Aluminum and Alloys – Application



http://www.alumitec.com.au/images/product-images/alloys/alloys01.jpg

http://www.aludiecasting.com/images/aluminium-alloy-casting.jpg

http://2.wlimg.com/product_images/bc-full/dir_14/405758/aluminium-alloy-wires-1732750.jpg

http://images.wisegeek.com/aluminum-foil.jpg

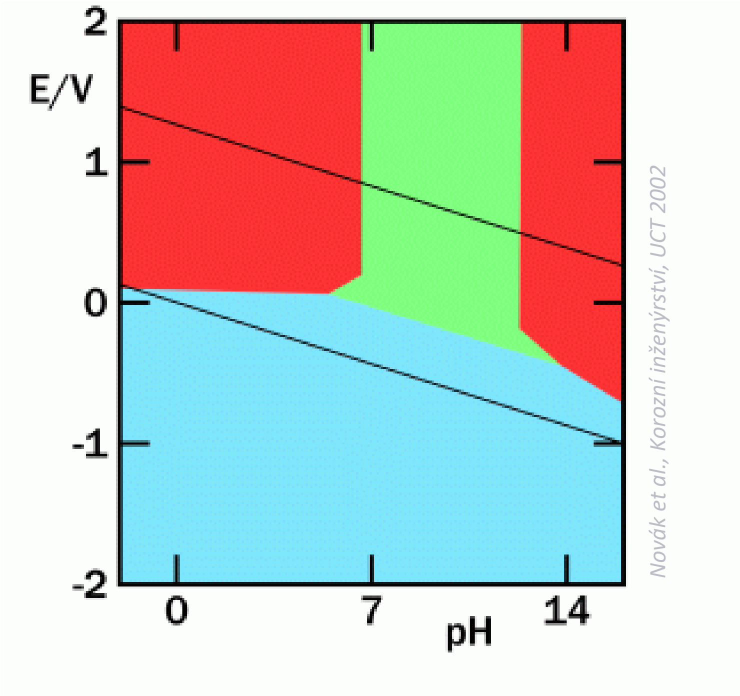
http://i.dailymail.co.uk/i/pix/2010/09/11/article-0-0810E9720000005DC-622_226x402.jpg

http://3.imimg.com/data3/SC/UU/MY-2/aluminium-windows-frames-250x250.jpg

http://www.pjlighthouse.com/wp-content/uploads/2012/08/aluminium-cookware-poisining-health-hazard.jpg

Copper and Alloys

- Very high electric and heat conductivity, formability
- High price, lower strength (non-alloyed), toxicity



- Ability to “passivate” – Cu_2O and other compounds (verdigris / měděnka)
- Low driving power to corrosion, good resistance especially in reduction conditions

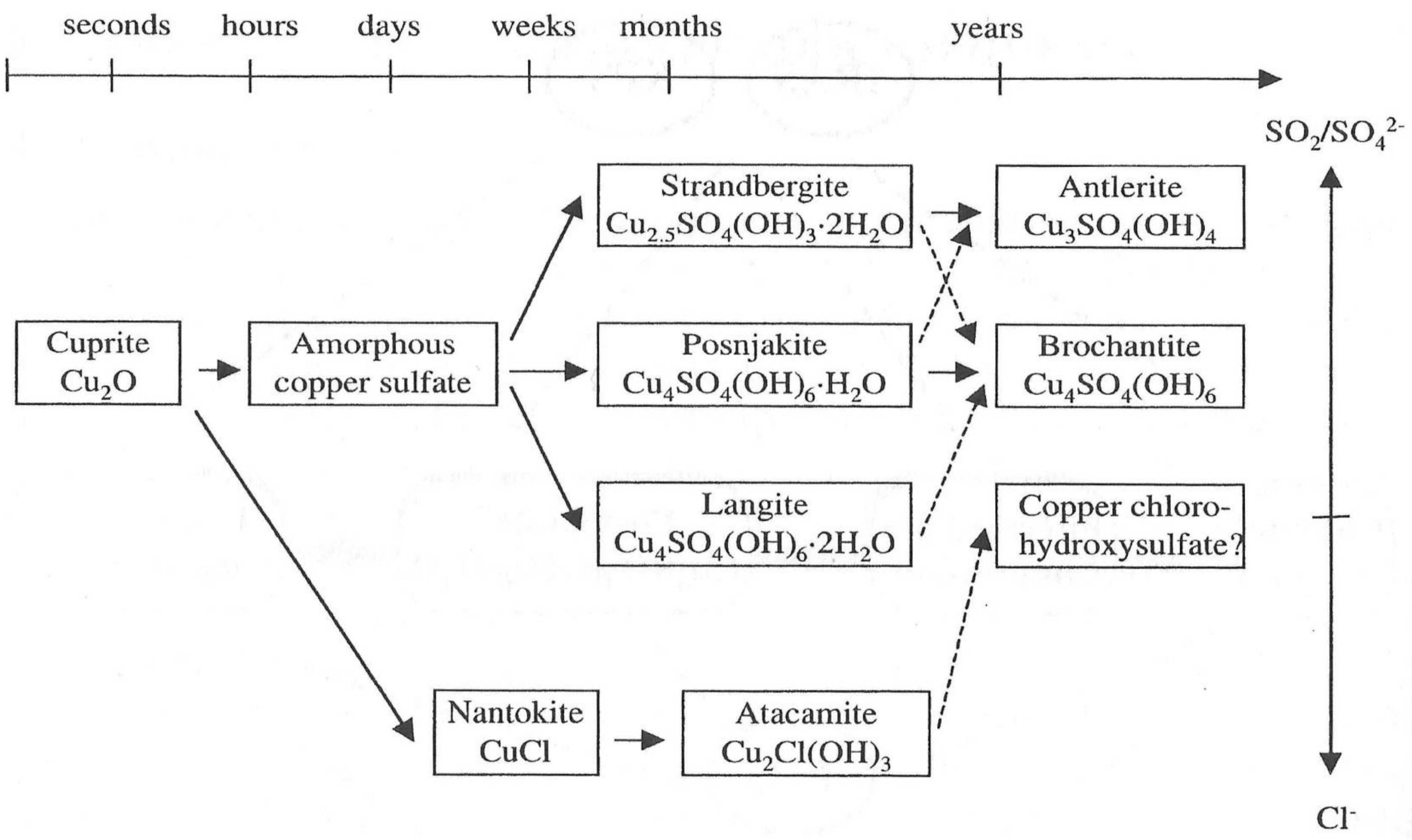

http://i2.stay.com/images/venue/194/76/f3ed29e3/copper-roof-palace-

Copper and Alloys

- **Non-alloyed copper**: Water and heating pipes, roofs, electric conductors, electronics
- **Brass** (Cu + 10–40 % Zn): Better mechanical properties, lower price; dezincification, SCC
- **Admiralty brass**: Cu + 30–40 % Zn + 1 % Sn (+P, As, Sb): Resistance against dezincification
- **Bronze** (Cu + 8–10 % Sn): Casting, sea water – valves, pumps
- Al bronze, Cu-Ni alloys

Copper and Alloys – Atmosphere

- Low corrosion rates:
  - Rural: ≈0.5 µm·year^{-1}
  - Urban: 1–2 µm·year^{-1}
  - Industrial: <2.5 µm·year^{-1}
  - Marine: ≈1 µm·year^{-1}
- Mechanism of the patina formation well described



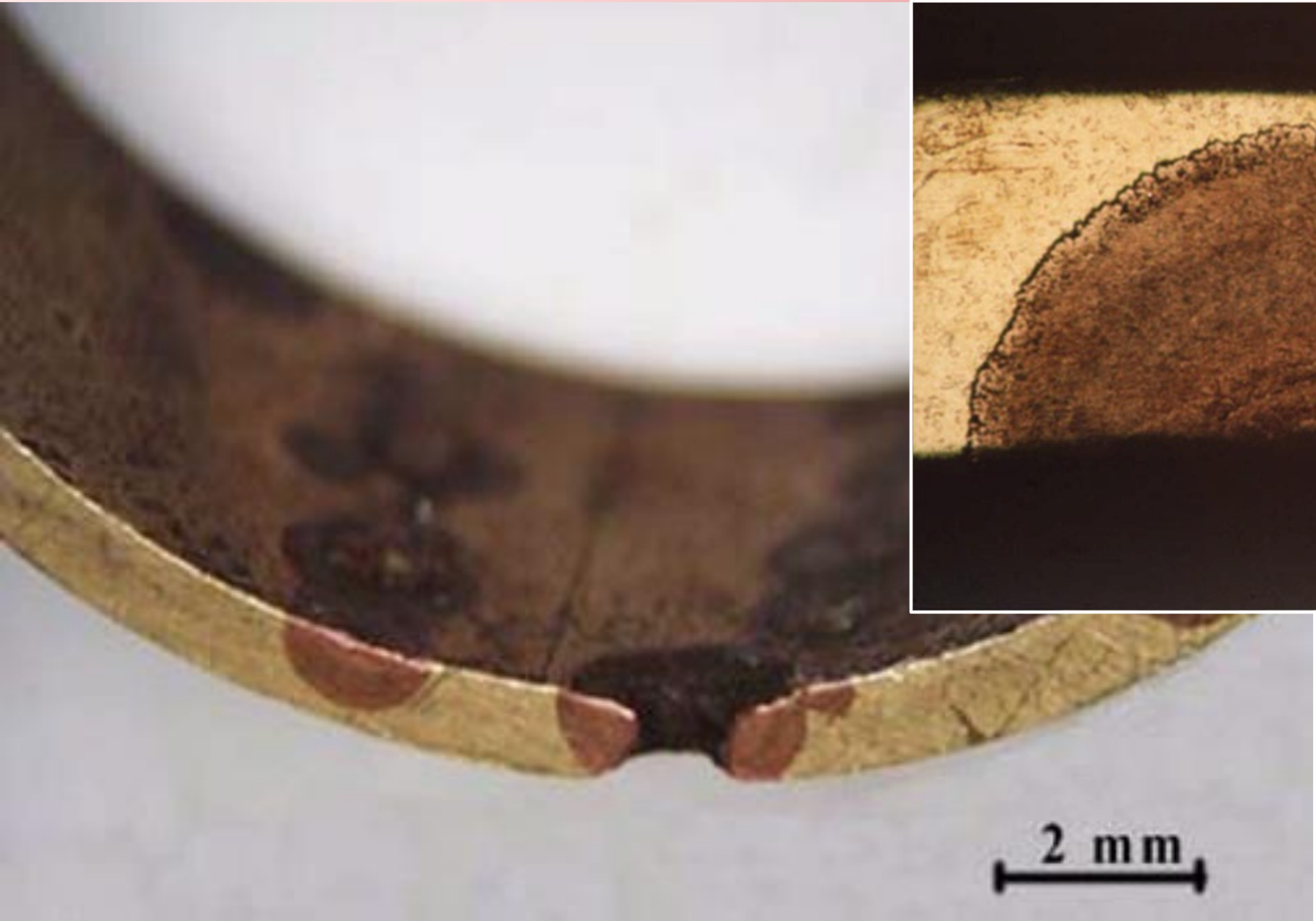
Krätschmer A.,Odnevall Wallinder I., Leygraf C., Corrosion Science 44 (2002), 425–450

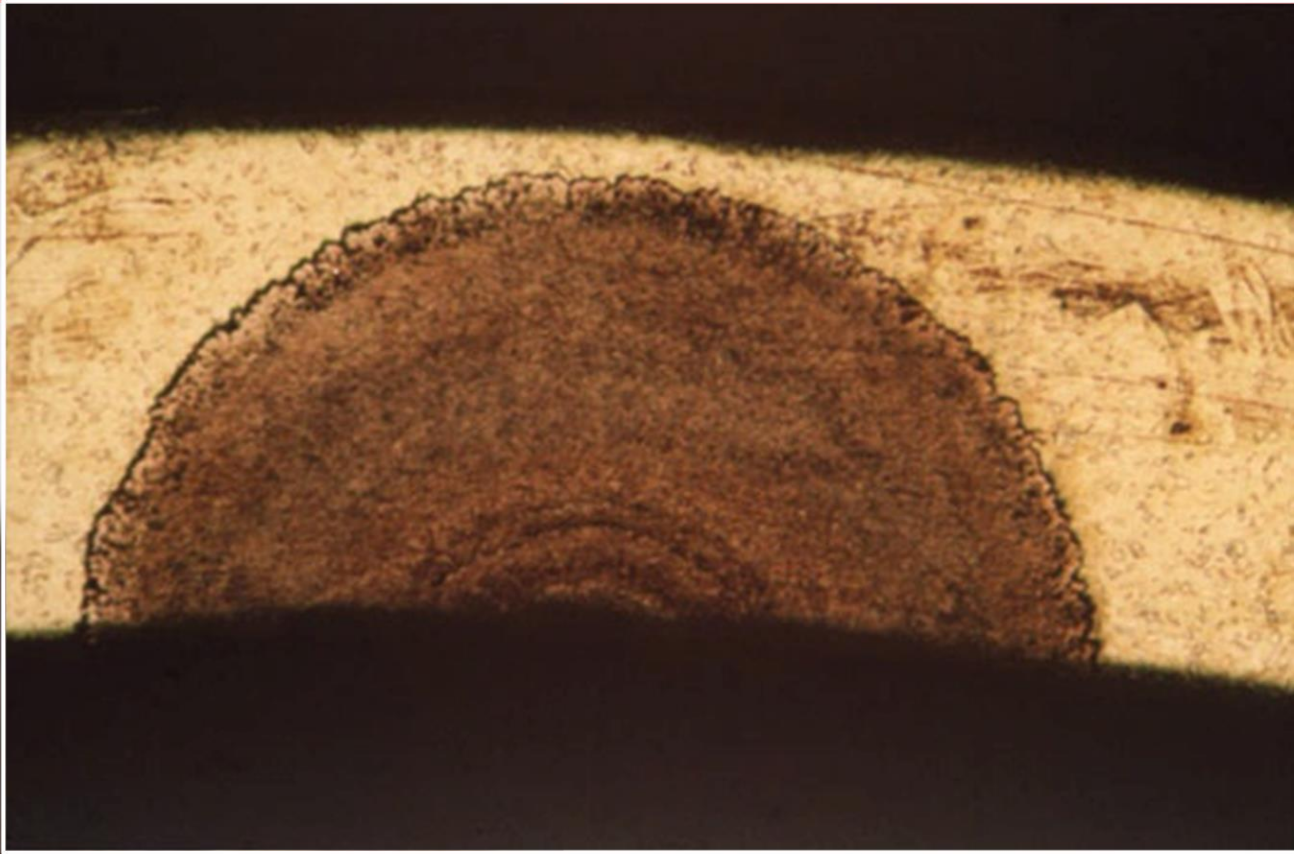
Copper and Alloys – Erosion corr.

Novák et al., Korozní inženýrství, UCT 2002

Erosion corrosion of brass pipes in flowing water

Copper Alloys – Dezincification

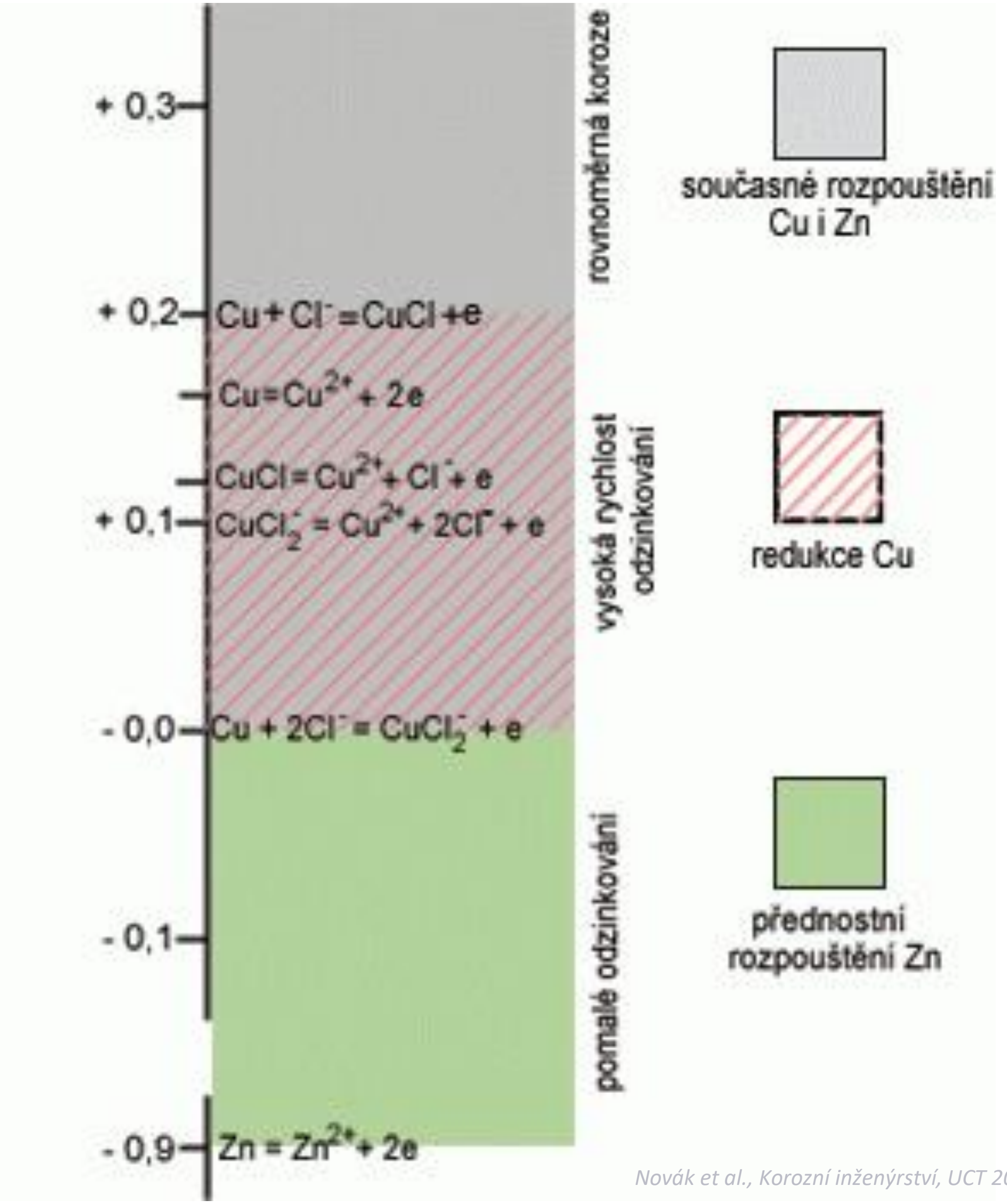




Novák et al., Korozní inženýrství, UCT 2002

Local dezincification of brass in water

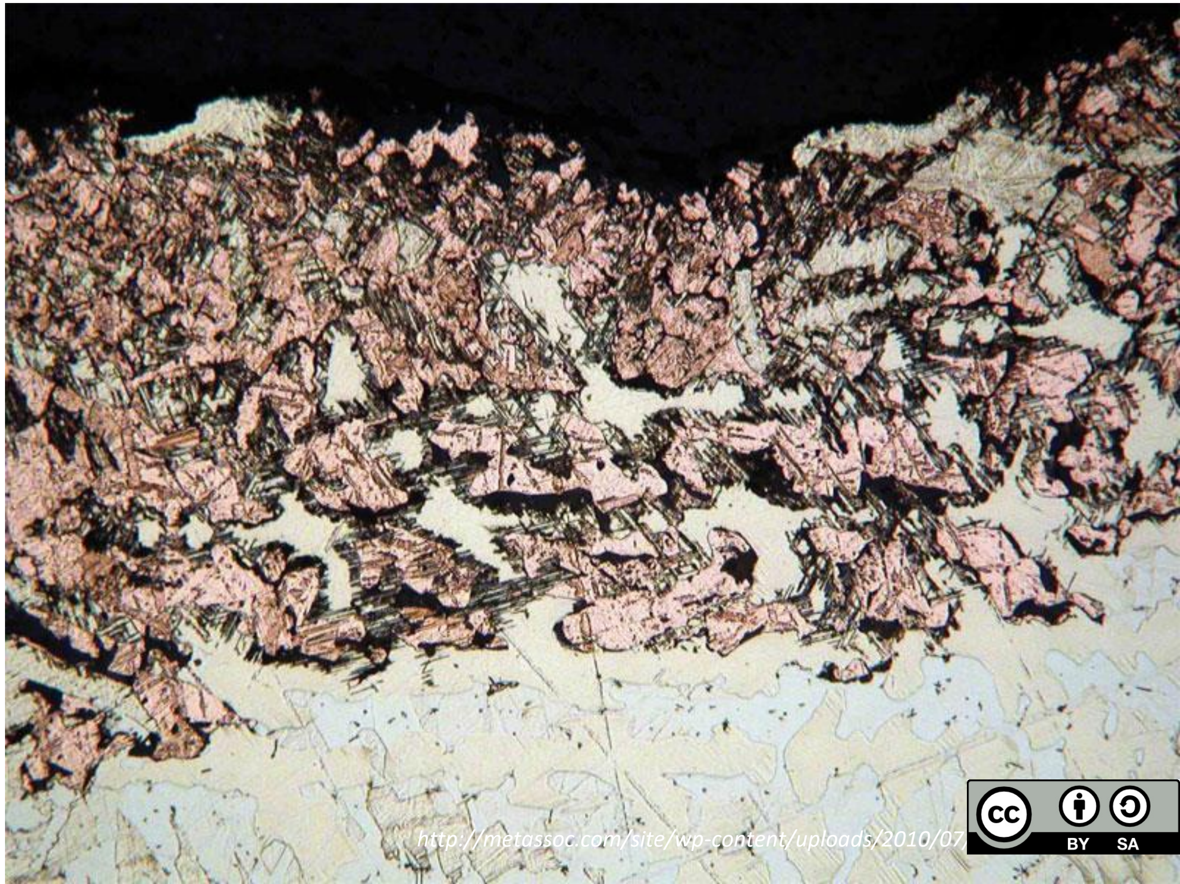
Copper Alloys – Dezincification



Novák et al., Korozní inženýrství, UCT 2002

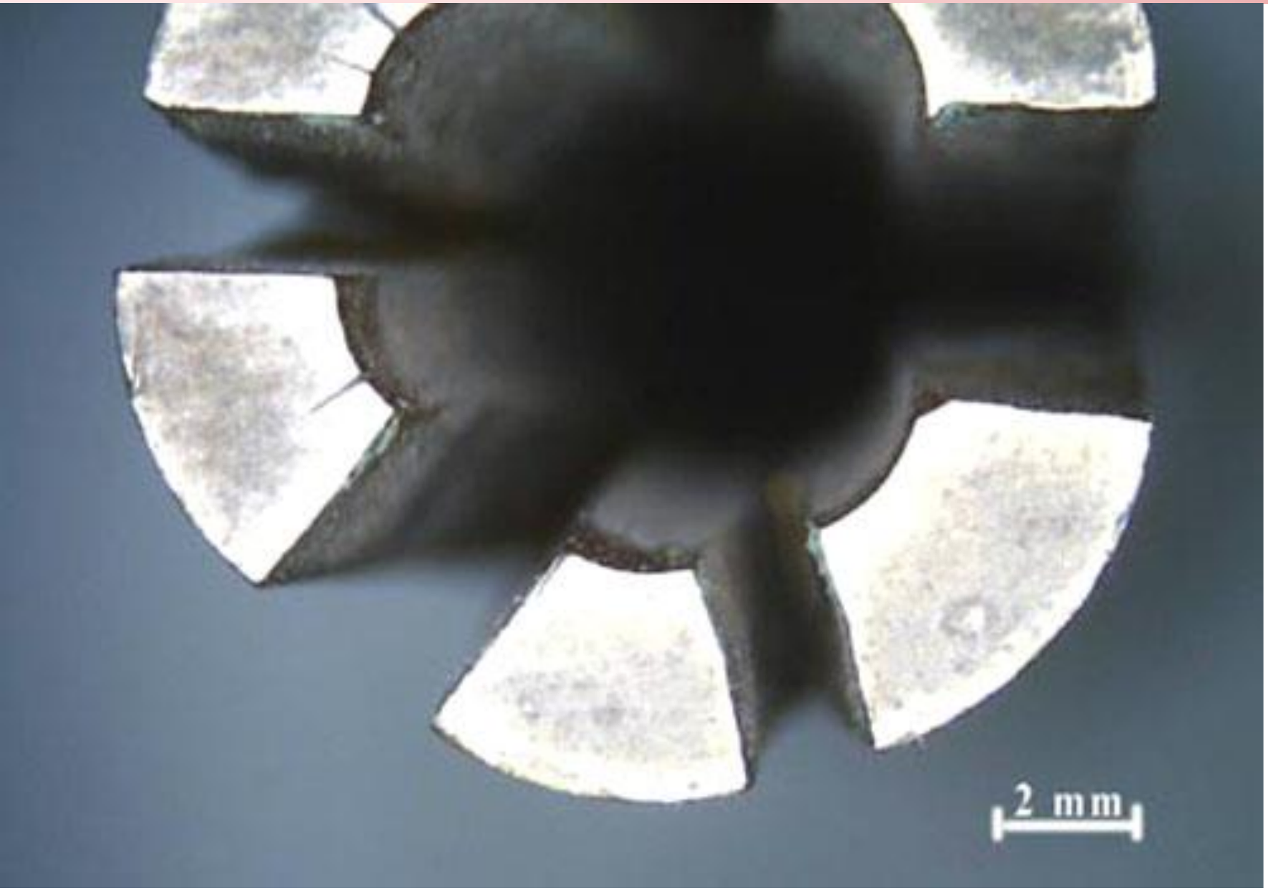
Phase α: Solid solution of copper and zinc, <35 % Zn
Phase β: Zinc-rich phase

α-brass: single-phase structure
β-brass: two-phase structure



http://metassoc.com/site/wp-content/uploads/2010/07/

Copper and Alloys – SCC / NH_4^+

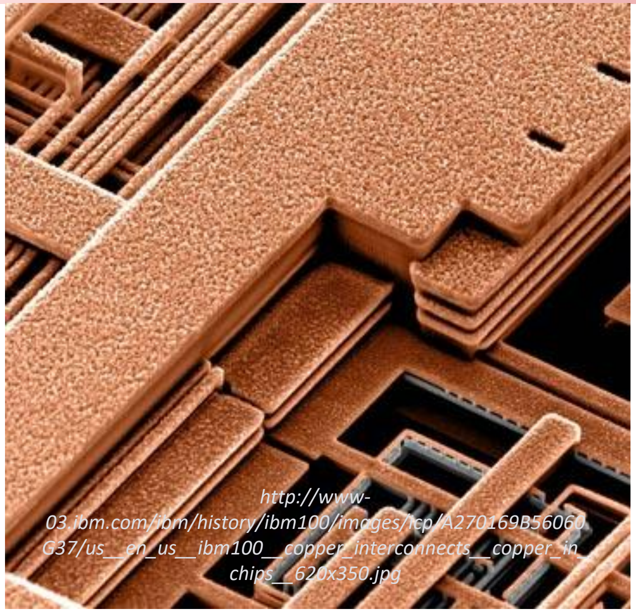


Novák et al., Korozní inženýrství, UCT 2002

Cold-formed brass pipe after exposure to humid atmosphere

Copper – Application

http://wand.images.worldnow.com/images/9932697_G.jpg

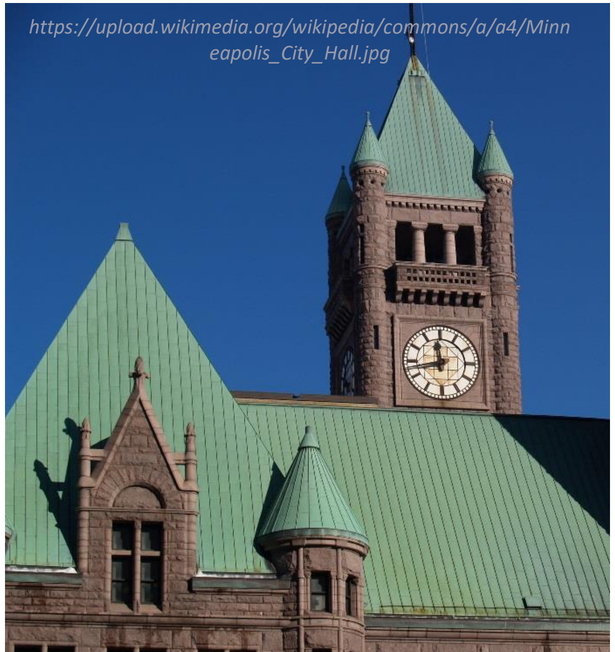


http://www-03.ibm.com/ibm/history/ibm100/images/icp/A270169B56060G37/us__en_us__ibm100__copper_interconnects__copper_in chips__620x350.jpg

http://www.onewayrooter.com/wp-content/uploads/2015/11/copper-pipes.jpg

http://c0590582.cdn.cloudfiles.rackspacecloud.com/jmackay-distillery.jpg

http://blog.marabu.bg/wp-content/uploads/2014/03/godishnina-ot-svatba-otpraznuvai-svoja-simvol-6.jpg



https://upload.wikimedia.org/wikipedia/commons/a/a4/Minneapolis_City_Hall.jpg

http://files.dnr.state.mn.us/mcvmagazine/issues/2013/sep-oct/img/copper/copper05.jpg

Brass – Application

http://www.lakshmiindustries.com/images/brass-copper-strips.jpg

http://www.melschire.com/wp-content/uploads/2014/04/compression-fttng.jpg

http://media.midwayusa.com/productimages/880x660/Primary/326/326620.jpg

http://cfnewsads.thomasnet.com/images/cmsimage/image/trumpet-brass.jpg

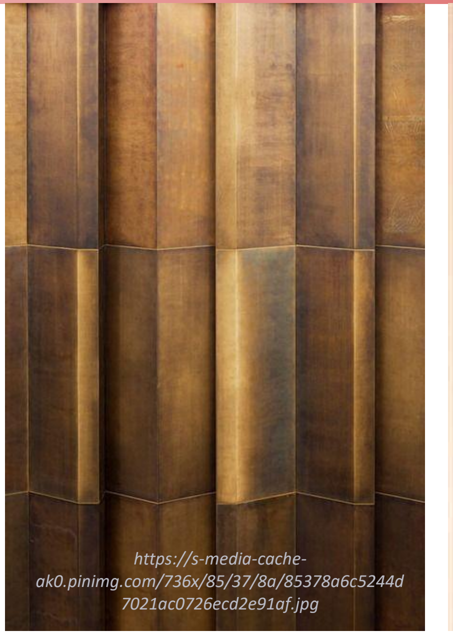
http://nothingbutpadlocks.com/uploads/products/1259171331_brass_padlocks.jpg

http://g02.s.alicdn.com/kf/HTB1fdVTJFXXXXXtXXXXq6xXFXXXs/221963420/HTB1fdVTJFXXXXXtXXXXq6xXFX

Bronze – Application

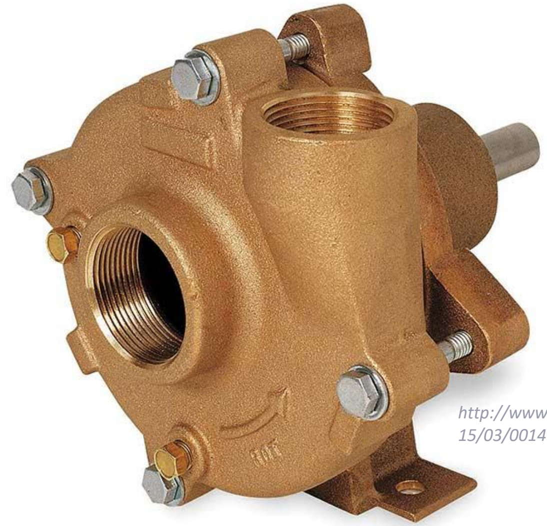
http://www.coinnews.net/wp-content/uploads/2013/06/Miss-Canada-Allegory-Bronze-Coin.jpg

http://static1.sw-cdn.net/rrstatic/img/materials/bronze-some-detail-is-lost.png



https://s-media-cache-ak0.pinimg.com/736x/85/37/8a/85378a6c5244d7021ac0726ecd2e91af.jpg

http://www.france-art-realisation.com/artists_createurs/nacera_sculpteur/clarice_bronze.jpg



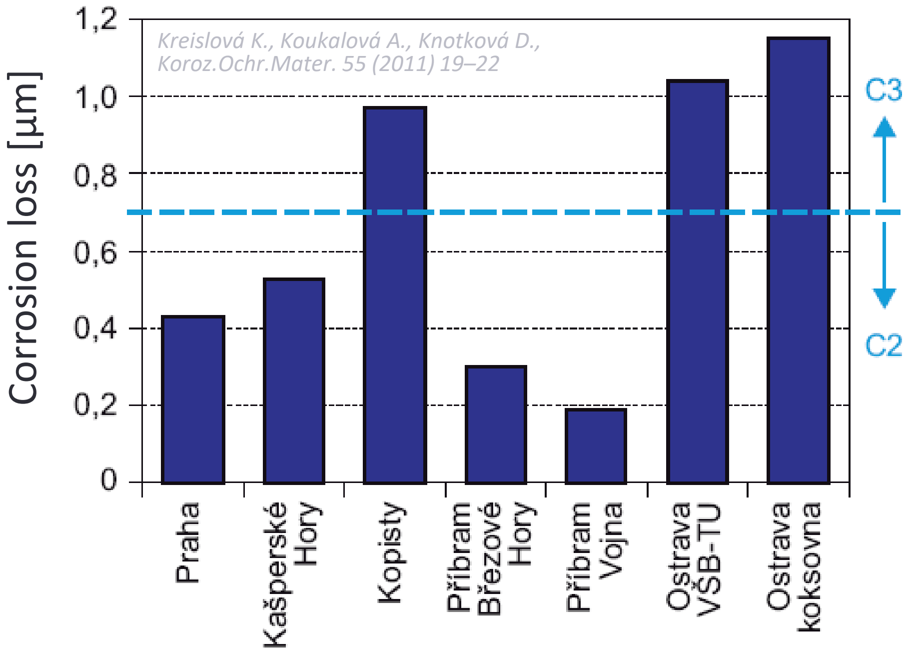
http://www.aerospecialties.com/app/uploads/2015/03/001463_TEEL-Centrifugal_Pump_01.jpg

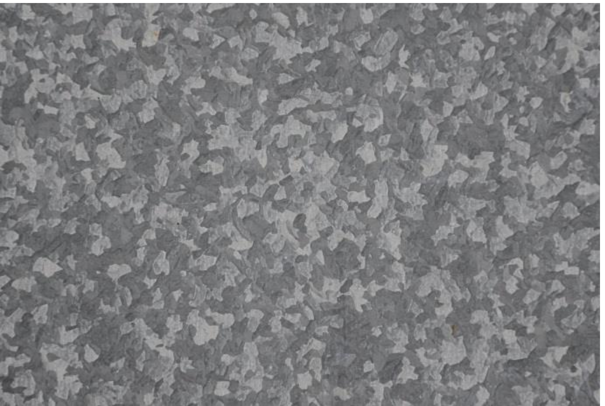
http://ecx.images-amazon.com/images/I/41BTXzAbLiL._SX342_.jpg

http://www.valves2u.com/website/Worthington%206L11%20Bronze%20Pump/Worthington%206L11%20Bronze%20Pump,%20New%20Surplus.jpg

Zinc and Zinc Coatings

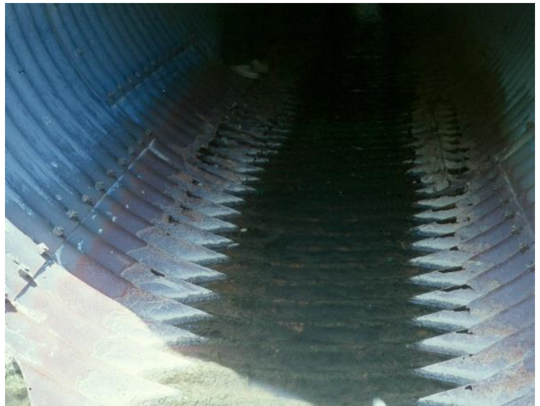
- Zinc coated steel is widely used in building, automotive and home appliance industries
- Low corrosion rates:
  - Urban: <1 µm·year^{-1}
  - Industrial: 1–15 µm·year^{-1}
  - Marine: 0.5–8 µm·year^{-1}
- Aesthetically acceptable appearance of zinc corrosion products

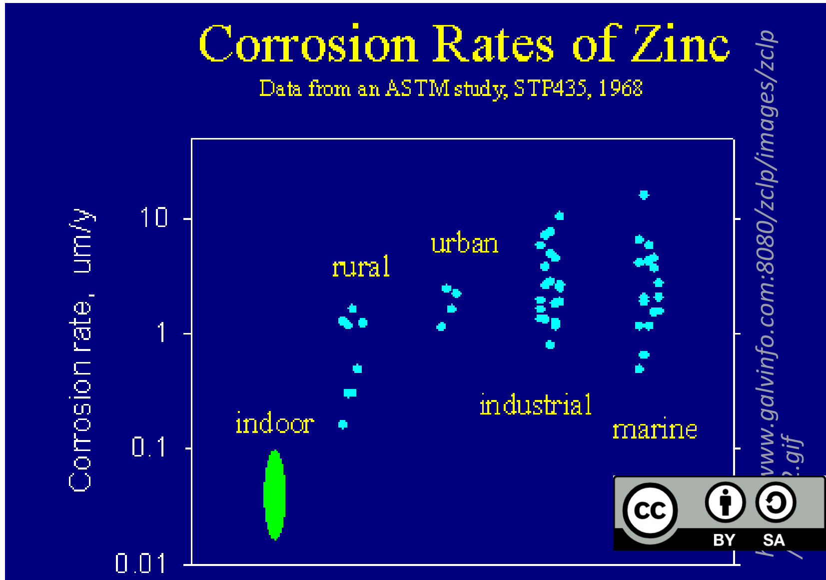




https://upload.wikimedia.org/wikipedia/commons/c/c4/Feuerverzinkte_Oberfl%C3%A4che.jpg

https://www.dot.state.oh.us/Divisions/Engineering/Structures/bridge%20operations%20and%20maintenance/PreventiveMaintenanceManual/BPMM/repairs/Photos/pic93.jpg





Zinc and Zinc Coatings

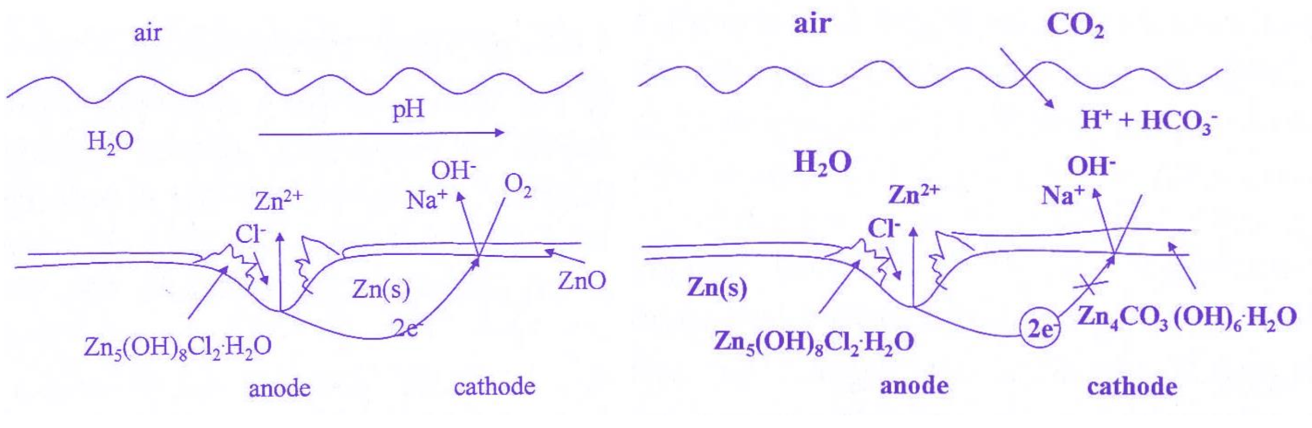
- Initial formation of zincite ZnO and $ZnOH_2$
- Stable corrosion products:
  - Hydrozincite $Zn_5(CO_3)_2(OH)_6$
  - Simonkolleite $Zn_5Cl_2(OH)_8 \cdot H_2O$
  - Gordaite $NaZn_4[Cl(OH)_6|SO_4] \cdot 6H_2O$

Bruno S., Zapponi M., Lazzarino H.A., Pedraza J.P., 3rd Symposium Coil coated steel, Paris, 2012

Substance	Hey index no.	Crystal system	Formula
Metal, oxides, and hydroxides			
Zincite	7.5.1	Cub.	ZnO
Wülfingite	7.5.4	Orth.	ε-$Zn(OH)_2$
Sulfides			
Wurtzite	3.4.3	Hex.	β-ZnS
Sulfites			
Zinc sulfite (h)		Mon.	$ZnSO_3 \cdot 2H_2O$
Sulfates			
Zinkosite	25.5.1	Orth.	$ZnSO_4$
Gunningite	25.5.1a	Mon.	$ZnSO_4 \cdot H_2O$
Boyleite	25.5.6	Mon.	$ZnSO_4 \cdot 4H_2O$
Bianchite	25.5.14	Mon.	$ZnSO_4 \cdot 6H_2O$
Goslarite	25.5.2	Orth	$ZnSO_4 \cdot 7H_2O$
Zinc hydroxysulfate (b)		Tric.	$Zn_4SO_4(OH)_6 \cdot 4H_2O$
Odnevallite*		Hex.	$NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$
Chlorides			
Simonkolleite		Hex.	$Zn_5Cl_2(OH)_8 \cdot H_2O$
Zinc oxychloride			$Zn_5Cl_2O_4 \cdot H_2O$
Zinc chlorosulfate		Mon.	$Zn_4Cl_2(OH)_4SO_4 \cdot 5H_2O$
Carbonates			
Smithsonite	11.6.1	Hex.	$ZnCO_3$
Zinc carbonate			$ZnCO_4 \cdot 4H_2O$
Zinc carbonate			$Zn_4CO_3(OH)_6$
Hydrozincite	11.6.3	Mon.	$Zn_5(CO_3)_2(OH)_6$
Zinc carbonate oxychloride			$Zn_a(CO_3)_b(OH)_cOCl$
Nitrates			
Zinc nitrate			$Zn(NO_3)_2$

Zinc and Zinc Coatings

- High corrosion rates in absence of CO_2 and permanent wetness: formation of non-protective corrosion products (ZnO)



No CO_2 350 ppm CO_2

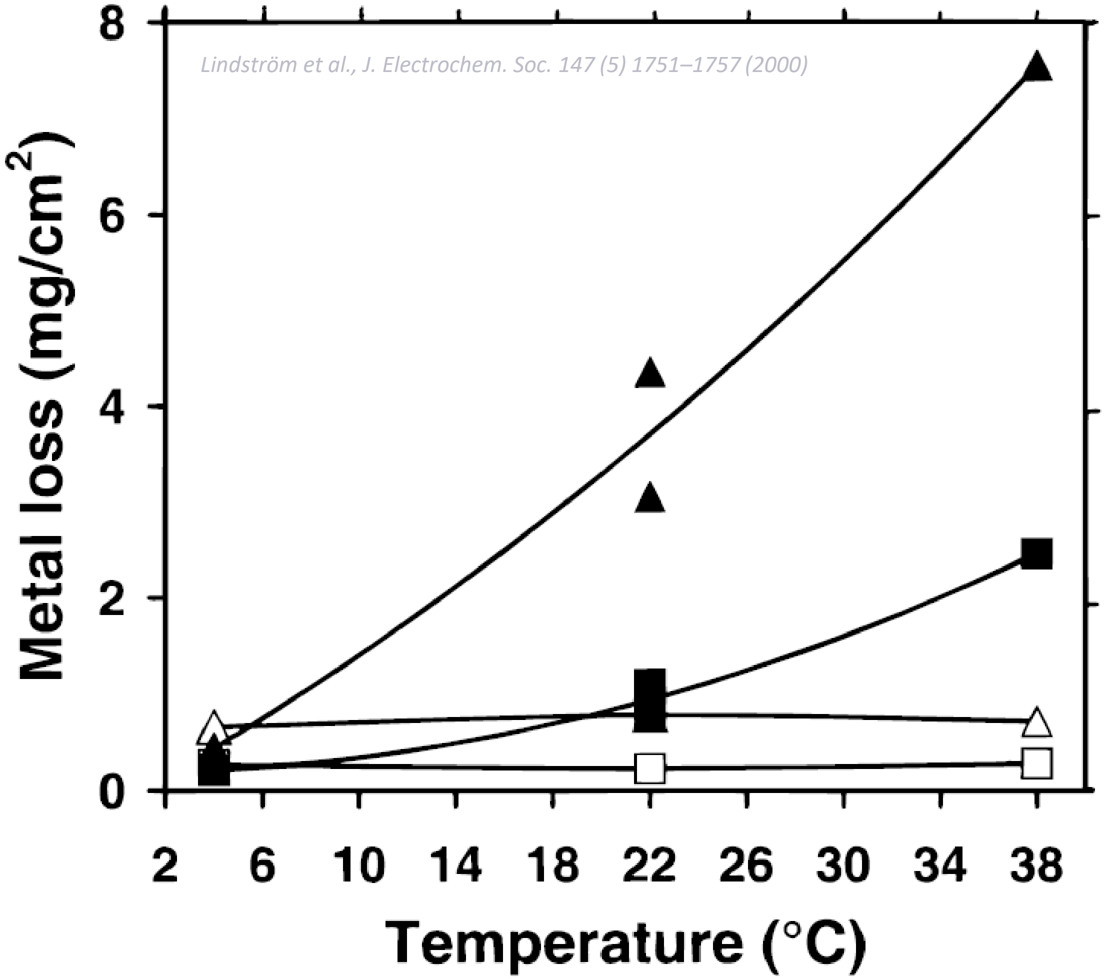
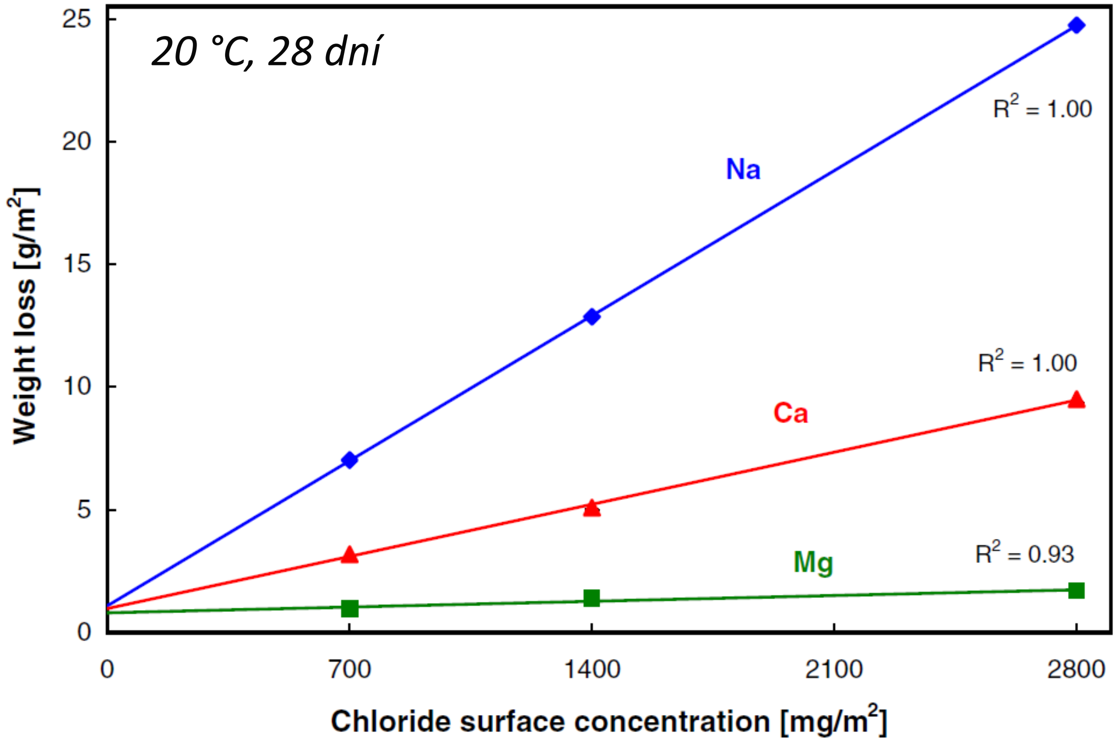


Figure 8. Metal loss as a function of exposure temperature: (▲) <1 ppm CO_2 and 70 μg/cm² NaCl; (■) <1 ppm CO_2 and 14 μg/cm² NaCl; (△) 350 ppm CO_2 and 70 μg/cm² NaCl; and (□) 350 ppm CO_2 and 14 μg/cm² NaCl. <1 ppm CO_2 at 22 and 38°C desiccator exposures.

Zinc and Zinc Coatings – ions

Prošek et al., Corros. Sci. 49 (2007) 2676–2693



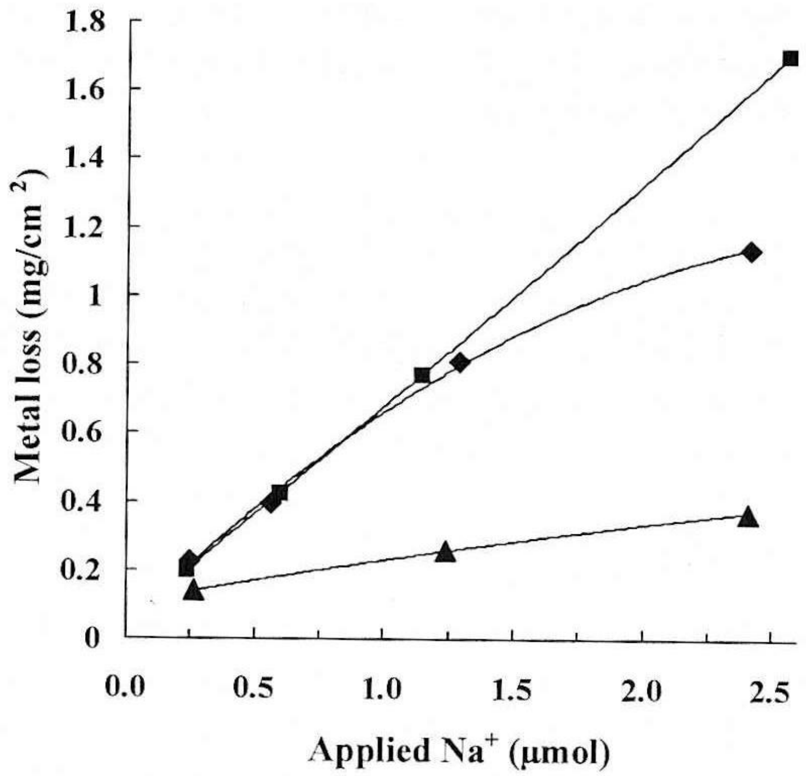
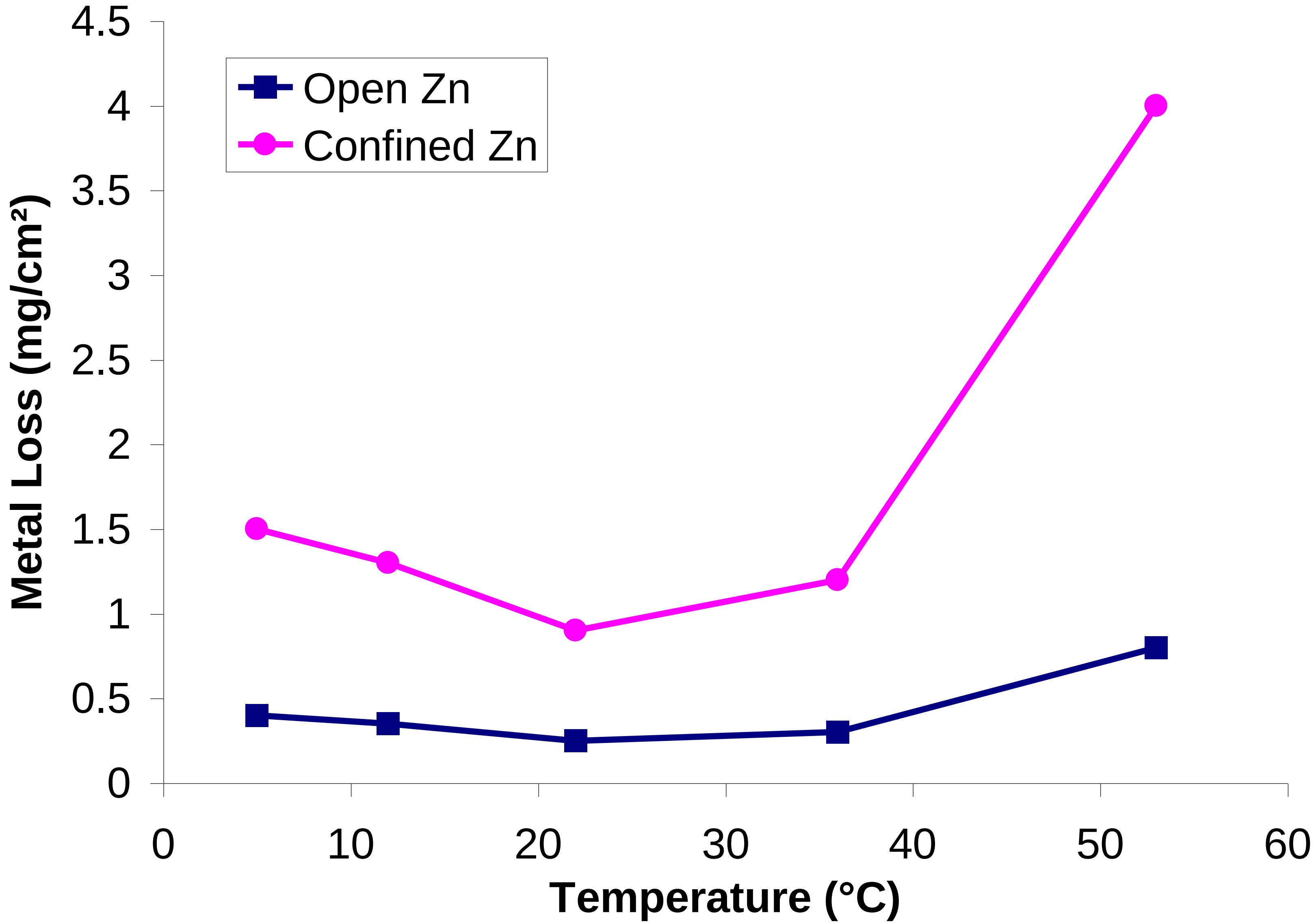


Figure 6.4 Metal loss as a function of applied amount of sodium; (■) Na2SO4, (◆) NaCl and (▲) NaNO3. The exposure time was four weeks, the relative humidity 95%, the temperature was 22°C and the CO2 concentration was 350 ppm.

Zinc and Zinc Coatings – T, config.



Rolled Zinc

- Roofing, currently also facades
- Life time over 100 years, grey patina
- High price
- Addition of titanium (0.1 wt. %) for higher strength („titanzinc“)

Malaga, Spain

https://www.vmzinc.es/proyectos/803-aeroport-de-malaga-espagne.html

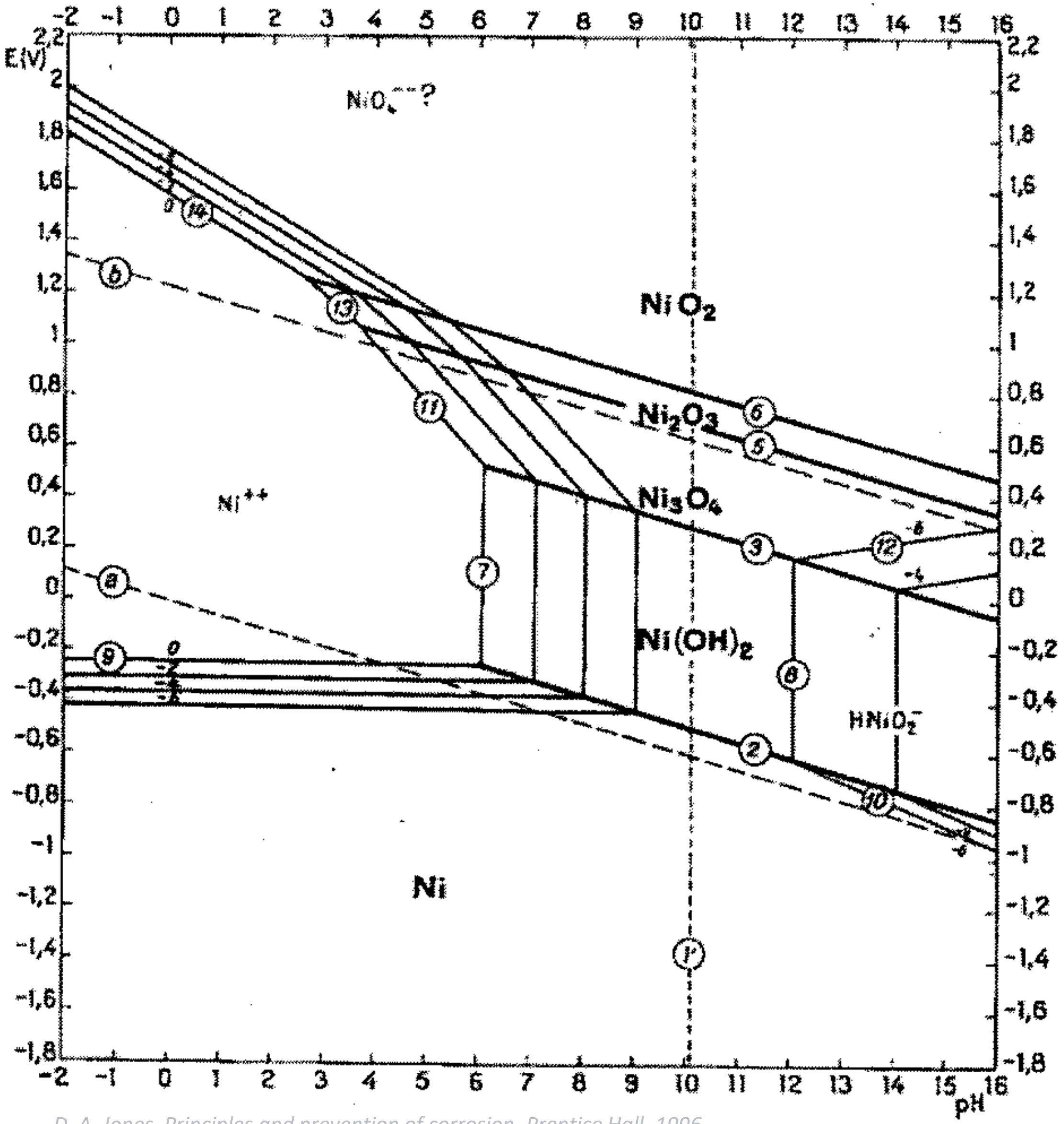
Praha

https://www.vmzinc.in/projects/558-siege-social-stival-otrokovice-czech-republic.html

Münster, Germany

https://www.vmzinc.dk/projekter/552-collective-housing-muenster-germany.html

Nickel and Alloys



D. A. Jones, Principles and prevention of corrosion, Prentice Hall, 1996

Passive in alkali solutions

Low corrosion rate in activity under acid conditions

Worse corrosion resistance in oxidizing acids

Nickel and Alloys

Alloy	EN	USN	Principal alloying elements, wt. %				
			Ni	Cr	Mo	Fe	Other
Ni							
200, 201	2.4060	N02200	99,2				
Ni-Cu							
400	2.4360	N04400	65			1,5	32 Cu
Ni-Cr-Fe							
600	2.4816	N06600	72	16		8	
601	2.5851	N06601	62	25		10	2.1 Al; 0.18 C
800	1.4876	N08800	32,5	21		44	
Ni-Cr-Fe-Mo							
825	2.4858	N08825	33	21	3	42	0.6 Ti; 0.2 Al
31			31	27	6,5	31	0.2 N; 1.2 Cu
33			31	33	1,6	32	0.4 N; 0.6 Cu
Ni-Cr-Mo-W							
C-276	2.4819	N10276	57	16	16	6	3.5 W
C-22		N06022	60	21	13	5	3 W
G-3	2.4619	N06985	45	22	7	19	2.0 Cu; 5.0 Co; 1.5 W
C-4	2.4610	N06455	66	16	16	1	0.3 Ti

Novák et al., Korozní inženýrství, UCT 2002

Alkali (NaOH, KOH)

Monel. Non-oxidizing acids, e.g. HF; heat exchangers

Inconel

Passivates in oxidizing acids due to presence of Cr

Cheaper, lower resistance (Fe); pitting, crevice; less SCC

Higher resistance against pitting and crevice corrosion

Very high resistance against pitting and crevice corr.

Nimonic. NiCr20Co20Ti2Al1 (about). Resistance at high temperature; turbines, combustion engi

Nickel and Alloys – Applications

http://1.imimg.com/data/N/W/MY-430436/Forged-Fittings_250x250.jpg

http://www.engineeringcapacity.com/__data/assets/image/0030/345198/ebp.jpg

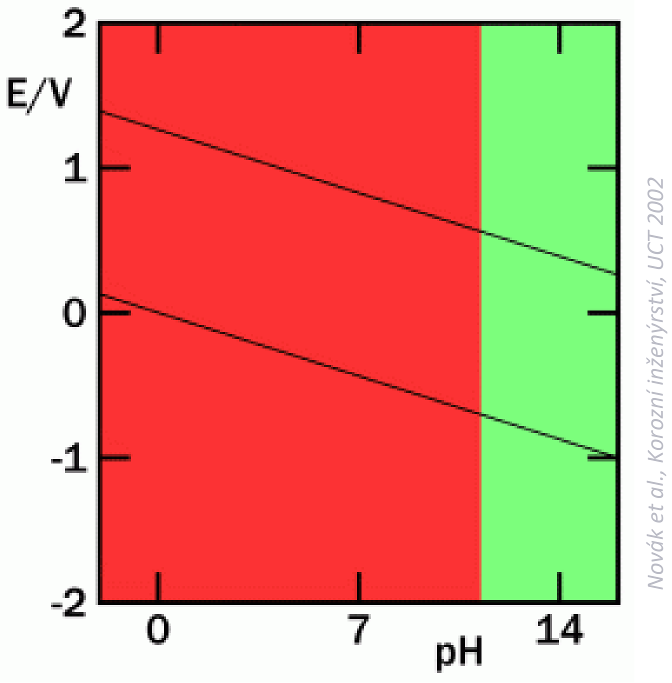
http://www.jamesduva.com/wp-content/uploads/2011/12/nickel-alloy.jpg

http://www.neonickel.com/wp-content/uploads/2014/01/Turbine.jpg

http://www.weldreality.com/stainless-steel-evaporators.gif

http://farm5.static.flickr.com/4130/5067465250_c280e2510e.jpg

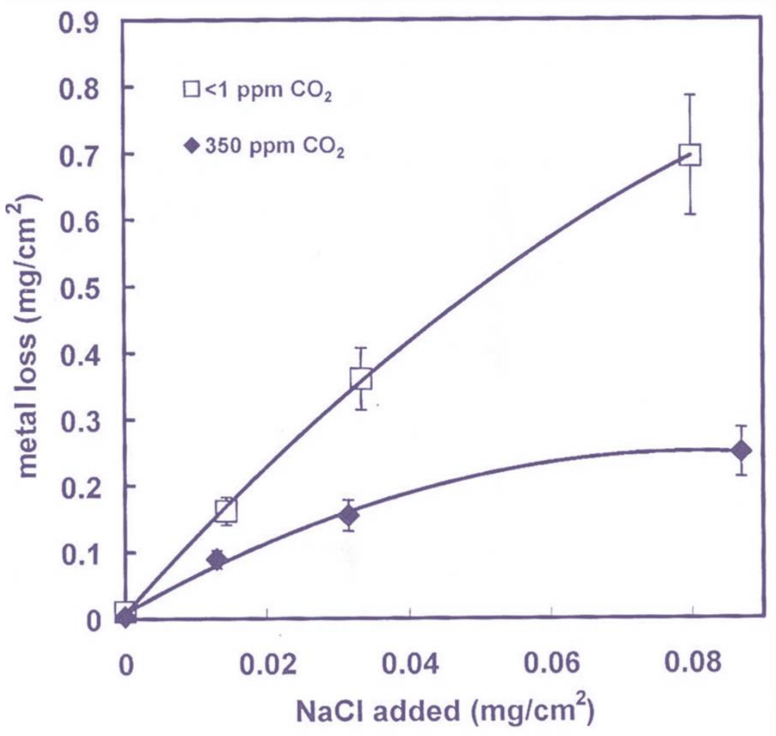
Magnesium Alloys



- Magnesium highly active
- Impurities (particularly heavy metals) undesirable
- Applicable only in less corrosive atmospheres
- Better than aluminum alloys from the viewpoint of strength-to-mass ratio
- Protection methods sought: Alloying, coatings
- If coatings fail, rapid corrosion degradation

Magnesium Alloys

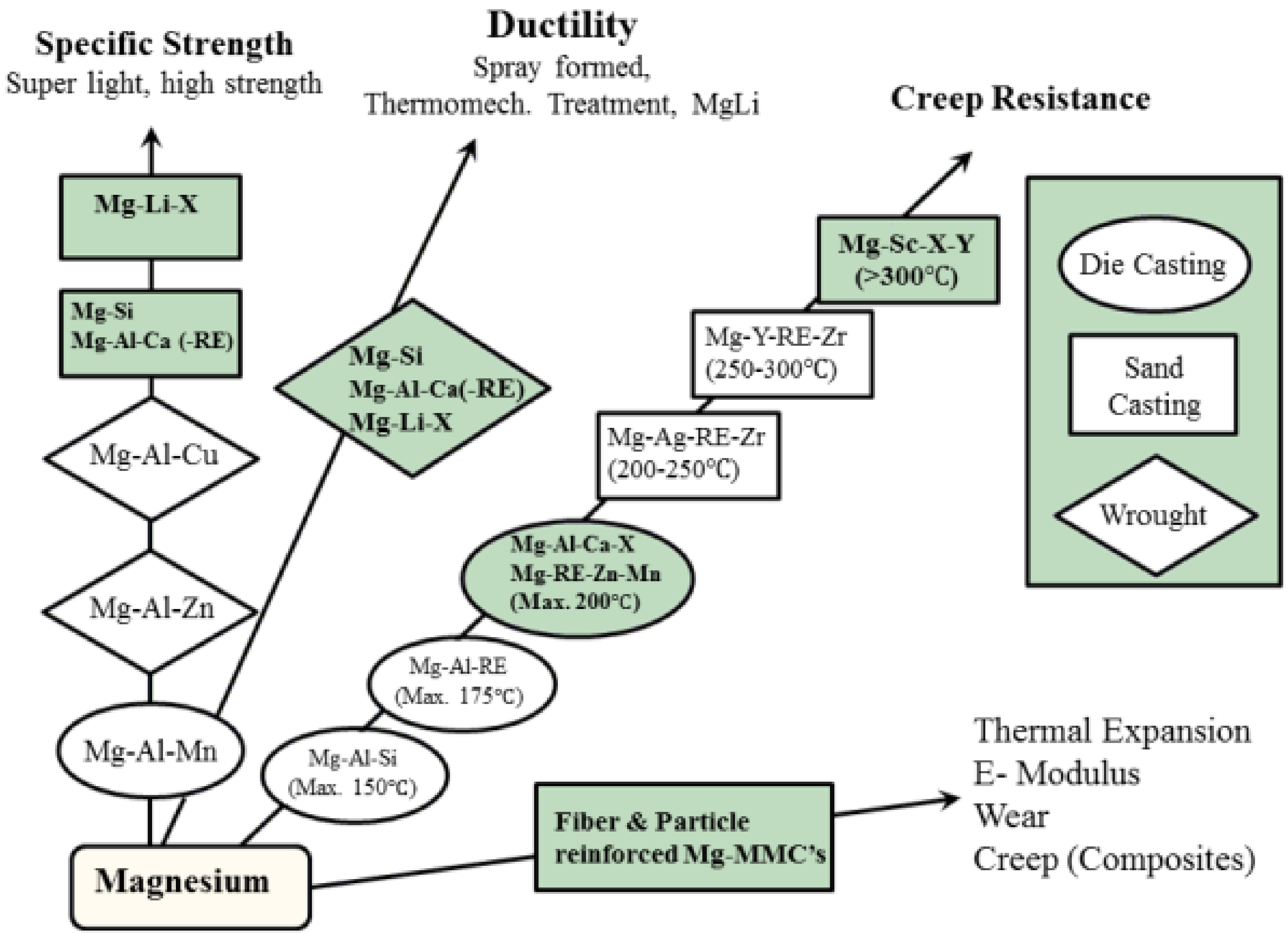
- Typical corrosion rates:
  - Rural: 4 µm/rok
  - Industrial: 10–20 µm/rok
  - Marine: 20 µm/rok
  - Tropical: 20–60 µm/rok



AZ91, 4 weeks, 95 % RH, 25 °C (data Lindström, 2003)

Corrosion product	Formula
Oxide/hydroxide	
Magnesium oxide	MgO
Magnesium hydroxide	$Mg(OH)_2$
Sulfates	
	$MgSO_4 \cdot 6H_2O$
	$MgSO_3 \cdot 6H_2O$
Chlorides	
	$Mg_2Cl(OH)_3 \cdot 4H_2O$
	MgOHCl
Carbonates	
Lansfordite	$MgCO_3 \cdot 5H_2O$
Giorgiosite	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$
Hydromagnesite	$3MgCO_3\ Mg(OH)_2 \cdot 3H_2O$
Hydrotalcite	$Mg_5Al_2(OH)_{16}\ CO_3 \cdot 4H_2O$

Magnesium Alloys

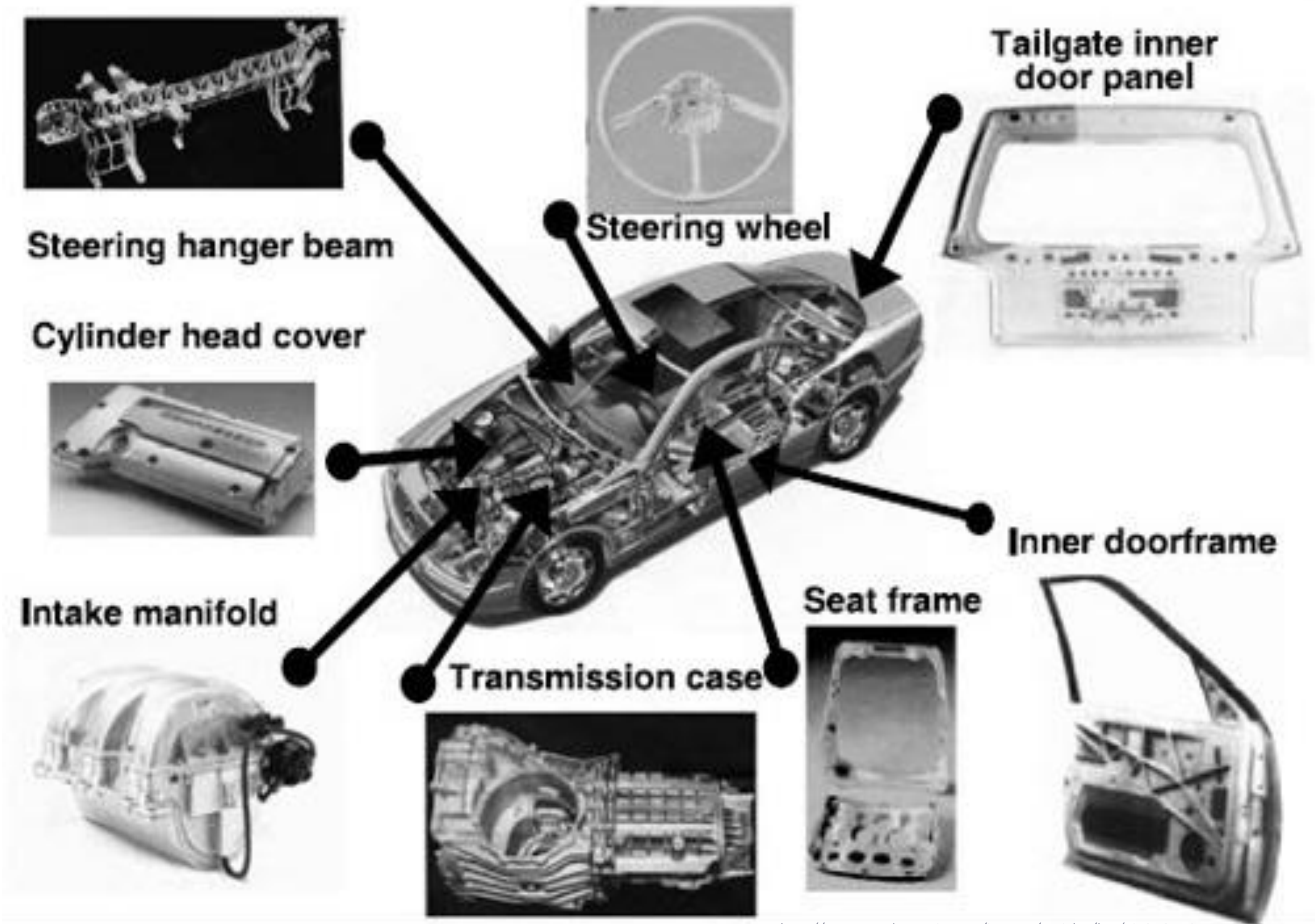


http://www.intechopen.com/source/html/37746/media/image1.png

Most common:

- AZ31 (MgAl3Zn1)
- AZ91 (MgAl9Zn1)
- AM60 (MgAl6Mn0.4)

Magnesium Alloys – Application

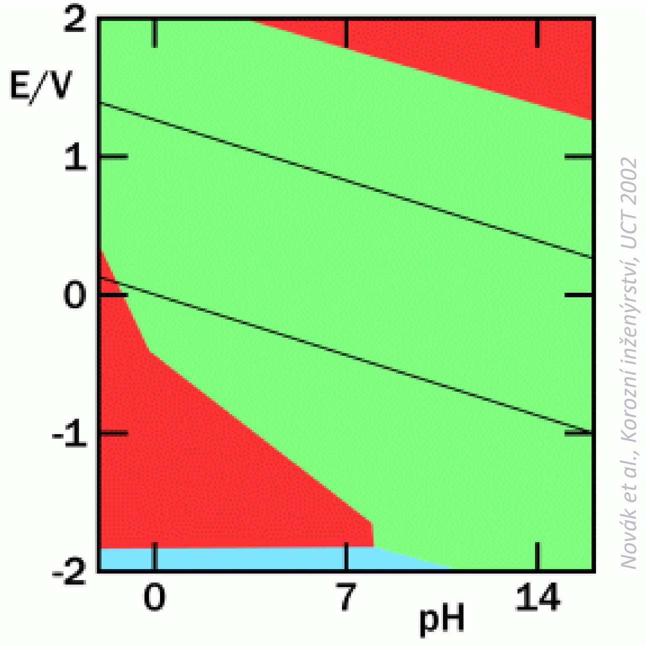


http://www.totalmateria.com/images/Articles/ktn/Fig246_1.jpg

http://www.hindustanmagnesium.com/solutions/Aerospace%20Image.jpg

http://www.imaging-resource.com/PRODS/NIKONV1/ZV1

Titanium and Alloys

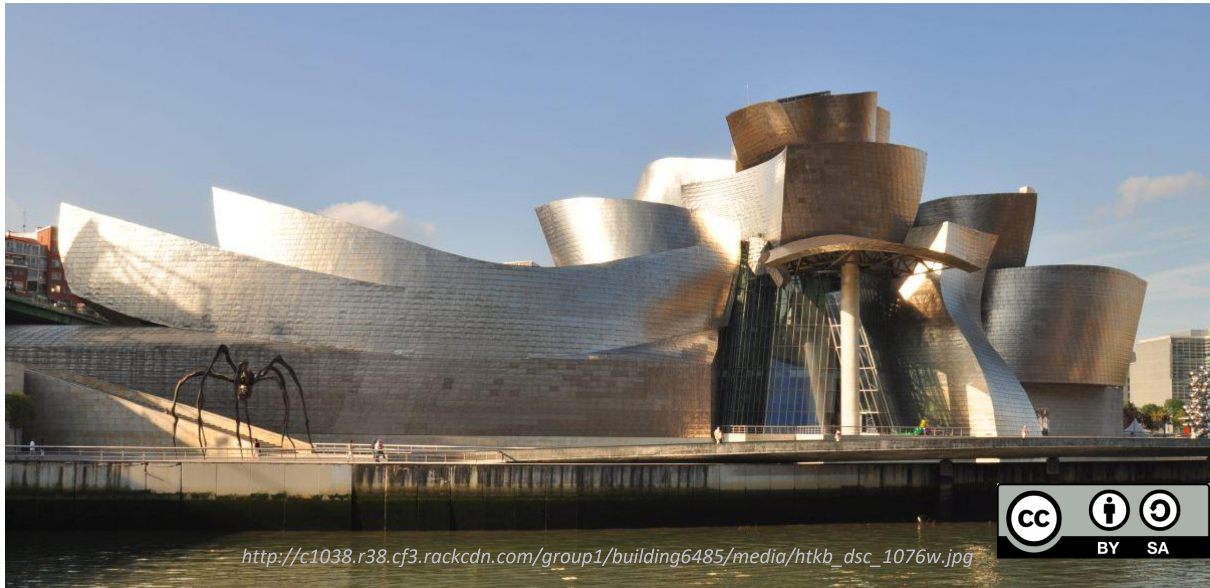


- Highly active
- Great ability to passivate due to formation of TiO_2 film
- Great corrosion resistance in oxidizing acids

- Worse stability in presence of reducing acids: alloying with Pd (≈0.1 %) to improve the ability to passivate
- Great resistance against pitting and crevice corrosion: crevice corrosion occurring only in concentrated chlorides at 70 °C and above
- Complexes with F: HF and F^- corrosive
- Explosive reaction with concentrated HNO_3
- Danger of H_{at} entry into structure, embrittlement (under specific cond.)

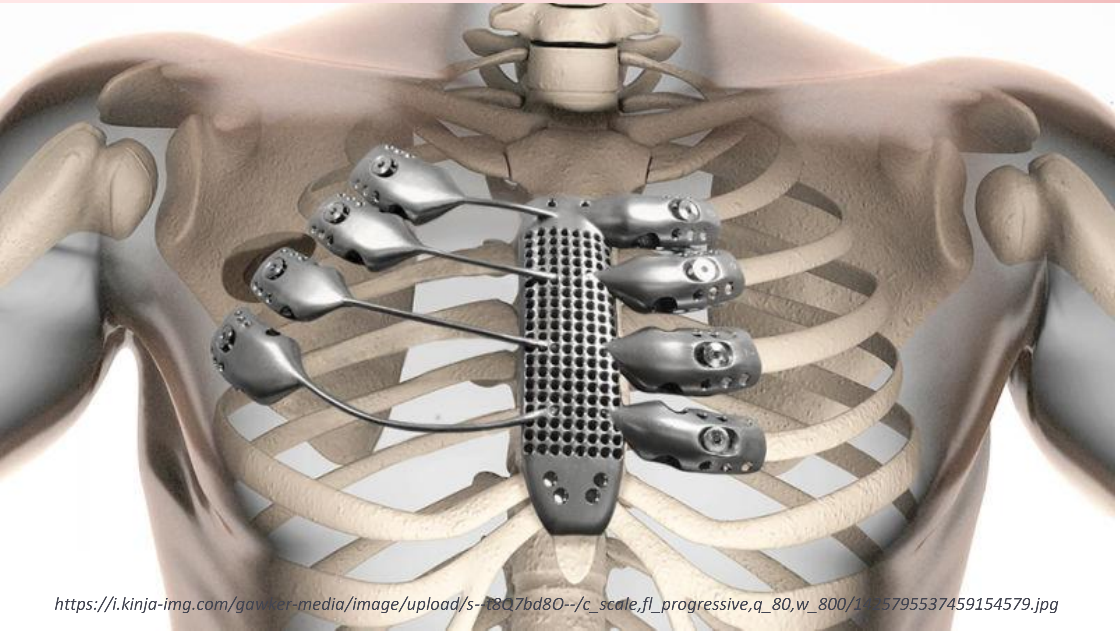
Titanium and Alloys

- **Grade 1–4:** Non-alloyed and low-alloyed Ti, forgeable, soft; use in chemical industry, limited use in architecture, automotive
- **Grade 5 (TiAl6V4)**: Most used, 50% applications of Ti; tough; turbines, engine parts, aeronautics, sport, sea water
- **Grade 23 (TiAl6V4)**: High purity, biomaterials – good biocompatibility
- **Grade 7, 11, 16, 17 (TiPd0.15, TiPd0.05)**: Higher resistance in reducing acids
- **and others**



http://c1038.r38.cf3.rackcdn.com/group1/building6485/media/htkb_dsc_1076w.jpg

Titanium and Alloys – Application



https://i.kinja-img.com/gawker-media/image/upload/s--t8Q7bd8O--/c_scale,fl_progressive,q_80,w_800/1...5795537459154579.jpg

http://www.sciaky.com/images/content/thumbs/titanium-parts.jpg

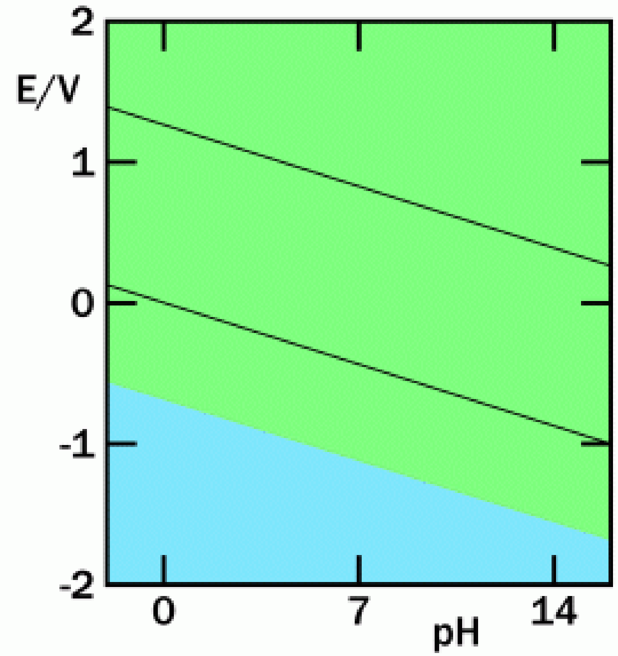
http://www.periodictable.com/Samples/022.8/s13.JPG

http://www.titanmf.com/wp-content/uploads/2014/03/Titanium-Shell-and-Tube-Heat-Exchanger-006-600x300_c.jpg

http://www.twinna.org.tw/UMemberAFile/52/5YP8kodfe
hhtQk66iHSTxjOB7g1APM6H68s.jpg

wikimedia.org

Tantalum

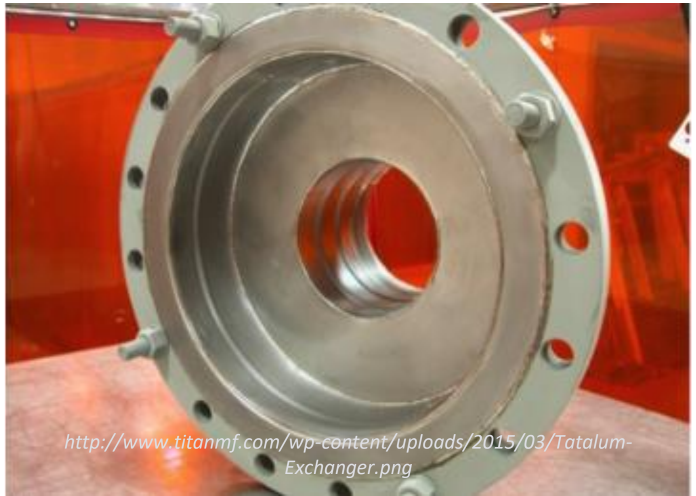


Novák et al., Korozní inženýrství, UCT 2002

- Strong ability to passivate
- Resistance similar to glass
- Stable in both oxidizing and reducing environments
- Used in production of acids

- Corrodes in presence of SO_2 and HF
- Brittle, expensive ⇨ Often coatings

http://hms2014tantalum.weebly.com/uploads/2/8/2/4/28241419/1398655955.png

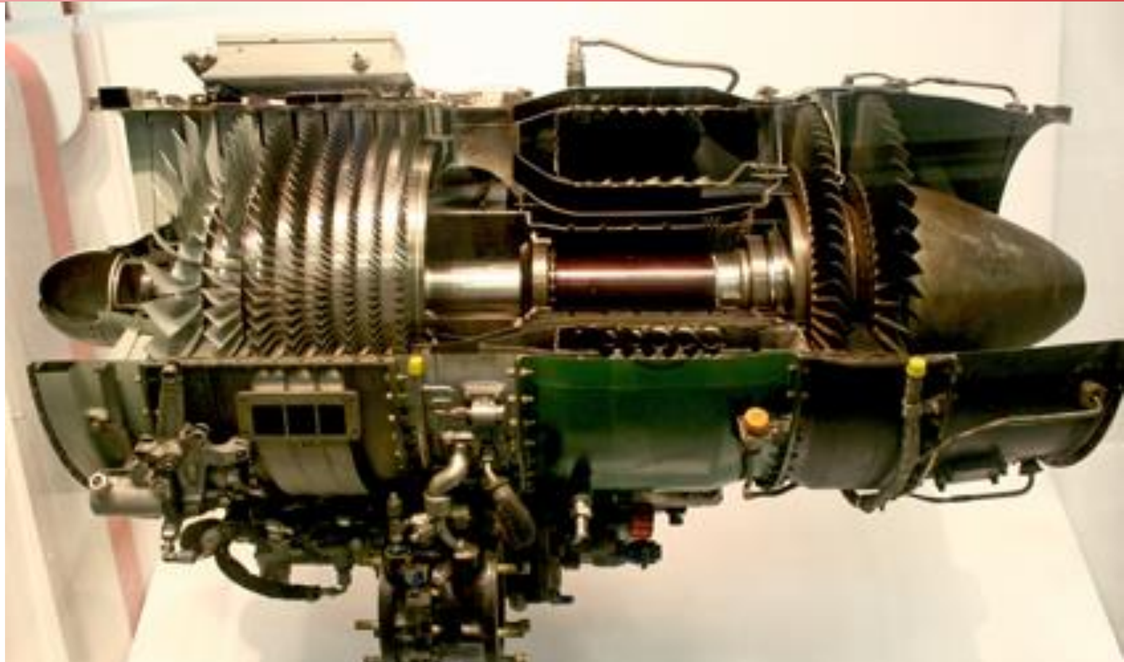


http://www.titanmf.com/wp-content/uploads/2015/03/Tatalum-Exchanger.png

http://www.titanmf.com/wp-content/uploads/Shell-and-Tube-Heat-Exchanger-001c_Medium-200x150.jpg

Cobalt Alloys

- Wear resistance, fatigue strength, high temperature resistance
- **Vitallium (CoCr30Mo5)**: Implants
- **Stellite (CoCr)**: Table accessories
- **Alacrite (CoCr20W15Ni10)**: Jet engines (aeronautics, aerospace), kg standard



http://www.steelforge.com/site/wp-content/uploads/2013/01/supperalloy.jpg

http://bonesmart.org/wp-content/uploads/2010/10/ConforMIS-iTotal-Knee-Implant.jpg

Lead

- Atmosphere: Protected with PbO, $PbSO_4$ or lead carbonates, corrosion rate less than 1 µm/year
- Earlier water piping and production and storage of H_2SO_4 (protective sulfate film)
- Toxicity and environmental aspects limit application

https://www.pca.state.mn.us/sites/default/files/styles/primary_840px_wide/public/non-lead-fishing-tackle-various-530.jpg?itok=Q9S5_DRo

https://qph.is.quoracdn.net/main-qimg-5c04788faf6943da7960725a082aa1ba?convert_to_webp=true

https://www.stpauls.co.uk/SM4/Mutable/Uploads/generic_image/T Cathedral%20dome.jpg

Copyright & Contact

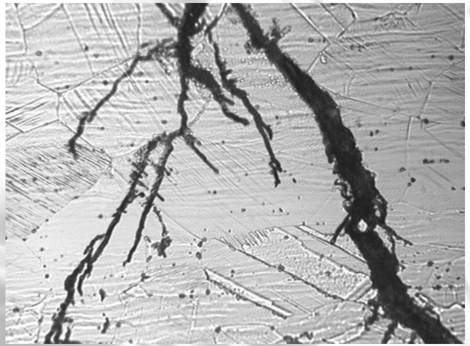
Tomáš Prošek, Ph.D.

University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS



www.vscht.cz

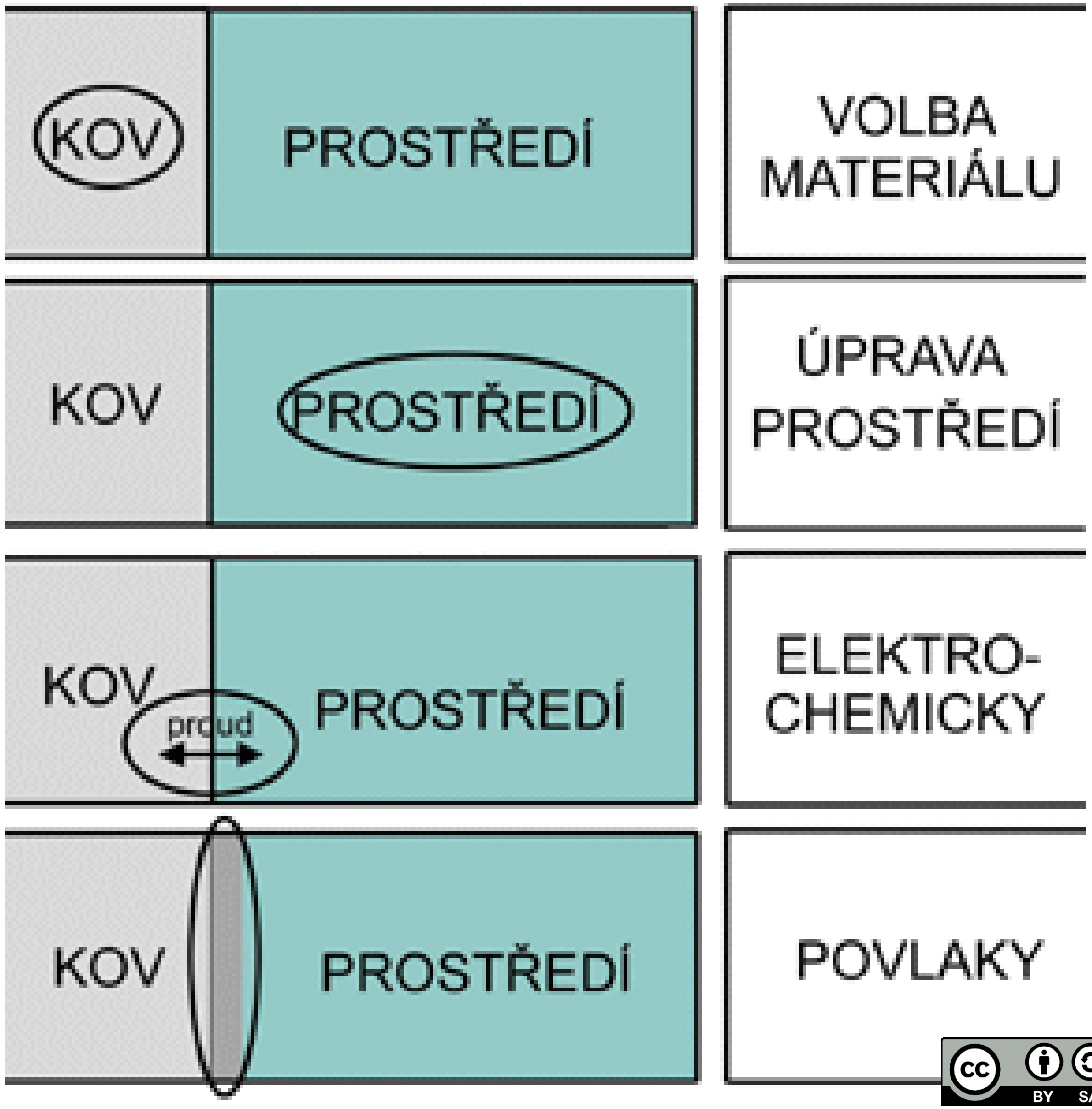
Corrosion Engineering

Tomáš Prošek

Principles of Corrosion Protection

Corrosion Protection Methods

- **Material selection**
- **Modification of the environment**
  - **Physical parameters**
  - **De-stimulation**
  - **Inhibition**
- **Electrochemical protection**
  - Cathodic
  - Anodic
- **Coatings**
- **Design**



Novák et al., Korozní inženýrství, UCT 2002

Material Selection

- About ¼ of the corrosion costs can be eliminated by the application of known corrosion protection methods
- Most efficient protection in the design phase; material selection crucial
- Material selection based on requirements on:
  - Mechanical properties (strength, wear resistance and others); → **Mass loss (corrosion depth) critical**
  - Further application properties (electric conductivity, optical)
  - Aesthetic properties

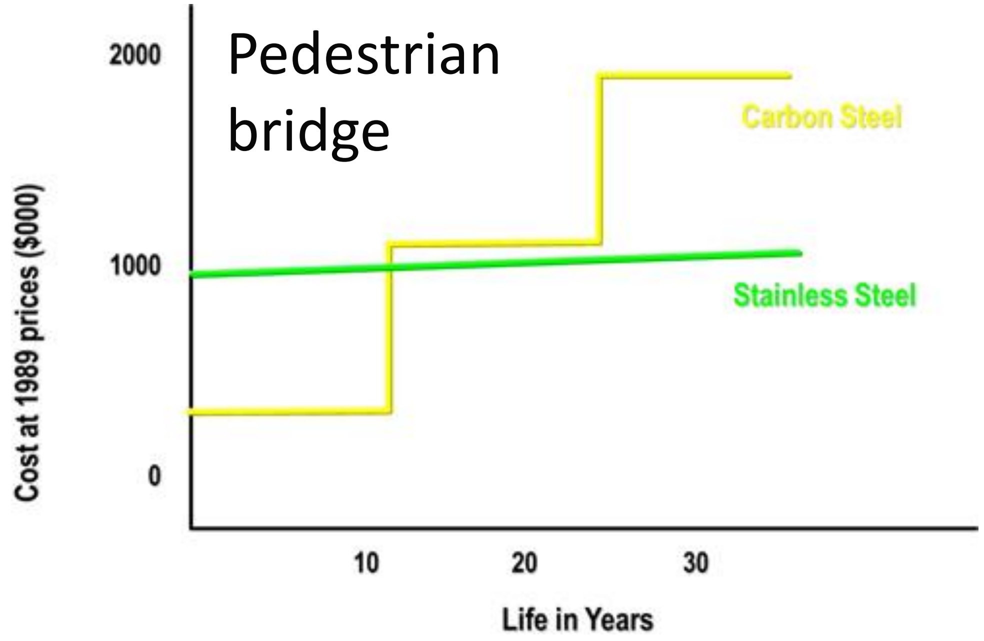
  (Further application properties, Aesthetic properties) → **Surface state critical**
  - Price
- Empirical experience available in handbooks: Dechema Corrosion Handbook, ASM Handbook of Corrosion, ad.; further resources: proceedings, journals

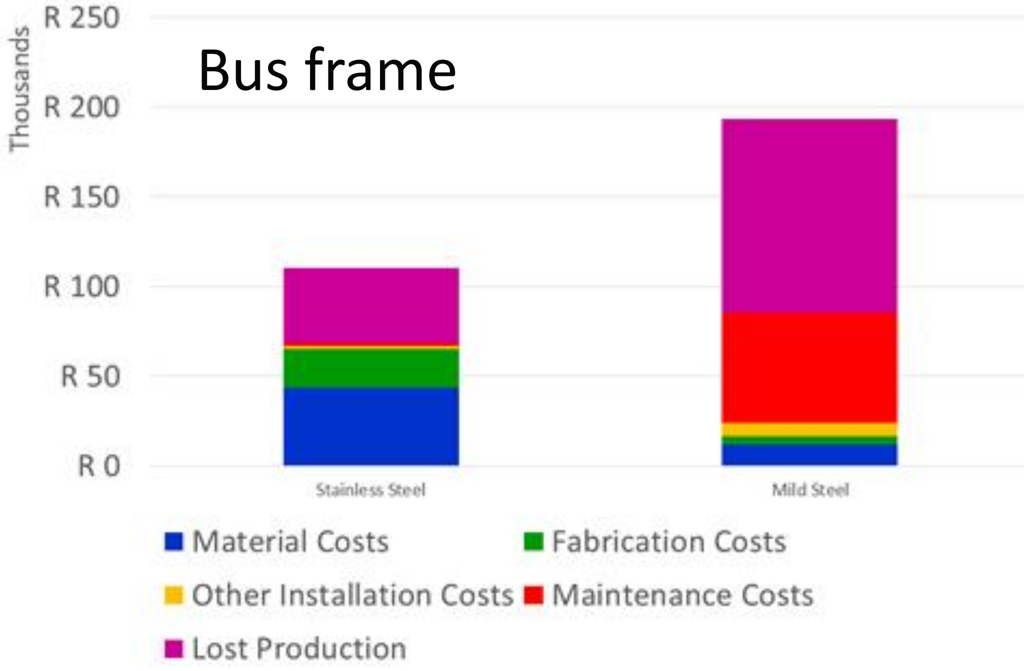
Total Cost of Ownership / LCA

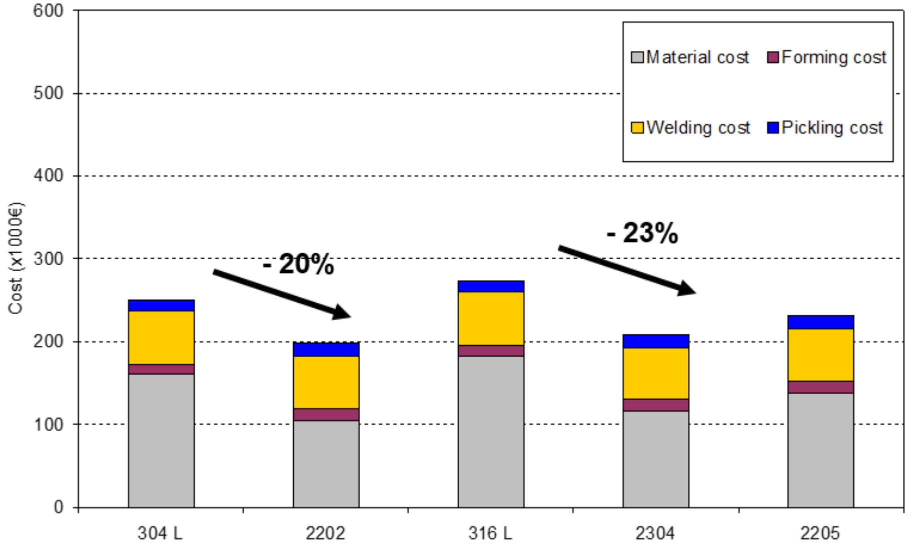
All Costs at Present Value Before Addition:					
Total life cycle cost (LCC)	Initial materials acquisition costs (AC)	Initial materials installation & fabrication costs (IC)	Operating & maintenance costs (OC)	Lost production costs during down-time (LP)	Replacement materials costs (RC)

$$TCO = AC + IC + \sum_{n=1}^{N} \frac{OC}{(1+i)^n} + \sum_{n=1}^{N} \frac{LP}{(1+i)^n} + \sum_{n=1}^{N} \frac{RC}{(1+i)^n}$$

Where: **N** = Desired service life **i** = Real interest rate **n** = Year of the event







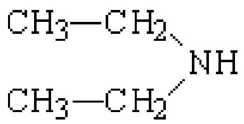
Storage tank
12 m diameter
18 m height

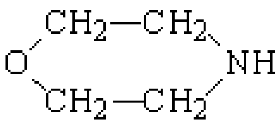
Environment Modification

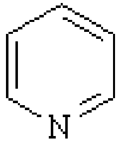
- **Change in physical parameters** – temperature, flow rate, irradiation
- **De-stimulation**
  - Removal of corrosive component(s)
  - Condition: Present in limited quantities and technologically unnecessary
  - Examples: Oxygen in power generation, H^+ ions (alkalization), chlorides and other ions from water solutions, water from crude oil and atmosphere
- **Inhibition**
  - Addition of small quantities (typically from 0.1 to 10 g/l) of a compound with a significant effect on corrosion rate
  - Systemization rather artificial, usually a combination of effect

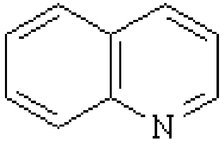
Inhibitors

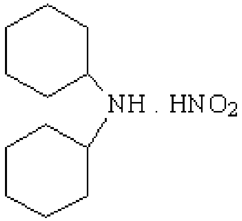
- **Passivation**: increased rate of cathodic reaction by direct reduction (Fe^{3+}, Ce^{4+}, CrO_4^{2-}, MoO_4^{2-}, VO_3^{3-}, NO_3^-) or by catalysis of reduction of other system components (Pt^{4+}, Pd^{2+}, Cu^{2+}); effect on anodic reaction (PO_4^{3-}, SiO_3^{2-})
- **Cathodic**: cathodic reaction blocking (As^{3+}, Sb^{3+}, Zn^{2+}, polyphosphates, CrO_4^{2-})
- **Adsorption**: surface blocking (typically organic compounds)

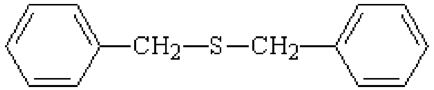

Diethylamine

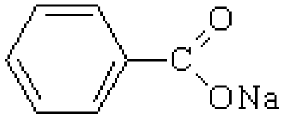

Morpholine

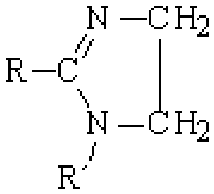

Pyridine

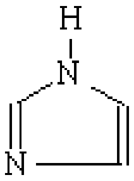

Chinoline

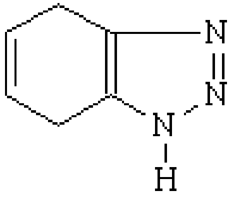

Dicyclohexylamine

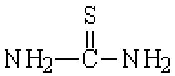

Diphenylsulfoxide

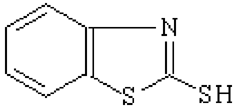

Sodium benzoate


Imidazoline


Imidazole


Benzenotriazole

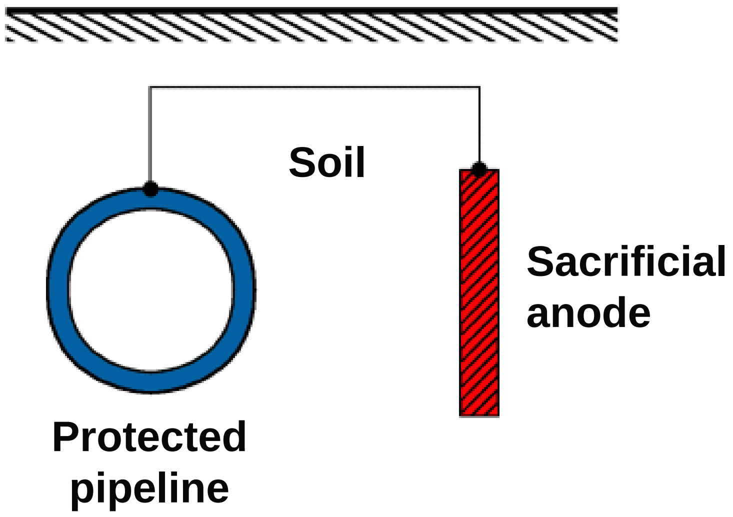

Thiourea

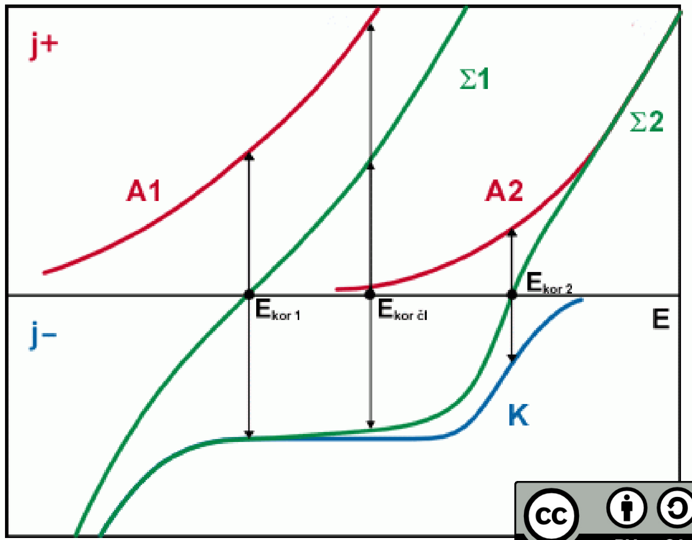

Mercaptobenzthiazole

- Soluble or volatile; often mixtures

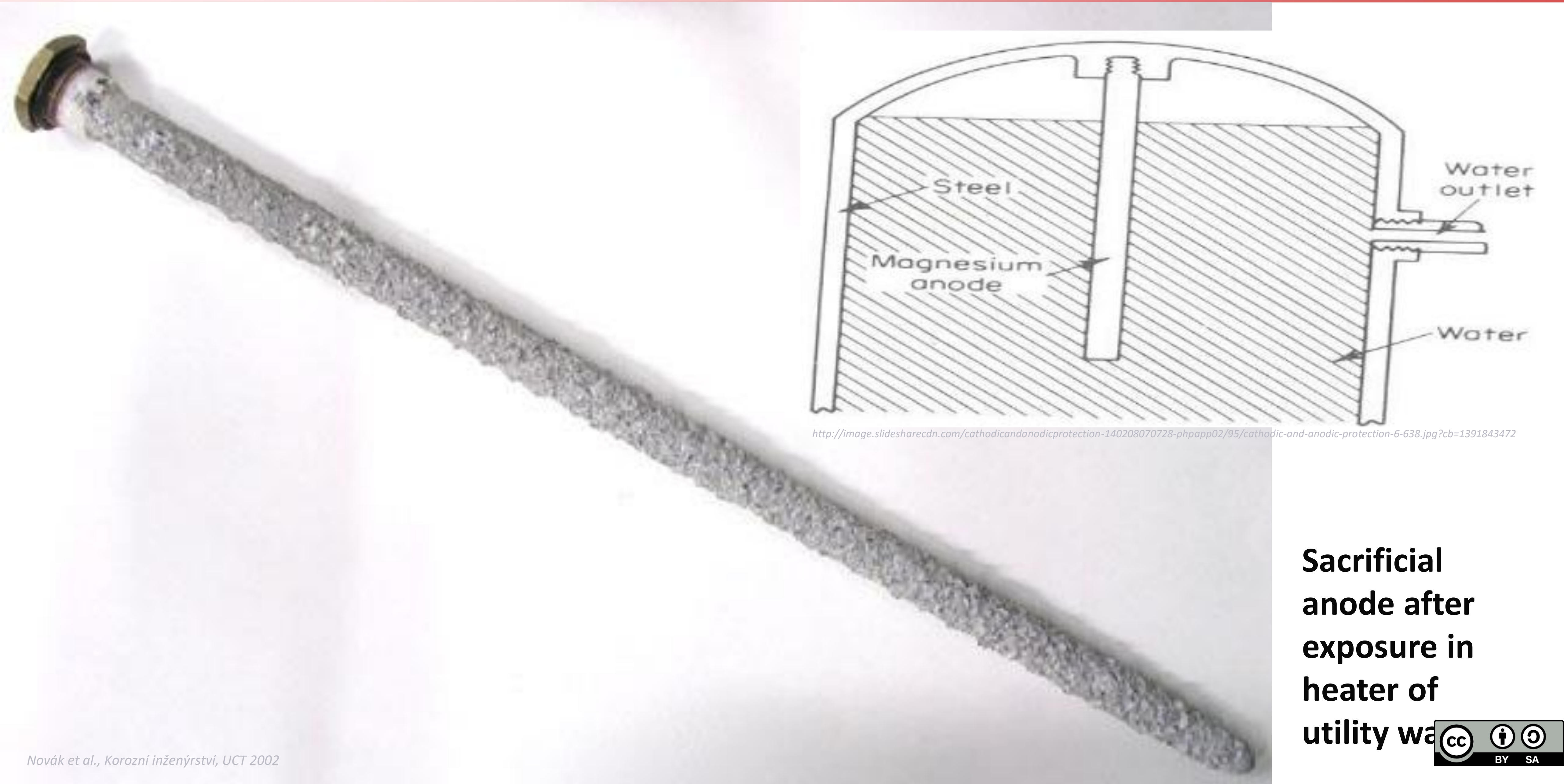
Electrochemical Protection

- Protection by direct current: change in potential
- **Cathodic protection by sacrificial anode**
  - Galvanic coatings, ships, buried structures, reinforcement in concrete
  - Zn, Mg, Al (for sea water, alloying necessary)
  - Protective current efficiency 50–90+ %
  - Long-term reliability without maintenance, lifetime limited
  - Throwing power limited by resistance of the environment





Protection by Sacrificial Anode



http://image.slidesharecdn.com/cathodicandanodicprotection-140208070728-phpapp02/95/cathodic-and-anodic-protection-6-638.jpg?cb=1391843472

Sacrificial anode after exposure in heater of utility wa

Novák et al., Korozní inženýrství, UCT 2002

Protection by Sacrificial Anode

http://www.cathodicme.com/images/sacpimg2.jpg

Sacrificial anodes

Protection by Sacrificial Anode

http://http://www.jonesboatchandlery.co.uk/media/wysiwyg/Boat_anode.jpg

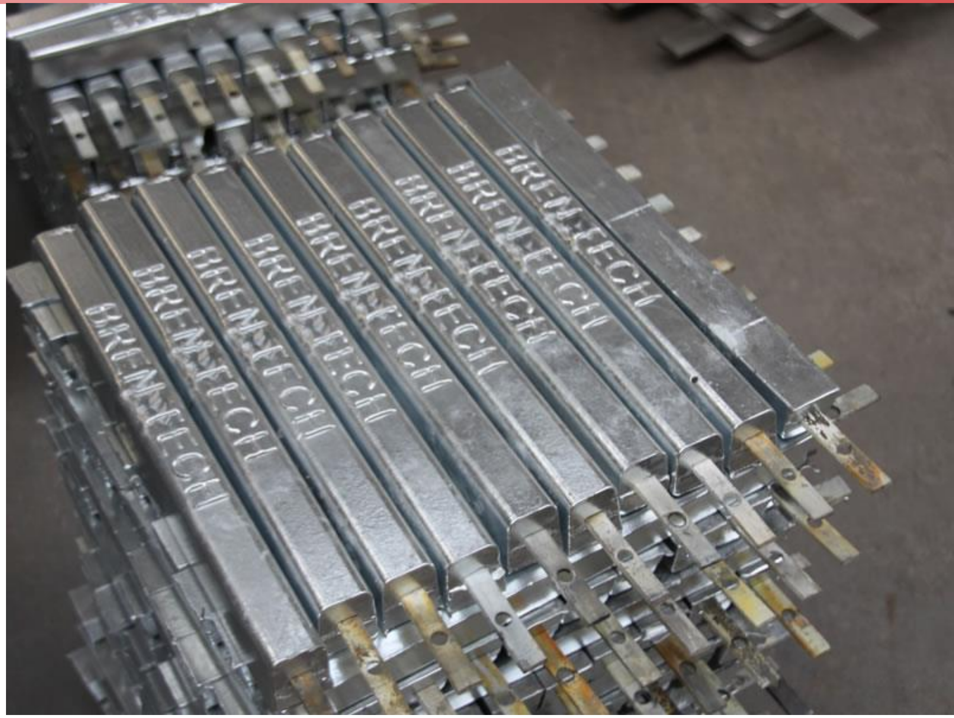
Used sacrificial anodes

http://www.amteccorrosion.co.uk/Photos%202008/old%20anodes.jpg

http://marineinsight.com/wp-content/uploads/2010/11/

Protection by Sacrificial Anode

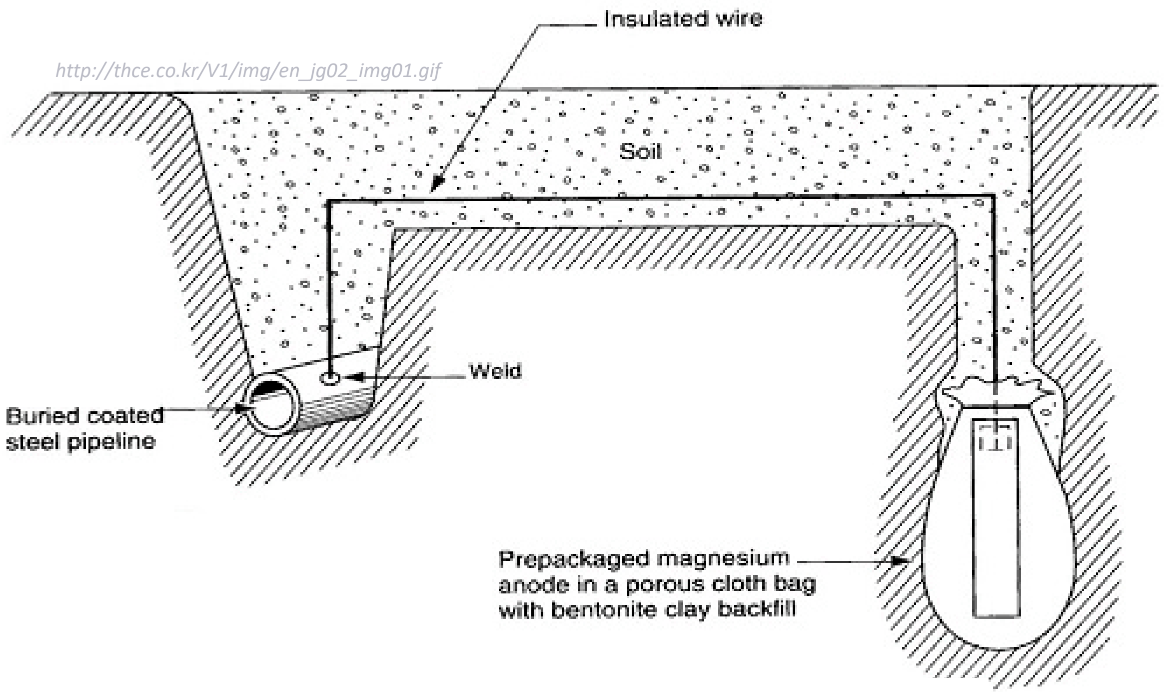
http://img.directindustry.com/images_di/photo-g/33780-6484855.jpg



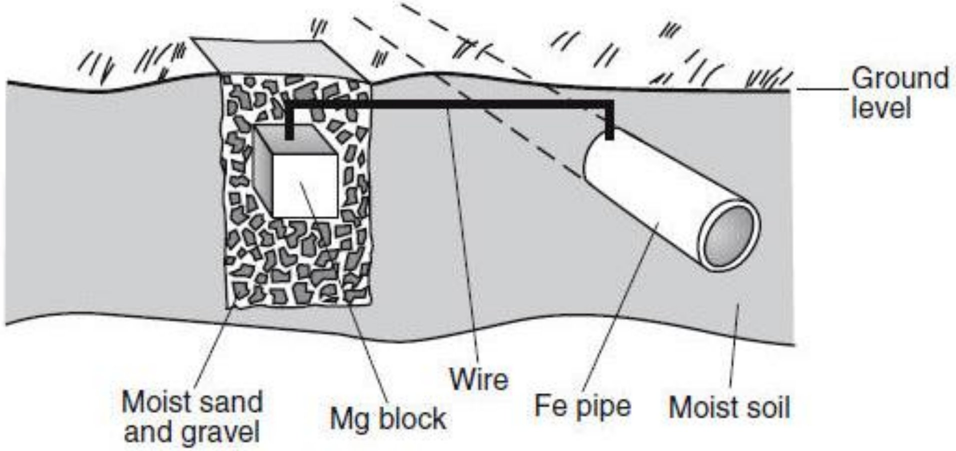
http://www.corrocogroup.com/cathodic-protection/1-2-2d.jpg

Sacrificial anodes for protection of steel bars in concrete

Protection by Sacrificial Anode



http://thce.co.kr/V1/img/en_jg02_img01.gif

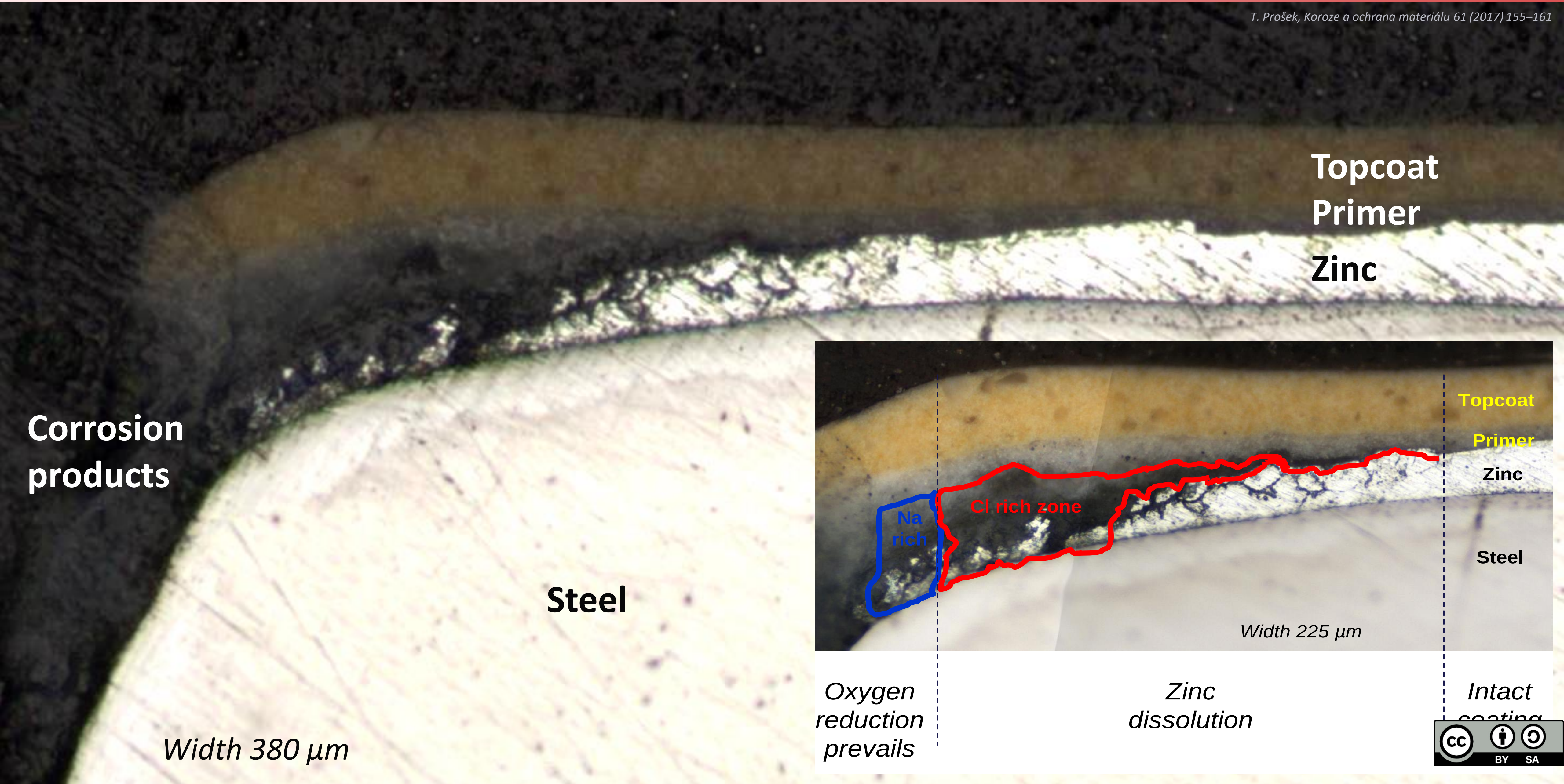


http://www.kentchemistry.com/RegentsExams/Aug2002/regent209.jpg

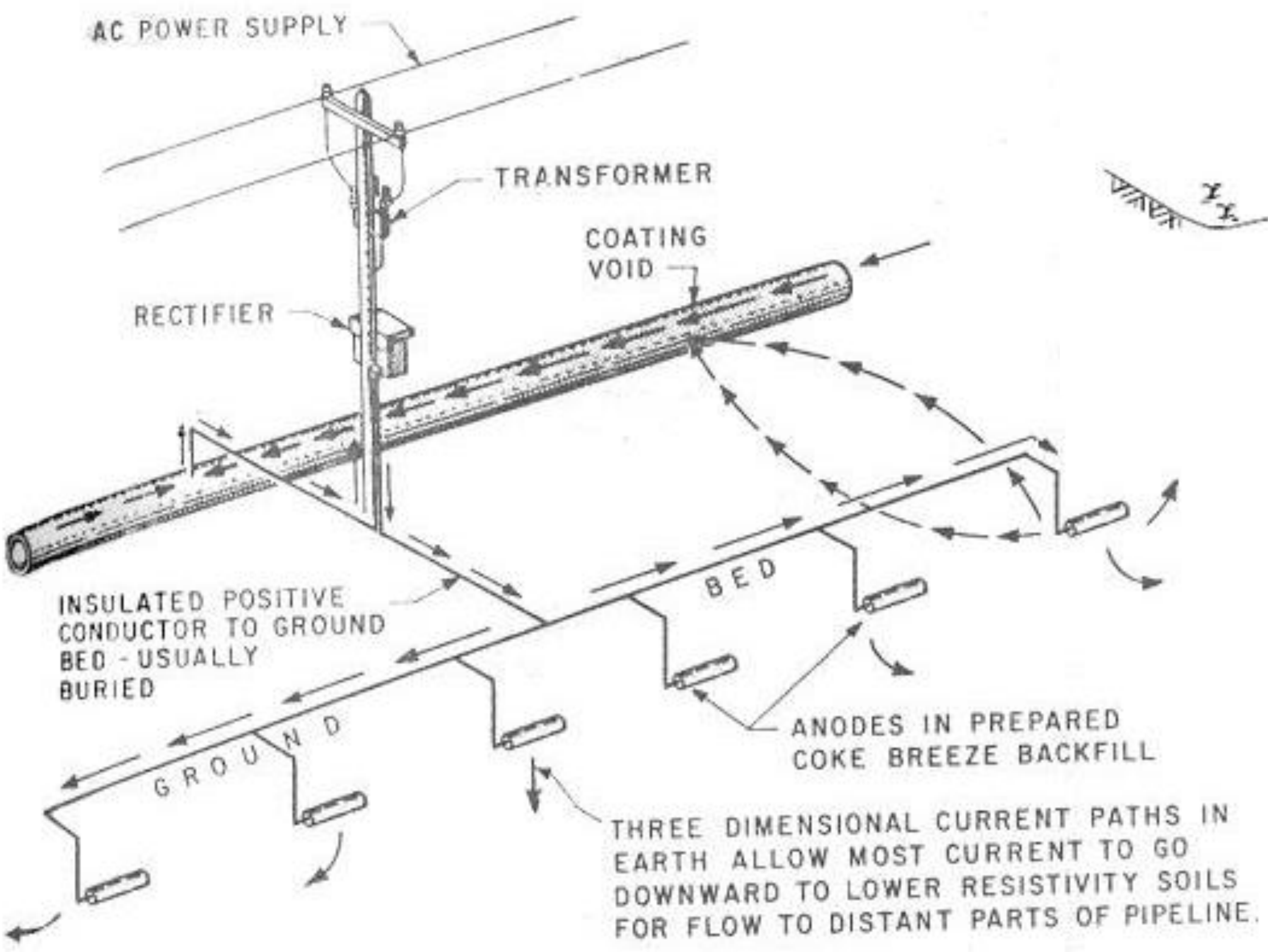
Novák et al., Korozní inženýrství, UCT 2002

Sacrificial anodes for protection of buried stru

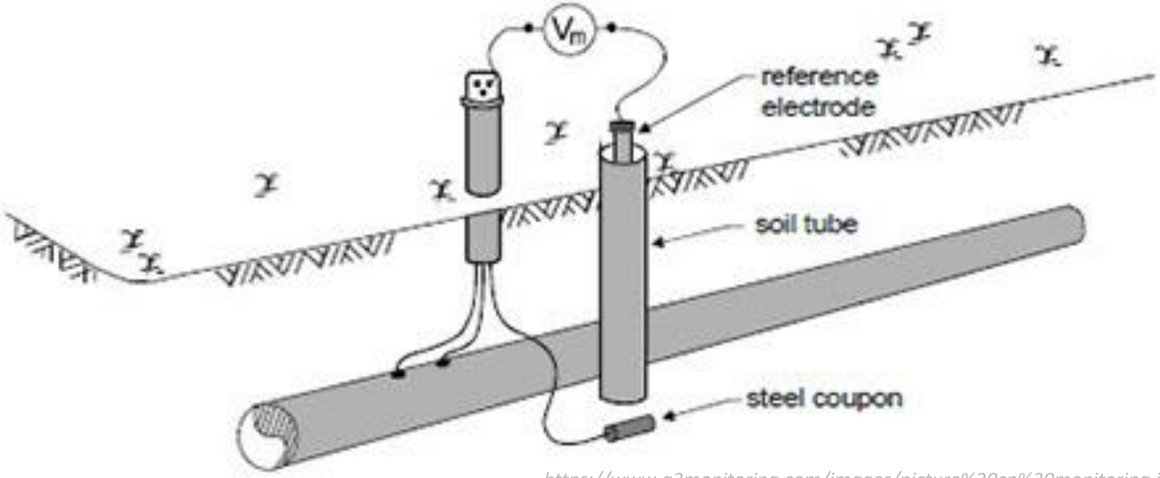
Protection by Sacrificial Anode



Cathodic Protection, External I

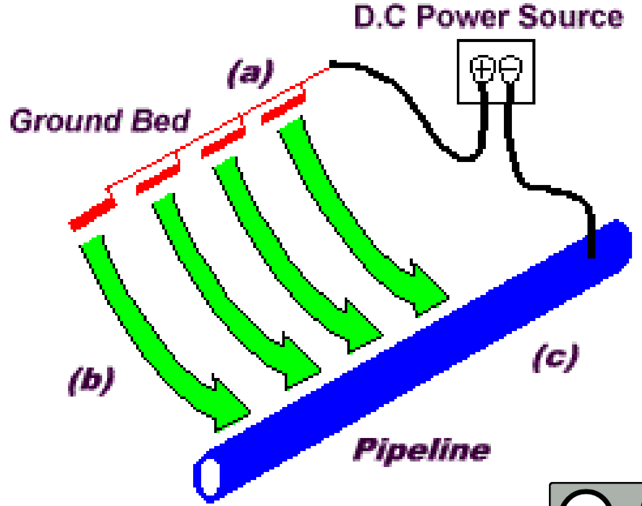


http://www.fadak.us/A.database/Metallurgy/Learn/L.002/Image/A.0053.12.jpg



https://www.a3monitoring.com/images/picture%20cp%20monitoring.jpg

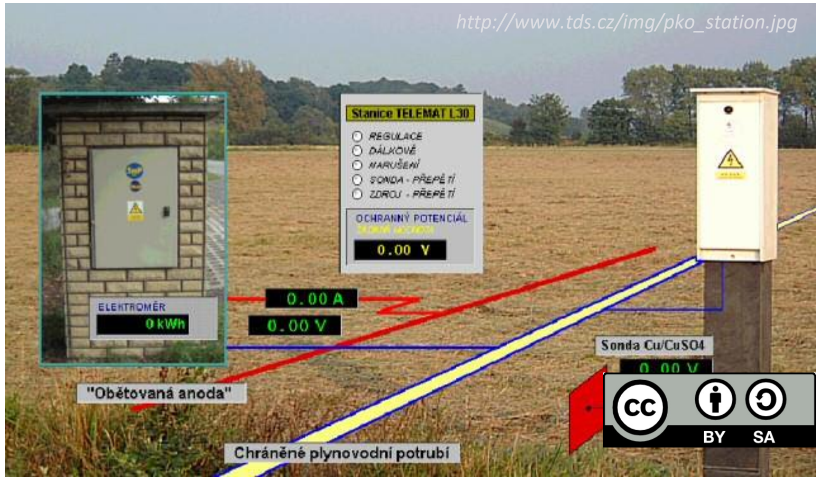
http://www.spaceweather.gc.ca/images/tech/e_pipediag.gif



Cathodic Protection, External I

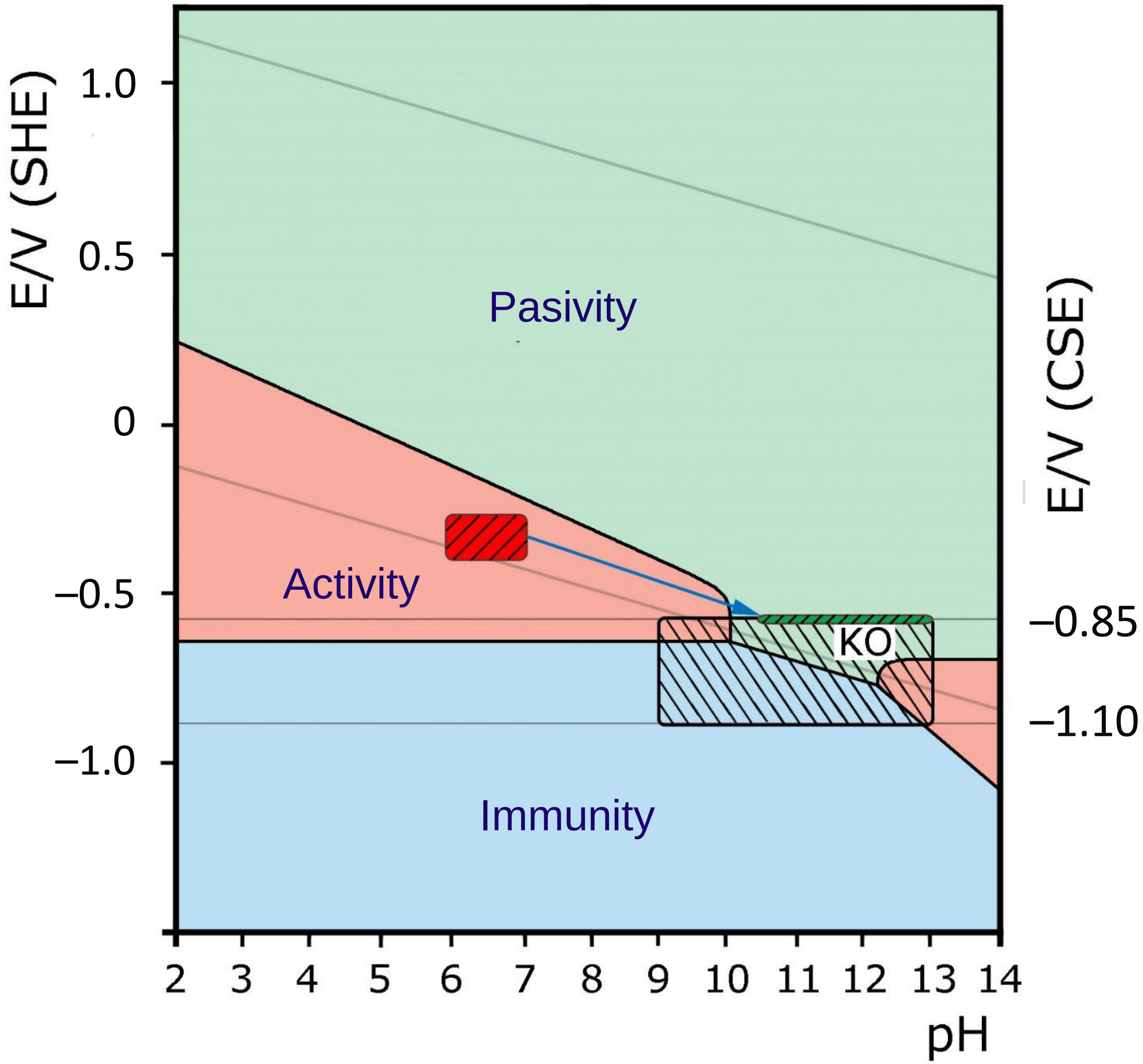
http://www.raychemrpg.com/ogd/cathodic_protection/plant_piping/plant_piping_6.jpg

https://upload.wikimedia.org/wikipedia/commons/6/65/Ku%C5%99%C3%AD_Kv%C4%9Btn%C3%A1_stanice_katodick%C3%A9_ochrany.jpg



http://www.tds.cz/img/pko_station.jpg

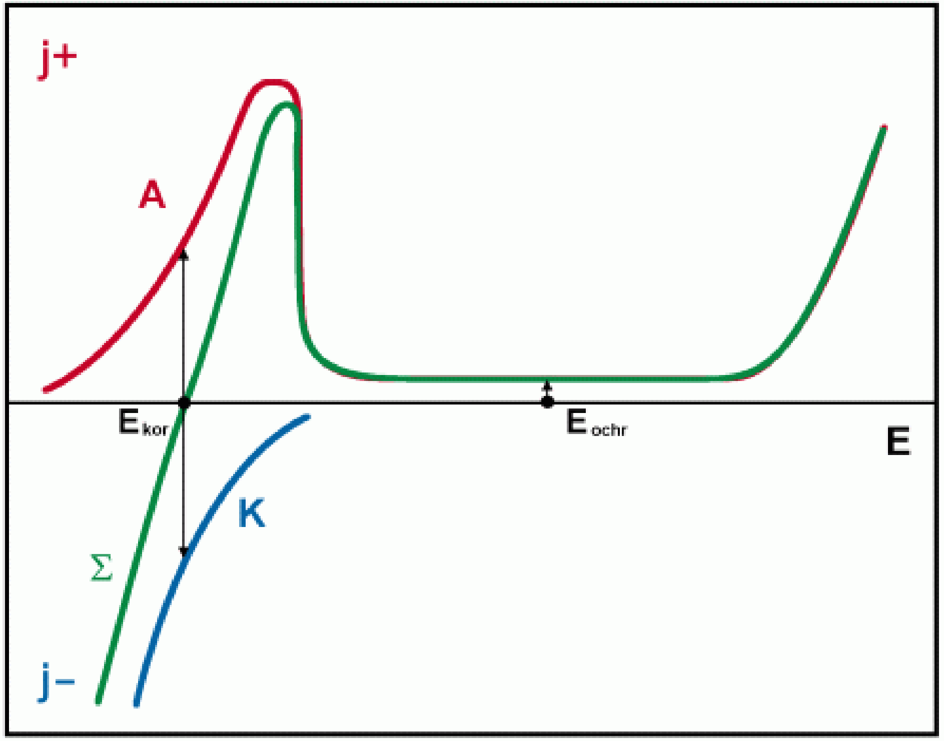
Cathodic Protection, External I



Cathodically protected steel in soil

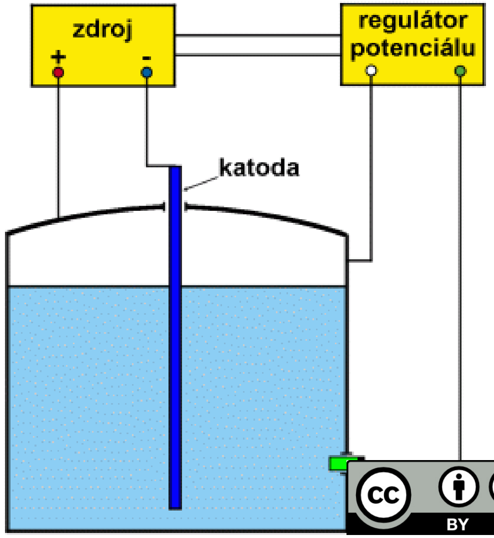
Anodic Protection

- Metals with ability to passivate and low corrosion rate in passivity
- E.g., stainless steel in sulfuric acid
- Risk of rapid damage in case of failure



Novák et al., Korozní inženýrství, UCT 2002

Cooling field with anodically protected coolers made of stainless steel FeCr18Ni10 in sulfuric acid production



Novák et al., Korozní inženýrství, UCT 2002

Anodic Protection

Cooling field made of cast iron in sulfuric acid production

Novák et al., Korozní inženýrství, UCT 2002

Detail of anodically protected cooler made of stainless steel FeCr18Ni10 in sulfuric acid prod

Protection by Coatings

- Optimal combination of mechanical and physical properties of basic material and coating – wear resistance, aesthetics, optical, corrosion properties
- Principal effect: **Barrier**
- Types of coatings:
  - Organic (paints), 70 %
  - Metallic, 20 %
  - Conversion coatings and passivation – phosphatation, chromate, blackening, …
  - Thick organic coatings – rubber, bitumen, polyethylene coatings
  - Enamel
  - Cement
  - Thermochemical (diffusion)

Organic Coatings

Novák et al., Korozní inženýrství, UCT 2002

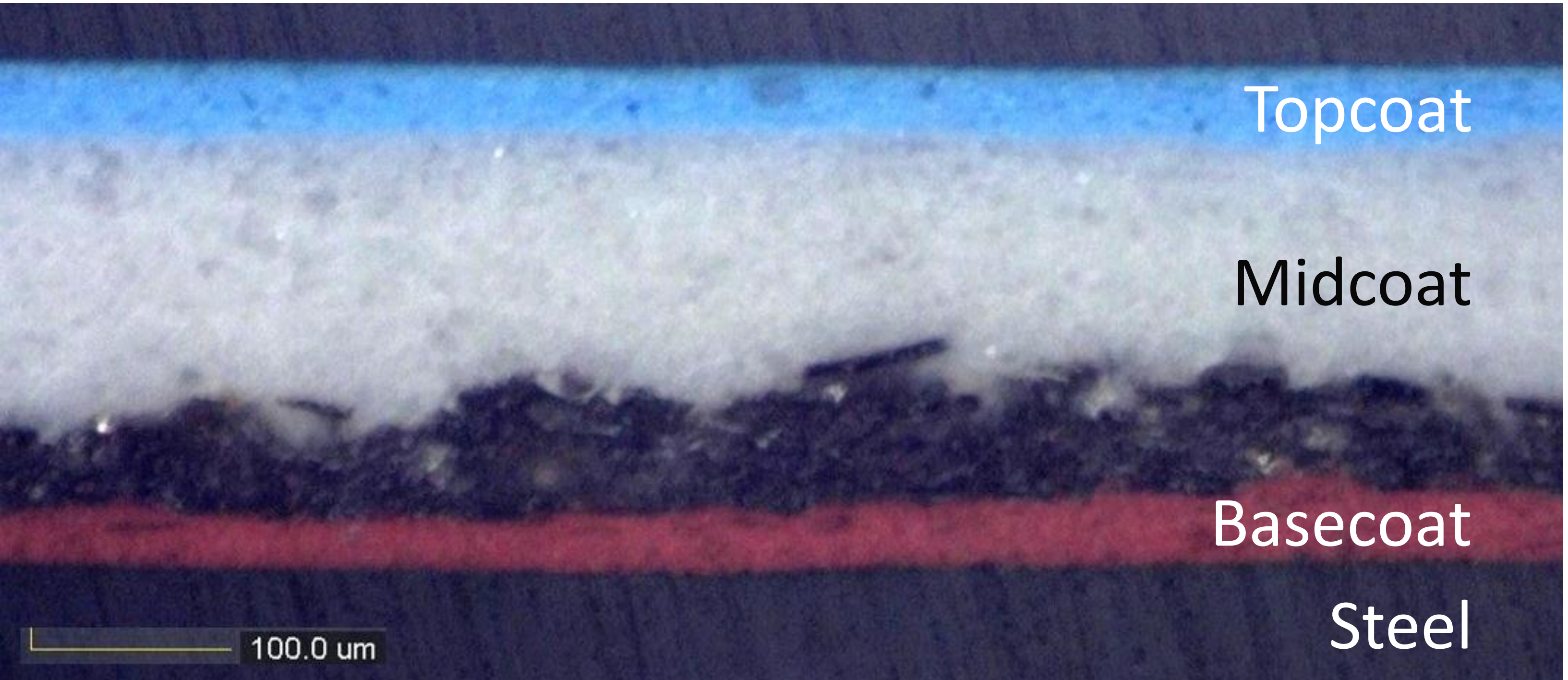
http://www.freevectors.net/files/large/CokeCan.jpg

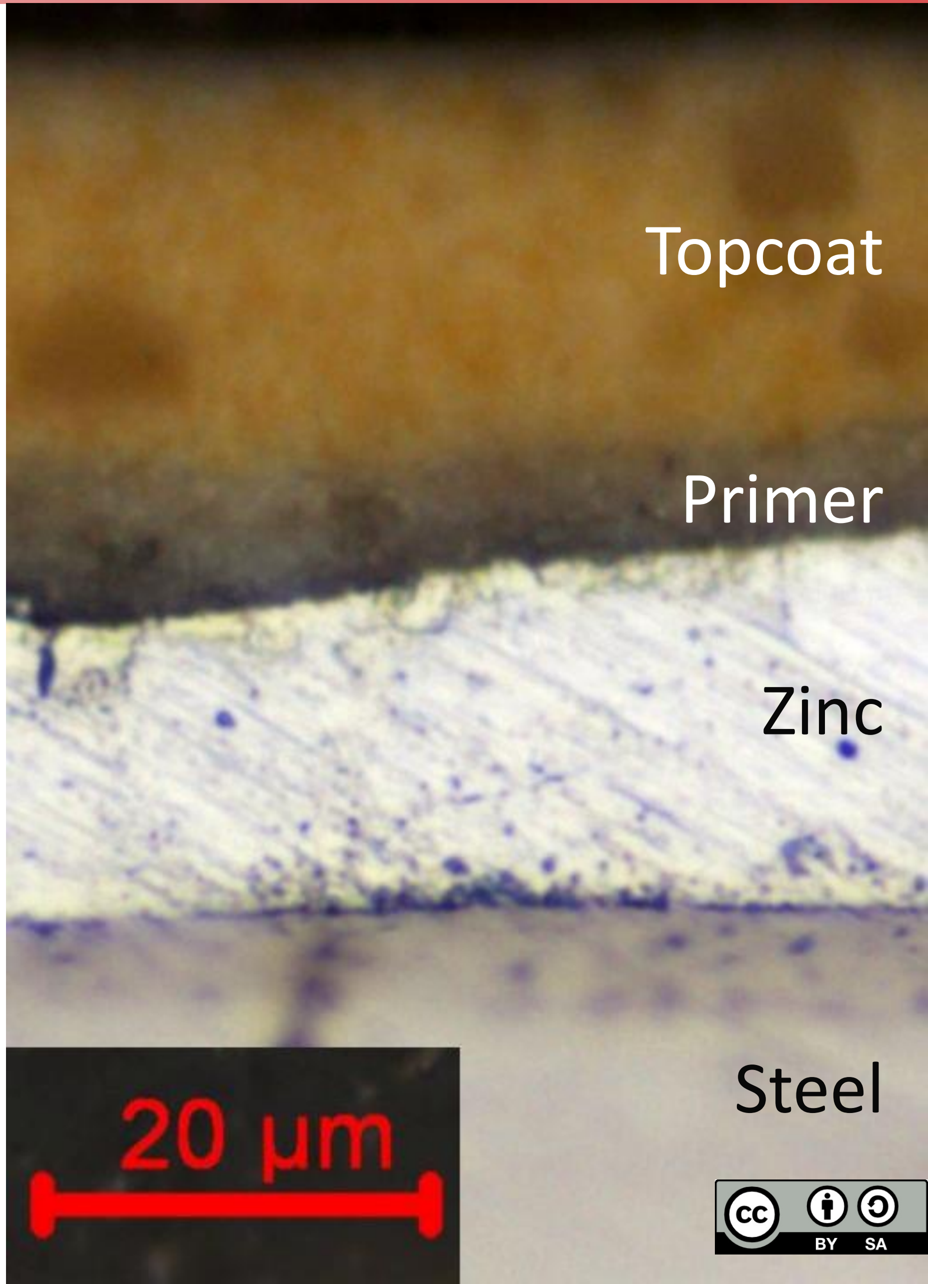
https://www.smlmarinepaints.co.uk/files/library/images/generic/how_not_to_paint.png

http://www.businesskorea.co.kr/sites/default/files/field/image/Samsung%20home%20appliances.jpg

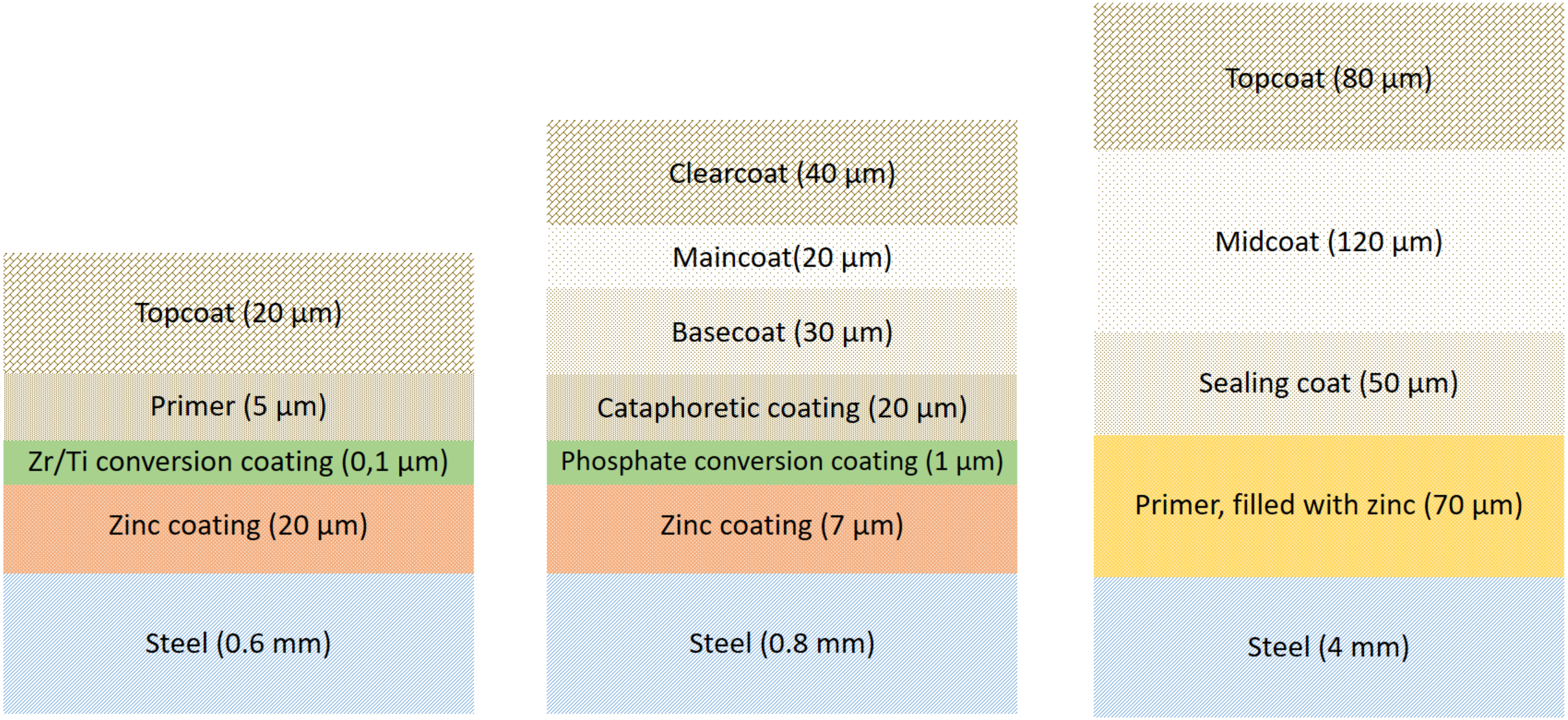
Organic Coatings

- Most common method of corrosion protection
- High efficiency (performance-to-cost ratio)
- Micrometers to hundreds of micrometers: short-term protection as well as heavy duty systems
- Duplex systems: combined with metallic coatings





Organic Coatings



Coil coated steel for roofing

Car body, Europe

Construction in marine atmosphere, expected lifetime 25 years

OC – Composition

- **Polymer binder**
- **Thinner** (except for powder) – real, colloid (dispersions)
- **Fillers** – structure reinforcement, better barrier effect, higher UV resistance, etc.; e.g. limestone, chalk, gypsum, talk
- **Pigments** – colour, covering, corrosion protection; TiO_2, $BaSO_4$, ZnO, graphite, …
- **Additives** – frothiness, dispersion agents, antibacterial, rheology, …

Triviální název	Pojivo
Akrylátové	Estery kyselin polyakrylové a polymetylakrylové
Alkydové	Polyestery vzniklé esterifikací polykarboxylových kyselin polyalkoholy [1]
Asfaltové	Přírodní a ropné asfalty, případně kamenouhelná smola [2]
Epoxidové	Epoxidová pryskyřice
Chlorkaučukové	Chlorovaný přírodní kaučuk nebo syntetický polyisopren
Nitrocelulózové	Deriváty nitrátů celulózy (acetobutyrátcelulózy, acetylceluloza, etylceluloza a benzylceluloza)
Olejové	Vysychavý rostlinný olej nebo olejopryskyřičné pojivo
Polyesterové	Produkty reakce diolů s vícesytnými kyselinami
Polyuretanové	Pryskyřice, vznikající reakcí vícefunkčních isokyanátů s látkami obsahujícími hydroxylové skupiny
Silikonové	Silikonová pryskyřice, obsahující řetězce –O–Si–O– (smíšené metylfenylpolysiloxany)
Vinylové	Polystyren, kopolymer vinylchloridu, chlorovaného PVC a chlorovaných polyolefinů

[1] Do této skupiny patří hmoty v ČR označované jako „syntetické" základní barvy nebo emaily. Jde o největší skupinu nátěrových hmot. [2] Mohou se kombinovat s epoxidy a polyuretany za vzniku epoxidehtů a polyuretandehtů.

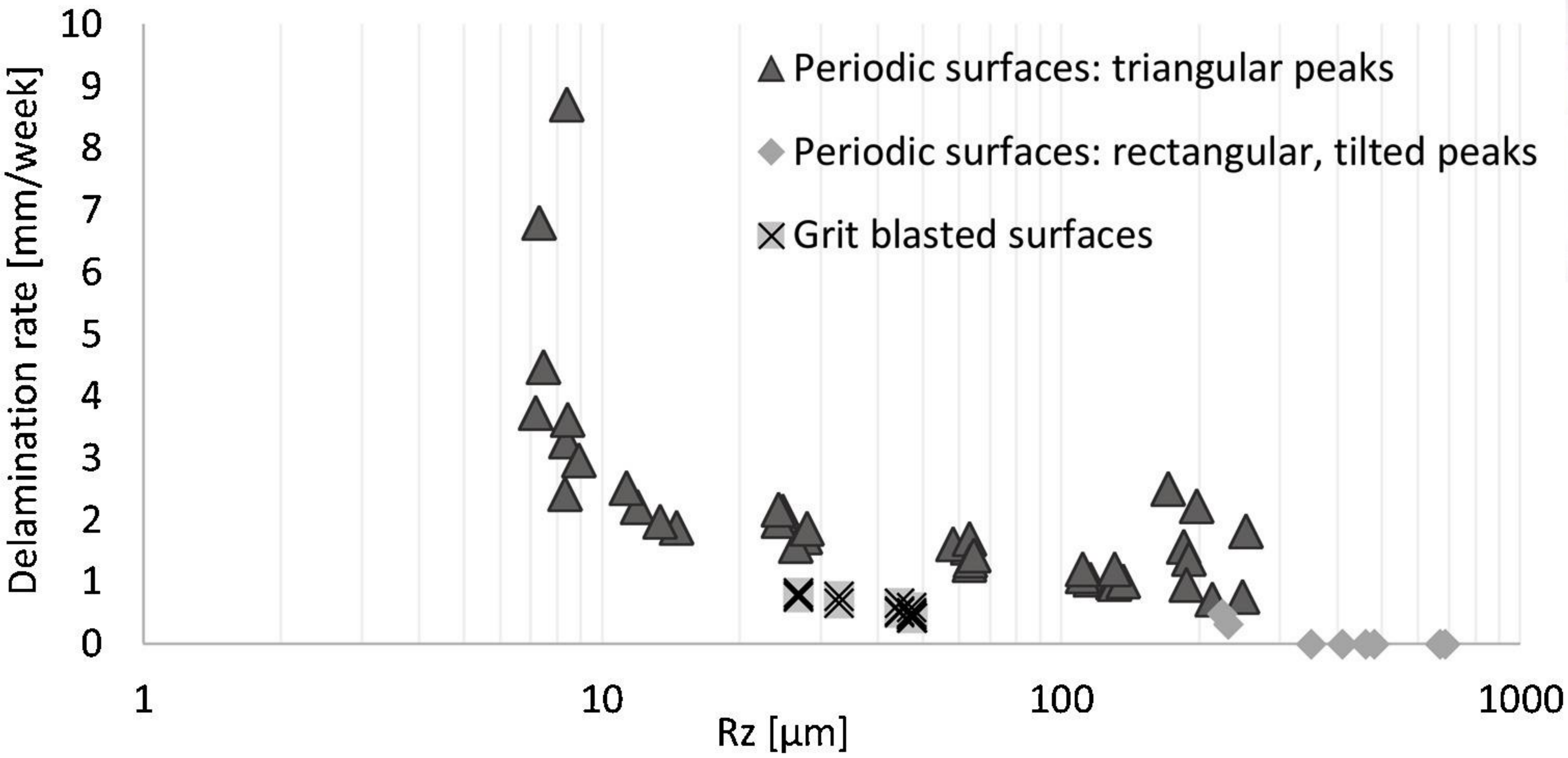
OC – Surface Preparation

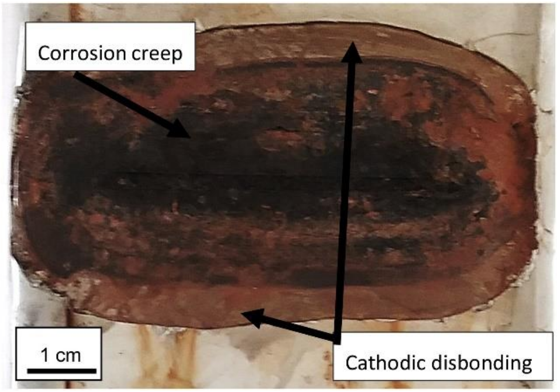
Novák et al., Korozní inženýrství, UCT 2002

Application of organic coating on untreated su

OC – Surface Preparation

- Clean surface = up to 10-fold higher coating lifetime
- Higher surface roughness = higher paint adherence = longer lifetime

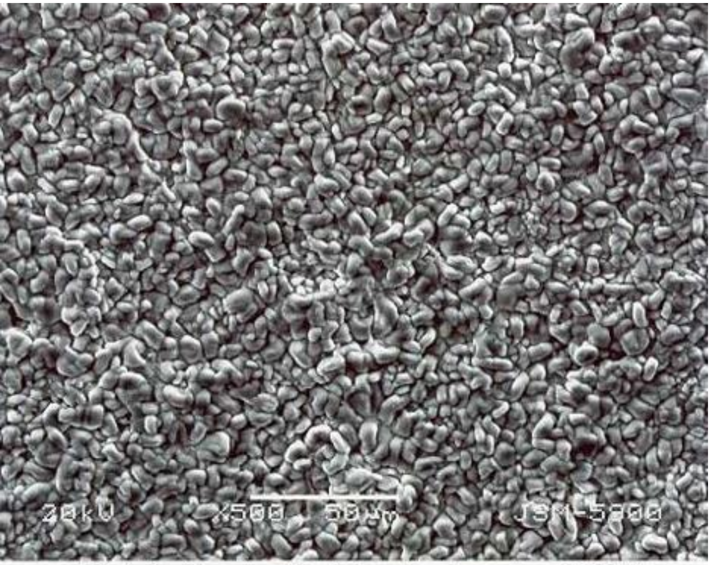




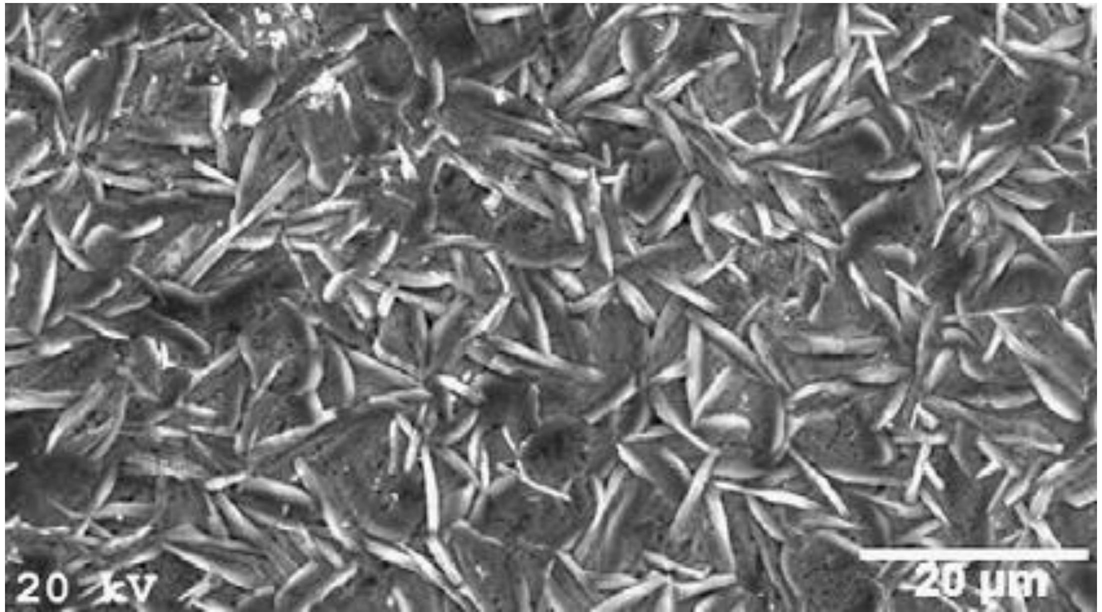
- Steel
- Two-component polyamine cured epoxy mastic coating
- DFT of 350–400 µm
- Corrosion test ISO 12944-9 (UVA, condensation, NSST)
- Delamination from defect

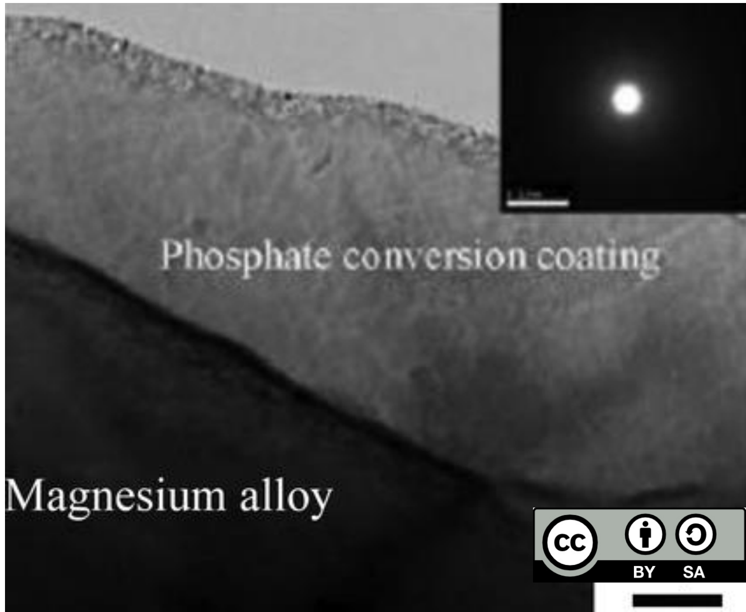
Hagen, C. M. H., et al. "The effect of surface roughness on corrosion resistance of machined and epoxy coated steel." Progress in Organic Coatings 130 (2019): 17-23.

OC – Conversion Coatings



SEM of calcium-modified zinc phosphate crystal (500X)





OC – Application

htt... ges.wisegeek.com/man-painting-a-white-wall.jpg

http://www.steelconstruction.info/images/thumb/b/b7/Roller_application.jpg/300px-Roller_application.jpg

https://www.thyssenkrupp-steel.com/media/content_1/compact/compact_20..._4/tk0414_d_3479_11_aufmacher_image_w886.jpg

https://i.ytimg.com/vi/YyCZIXf7o-Y/maxresdefault.jpg

https://i.ytimg.com/vi/YyCZIXf7o... /maxresdefault.jpg

http://...rehabsteel.com/wp-content/uploads/2014/05/color-coils1.jpg

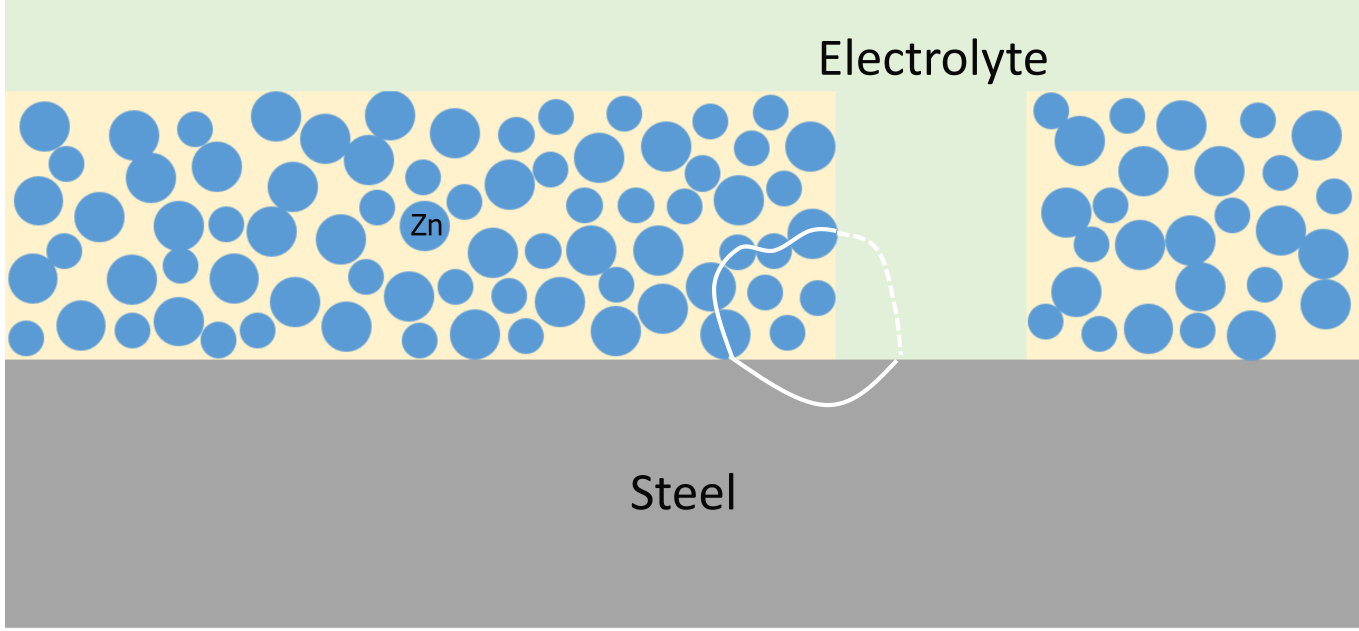
OC – Thickness Verification

Measurement of coating thickness

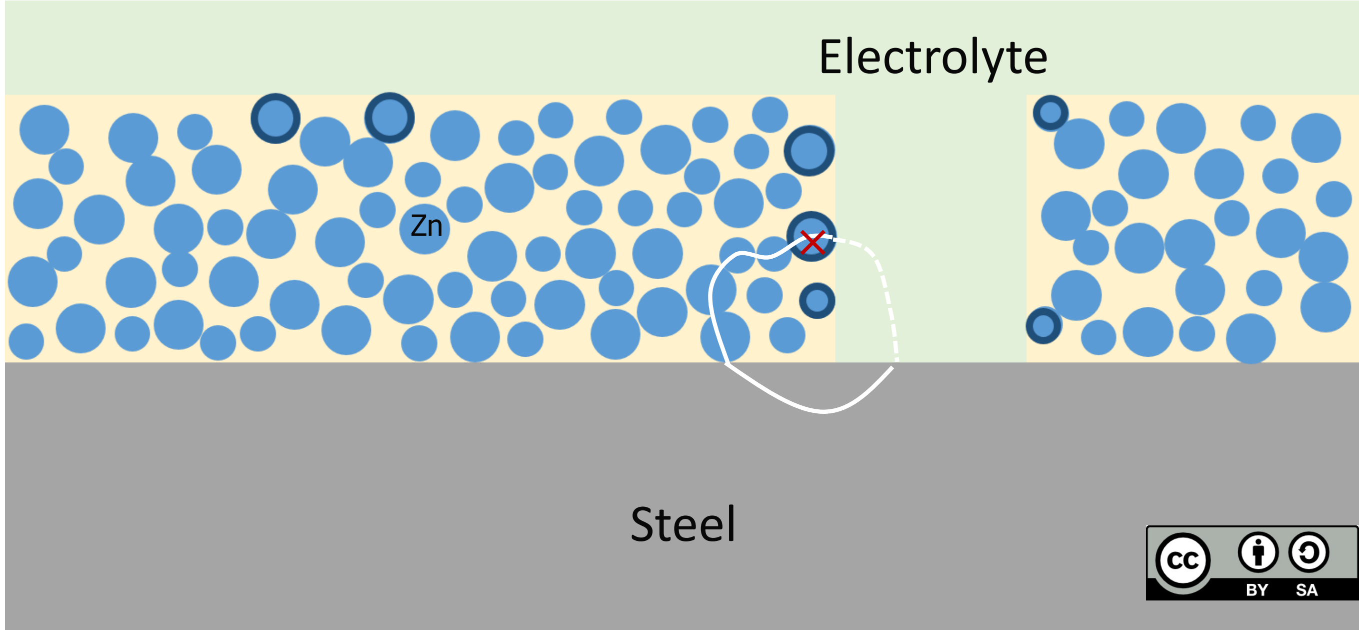
Novák et al., Korozní inže

OC – Protection Mechanism

- **Galvanic (electrochemical)**
  - Coatings filled with metallic (Zn, Zn-Al) pigments
  - Polarization of steel towards negative potentials (cathodic protection) in defects
  - Short-term effect

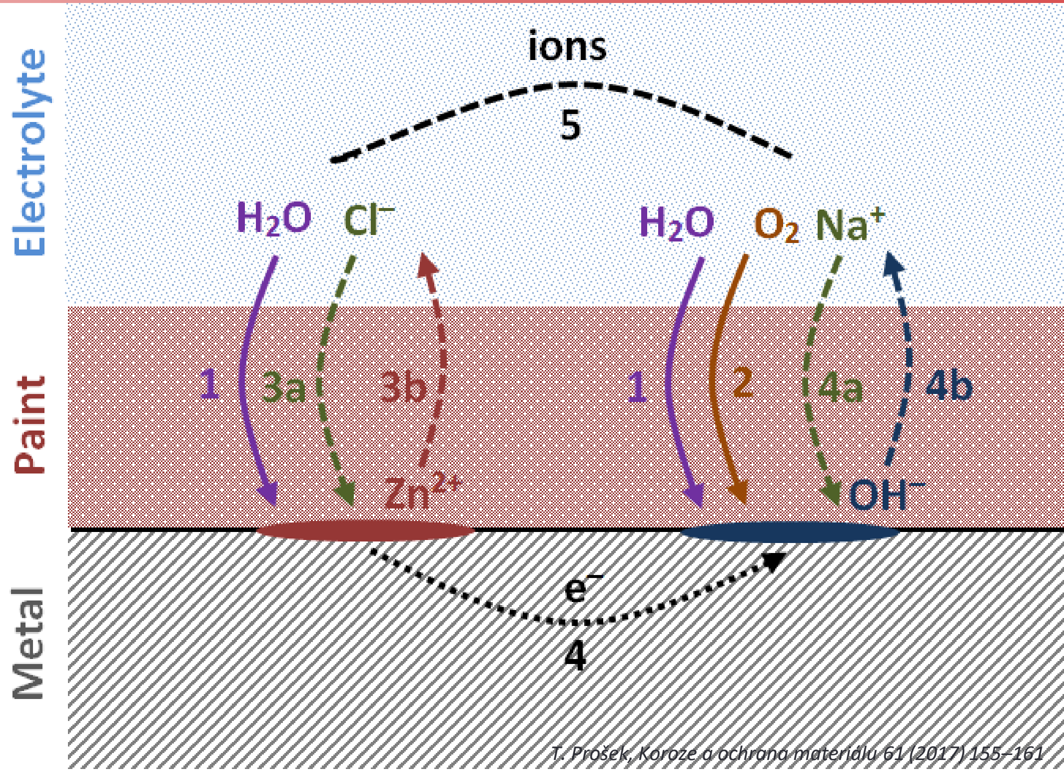


- **Inhibition**
  - Release of anticorrosion pigments in defects



OC – Protection Mechanism

- **Barrier effect**
  - Primary; physical barrier between corrosive environment and metal
  - Limits access of water, oxygen and/or ions to the metal surface = blocking the electrochemical reaction
  - **Water**: rapid saturation (hours/days), 0.1's to 1's volume %
  - **Oxygen**: transport rate sufficient for corrosion rates in 0.1's to 1's mm/year
  - **Ions**: Most probably the critical factor



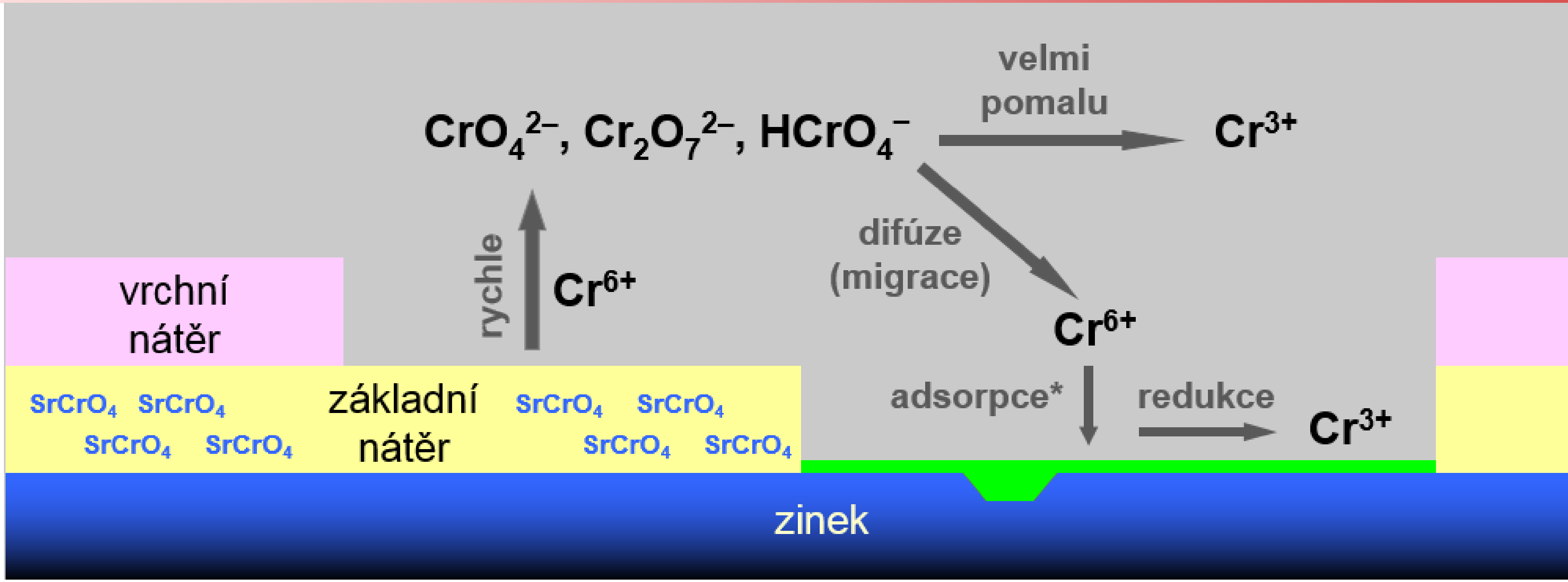
$Zn \leftrightarrow Zn^{2+} + 2e^-$ $O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$

Transport processes

1. **Water**
2. **Oxygen**
3. **Ions from and to anodic sites**
4. **Ions from and to cathodic cites**
5. Electrons in metal
6. Ions in electrolyte

OC – Defects

- Defects are regularly present – micro (**porosity**), macro (**scribes, cut edges**)



T. Prošek, Koroze a ochrana materiálu 61 (2017) 155–161

- Inhibitors in primer coats: ideally self-healing
- Traditionally Pb_3O_4, chromates; toxicity → phosphates, silicates, borates, molybdates, nano-encapsulation
- Metallic pigments (Zn, Zn-Al): Pore sealing, inhibition, short-term cathodic protection

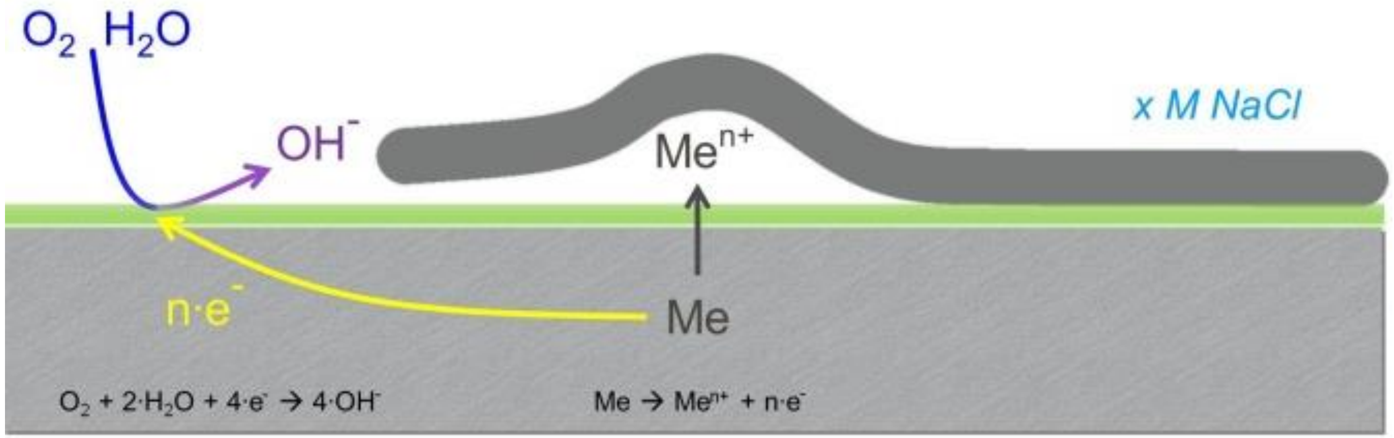
OC – Degradation

Novák et al., Korozní inženýrství, UCT 2002

http://i170.photobucket.com/albums/u244/heydoog/63%20Impala%20in%20the%20snow/weatheringandcelluclay7.jpg

OC – Anodic Delamination

- Typical of zinc protected steel
- Cathodic protection of defect
- Slow, natural and desirable process

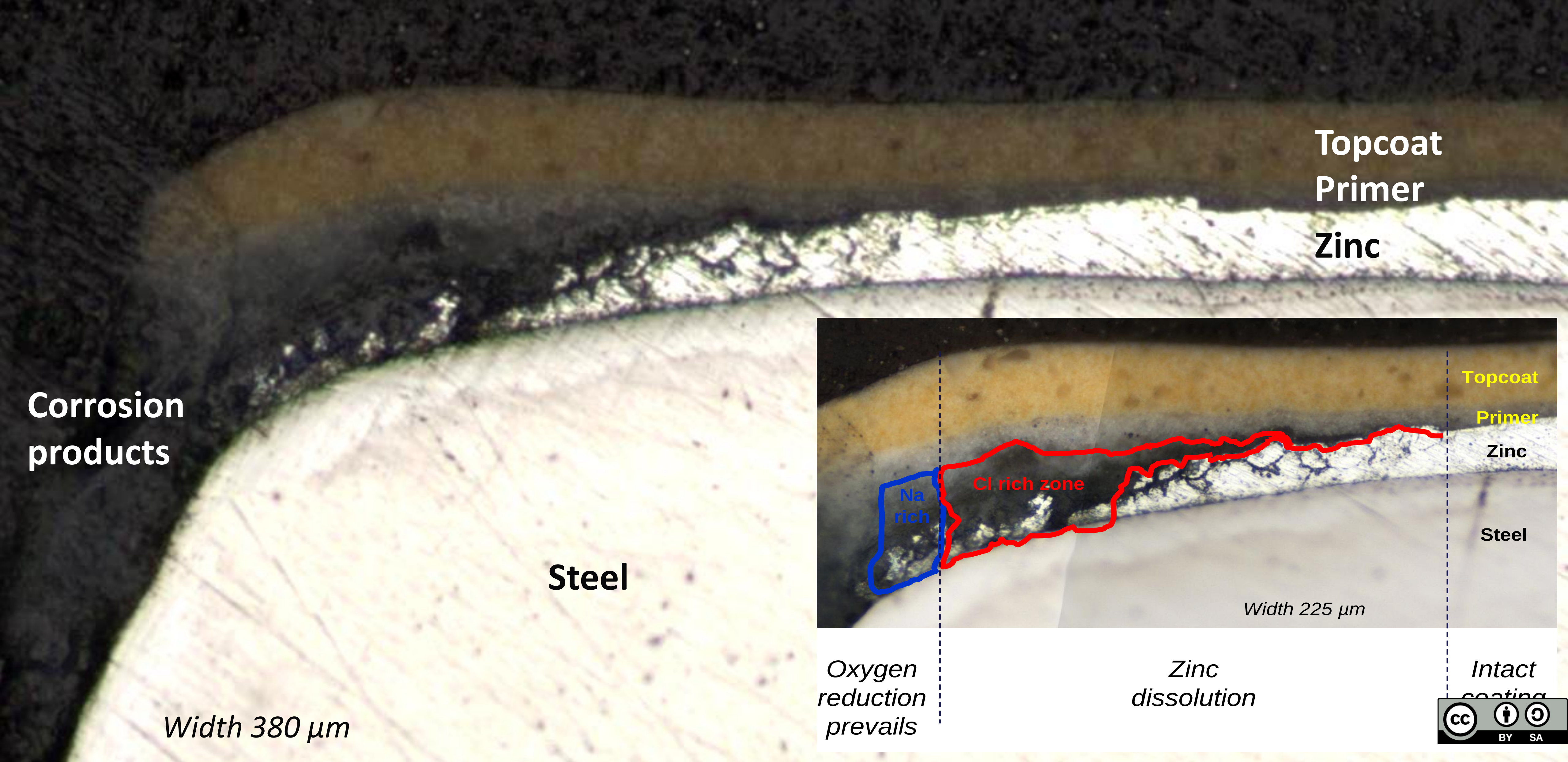


http://www.jcse.org/volume2/paper15/v2p15f3.jpg

T. Prošek, Koroze a ochrana materiálu 61 (2017) 155–161

OC – Anodic Delamination

T. Prošek, Koroze a ochrana materiálu 61 (2017) 155–161



OC – Anodic Delamination

Steel, Zn-Al-Mg coating, exposure to marine climate

Width 1.9 mm

- Delamination rate controlled by the ratio of zinc coating thickness and defect size

Zinc 7 µm

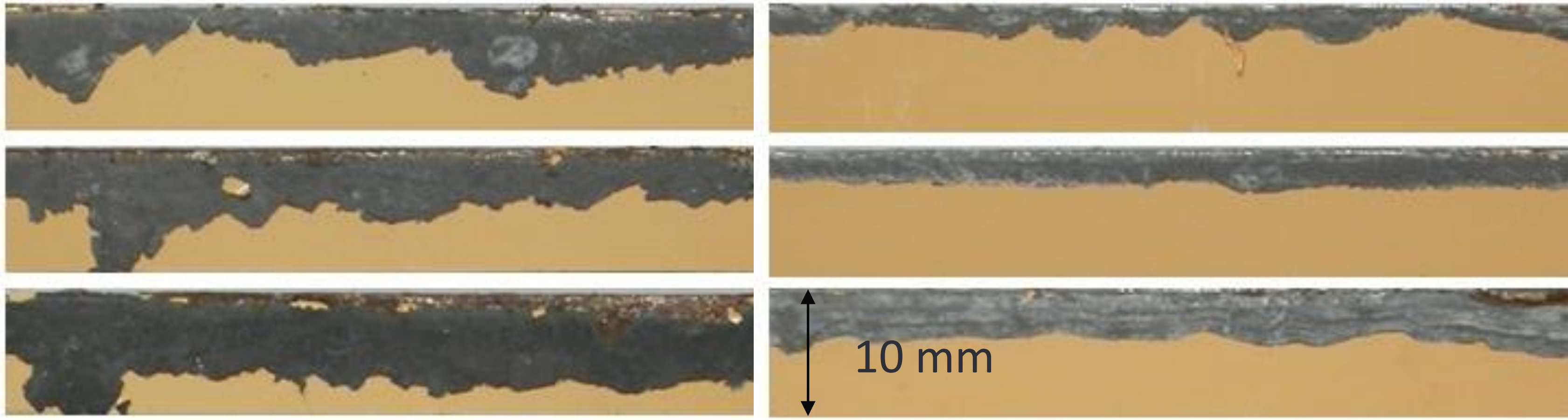
Zinc 20 µm

Steel

0.5 mm

1.0 mm

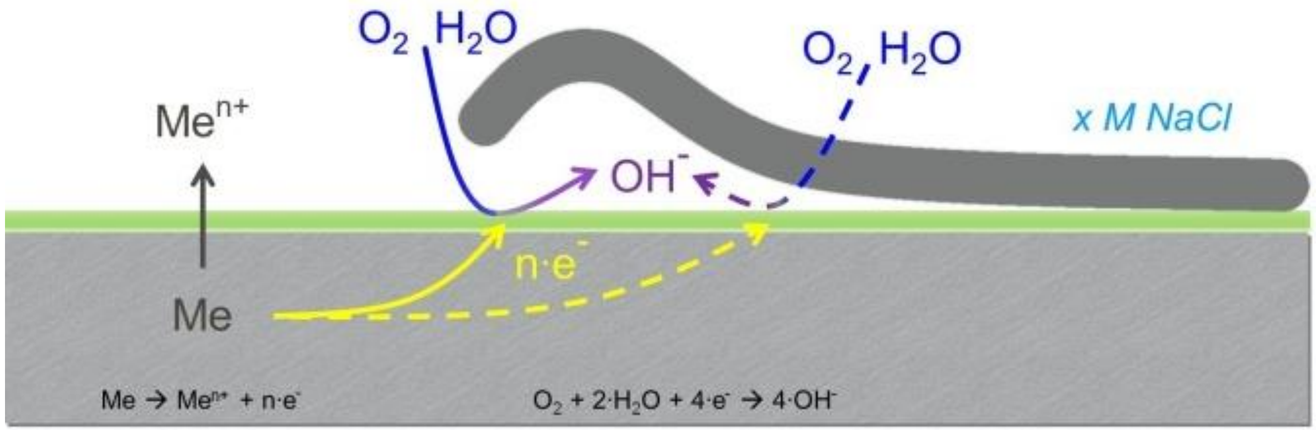
2.5 mm

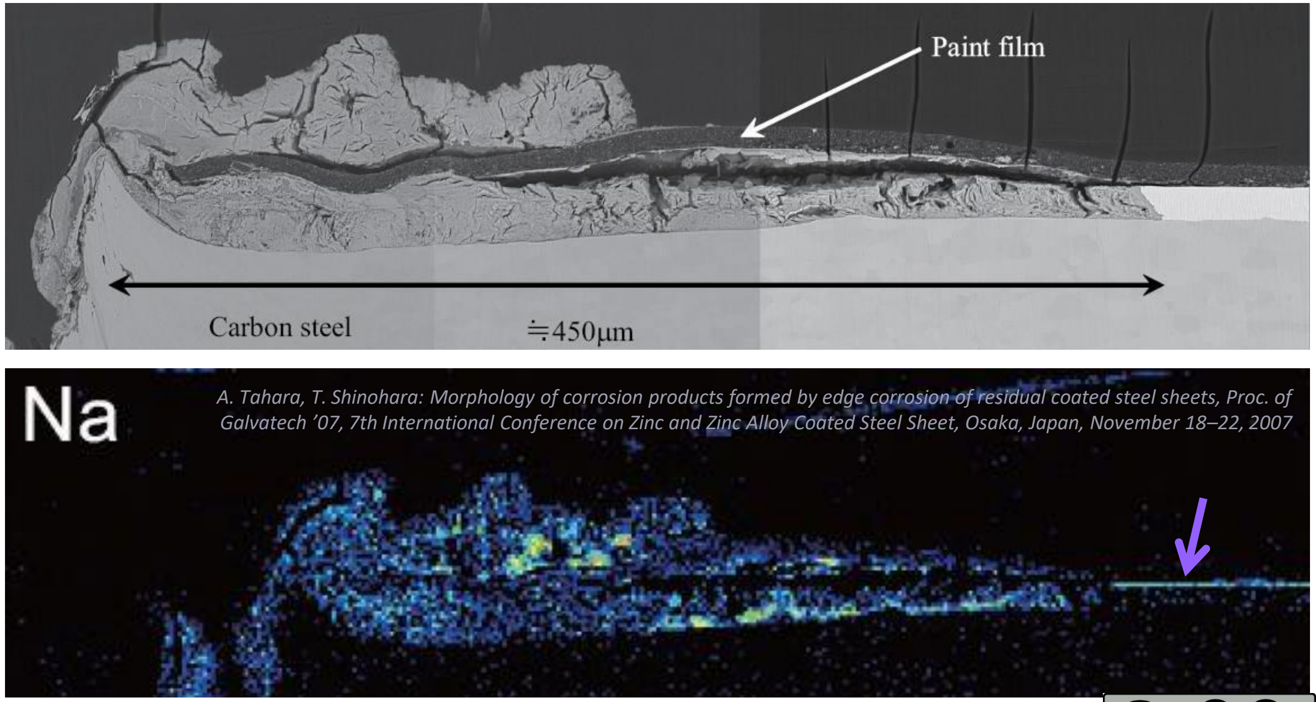


Steel, zinc coating, „mud test"

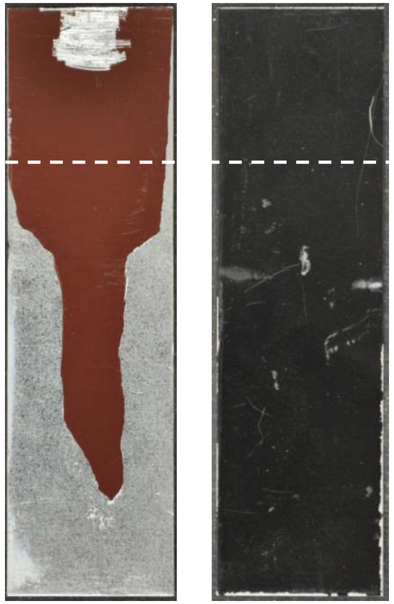
OC – Cathodic Delamination

- **Alkalization** of the interface between metal and organic coating → **loss of adhesion**
- Testing: **Cathodic polarization**
  - External current
  - Anode made of active metal (Mg)





A. Tahara, T. Shinohara: Morphology of corrosion products formed by edge corrosion of residual coated steel sheets, Proc. of Galvatech '07, 7th International Conference on Zinc and Zinc Alloy Coated Steel Sheet, Osaka, Japan, November 18–22, 2007



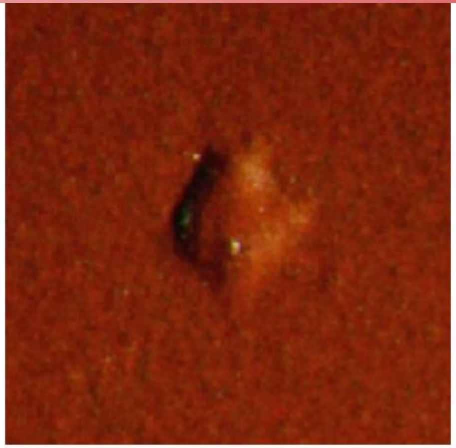
50×25 mm

Steel, zinc coating, tropical marine climate

OC – Blistering

- **Local defects**
- Classification according to ČSN EN ISO 4628-2
- Several mechanisms

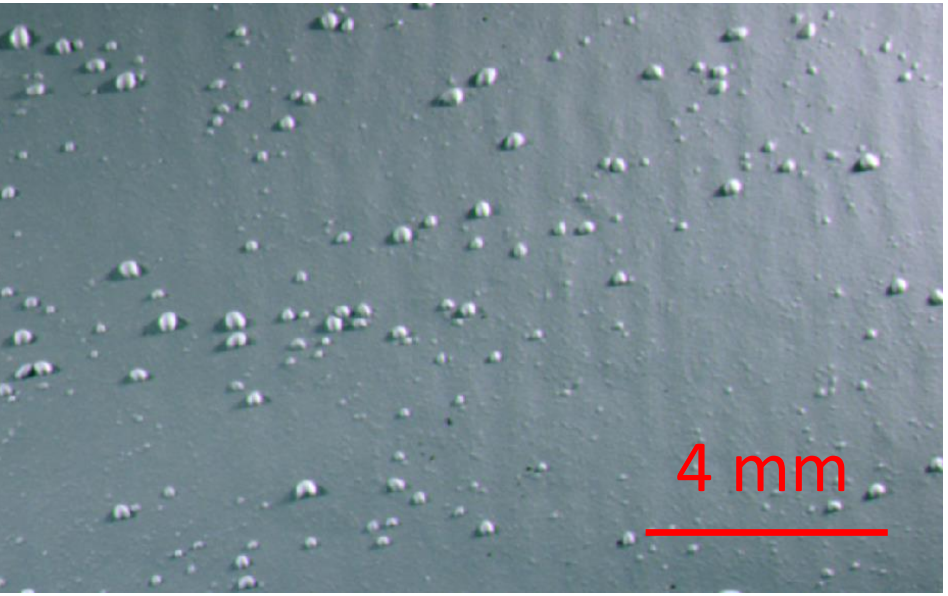
↔1.4 mm



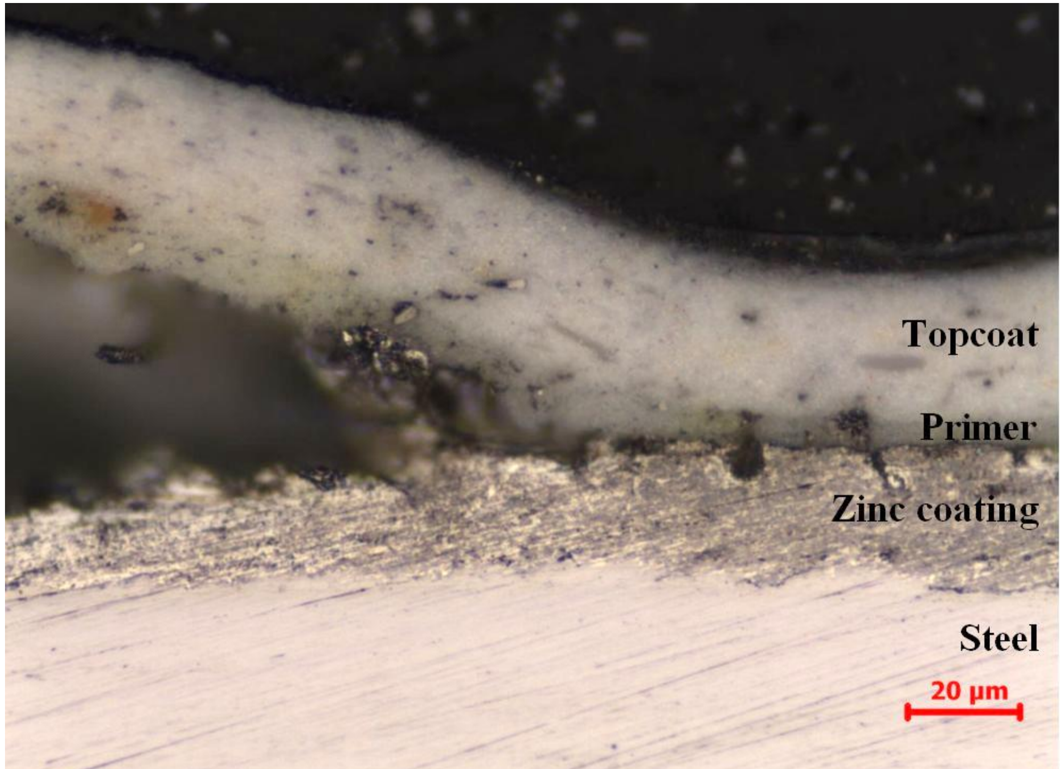
↔1.1 mm

↔12.4 mm

Marine climate, 4,5 years



Constant condensation test, 60 °C, 1450 hours



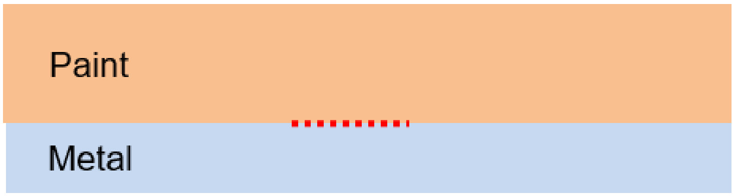
Cyclic tropical test, 50 °C; 15×15 mm

OC – Blistering

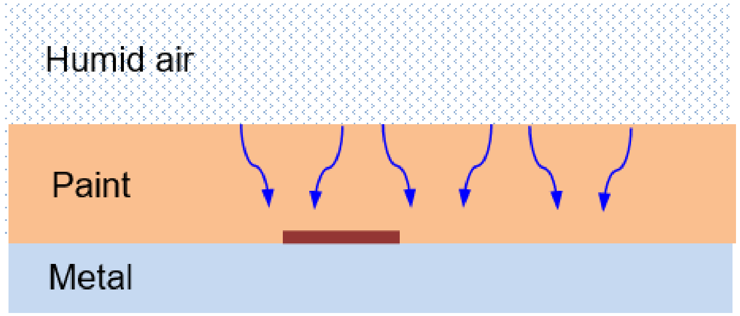
Novák et al., Korozní inženýrství, UCT 2002

OC – Blistering, Mechanism

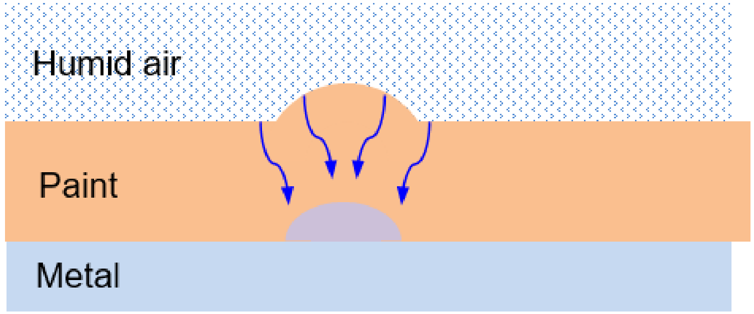
• Osmotic blistering



Soluble salt is present at the paint/metal interface

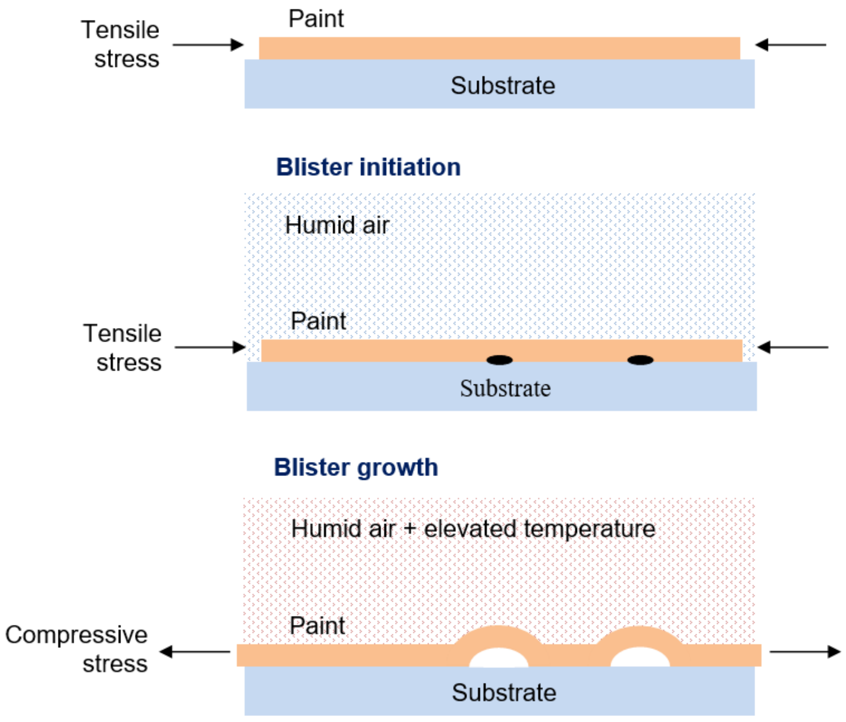


Water penetrates through paint and water clusters form due to local de-adhesion



Osmosis is the driving force of further water transport to the interface; the solution dilutes, its volume grows and blister appears

• Stress-induced blistering



Water penetrates organic coating and water clusters form due to local de-adhesion

Paint expand at elevated temperature, stress becomes compressive and blisters form; they are reversible (may disappear at lower temperature) until plastic deformation of the paint takes place or are filled with corrosion products; can be empty

T. Prošek, Koroze a ochrana materiálu 61 (2017) 155–161

• Cathodic blistering

OC – Loss of Adhesion

- Perfect paint adhesion is necessary for good corrosion protection
- Global loss of adhesion can be caused by:
  - Presence of soluble contaminants
  - Presence of corrosion products, in particular non-adherent
  - Failure of conversion coating
  - Incompatibility of paint system layers
  - Dramatic UV degradation

Steel, zinc coating
Volkswagen PV1200 test, 11 cycles (days)
120×90 mm

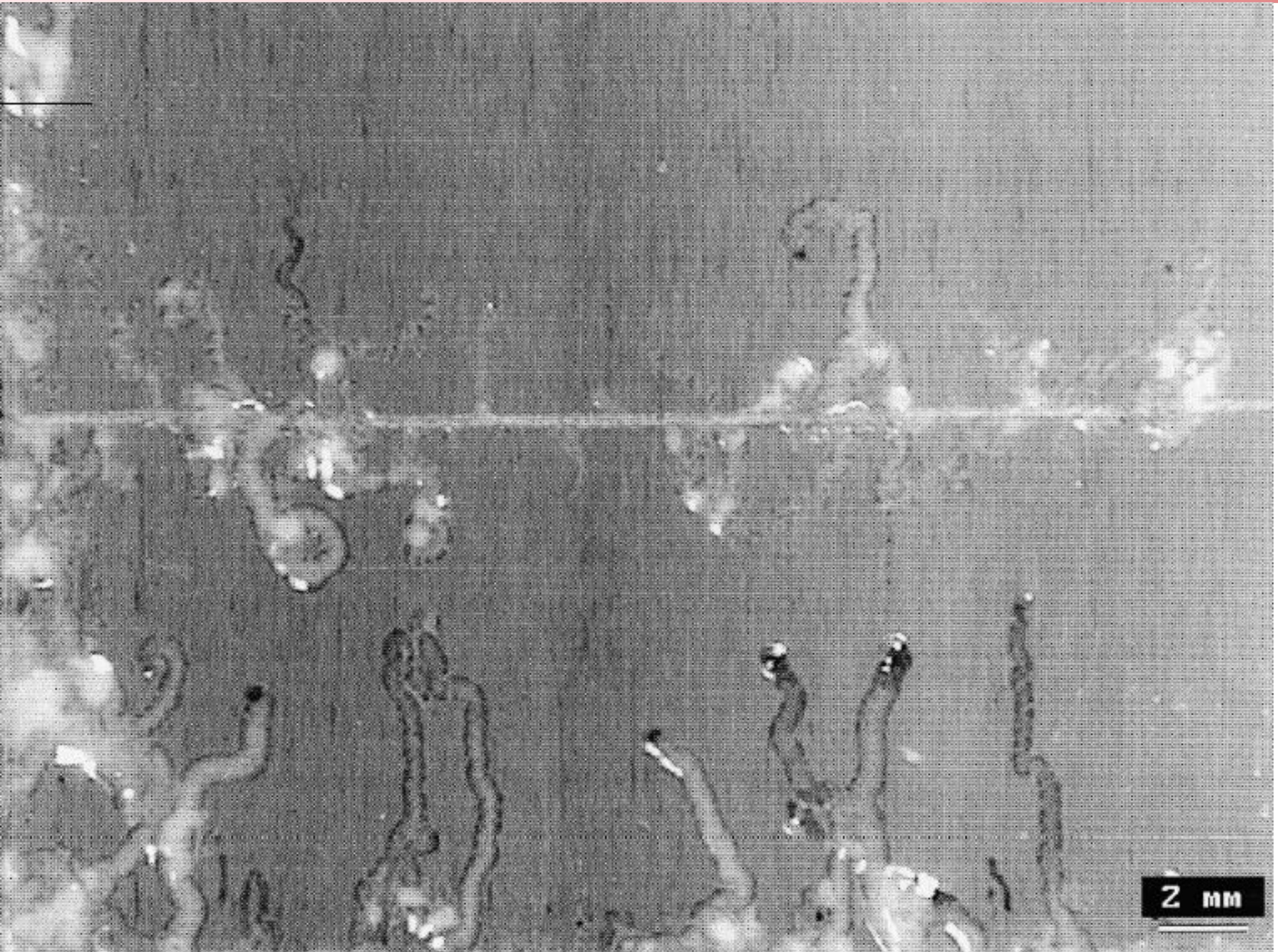
OC – Chalking

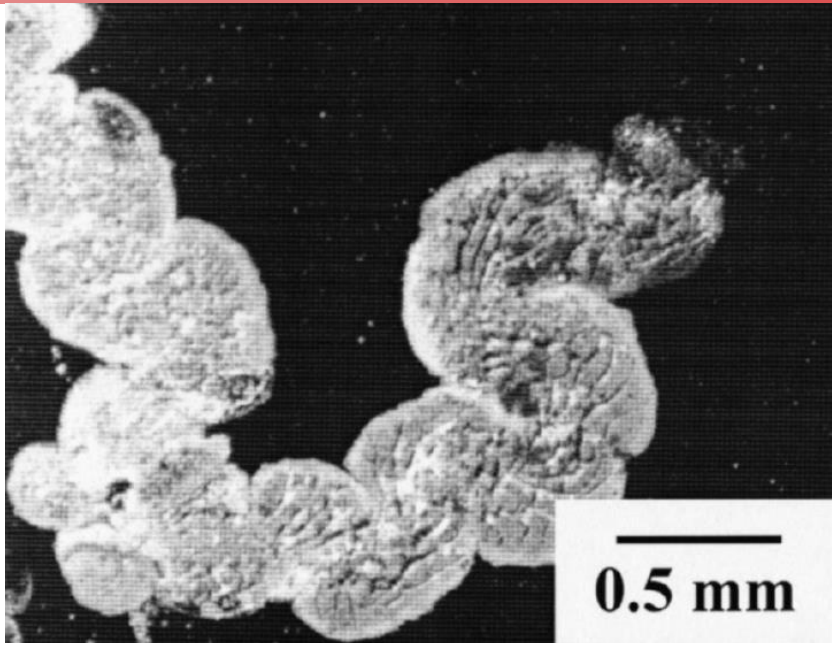
- Global degradation of topcoat
- Usually photochemical degradation of polymeric binders (UV, O_2)
- **Release of pigment particles from polymeric structure** and loss of gloss and colour changes
- Specific of different binders
- Resistance can be improved by stabilizers, antioxidants, UV absorbers and quenchers

http://www.harwoodservices.com/problem-solver/chalking

- Initially only aesthetic problem, in long run a drop in barrier effect
- **Tests**: UV irradiation in combination with humidity, possibly with corrosive environment

OC – Filiform Corrosion





Filiform (nitková, filigránská) corrosion of aluminum with epoxy paint

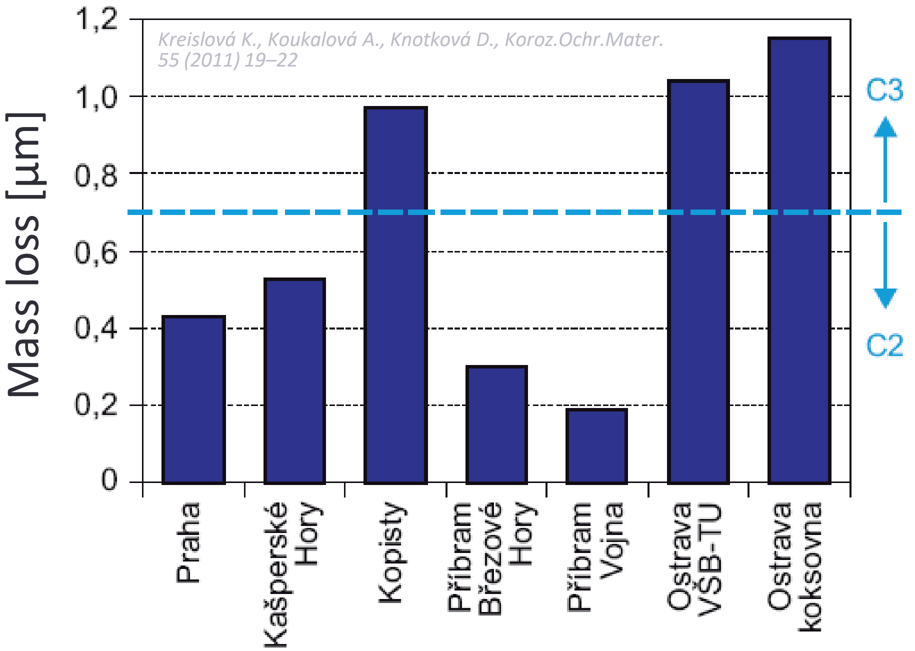
Metallic Coatings

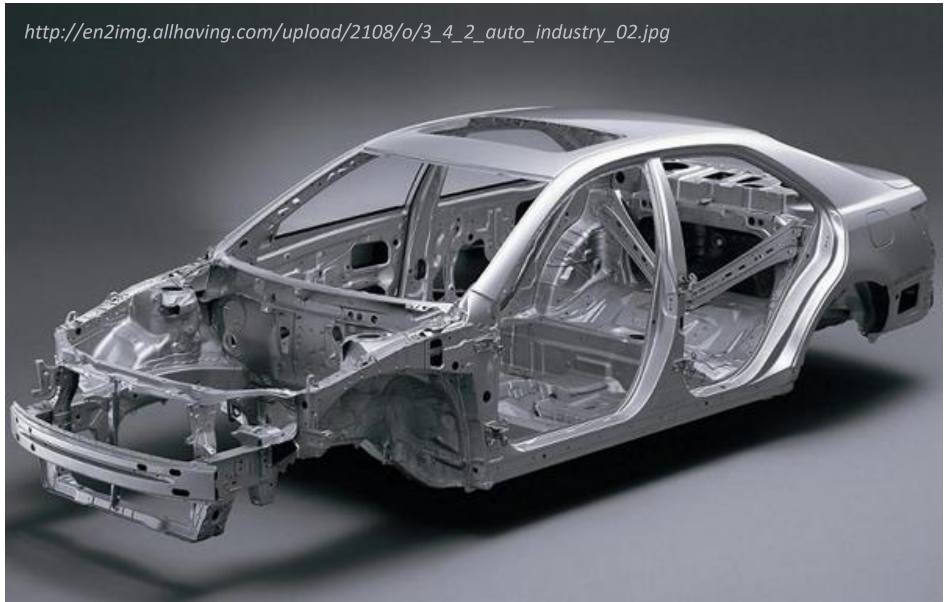
- Under most conditions, **only zinc and certain zinc alloy coatings able to protect steel cathodically**, others provide only barrier protection
- Zinc coatings:
  - Building and automotive industry, home appliances
  - Low corrosion rate
  - Aesthetically acceptable appearance of corrosion products
- Other coatings: Al, Sn, Ni, Cr, Cu, rare metals

Postup povlakování	Obvyklá tloušťka vrstvy	Typické použití (povlak/podklad)	Poznámka
Žárové kontinuální	7–40 μm	Zn/ocel Zn-Al/ocel Al-Si/ocel	Dominantní proces pro plechy a drát
Žárové vsázkové	40–200 μm	Zn/ocel	Konstrukčně složitější a rozměrné výrobky
Žárový nástřik	80–300 μm	Zn/ocel Zn-Al/ocel Al/ocel	Velmi rozměrné výrobky
Elektrolytické (galvanické)	1–25 μm	Zn/ocel Zn-Ni/ocel Cr/RM Au/RM Sn/ocel	Drobnější díly vsázkově, v menší míře kontinuální proces pro plech
Bezproudé z roztoku	<1–50 μm	Ni/RM	Podklad pod dekorativní chromové povlaky
Depozice ve vakuu	<1–10 μm	Al/RM	PVD, CVD, iontová implantace
Termochemický	<1–80 μm	Zn/ocel	
Plátování	<0,071–10 mm	Ni/ocel Zn/ocel Au/RM	Nanášení naválcováním a dalšími postupy

Metallic Coatings – Zinc

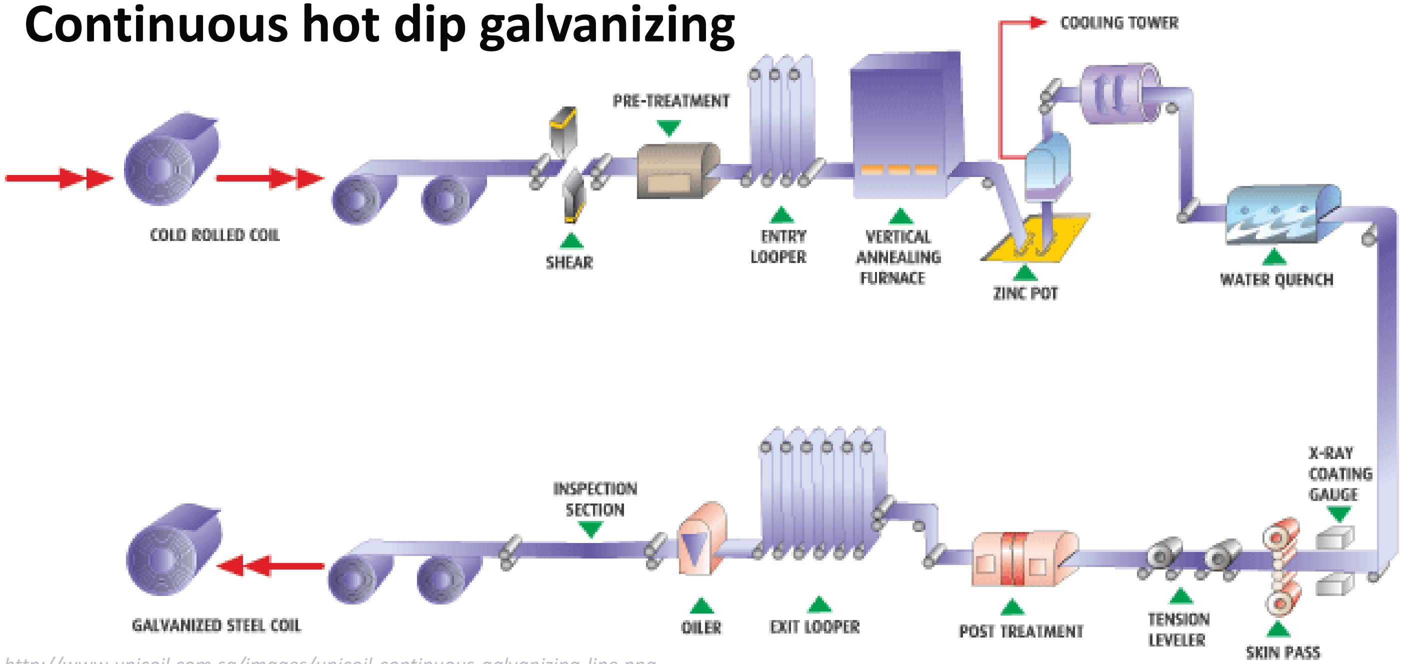
- Stable corrosion products
- High corrosion rate in absence of CO_2 and at constant humidity, acids
- Alloy coatings: Zn-5Al, Zn-55Al, Zn-Mg, Zn-Al-Mg, Zn-Ni, Zn-Fe





Metallic Coatings – Application

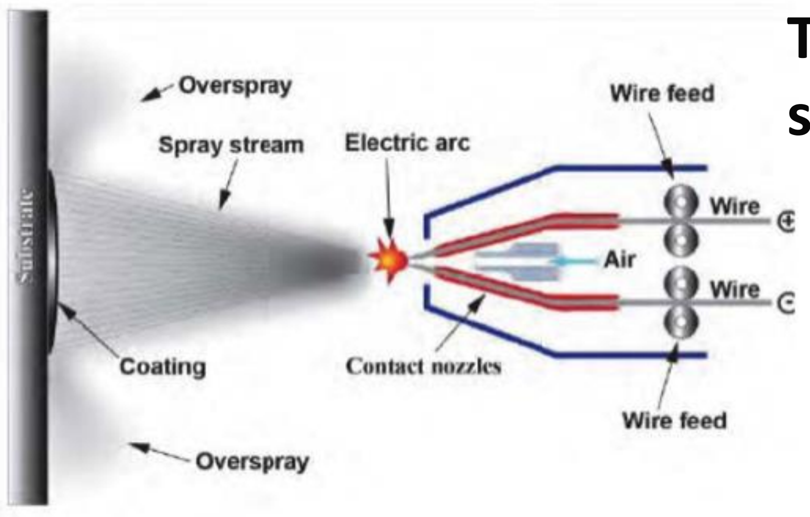
Continuous hot dip galvanizing



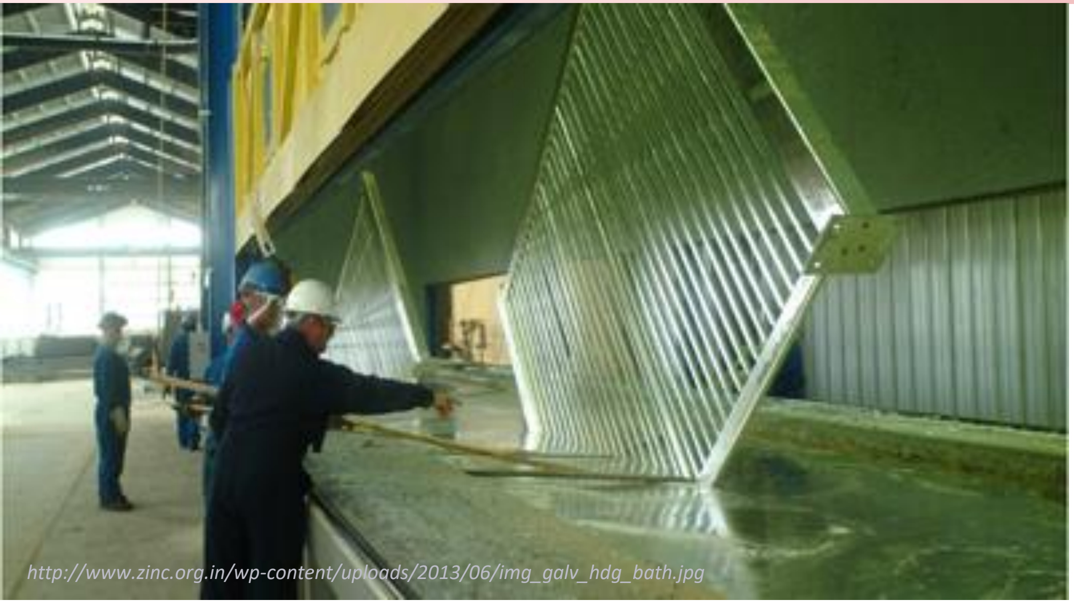
http://www.unicoil.com.sa/images/unicoil-continuous-galvanizing-line.png

http://www.gobizkorea.com/att/cat/1138175000/tp_html/img/1138175000_cat_1_large_img1_2.jpg

Thermal spraying

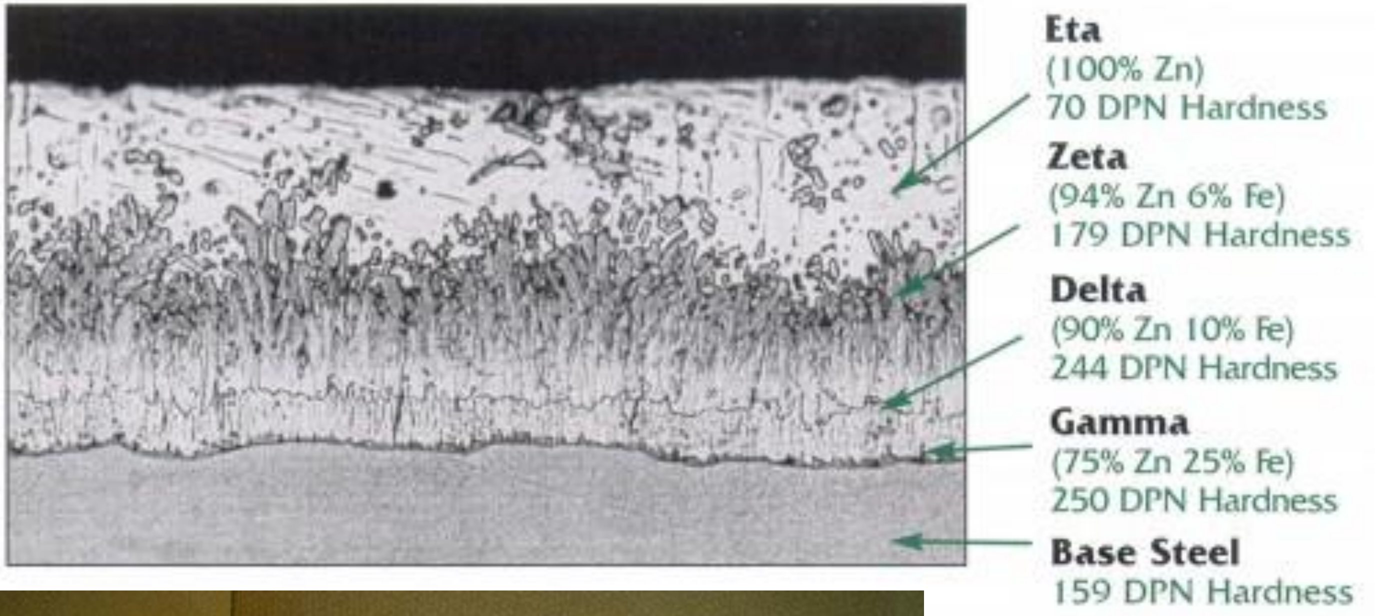


Metallic Coatings – Application



http://www.zinc.org.in/wp-content/uploads/2013/06/img_galv_hdg_bath.jpg

http://www.galvanizeit.org/uploads/default/_500/galv_coat.jpg

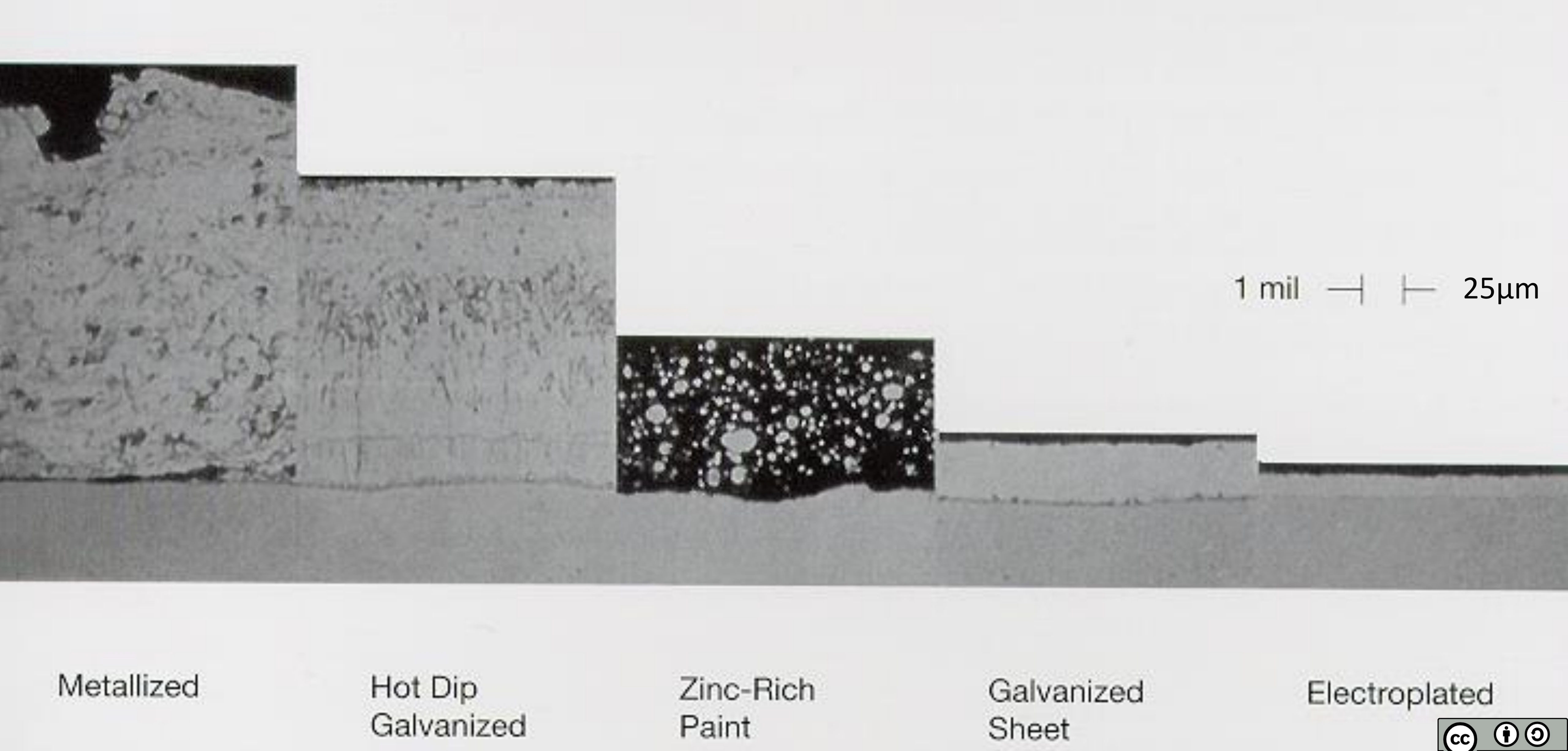


http://www.brista.de/bilder/normale-bilder/feuerverzinken.jpg

Novák et al., Korozní inženýrství, UCT 2002

Batch hot dip galvanizi

Metallic Coatings – Zinc



Metallic Coatings – Chromium

http://www.aclassmetal.com.au/images/chrome_plated_tap_mixer_.jpg

https://upload.wikimedia.org/wikipedia/commons/e/e1/Motorcycle_Reflections_bw_edit.jpg

https://c2.staticflickr.com/4/3393/3499013648_a8a4ae5099_b.jpg

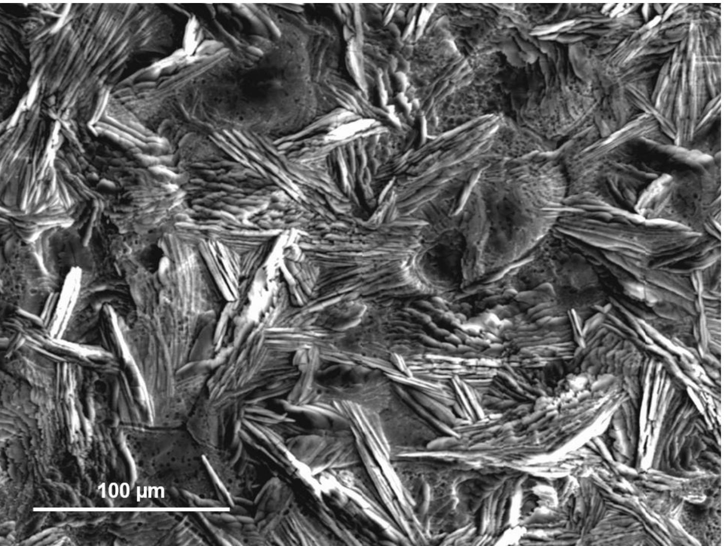
http://www.chromovani-zajic.cz/Foto/bigHridel1.jpg

http://www.rosik.pl/files/IMG_3208%20kopia%5b1%5d.jpg

http://custompolishchromeplating.com/wp-content/uploads/2013/08/chrome-plating-process.jpg

Conversion Coat., Passivation

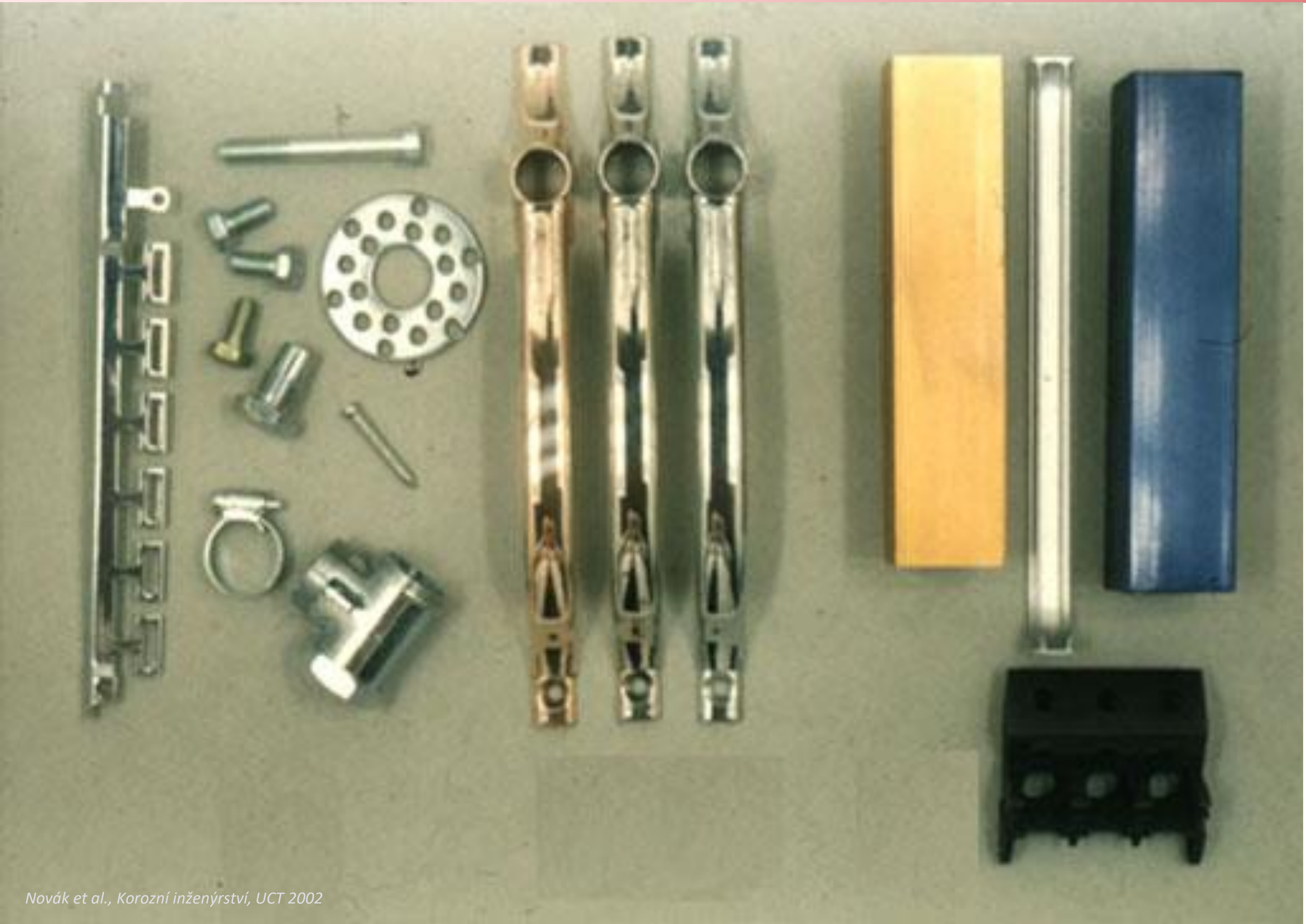
- Formation of thin films by chemical reactions between metals and baths
- **Passivation**: Thinner (<10 nm), self-healing films
- **Conversion coating**: Self-healing not possible, usually thicker (>10 nm)
- Usually good basis for painting – large specific area, metal-paint anchor
- Oxidic (anodization of aluminum, blackening of steel), phosphate-based (phosphatation of zinc, steel, magnesium and aluminum), chromate (chromating of aluminum, zinc and tin), silanes, Zr-Ti, etc.



Structure of zinc phosphate conversion coating (SEM)

Phosphating: Precipitation of insoluble phosphate (zinc phosphate, $Zn_3(PO_4)_2$; iron (III) phosphate, $FePO_4$) films by reactions with acidic phosphate solutions

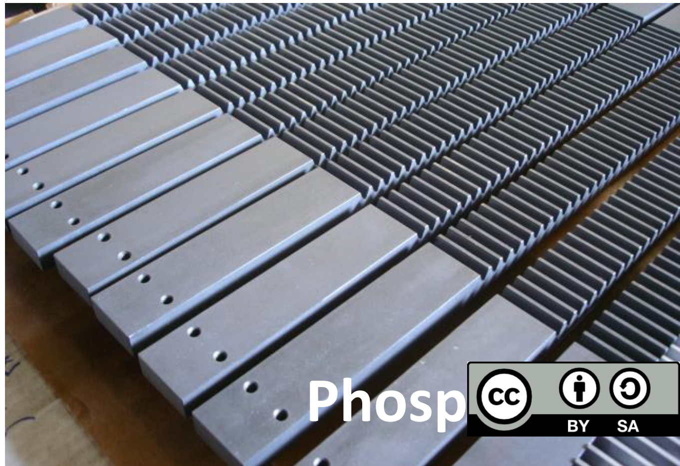
Conversion Coat., Passivation



Novák et al., Korozní inženýrství, UCT 2002

http://www.esako.cz/editor/image/stranky3_galerie/tn_zoom_obrazek_896.jpg

http://www.chromtech.cz/files/cache/0afbec80f461e81bb33a85c8b0a5354f_f85.JPG



http://www.rosma.cz/galerie/galvanovna/fosfatovani/dsc05381.jpg

Thick Non-Metallic Coatings

Novák et al., Korozní inženýrství, UCT 2002

Rubber lining

Acid-proof brick lining of floor in chemical production site

Novák et al., Korozní inženýrství, UCT 2002

Thick Non-Metallic Coatings

Novák et al., Korozní inženýrství, UCT 2002

Ena

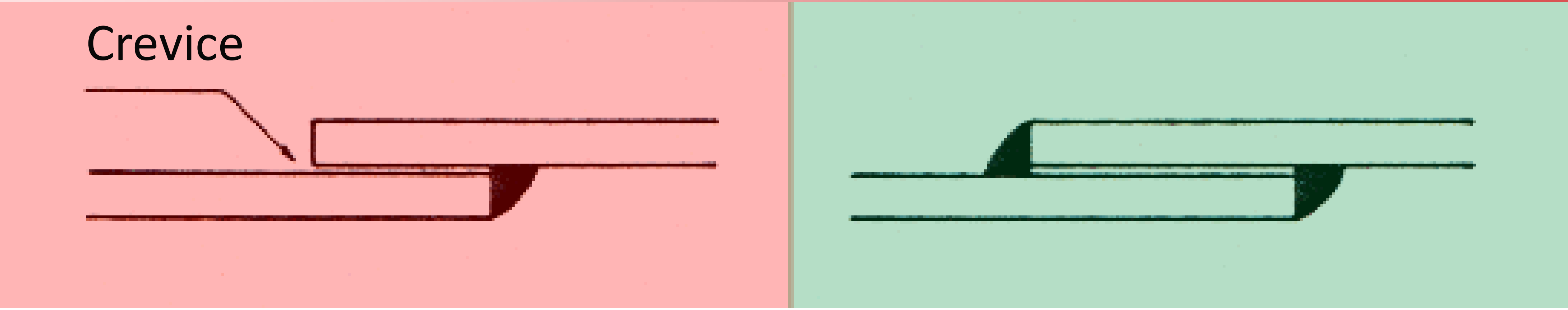
Design

Basic approaches:

- **Uniformity of conditions** (flow, temperature, composition …)
- **Good accessibility** (inspection, re-painting, repairs, cleaning)
- **Shorten contact time between corrosive environment and metal**
- **Limit risk of galvanic coupling**

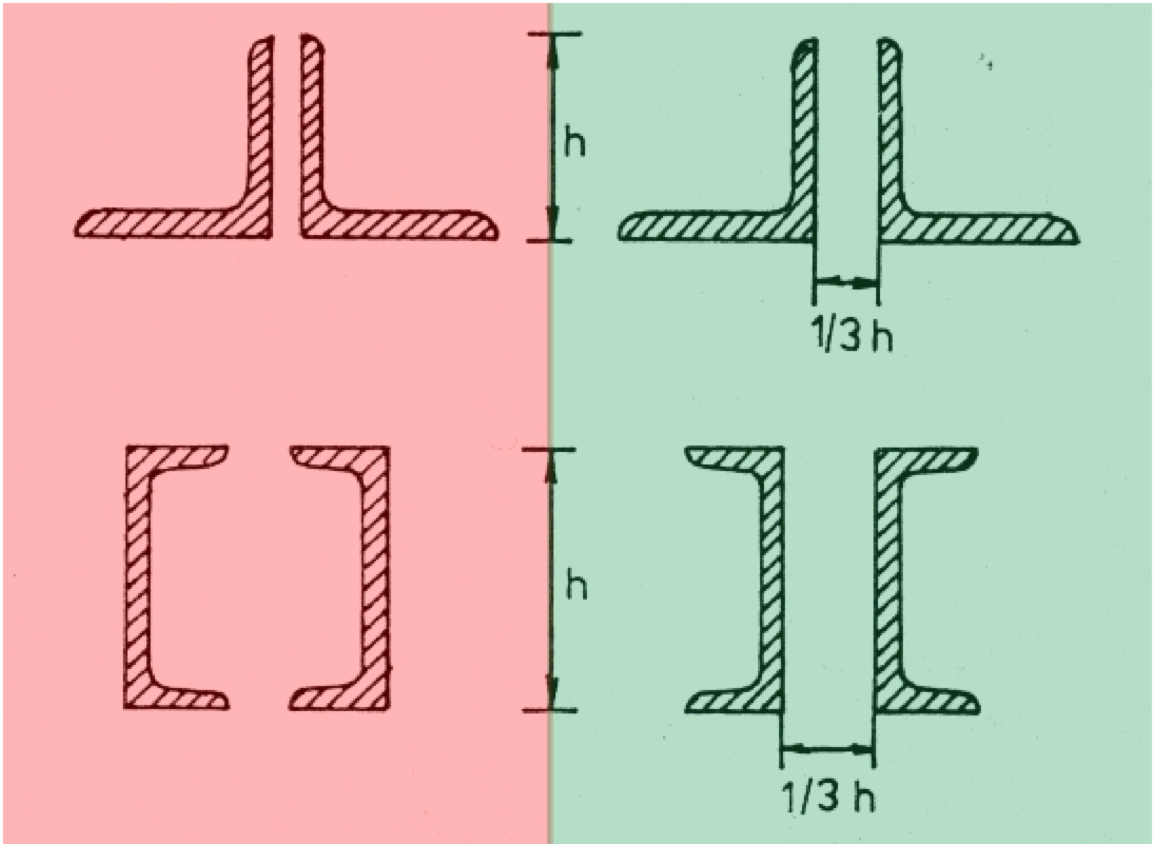
Design

Prevention of crevice formation

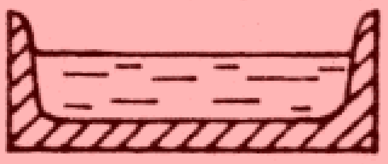


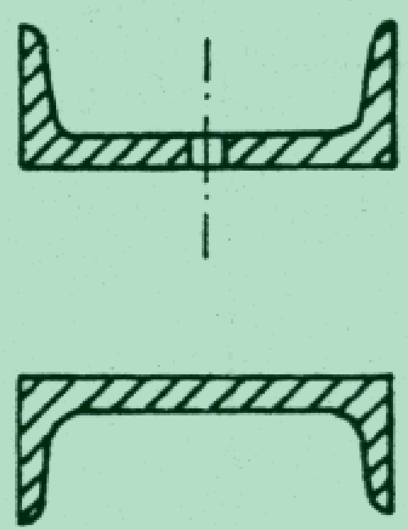
Novák et al., Korozní inženýrství, UCT 2002

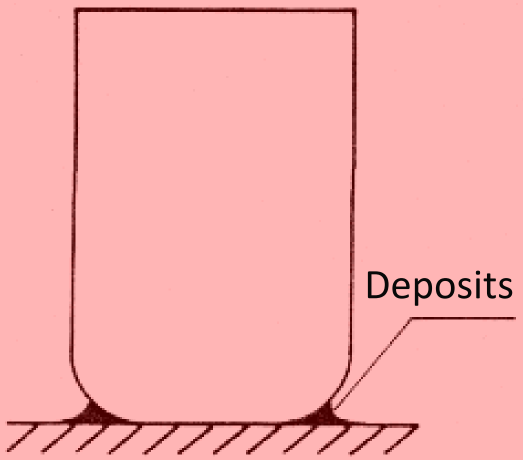
Accessibility of painted parts (for re-painting)

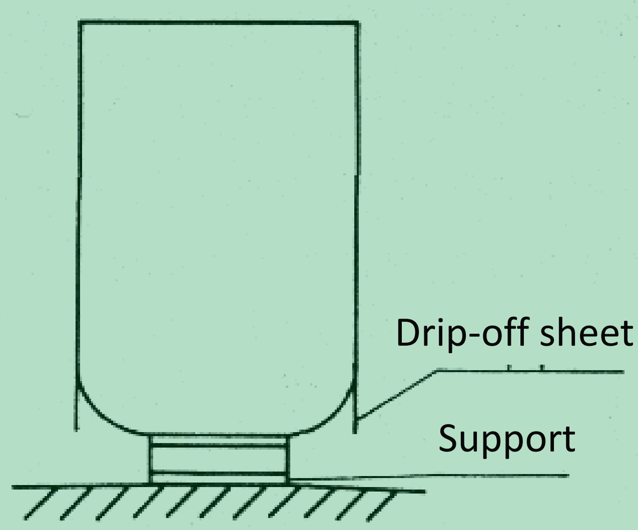


Design



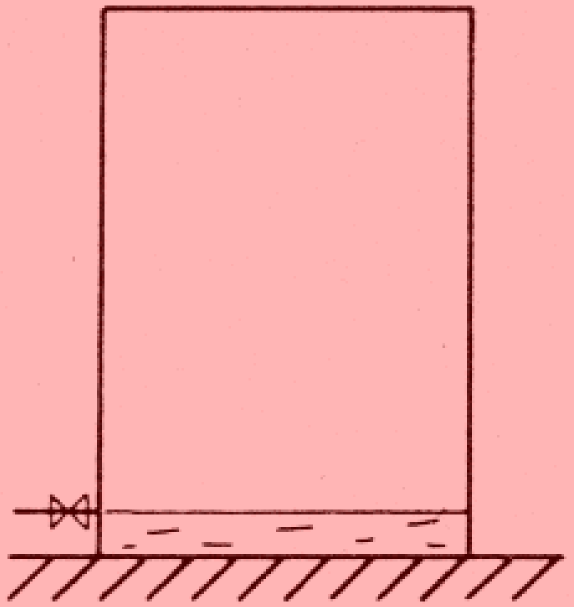


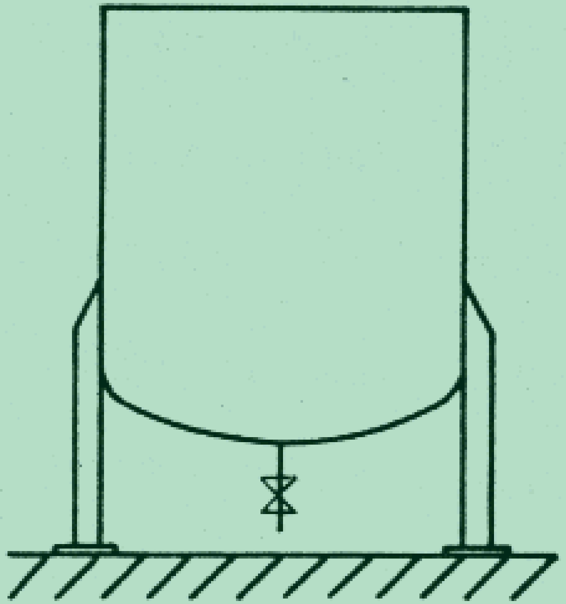




Novák et al., Korozní inženýrství, UCT 2002

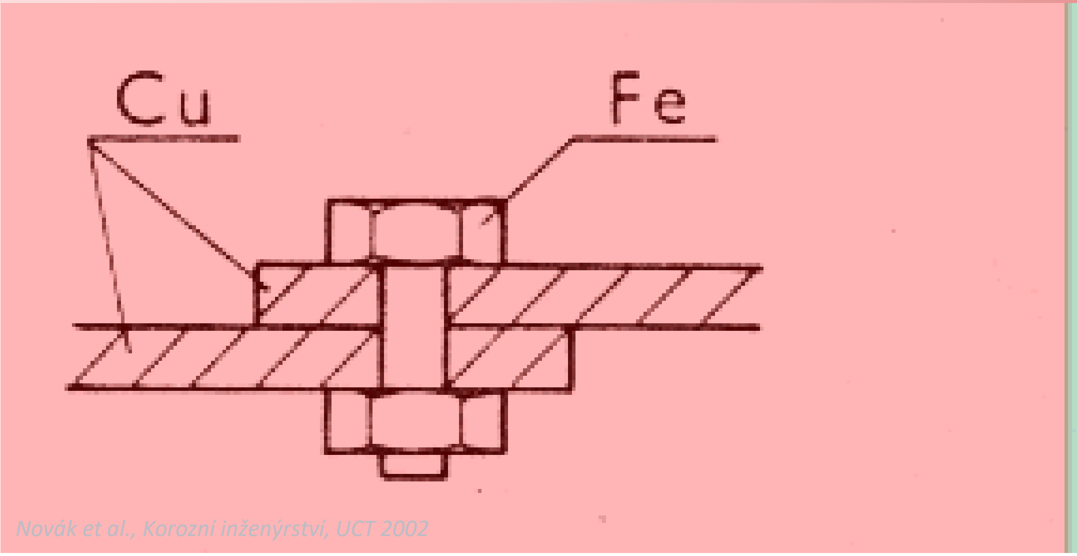
Prevention of liquid and deposit retention

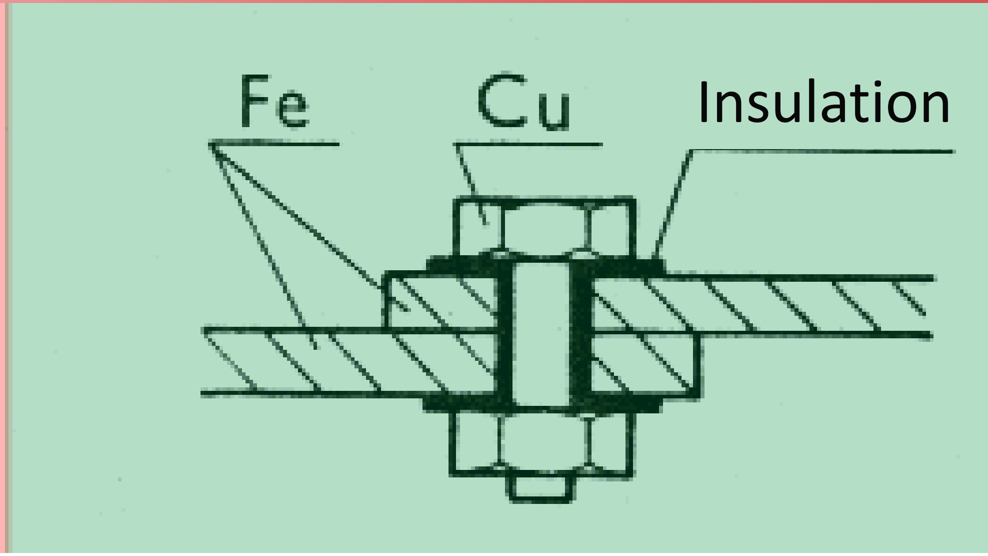




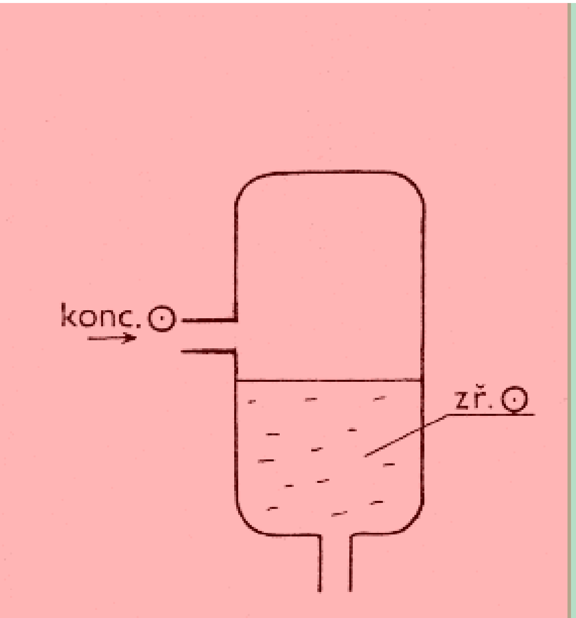
Design

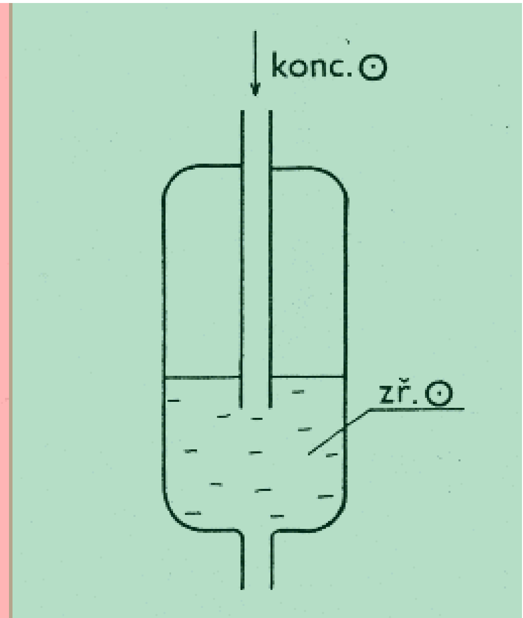
Prevention of galvanic coupling



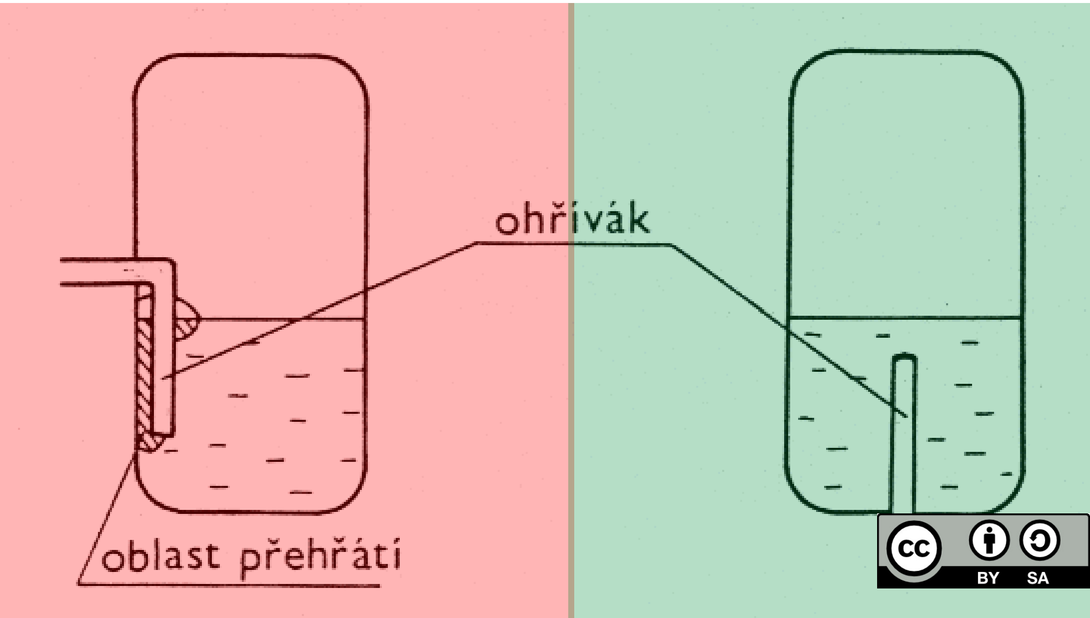


Formation of concentration galvanic couple



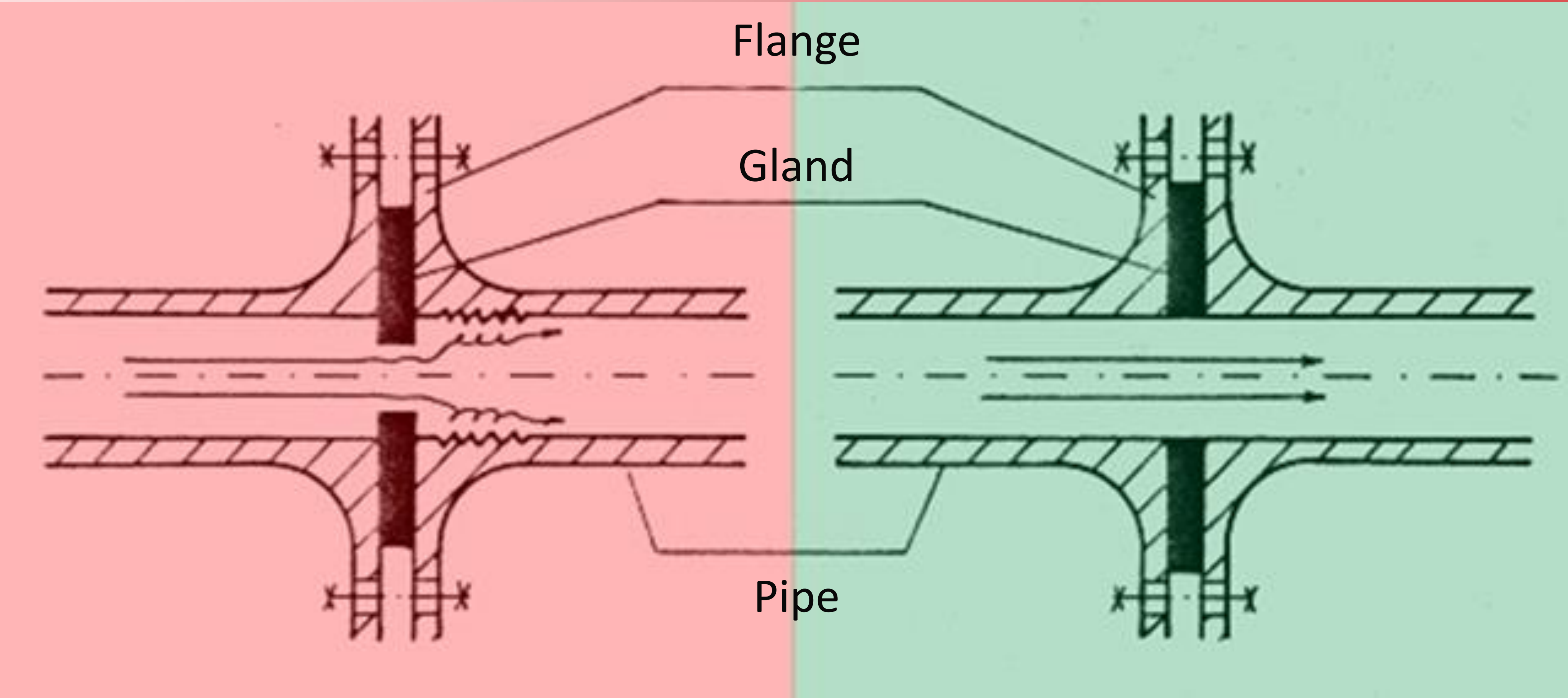


Thermogalvanic couple due to heating



Design

Uniform flow



Novák et al., Korozní inženýrství, UCT 2002

Copyright & Contact

Tomáš Prošek, Ph.D.

University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

www.vscht.cz

Corrosion Engineering

Tomáš Prošek

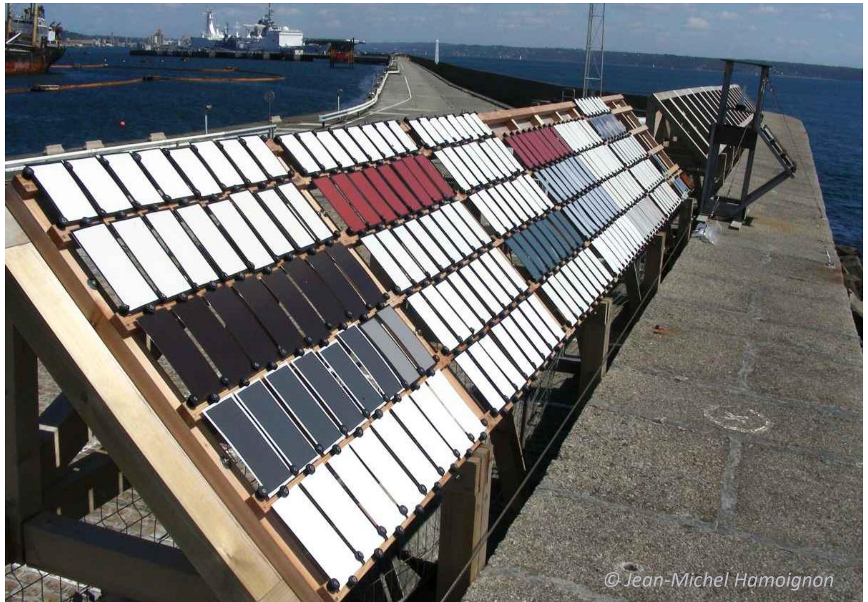
Corrosion Testing

Content

- Principles and goals of corrosion testing
- Assessment of corrosion degradation
- Exposure tests in natural environment
- Accelerated corrosion tests
- Laboratory tests
- Laboratory measurements
- Summary

Goals of Corrosion Testing

- **Minimization of corrosion losses**
- Application:
  - **Selection of materials** with optimal corrosion resistance for a given application
  - **Lifetime prediction** for inspection and replacement planning, warranty
  - **Development of new materials and anticorrosion methods**
  - **Quality control**



New Trends in Corrosion Testing

- **Material selection for new environments**
  - Deep sea mining: H_2S, high temperature and pressure
  - Deicing salts for winter treatment of roads: $MgCl_2$, $CaCl_2$, organic mixtures
- **Development of new materials**
  - High strength steels for automotive industry
  - Alloyed zinc coatings: Zn-Al-Mg, Zn-Mg...
  - Environmentally friendly surface treatment
  - Water-based paints
  - Functional and thin coatings
  - Nanomaterials
  - New light Al and Mg alloys

⇨ **Often need of new or improved testing methods**

Options

- **Field exposure tests**
  - \+ Reliable, real conditions
  - − Time consuming, expensive
- **Standardized accelerated corrosion tests**
  - \+ Rapid and relatively cheap
  - − Can be unreliable
- **Lab tests**
  - Specific problems, often development
- **Lab measurement**
  - Measurement of parameters with obvious effects on corrosion stability

Assessment of Corrosion State

- Visual
- Mass loss (or gain)
- Presence of non-uniform corrosion
- Corrosion depth
- Loss of mechanical properties
- Changes in other properties

© Tomáš Prošek

Assessment – Visual

- Extent and morphology
- Degradation has to be accompanied with the **formation of corrosion products** or **other visible changes**
- Less useful for non-uniform corrosion, e.g. SCC or pitting corrosion

Steel, NaCl deposits, 20 °C, 80% RH

Assessment – Visual

- **Corrosion products:**
  - **Degree of rusting**: EN ISO 4628-3 *Paints and varnishes — Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 3: Assessment of degree of rusting*

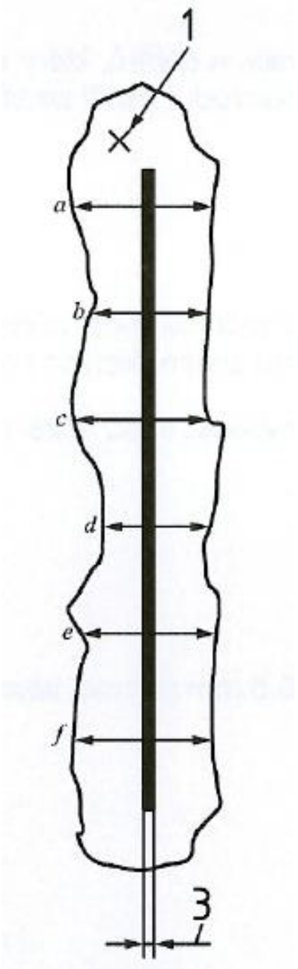
Degree of rusting	Rusted area %
Ri 0	0
Ri 1	0,05
Ri 2	0,5
Ri 3	1
Ri 4	8
Ri 5	40 až 50

  - **Time to formation** of corrosion products (e.g. to 5% coverage)
  - Image analysis and **calculation of the area** covered with corrosion products

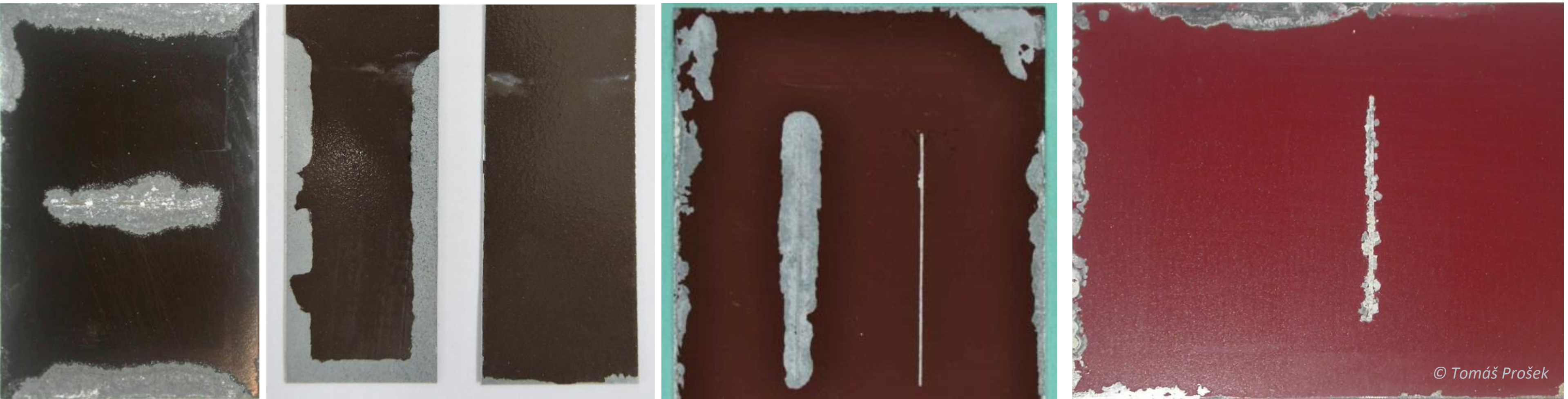
➢ *Practical for steel, worse for e.g. zinc*

Assessment – Visual

- **Paint delamination** from defects:
  - **Mean distance**: EN ISO 4628-8 *Paints and varnishes — Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 8: Assessment of degree of delamination and corrosion around a scribe or other artificial defect*
  - **Maximal distance or area** can also be evaluated

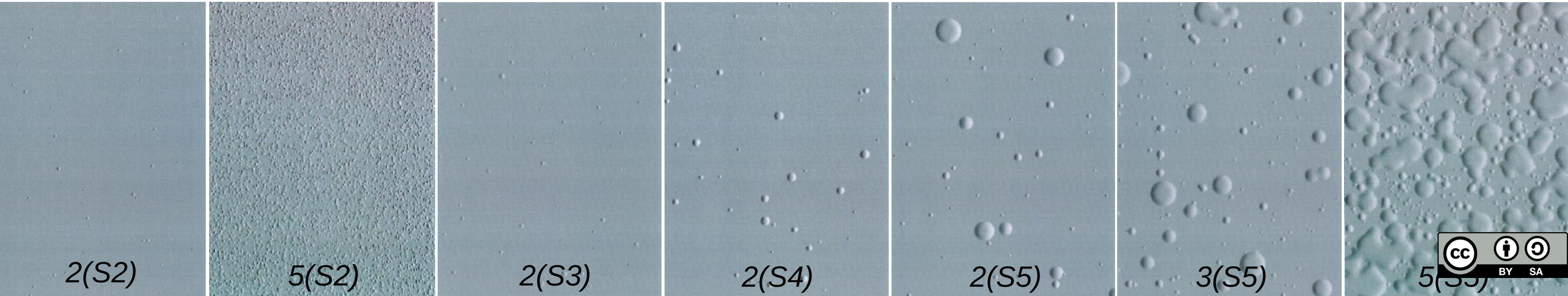


$$d_1 = \frac{a+b+c+d+e+f}{6}$$



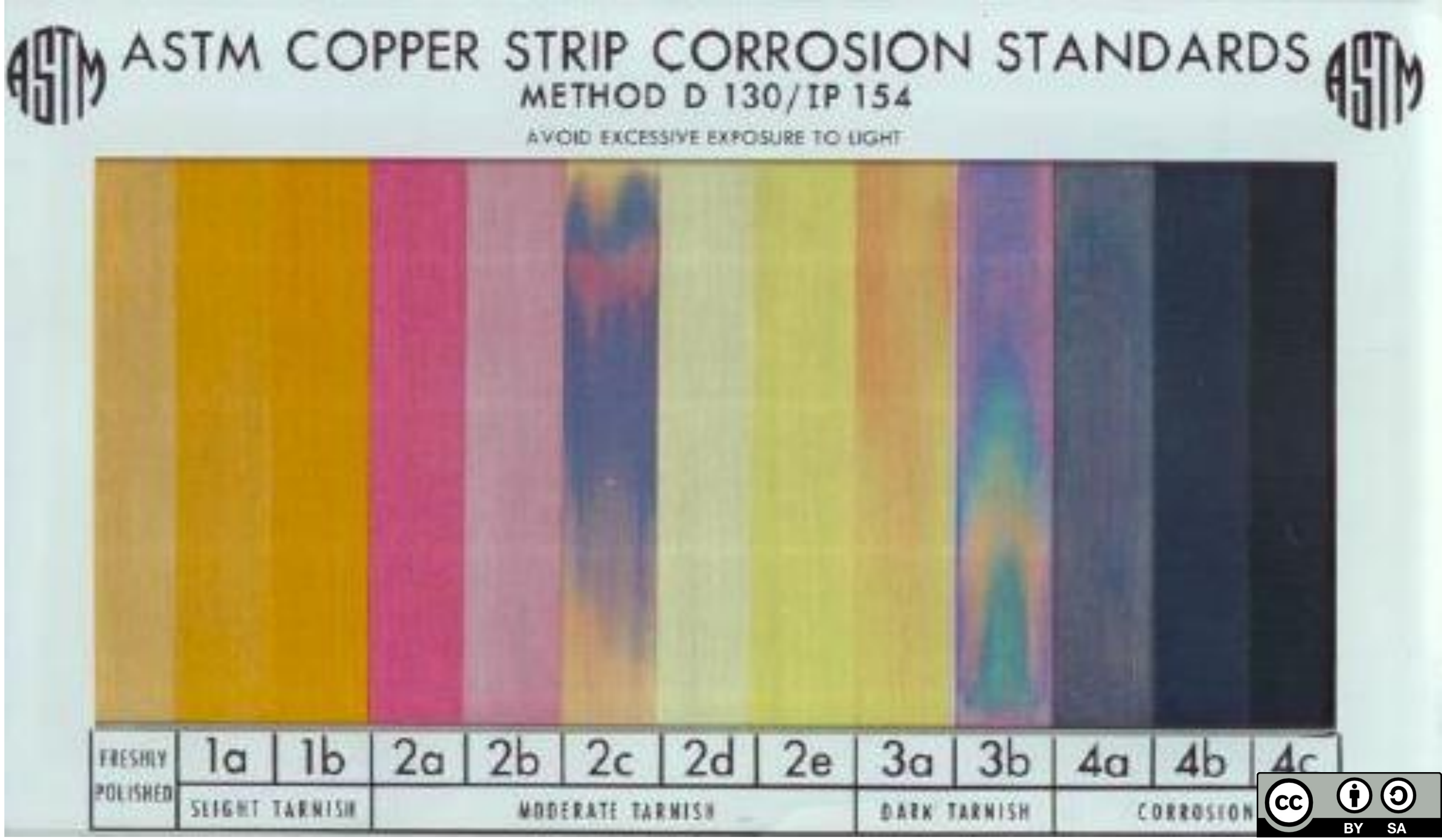
Assessment – Visual

- **Paint blistering (puchýřkování)**:
  - **Size and density**: EN ISO 4628-2 *Paints and varnishes — Evaluation of degradation of coatings — Designation of quantity and size of defects, and of intensity of uniform changes in appearance — Part 2: Assessment of degree of blistering*: <2(S2), 2(S2) … 5(S5)
  - ➢ Scatter in scores between operators, trials to use digital image analysis



Assessment – Visual

- **Chalking** (EN ISO 4628-6, 7)
- **Cracking** (EN ISO 4628-4)
- **Flaking** (EN ISO 4628-5)
- **Filiform corrosion** (EN ISO 4628-10)
- **Loss of gloss of copper** (assessment of indoor air corrosivity)

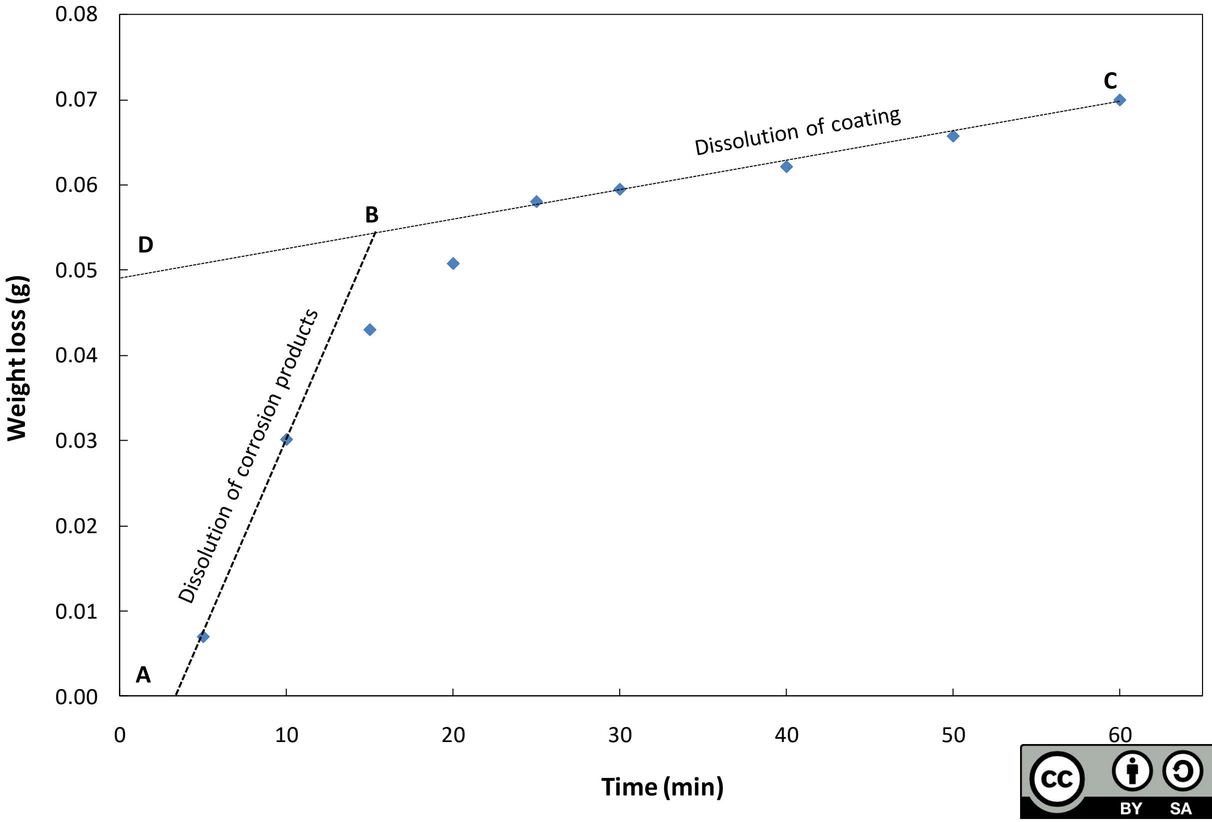


Assessment – Mass Loss

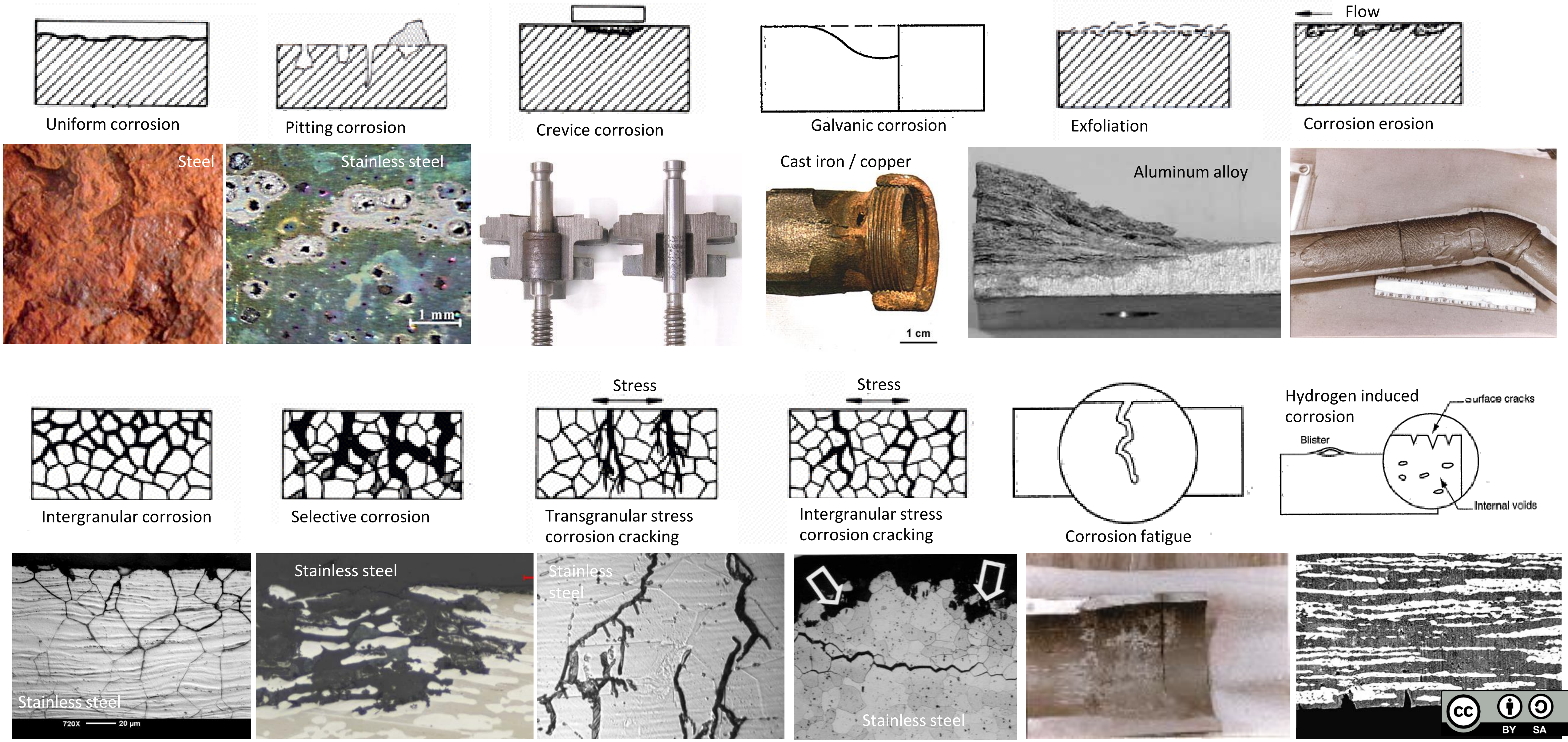
- Mostly used for uniform corrosion
- Chemical agent dissolving corrosion products with minimal corrosivity towards metal itself
  - Zinc: Saturated glycine solution (NH_2CH_2COOH)
  - Steel: Concentrated HCl + 20 g Sb_2O_3, 50 g $SnCl_2$ in 1 liter
- Given in g/m², g/m² year, µm/year

ISO 8407 *Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens*

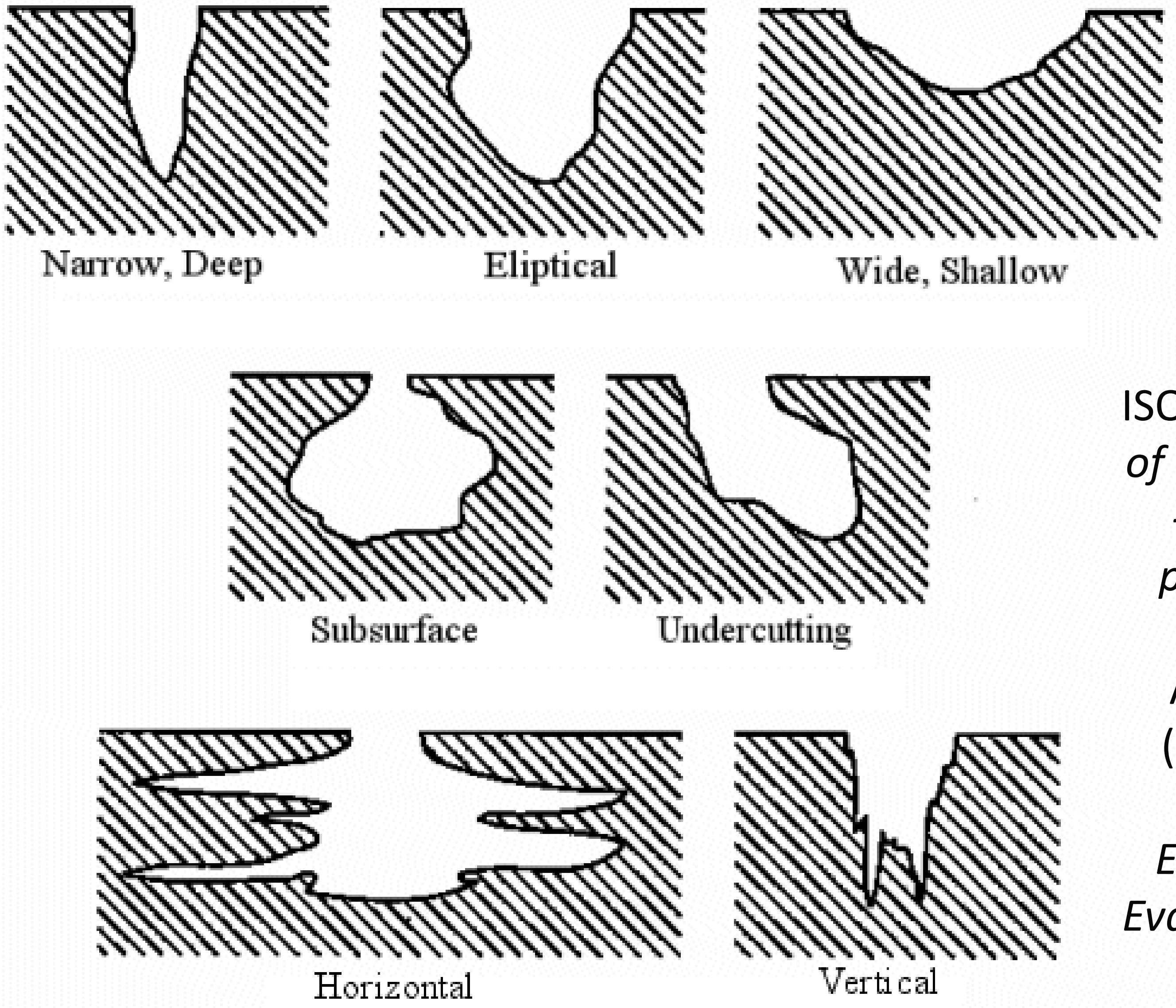
ASTM G1 – 03 (2011) *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*



Assessment – Non-Uniform

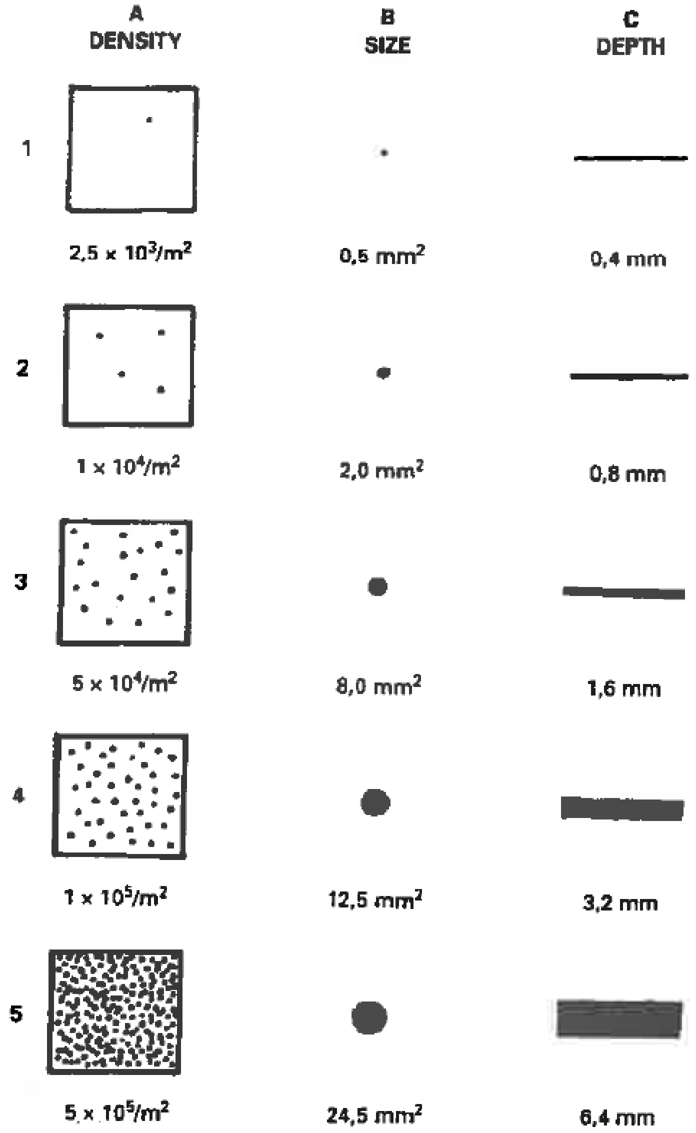


Assessment – Pitting Corrosion



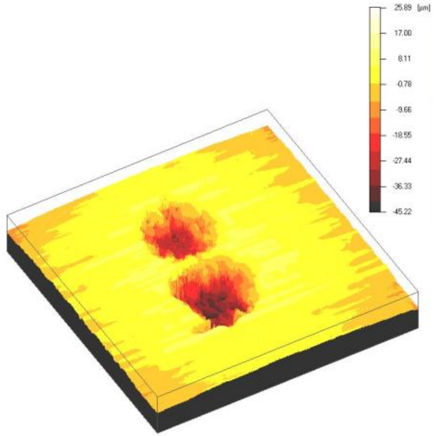
ISO 11463 *Corrosion of metals and alloys – Evaluation of pitting corrosion*

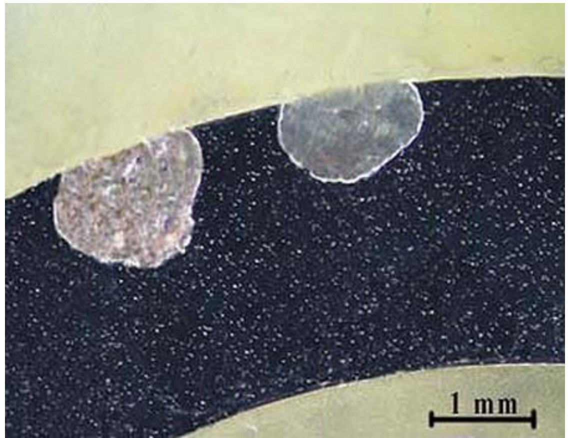
ASTM G46 – 94 (2013) *Standard Guide for Examination and Evaluation of Pitting Corrosion*

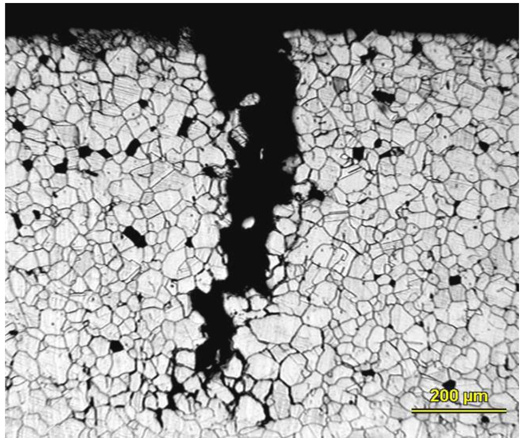


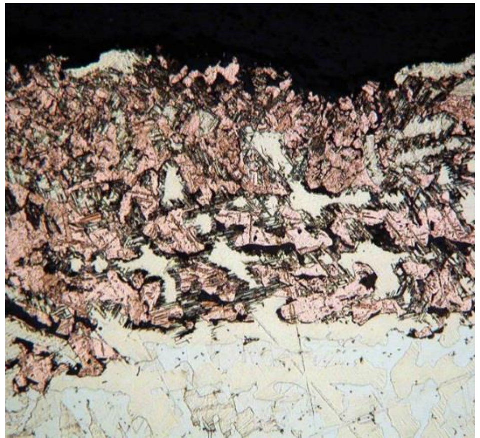
Assessment – Corrosion Depth

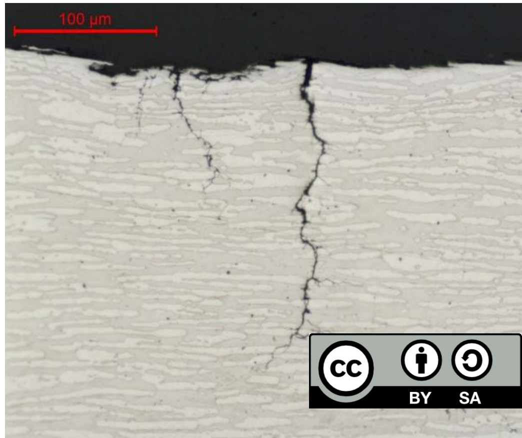
- For non-uniform corrosion, mass loss is usually not representative
- Maximal depth practically most important; assessed by:
  - **Metallography at cross-section** (location selection, time consuming)
  - **Sequential polishing** (time consuming, sample destruction)
  - **Micrometer gauge with sharp tip** (only defects with larger mouth)
  - **Profilometry** (only defects with larger mouth)
  - **Advanced techniques**: X-Ray, tomography





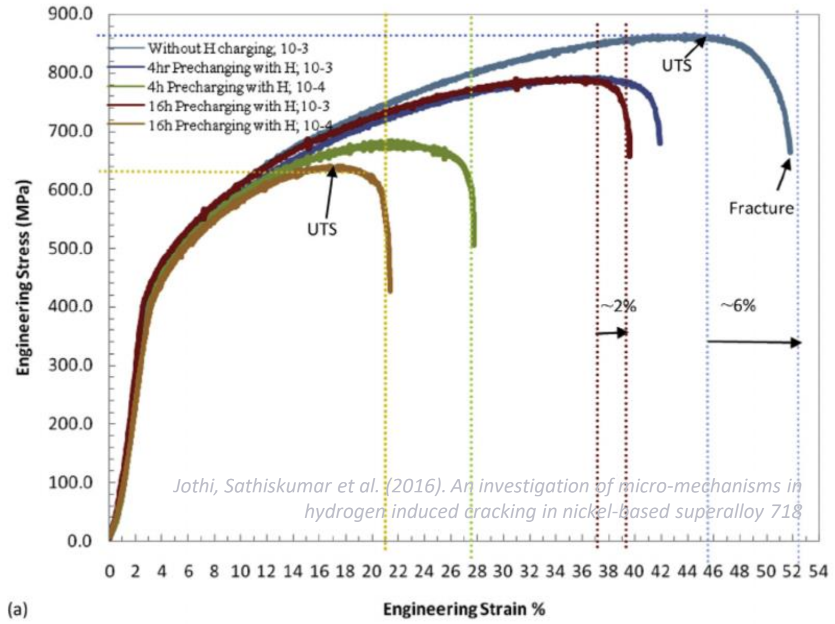




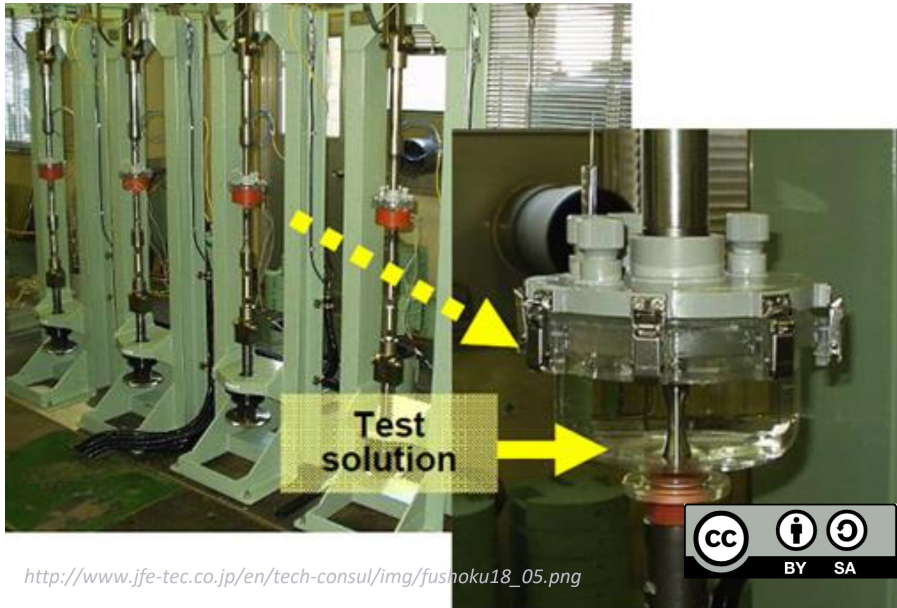


Assessment – Mechanical Prop.

- Usual for safety-critical parts with danger of brittle failure
- Either corrosion test with applied mechanical stress or mechanical test after corrosion test



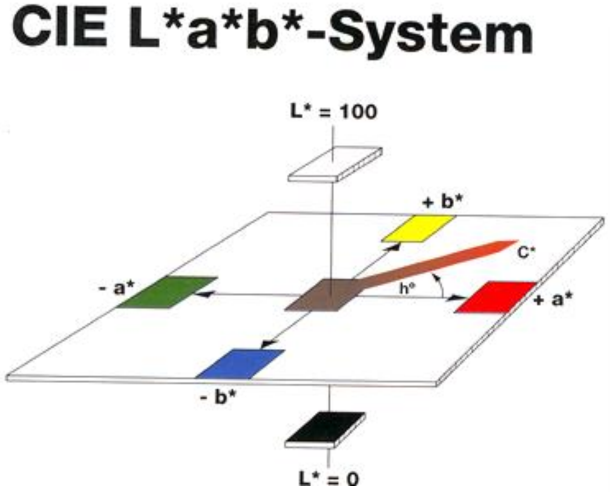
Jothi, Sathiskumar et al. (2016). An investigation of micro-mechanisms in hydrogen induced cracking in nickel-based superalloy 718



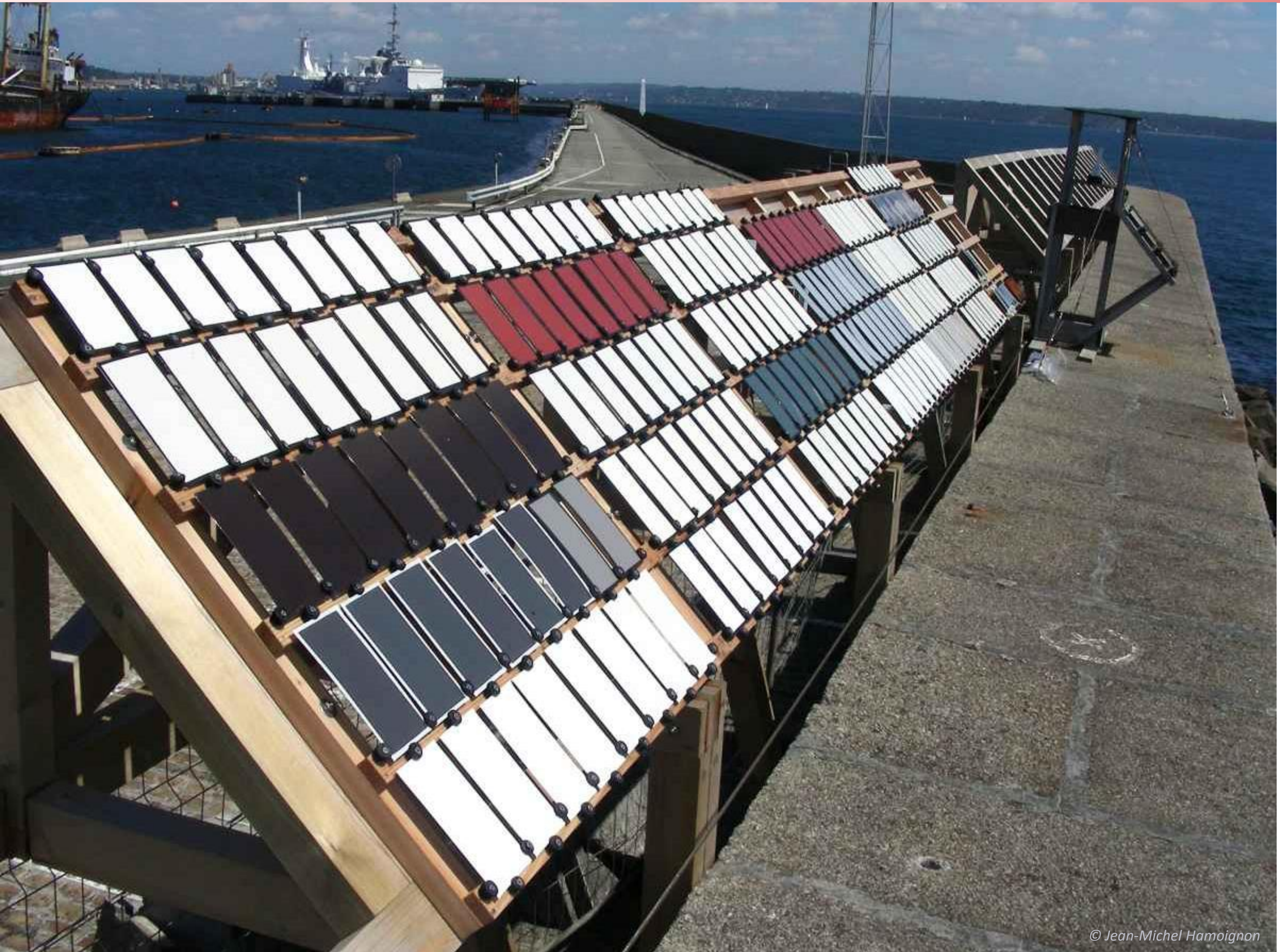
http://www.jfe-tec.co.jp/en/tech-consul/img/fushoku18_05.png

Assessment – Other Properties

- Electrical resistance (proportional to thickness)
- Gloss, colour (organic coatings)
- Functional properties: antibacterial, self-cleaning, heat-reflective
- Changes in the environment – released corrosion products (Cu, Zn, …), reduction of components (H_2, …)



Field Exposure Tests



Exposure Tests – Principles

- Exposure to conditions **as close as possible to real applications** regarding:
  - Composition and physical parameters of environment
  - Surface state (surface treatment, processing, installation, …)
  - Position and geometry

- Used mainly for:
  - **Outdoor atmospheric corrosion** (construction, transport)
  - Indoor atmospheric corrosion (objects of cultural heritage, electronics)
  - Seawater corrosion (oil & gas, marine transport)
  - Corrosion on power generation
  - Automotive industry

Outdoor Exposure – Effects

- Rainfall and variations of relative humidity
- Temperature
- Concentration of activators, mainly chlorides (Cl^-) and sulphur dioxide (SO_2)

but also:

- UV radiation (organic coatings)
- Degree of sheltering (rainfall, irradiation)
- Wind, specimen orientation, surface preparation
- Presence of other pollutants (NO_x, HNO_3, O_3, ...), dust deposition, …

→ Too many parameters; need for simplification

Outdoor Exposure – Effects

Standards define how to handle climatic and exposure parameters:

- Important + Incontrollable ➲ **Measure** (T, RH)
- Important + Controllable ➲ **Fix** (inclination, orientation)
- Unimportant ➲ **Omit**

- Can differ for individual types of sites and materials

Outdoor Exposure – Standards

- Basic requirements for field testing defined by ISO standards:
  - **(ČSN) EN ISO 8565:2012** *Metals and alloys – Atmospheric corrosion testing – **General requirements for field tests***
  - **(ČSN) EN ISO 9223:2012** *Corrosion of metals and alloys – Corrosivity of atmosphere – **Classification***
  - **(ČSN) EN ISO 9224:2012** *Corrosion of metals and alloys — Corrosivity of atmospheres – **Guiding values for the corrosivity categories***
  - **(ČSN) EN ISO 9225:2012** *Corrosion of metals and alloys – Corrosivity of atmospheres – **Measurement of pollution***
  - **(ČSN) EN ISO 9226:2012** *Corrosion of metals and alloys – Corrosivity of atmospheres – **Determination of corrosion rate of standard specimens for the evaluation of corrosivity***
  - **(ČSN) EN ISO 12944-2:1998** *Paints and varnishes – Corrosion protection of steel structures by protective paint systems – Part 2: **Classification of environments*** (for water, soil and atmosphere)
- Additional standards for specific materials, environments and applications

Outdoor Exposure – Types

Main corrosion factors

Atmospheres [a] → ↓Parameters	Rural	Urban	Industrial	Marine/ Industrial	Marine	High UV
Rainfall	X	X	X	X	X	X
Temperature	X	X	X	X	X	X
[Dew point]	[X]	[X]	[X]	[X]	[X]	[X]
[SO_2 of rain]	-	[X]	[X]	[X]	-	-
SO_2 of air	-	X	X	X	-	-
NO_x	X	X	X	X	-	-
Cl^-	-	-	-	X	X	-
[pH of rain]	[X]	[X]	[X]	[X]	[X]	[X]
Relative Humidity	X	X	X	X	X	X
Total Radiation	X	X	X	X	X	X
[Time of wetness]	[X]	[X]	[X]	[X]	[X]	[X]

(ČSN) EN ISO 12944-2
(ČSN) EN ISO 9223

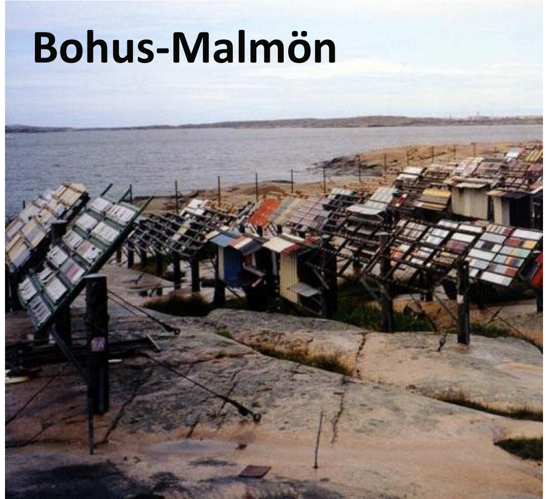
X Required
[X] Optional

Basic information on the type of atmosphere in view of expected corrosivity

Outdoor Exposure – Classes

- Corrosivity according to (ČSN) EN ISO 9223 standard:
  - Yearly exposure of carbon steel, zinc, aluminum and copper coupons
  - 45°, facing south (for northern hemisphere) or sea
  - Removal of corrosion products
  - Measurement of mass loss

Carbon steel, marine climate, 1 year



Outdoor Exposure – Classes

Corrosivity class	Corrosion rate (loss) r_{corr}				
	Unit	Steel	Zinc	Copper	Aluminum
C1 Very low	$g/(m^2{\cdot}a)$	$r_{corr} \leq 10$	$r_{corr} \leq 0{,}7$	$r_{corr} \leq 0{,}9$	negligible
	μm/a	$r_{corr} \leq 1{,}3$	$r_{corr} \leq 0{,}1$	$r_{corr} \leq 0{,}1$	—
C2 Low	$g/(m^2{\cdot}a)$	$10 < r_{corr} \leq 200$	$0{,}7 < r_{corr} \leq 5$	$0{,}9 < r_{corr} \leq 5$	$r_{corr} \leq 0{,}6$
	μm/a	$1{,}3 < r_{corr} \leq 25$	$0{,}1 < r_{corr} \leq 0{,}7$	$0{,}1 < r_{corr} \leq 0{,}6$	—
C3 Medium	$g/(m^2{\cdot}a)$	$200 < r_{corr} \leq 400$	$5 < r_{corr} \leq 15$	$5 < r_{corr} \leq 12$	$0{,}6 < r_{corr} \leq 2$
	μm/a	$25 < r_{corr} \leq 50$	$0{,}7 < r_{corr} \leq 2{,}1$	$0{,}6 < r_{corr} \leq 1{,}3$	—
C4 High	$g/(m^2{\cdot}a)$	$400 < r_{corr} \leq 650$	$15 < r_{corr} \leq 30$	$12 < r_{corr} \leq 25$	$2 < r_{corr} \leq 5$
	μm/a	$50 < r_{corr} \leq 80$	$2{,}1 < r_{corr} \leq 4{,}2$	$1{,}3 < r_{corr} \leq 2{,}8$	—
C5 Very high	$g/(m^2{\cdot}a)$	$650 < r_{corr} \leq 1500$	$30 < r_{corr} \leq 60$	$25 < r_{corr} \leq 50$	$5 < r_{corr} \leq 10$
	μm/a	$80 < r_{corr} \leq 200$	$4{,}2 < r_{corr} \leq 8{,}4$	$2{,}8 < r_{corr} \leq 5{,}6$	—
CX Extreme	$g/(m^2{\cdot}a)$	$1\,500 < r_{corr} \leq 5\,500$	$60 < r_{corr} \leq 180$	$50 < r_{corr} \leq 90$	$r_{corr} > 10$
	μm/a	$200 < r_{corr} \leq 700$	$8{,}4 < r_{corr} \leq 25$	$5{,}6 < r_{corr} \leq 10$	—

(ČSN) EN ISO 9223

The classification used for other materials as well (organic coatings, plastics, stone, ...)

Outdoor Exposure – Classes

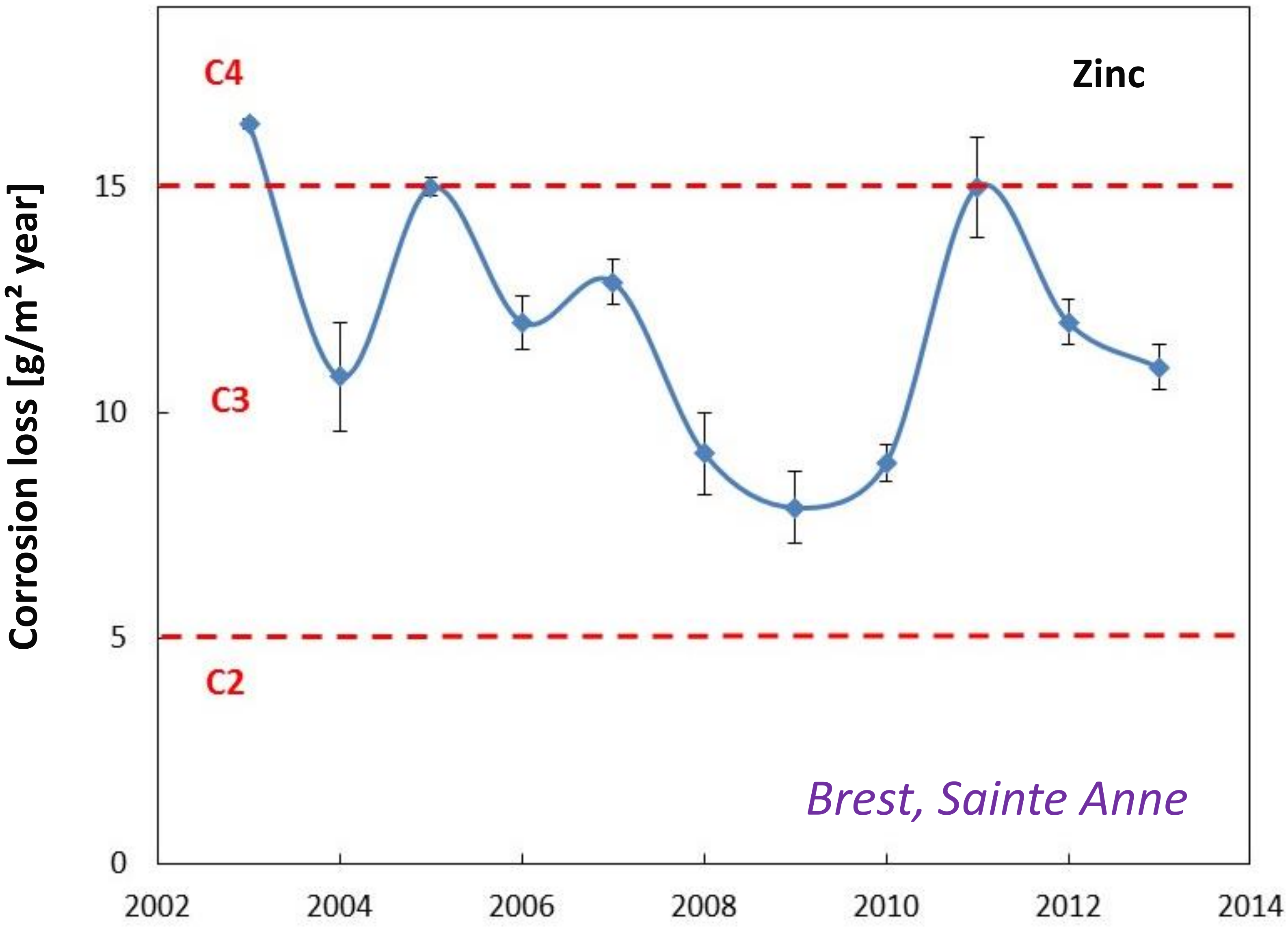
Sainte Anne, Brest, France, 2010

		Steel	Zinc	Copper	Aluminum
Corrosion rate	g/m² year	692 ± 43	8.9 ± 0.4	20.1 ± 0.8	0.6 ± 0.1
	µm/year	88 ± 5	1.2 ± 0.1	2.3 ± 0.1	0.2 ± 0.0
Corrosivity class		C5 / Very high	C3 / Medium	C4 / High	C3 / Moderate

Base navale, Brest, France, 2010

		Steel	Zinc	Copper	Aluminum
Corrosion rate	g/m² year	747 ± 55	12.7 ± 1.3	42.0 ± 4.4	1.2 ± 0.1
	µm/year	95 ± 7	1.8 ± 0.2	4.7 ± 0.5	0.4 ± 0.0
Corrosivity class		C5 / Very high	C3 / Medium	C5 / Very high	C3 / Moderate

Outdoor Exposure – Classes



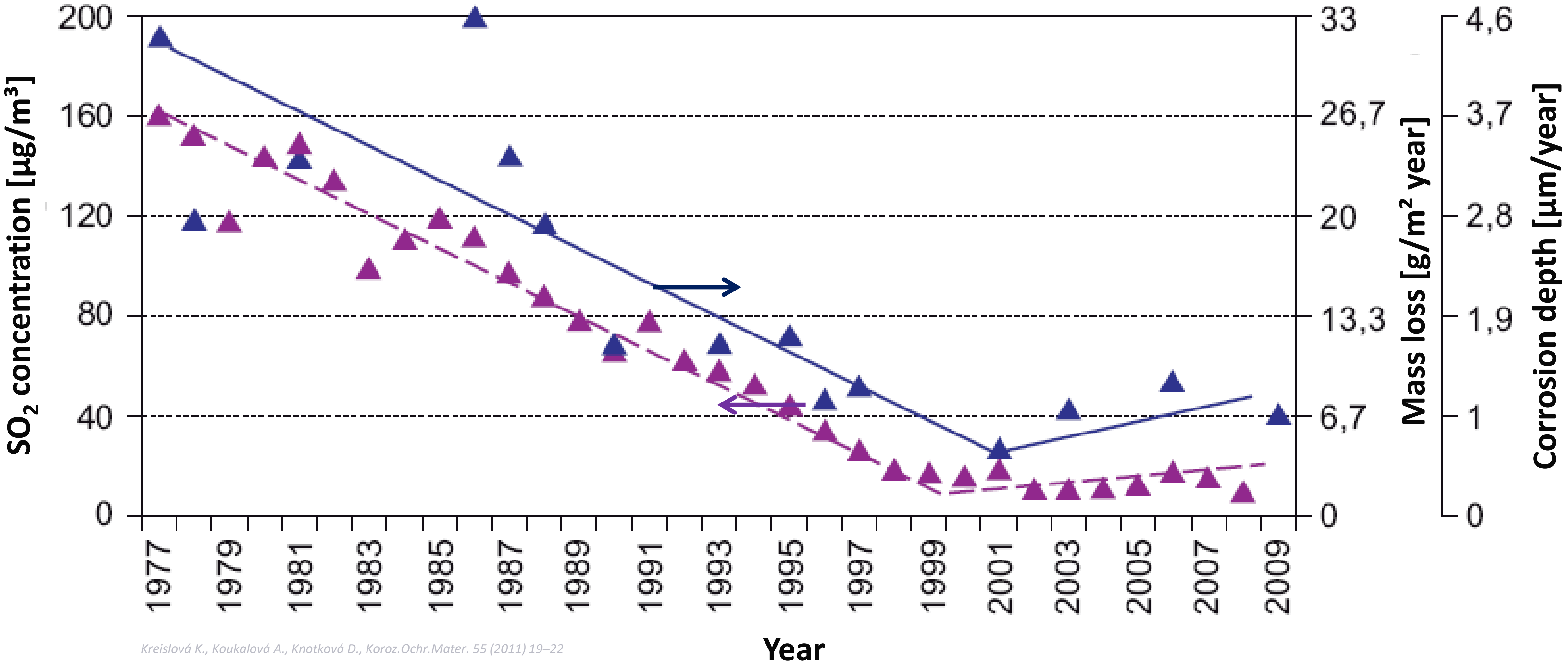
Outdoor Exposure – Sites

- Marine tropical: Florida, USA (Q-Lab)
- Marine: Brest, F; Bohus-Malmön, SE
- Industrial: Kopisty (SVUOM); Ostrava-Radvanice (UCT); Shenyang, CN
- Rural: Kašperské Hory (SVUOM)
- Urban:
  Praha (SVUOM)
  Kralupy (UCT)

Type	Name	T [°C]	RH [%]	Precipitation [mm/year]	Cl⁻ depos. [mg/m²day]	SO_2 [µg/m³]	WL steel [g/m²/year]	WL zinc [g/m²/year]
Marine	Brest	12	79–85	840–1320	140–1850	Low	750–860	9.1–16.4
Marine	Bohus-Malmön Kvarnvik	6–9	75–81	620–860	160–1160	Low	340–1330	6.2–13.4
Marine / Industrial	Qingdao	13–14	73–74	500–930	16–30	[1]	320–340	3.5–7.4
Industrial	Ostrava	8	80	700	Low	17	570	9
Industrial	Kopisty	9	79	500	Low	14	180	7
Industrial	Jiangjin	19	79–81	1080–1140	0–1	54–231	260–290	7.6–10.6
Urban	Praha	10	68	520	Low	7	60	3
Urban	Shenyang	10	63–65	440–790	2	33	140–170	6.7–8.7
Rural	Langonnet	10–11	83–85	1080–1350	8	Low	170	7.7–10.4
High UV	Dubai	29	57	94	3	10–11	NA	NA

WL … Weight loss in 1st year; NA … Not available; [1] 36–57 mg/m²day

Outdoor Exposure – Kopisty



Kreislová K., Koukalová A., Knotková D., Koroz.Ochr.Mater. 55 (2011) 19–22

Outdoor Exposure – Requirements

- Samples exposed facing south (for northern hemisphere); marine sites: facing sea
- Orientation 45° to horizontal
- Climatic data measured and reported
- Samples of 150×100 mm or any other
- Corrosion rate measured in parallel using zinc, steel, copper and aluminum
- All specimens should be mounted on the same day
- Avoid galvanic effects

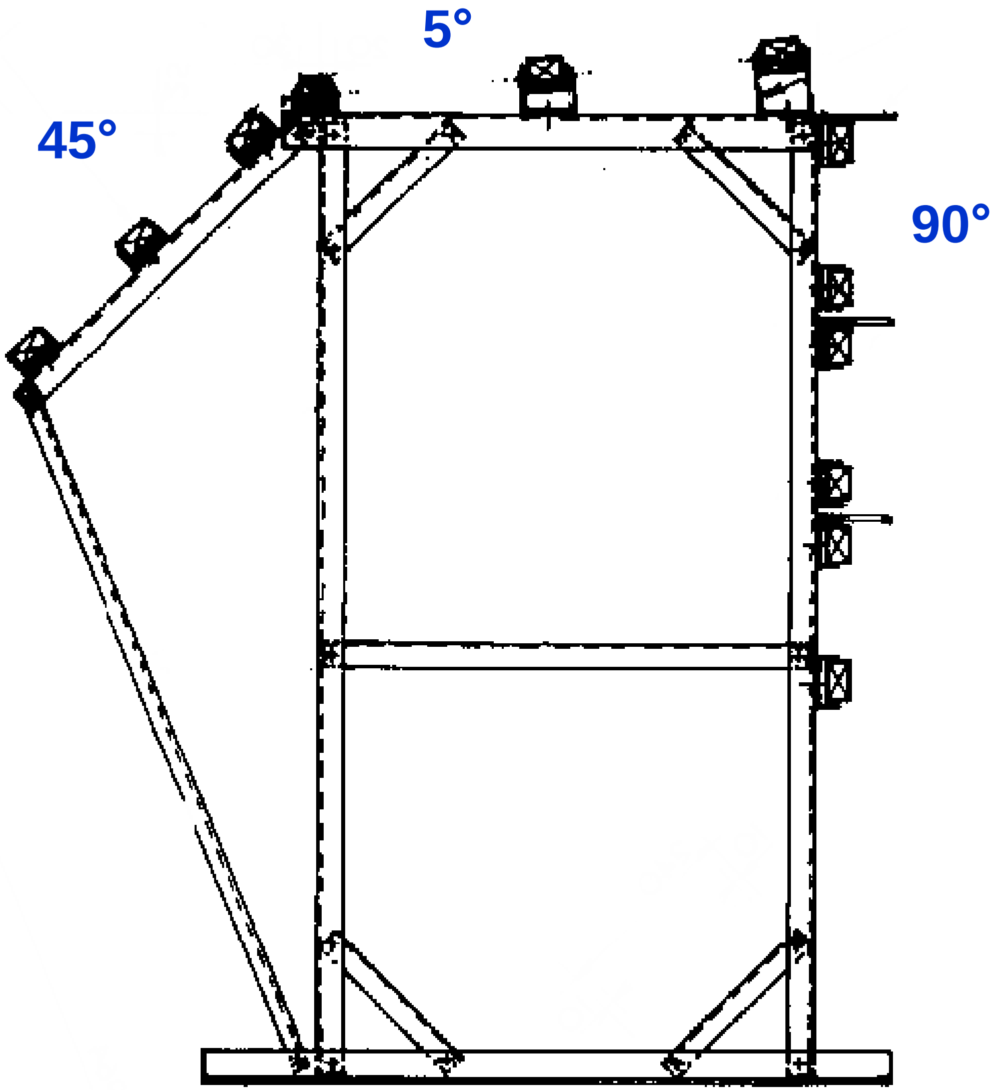
Outdoor Exposure – ECCA

- Standards developed by European Coil Coating Association for building materials
- Addition to the ISO system
- Provides more relevant modes of degradation of pre-painted materials

- (ČSN) EN 13523-19 (2011) *Coil coated metals – Test methods – Part 19:* ***Panel design and method of atmospheric exposure testing*** specifies conditions of outdoor exposure testing
- (ČSN) EN 13523-21 (2010) *Coil coated metals – Test methods – Part 21:* ***Evaluation of outdoor exposed panels*** describes the evaluation of panels

Outdoor Exposure – ECCA

- **ECCA racks**
  - 45° south
  - 5° south
  - 90° north



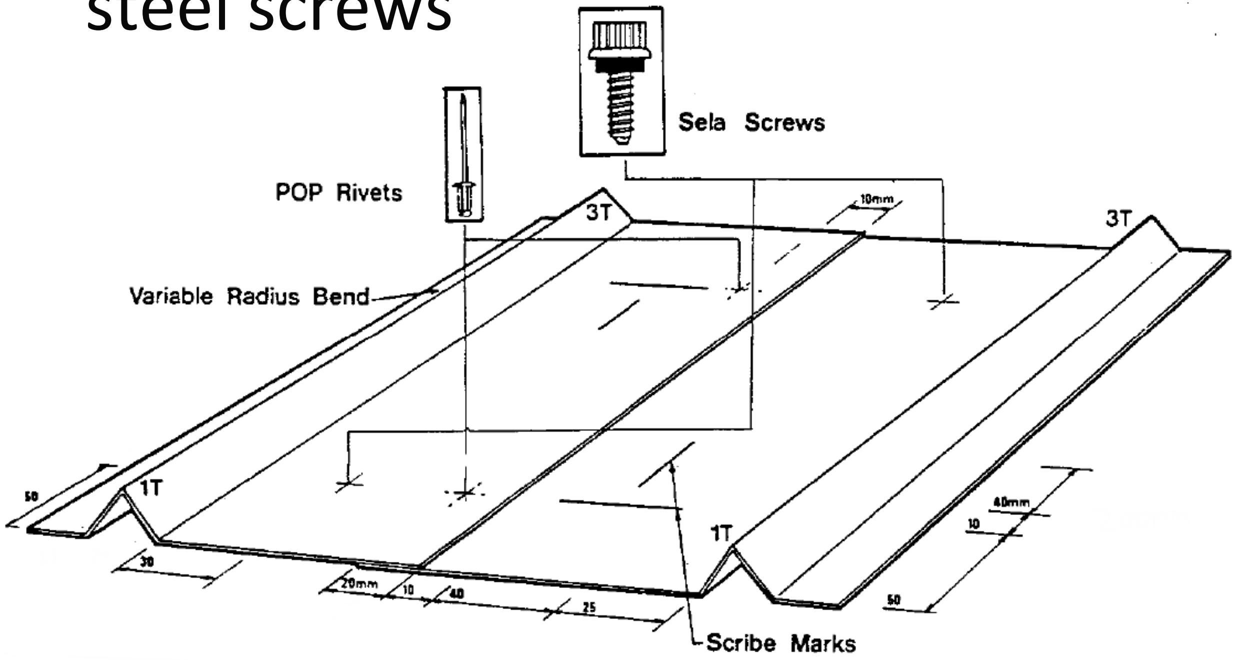
Outdoor Exposure – ECCA

Effect of panel orientation:

- Sainte Anne, Brest, carbon steel, from October 2007 until October 2008
- 90° north – most aggressive for most non-painted and painted materials under high chloride deposition

Outdoor Exposure – ECCA

- **Specific panel design for each orientation as a function of studied properties**
- E.g., 90° N simulating side claddings:
  - Corrosion in the unwashed area under overhang
  - Overlapped panels with variable radius bend, scribe marks and stainless steel screws



Outdoor Exposure – ECCA

- Evaluation following standard EN 13523-21

After
6 months,
then yearly

Panel Identification N°	Start of exposure	Date of inspection	Accumulative time of exposure	Exposure Site	Angle
	22/02/2007	02/03/2009	24 months	Sainte Anne BREST (France)	90° North
Description: ND	Substrate ND	Coating type ND	Colour Blue	Other (surface treatment) ND	

Property/Area inspected	Measured values / Results of inspection											Other observations
Gloss (60°) EN 15323-2	initial gloss			Gloss after exposure			Change in Gloss			Gloss Retention %		
	26,8			25,8			1			4		
Coulour EN 13523-3	initial colour			Colour after exposure			Couour change			Colour différences		
	L*	a*	b*	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE		
	41,79	-1,77	-11,12	41,55	-2,09	-10,84	0,24	0,32	-0,28	0,49		
Edges	Filiform corrosion Size			Delamination		Blistering			Rusting			
	mean	max.	% affected	mm	% affected	Size	Number	% affected	Colour of rusting WR or RR	% affected	Number of the spots	
side	0	0	0	0,5	50	0	0	0	WR	10	_	
top	0	0	0	1,0	70	1,0	1	_	WR	100	_	
bottom	0	0	0	0,5	20	0	0	0	0	0	0	
overlap	0	0	0	1,0	50	0	0	0	WR + RR	30	2 spots for RR	
Overall surface	Cracking prEN ISO 4628-4			Flaking prEN ISO 4628-5		Blistering prEN ISO 4628-2			Rusting prEN ISO 4628-3			
	Size		Quantity	Size	Quantity	Size		Quantity	Size		Quantity	
	no		no	no	no	no		no	no		no	
Bends	Cracking Leng in mm from 1T			Flaking prEN ISO 4628-5		Blistering prEN ISO 4628-2			Rusting prEN ISO 4628-3			
				Size	Quantity	Size		Quantity	Size		Quantity	
	no			no	no	no		no	no		no	
Areas around screws	type of degradation Initial Scratches			Size (mm): 0								
Areas around rivets	type of degradation Initial Scratches			Size (mm): 0								
Scribe	Delamination 0			Area affected (%)		Blisters ☐	Rust ☐		Filiform corrosion ☐			
Reverse side	white Rust											

Accelerated Tests

Accelerated Tests – Requirements

What should a corrosion test be capable of?

- **Acceleration** of corrosion processes with identical mechanism
- **Simulation of service conditions** in view of main corrosion factors
- Corresponding **material and geometry ranking**
- Enable co-simulation of **other possible interactive mechanisms**, such as heat, solar impact or mechanical stress and fatigue

Accelerated Tests – Acceleration

How to accelerate corrosion?

- Higher **temperature** boosts kinetics of corrosion reactions
- **Changes in chemical composition**, e.g. chloride concentration
- **pH changes**, mostly acidification
- **Increasing relative humidity**
- **Cyclic wetting and drying** lead to change in electrolyte concentration
- **Defects** such as **scribes, cut edges**
- **Geometry or orientation** increasing tendency of a product to corrosion degradation, e.g. artificial crevices
- **Mechanical load,** relevant to SCC, corrosion fatigue, etc.

Accelerated Tests – SST

- Salt spray test
- Firstly used in 1914
- First standard (ASTM B117) from 1939
- (ČSN) EN ISO 9227, (ČSN) EN ISO 7253, ASTM G85 and many others
- Still most used corrosion test
- Usually 35 °C, 5 wt. % NaCl, pH 6.5–7.2, 2–1000+ hours (**NSST**)
- **ASS**: NaCl solution acidified by CH_3COOH
- **CASS**: CH_3COOH and $CuCl_2$

Accelerated Tests – SST

- \+ **Many reference data**
- \+ **Widely used quality control tool**
- \+ **Cheap**
- +/– **Extreme corrosivity**: High chloride load, permanent wetness, good access of O_2: mass loss 5 µm/day (40 g/m²·day) for carbon steel
- – **Unrealistic test conditions** leading to poor correlation with service (real world) performance
- – **Important variations in results** between parallel samples, between cabinets and labs, mainly due to high sensitivity to chloride deposition (15 ml/h per 80 cm²): *calibration certificate and reference samples should be required*

Accelerated Tests – Cyclic

- Initiative of automotive industry (1980's to 1990's)
- **More realistic conditions** due to repeated cycles of:
  - **Chloride contamination** (fog, rain, immersion)
  - **Drying phase**
  - **Wetting phase**
- **1st generation**: Lower, but still high Cl^- deposition
- **2nd generation**: Dramatically lower Cl^- deposition
- New trends: Further technical phases such as freezing or rapid temperature changes

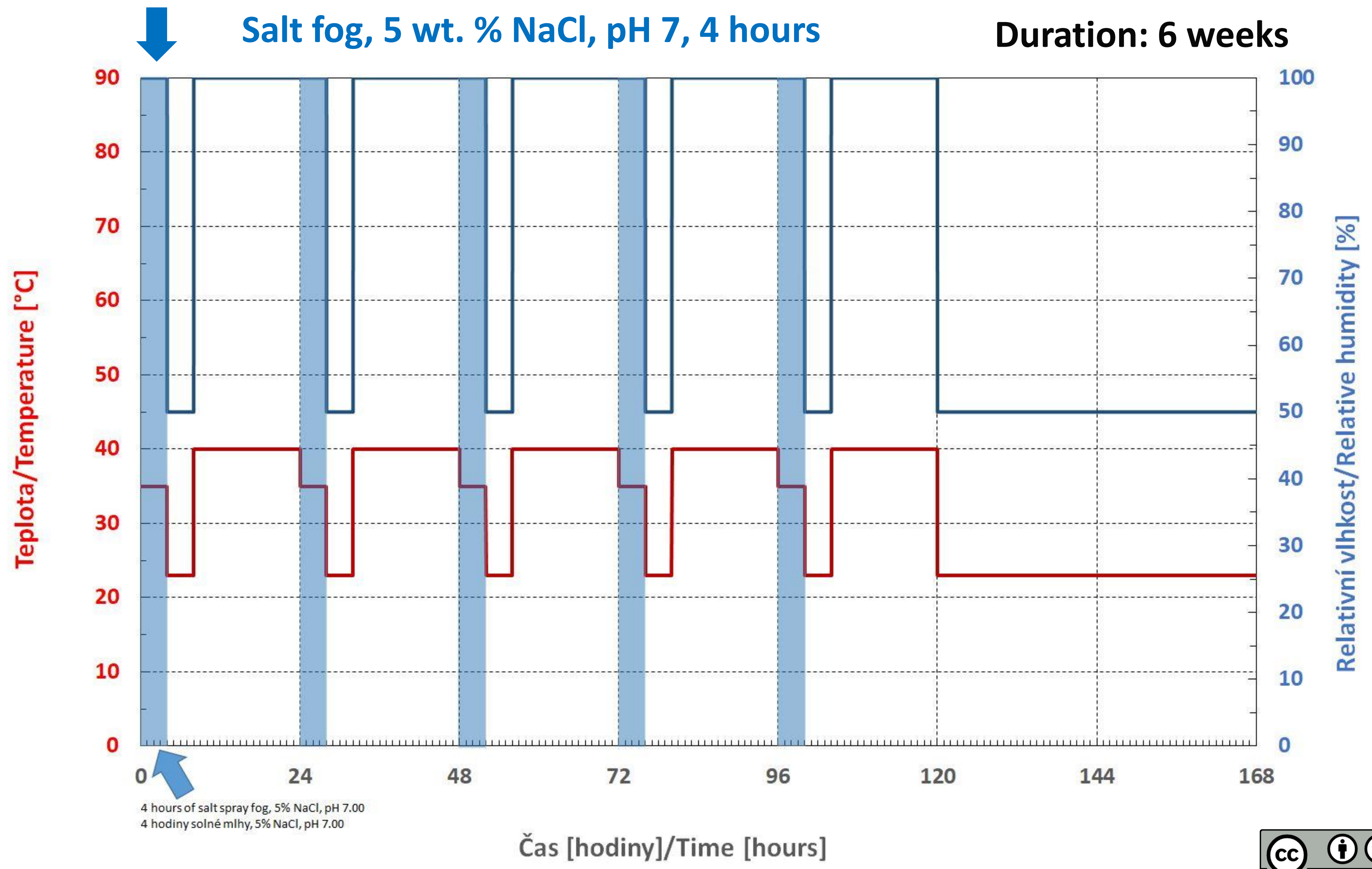
→ Significantly better prediction of material performance

Accelerated Tests – Cyclic

	Standard	Activation phase: Salt solution pH Deposition rate per 80 cm²	Activation phase: Frequency	Activation phase: Chloride deposition; mg/cm²/test *Approximatelly*	T [° C] RH [%]	Duration [days]
1	Renault **ECC1** D172028	NaCl 1%, pH 4 5 ml/h	30 min/day 3.5 h/week	8	35.. ..20,1h35 35.. ..55,2h40 35.. ..90,1h20	42
2	Volvo Car Corp **VICT** VCS1027,149, STD 423-0014	NaCl 1%, pH 4 120 ml/h (15 mm/h)	3x15 min twice a week 1.5 h/week	27	45.. ..50, 4h 35.. ..95, 4h	42
3	**VDA** 621-415	NaCl 5%, pH 6.5-7.2 1.5 ml/h	24 h/week	136	40.. ..100, 8h 18-28.. ..50, 16h 23.. ..50, 48h	70
4	Scania **SICT** STD4233, ISO 16701	NaCl 1%, pH 4	Immersion 1 h twice a week	?	35.. ..45, 2h 35.. ..90, 7h	84
5	Daimler **KWT**	NaCl 1%, pH 6.5-7.2, 2 ml/h	2 h/day (4 days) 8 h/week	7.3	-15.. ..50 up to 50.. ..up to 100	42
6	PSA **TCAC** D13 5486	NaCl 1%, pH 4 3 ml/h	1 h twice a week	5.4	35.. ..85, 7h 35.. ..45	84
7	VDA 233-102, SEP 1850, **N-VDA**	NaCl 1%, pH 6.5-7.2 2 ml/h	3h (3 × week) 9 h/week	8.1	-15.. ..50 up to 50.. ..up to 100	42
8	New Volvo/Ford CETP 00.00-L-467 **VOLVO/FORD**	NaCl 0.5% ~120-160 ml/h	10+3+3+3 min / 6 h (wet phase) 5 days/week		25.. ..95, 6h 50.. ..70,15h30	42
9	Nissan M 0158 **CCT IV**	NaCl 5%, pH 6.5-7.2 1.5 ml/h	10 min/day 1h10/week	4	60.. ..30, 160mn 60.. ..95, 80min	42
10	Volkswagen **PV1210**	NaCl 5%, pH 6.5-7.2 1.5 ml/h	4 h (5 × week)	113	40.. ..100, 16h 22.. ..50, 4h	42
11	Neutral salt spray ISO 9227 **NSST**	NaCl 5%, pH 6.5-7.2 15 ml/h	Permanent	383	35.. ..100	

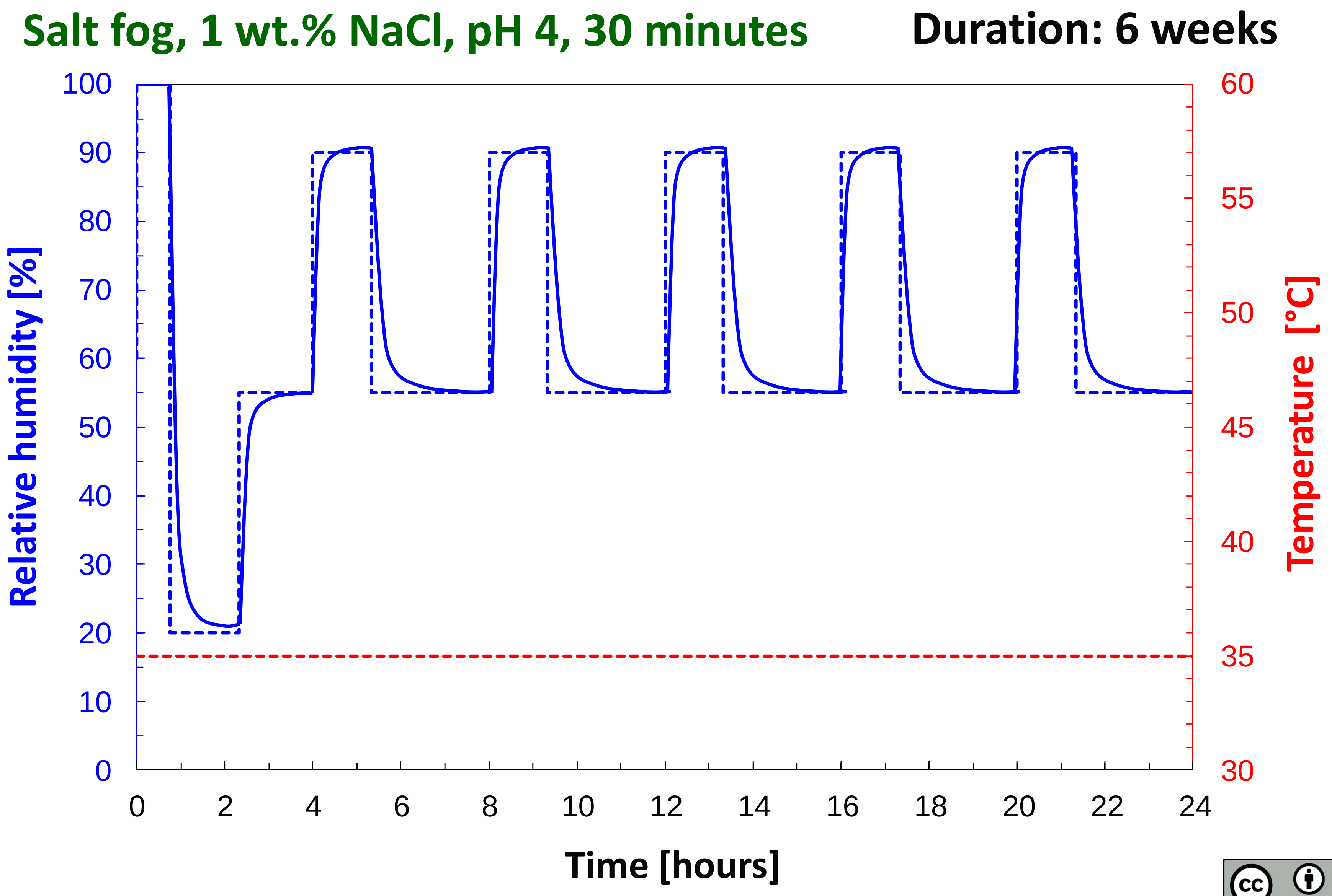
Accelerated Tests – PV 1210

Volkswagen PV 1210



Accelerated Tests – ECC1

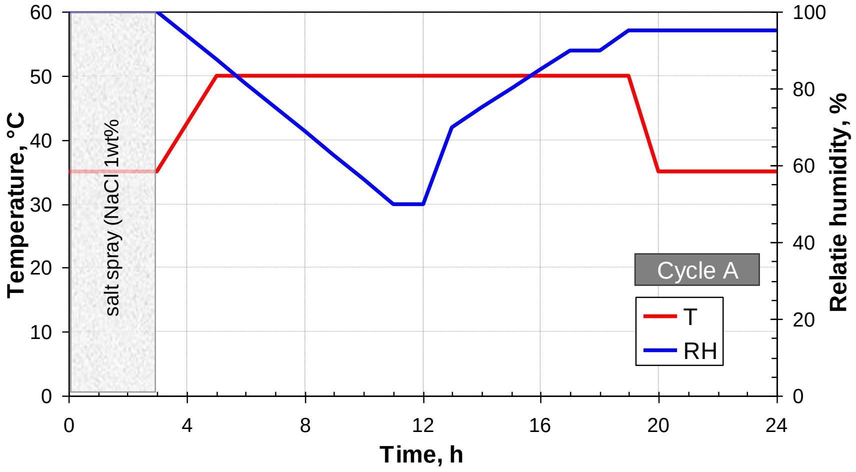
Renault
ECC1 D17
2028

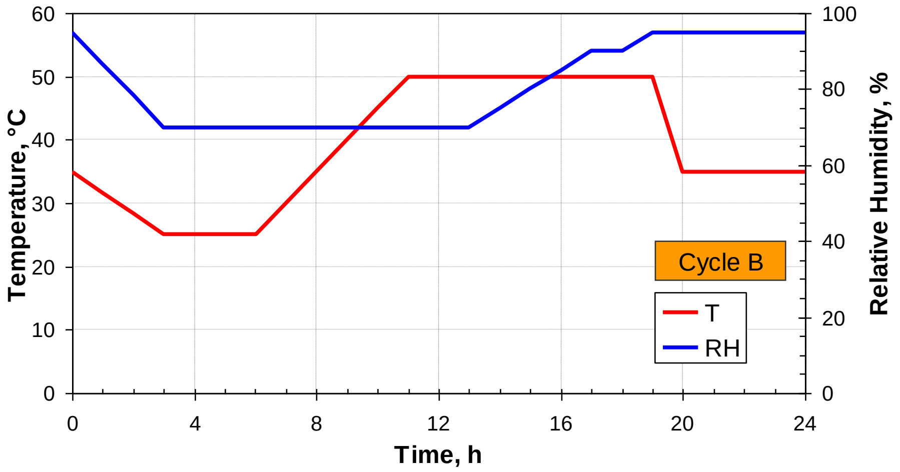


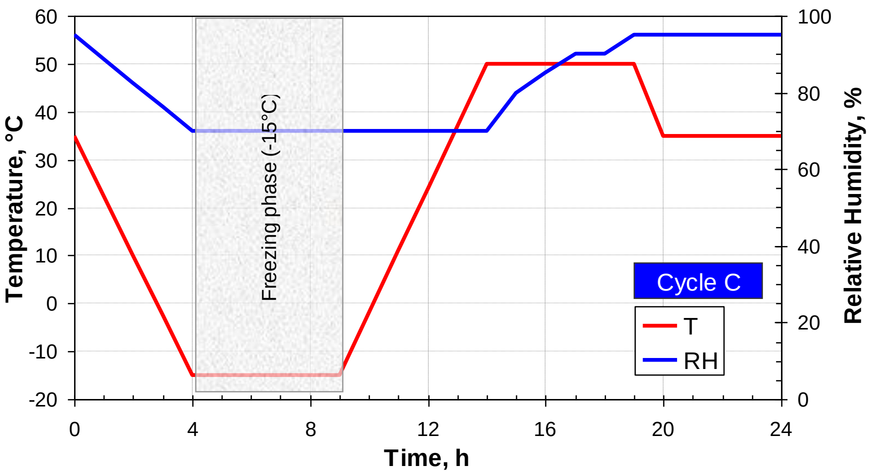
Accelerated Tests – N-VDA

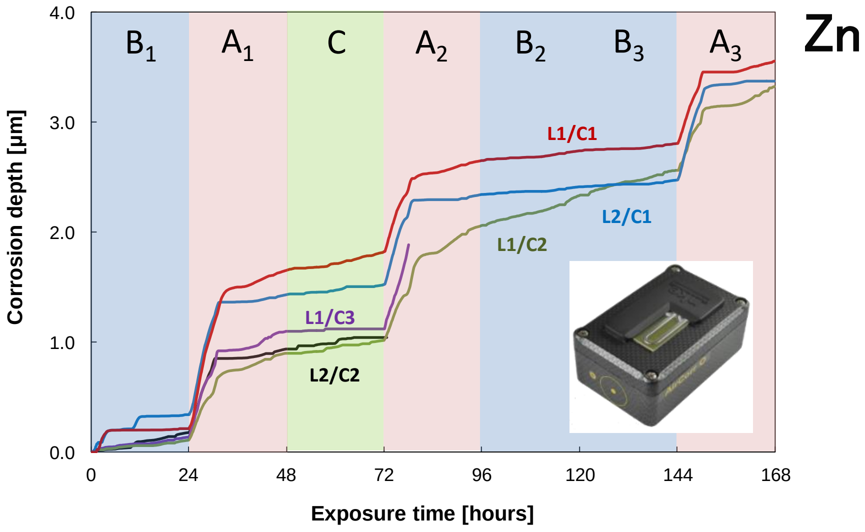
VDA 233-102
SEP 1850
N-VDA

6 weeks
sub-cycles
B-A-C-A-B-B-A





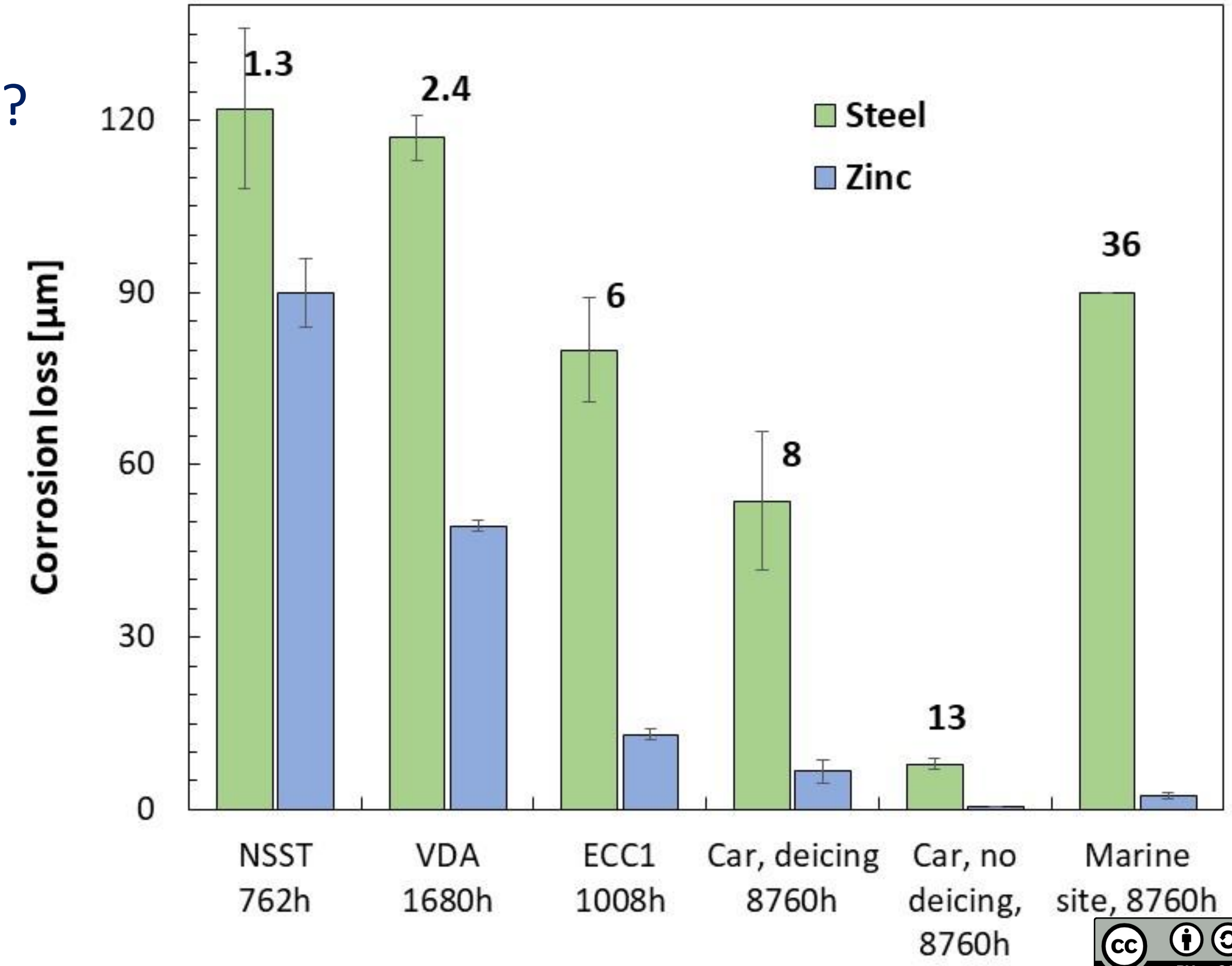




Accelerated Tests – Comparison

- **Example 1**: Does it make sense to apply a zinc coating?
  - NSST: Similar corrosion losses of steel and zinc
  - **Only the tests of the 2nd generation provide the correct ranking**

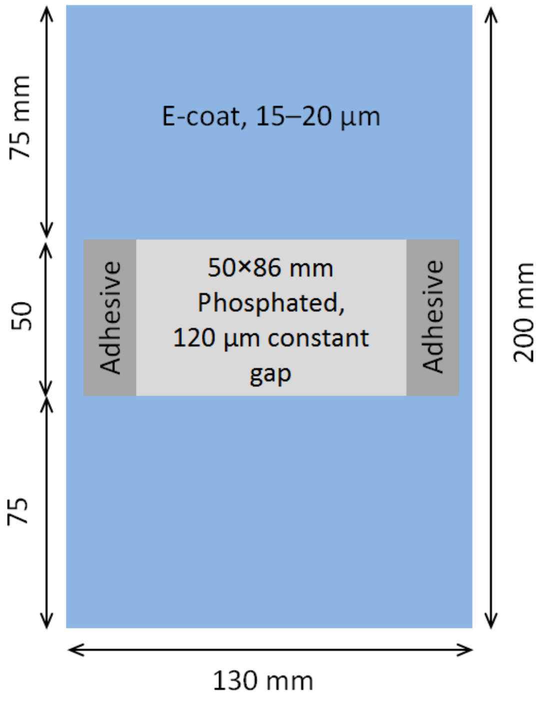
Data: N. LeBozec, N. Blandin, D. Thierry, Materials and Corrosion 59 (2008) 889–894



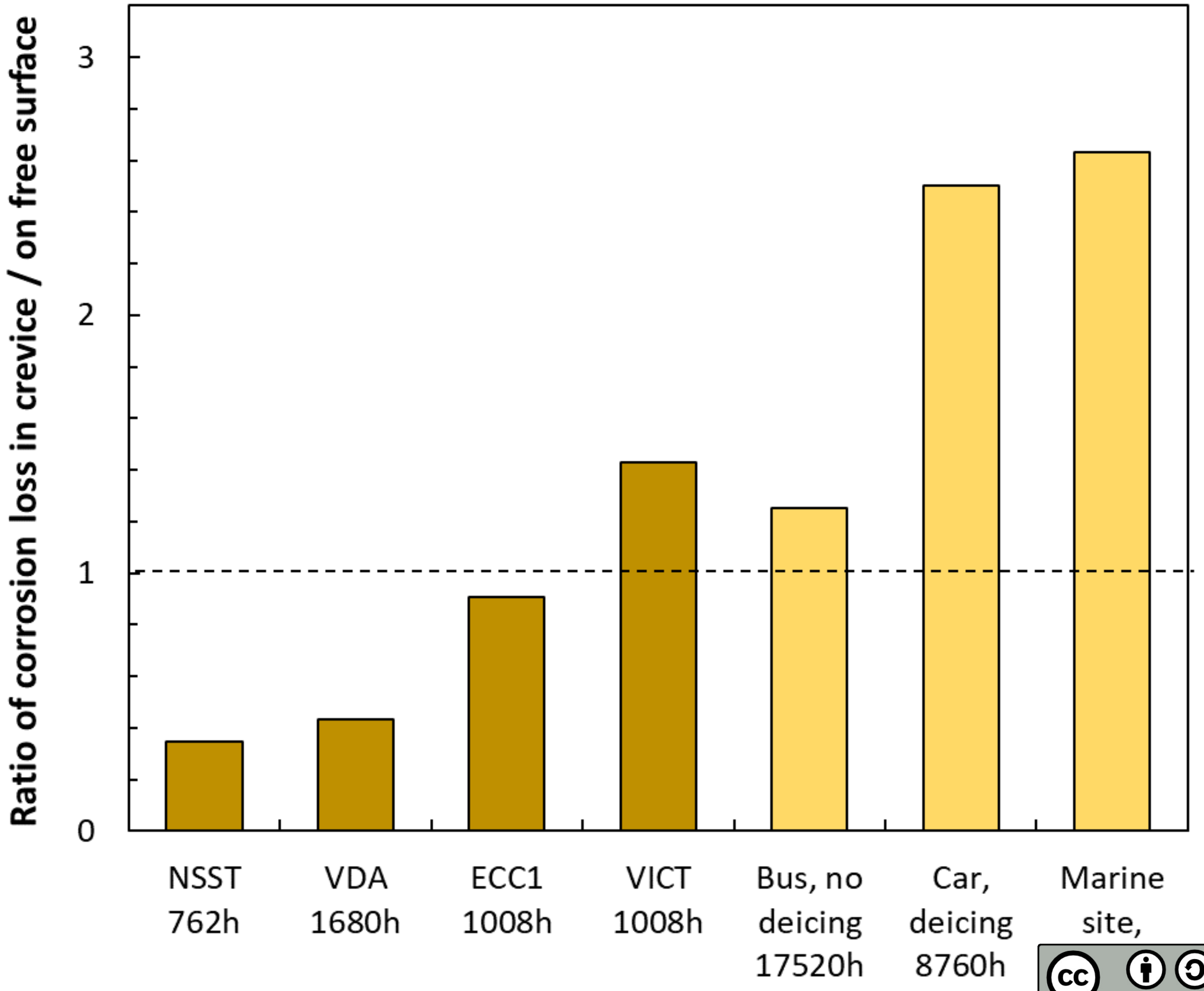
Accelerated Tests – Comparison

- **Example 2:** Lap joints

- Lap joint corrosion critical for car bodies
- Samples with model crevices with non-protected surface



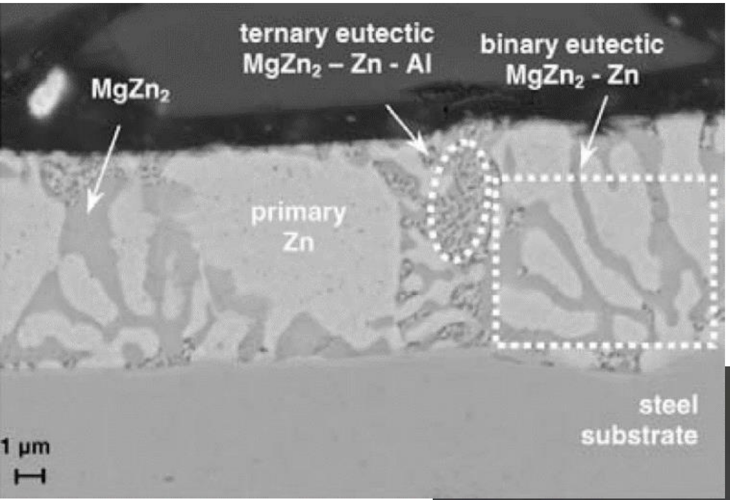
Data: N. LeBozec, N. Blandin, D. Thierry, Materials and Corrosion 59 (2008) 889–894

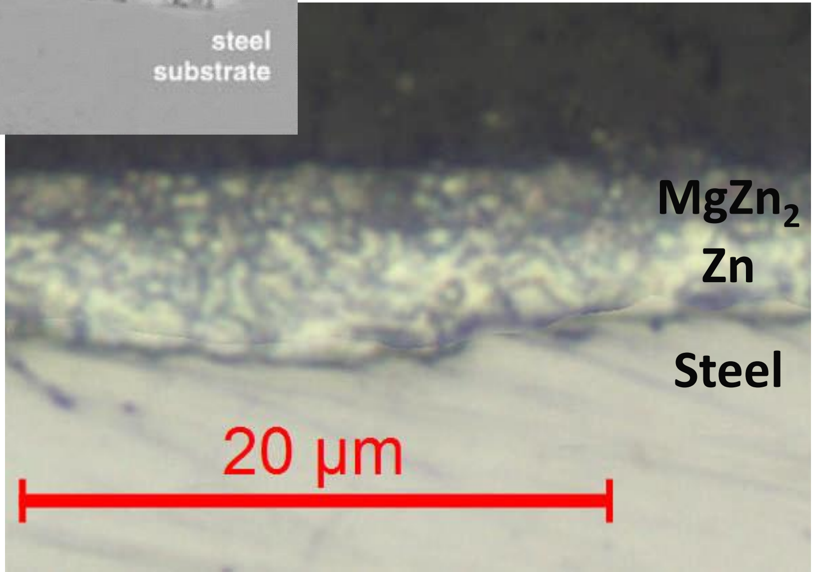


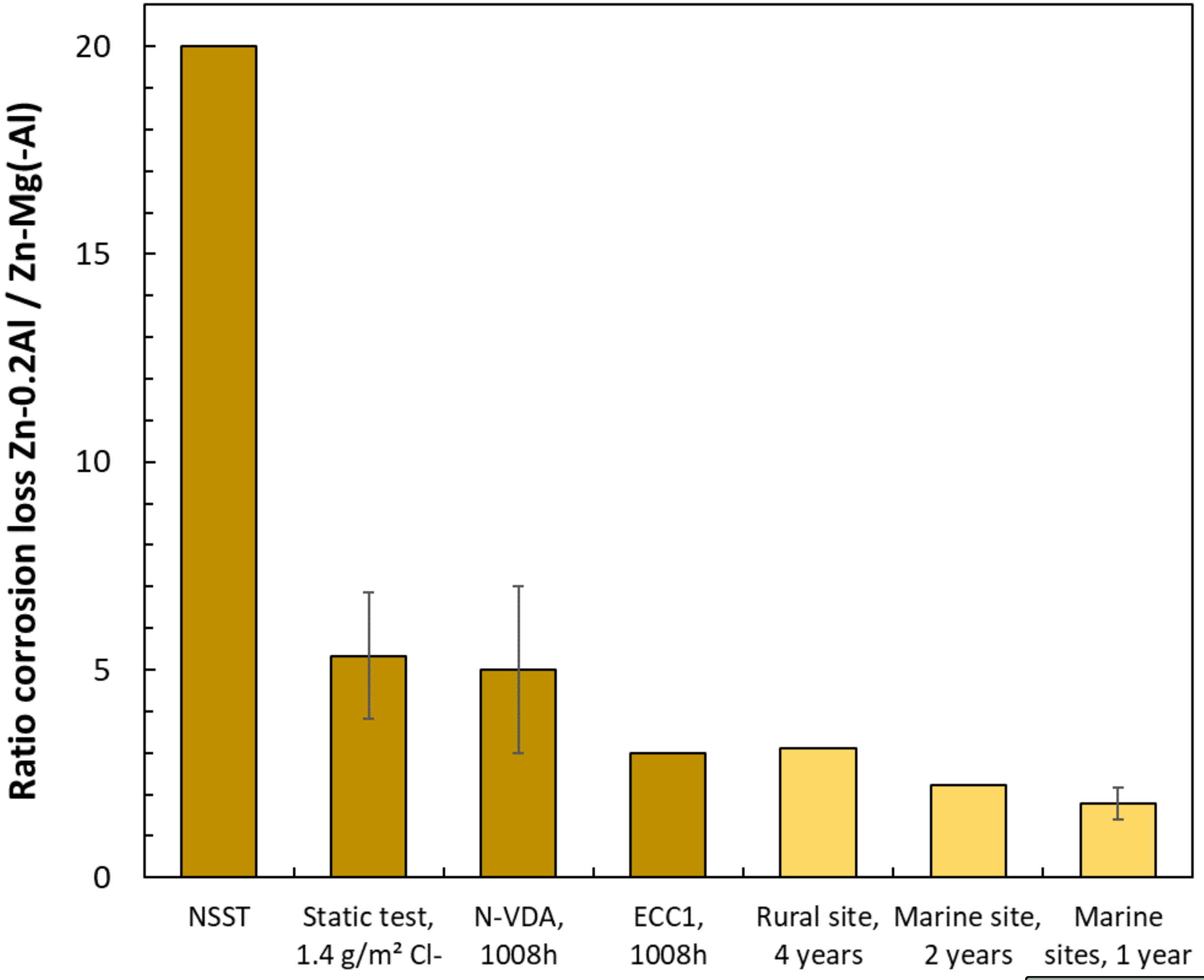
Accelerated Tests – Comparison

- **Example 3**: Alloy Zn coatings

- Zn-Mg and Zn-Al-Mg coatings perspective for many applications: weldability, formability, corrosion resistance







Accelerated Tests – Summary

- Salt spray test
  - Unrealistic
  - Missing correlation to results of exposure under service conditions
  - Applicable to quality control

- Cyclic accelerated tests **simulate better real environments** and they are optimal for **material selection, lifetime assessment** and **development of new anticorrosion measures** (especially for combined materials)

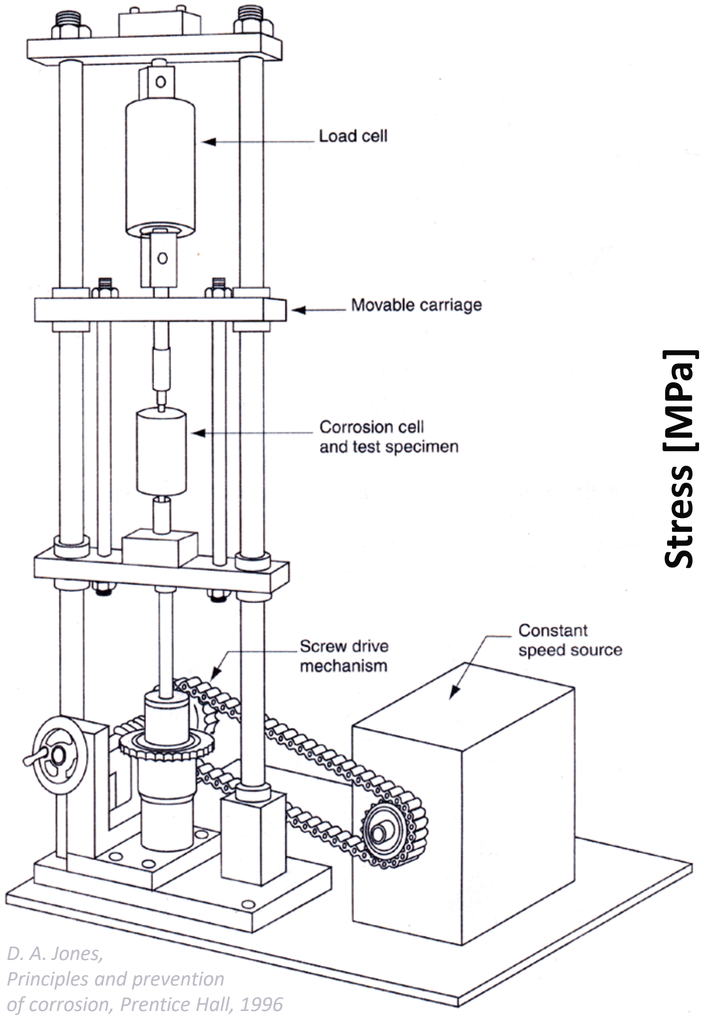
Accelerated Tests – Other Fields

- Many accelerated tests used in oil & gas, power generation, etc., e.g.:

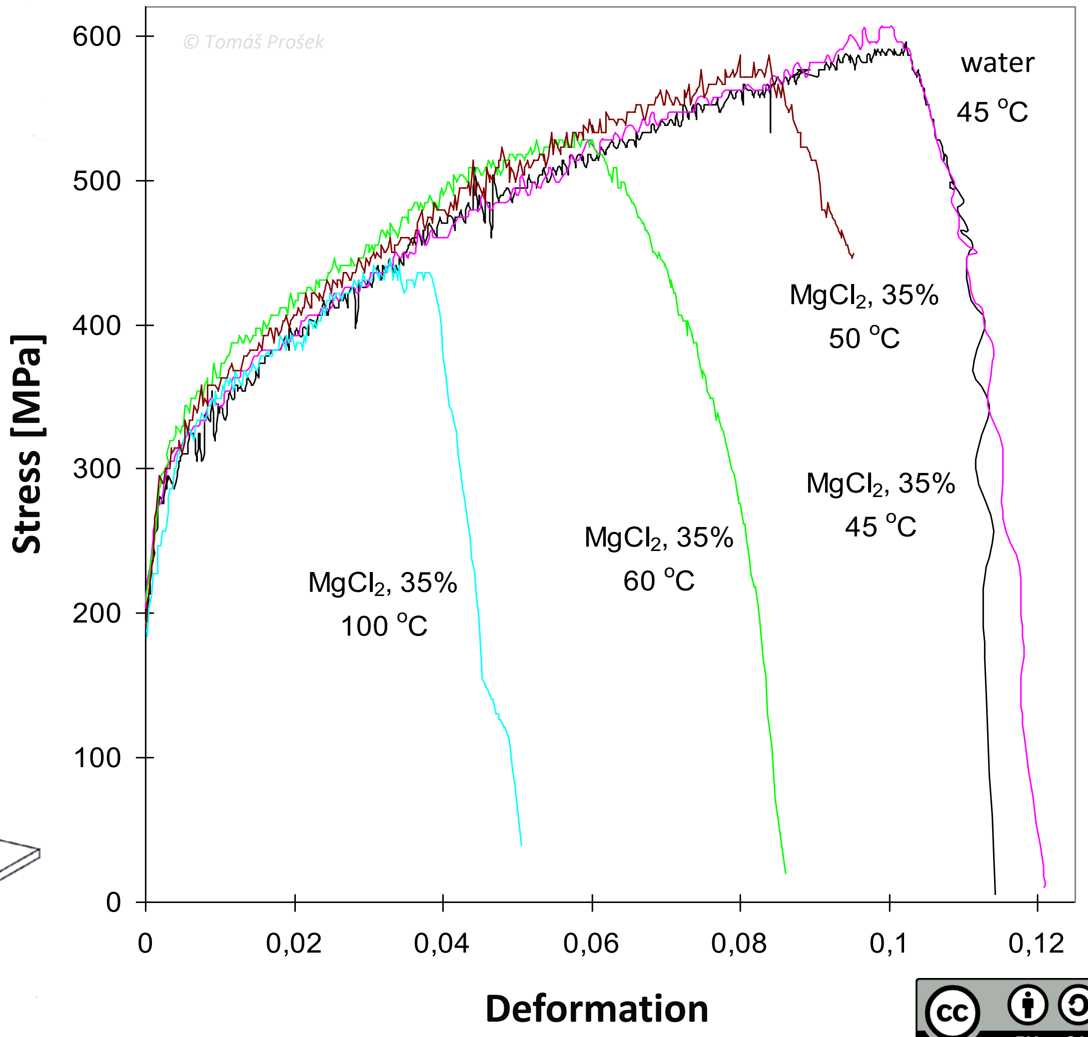
Stress corrosion cracking: Slow strain rate test (SSRT)

ASTM G129-00, Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking

ČSN ISO 7539-7, Zkouška koroze za napětí, Část 7: Zkoušení při malé rychlosti deformace



D. A. Jones, Principles and prevention of corrosion, Prentice Hall, 1996

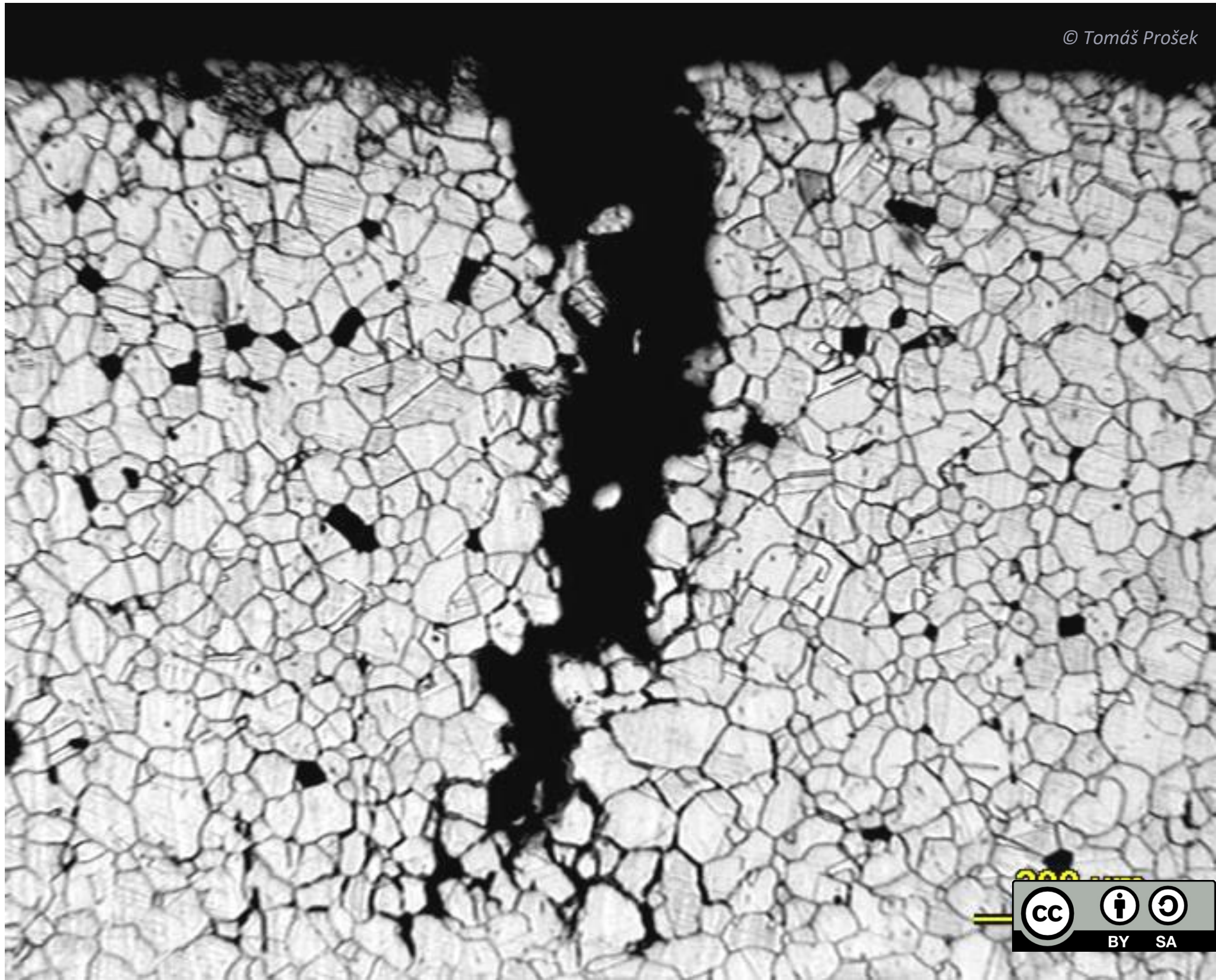


Accelerated Tests – Other Fields

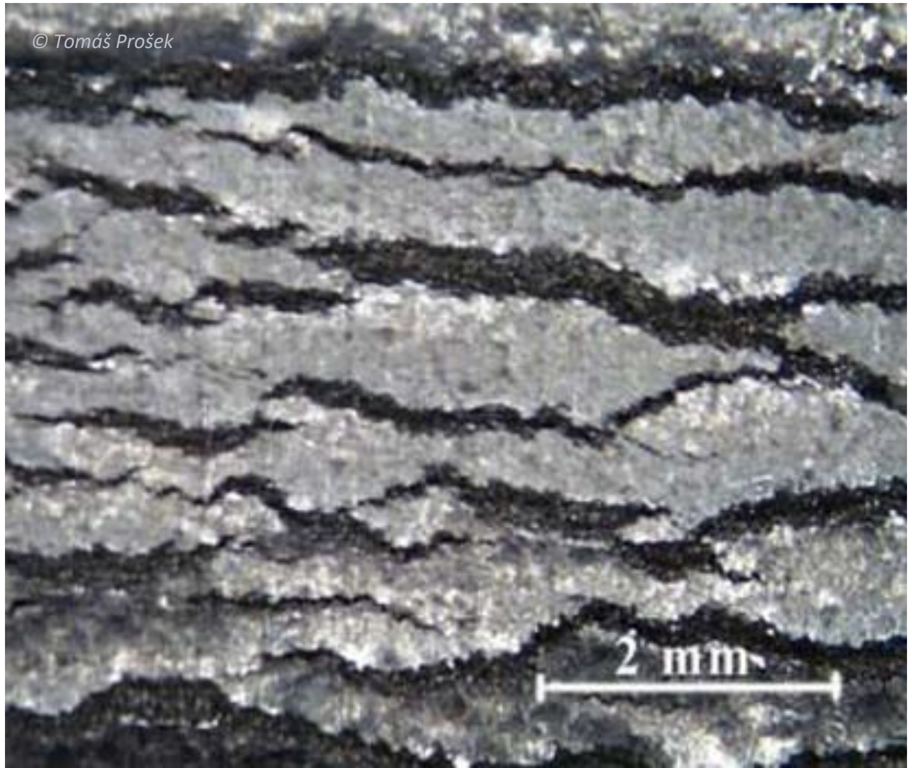
Intergranular corrosion of stainless steel

- Boiling 16 vol.% sulfuric acid with Cu shavings for 15 hours, then bending

ASTM A262 – 15, Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels, Practice E

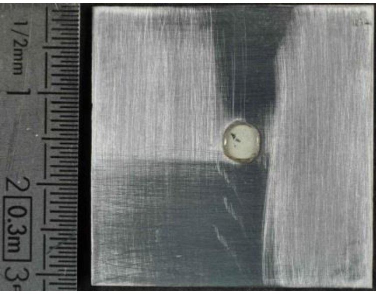


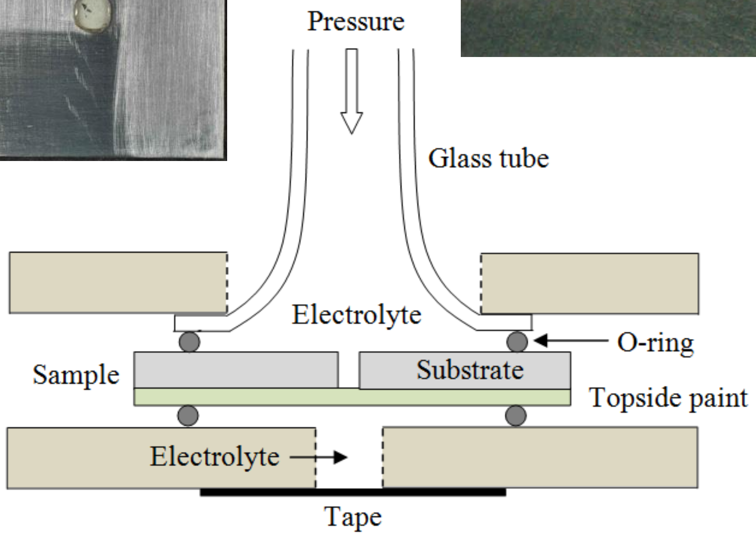
Stainless steel FeCr18Ni9, Strauss solution, after bending

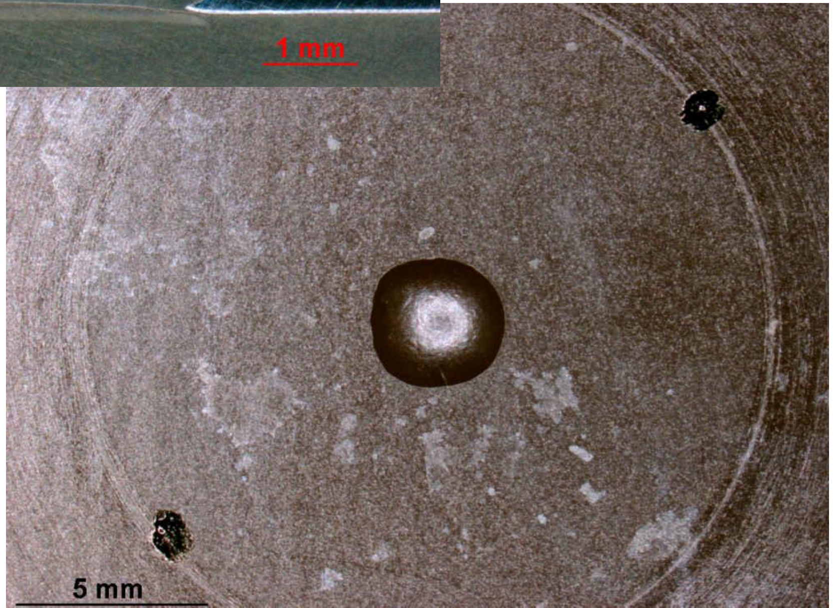


Lab Tests

- If an appropriate standardized accelerated test is unavailable
- Usually in research, but can be useful for material selection and other technical problems as well
- Focused on specific degradation mechanisms
- Example: Pressurized Blister Test (adhesion of organic coatings)







Lab Measurements

- Limited use
- Parameter correlating with corrosion resistance
- Link between the parameter and corrosion resistance needs to be well known and straightforward
- Examples:
  - Thickness of metallic or organic coating
  - Coating adhesion
  - Impedance response of coatings (electrochemical impedance spectroscopy)
  - Chemical composition (of stainless steel, aluminum alloys, …)

Summary

- Although time consuming and expensive, **tests in service environments provide the most valuable data;** they are irreplaceable at the final stages of **testing and qualification of new materials or anticorrosion solutions**
- **Standardized accelerated corrosion tests**
  - **Necessary for quality control and in early phases of product development**
  - **Applicability for lifetime assessment is limited**, because real environments are more complex
  - **There is space for optimization** based on comparison of results from service conditions
- **Lab tests** can be used when no relevant standardized test is available
- **Lab measurements** are complementary and can be used only if there is a clear correlation between corrosion resistance and the parameter measured

Copyright & Contact

Tomáš Prošek, Ph.D.

University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

www.vscht.cz

Corrosion Engineering

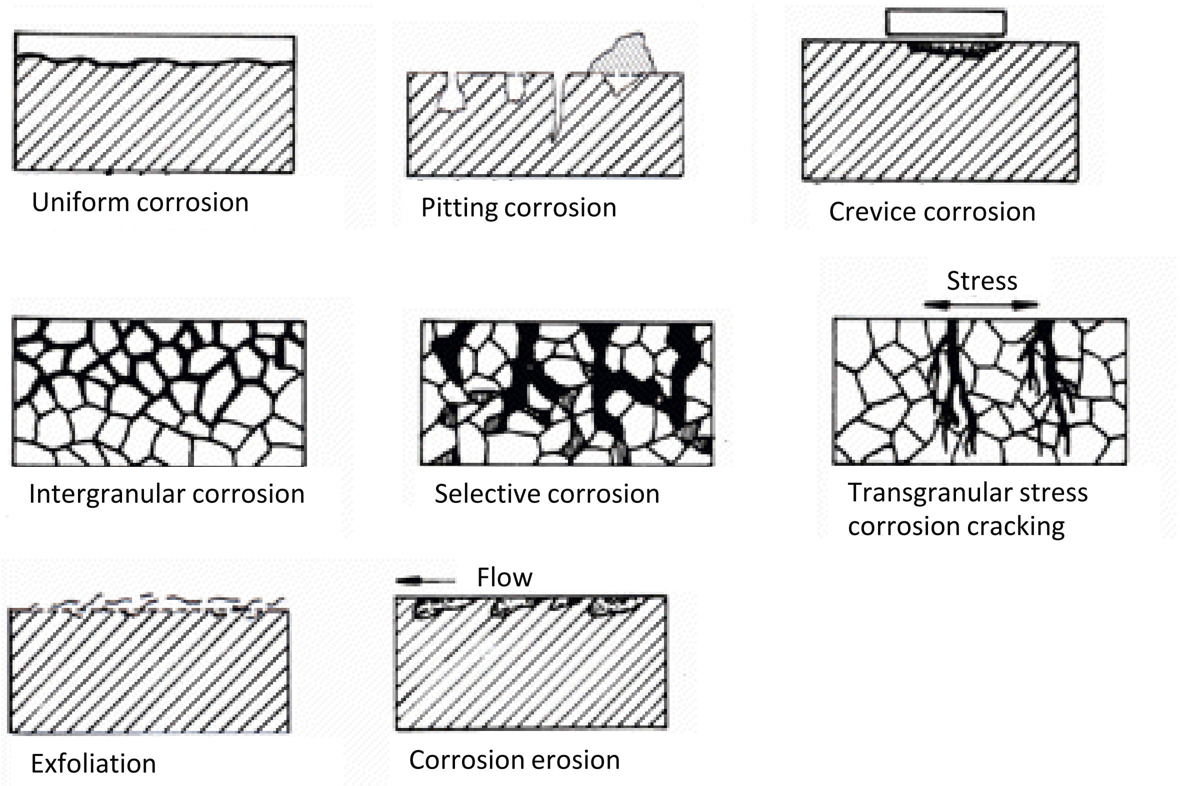
Milan Kouřil

Measurement of Corrosion Rate and Corrosion Monitoring

Meas. of v_{cor} and Corr. Monitoring

- **Quantitative data on corrosion properties**
  - Comparison of corrosion resistance of different materials – material selection, efficiency of anticorrosion measures
  - Lifetime prediction
- **Under operation**
  - Inspection
  - Corrosion monitoring
- **Lab conditions**
  - Simulation of service conditions
  - Accelerated tests

Corrosion Rate



- **Thickness reduction in time:**

  [mm/a], [mm/a], [mpy]

- **Mass loss per area in time:**

  [g/m^2·h]

Corrosion is an electrochemical process

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$H^+ + 2e^- \rightarrow H_2$$

$$O_2 + 2H_2O + 2e^- \rightarrow 4OH^-$$

Electrochemical methods [A/m^2]

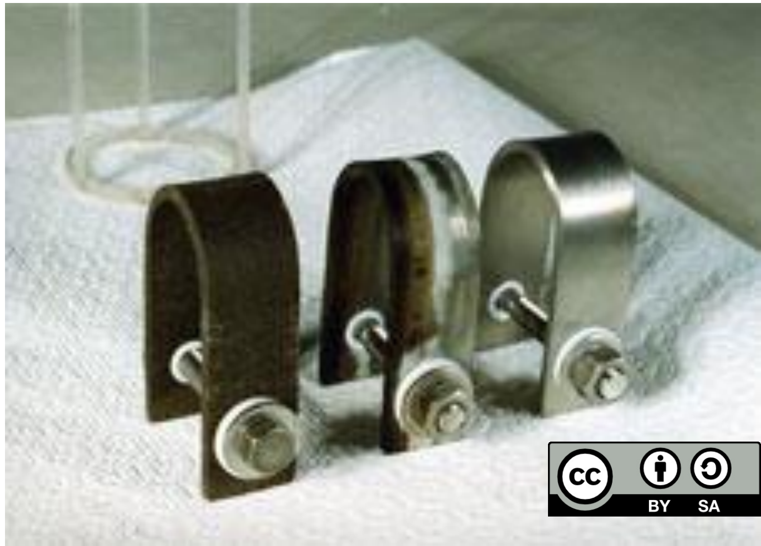
Analysis of corrosion environment

Corrosion Monitoring Methods

Method	Measures	Response	Measurement on
Electrochemical: • Free corrosion potential • LPR (polarization resistance) • ZRA (galvanic current) • EN (electrochemical noise) • Impedance techniques	 Indirectly corrosion rate Actual corrosion rate Corrosion degradation Non-uniform corrosion Corrosion rate	Immediate	 Probe or facility Probe under operation Probe under operation Probe under operation Probe under operation
Acoustic emission	Formation of cracks, leaks, erosion by particles	Immediate	Facility under operation
Electric resistance (resistometric)	Corrosion degradation	Medium	Probe under operation
Analysis of corrosion environment	Total corrosion of facility	Slow	Facility under operation
Released hydrogen	Uniform corrosion, hydrogen embrittlement	Slow	Probe or facility under operation
Ultrasound	Uniform corrosion, presence of cracks and pits	Slow	Facility under operation or during shutdown
Electromagnetic, induction	Distribution of non-uniform corrosion	Slow	Facility during shutdown
Visual inspection	Distribution of corrosion degradation, pits, cracks	Slow	Facility during shutdown
Radiation	Distribution of non-uniform corrosion	Slow	Facility under operation or during shutdown
Thermography	Distribution of corrosion degradation	Slow	Facility under operation
Changes in mass and dimension	Average corrosion rate	Very slow	Facility under operation or during s

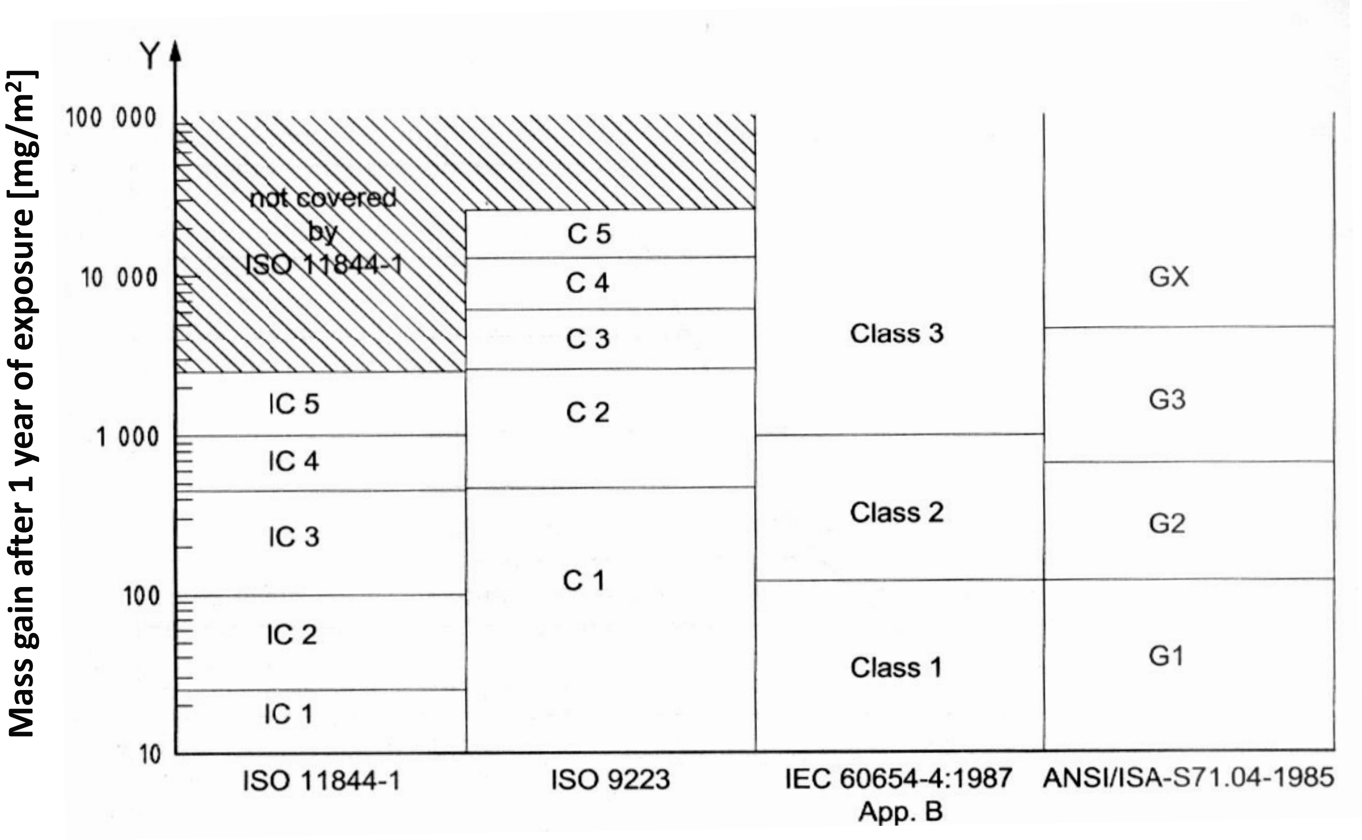
Corrosion Coupons

- Corrosion coupon = sample of material exposed to real environment
- Evaluation
  - Change in mass after given exposure time – **average corrosion depth (mm/a)**, (ČSN) EN ISO 8407 sets rules for removal of corrosion products
  - Type of corrosion degradation – uniform corrosion, pitting – depth of attack
- Implementation
  - To be representative, parallel samples needed
  - Sample removal during operation
  - Critical location – weld, crevice, etc.
  - Dependence of corrosion rate on time: periodical sample removal



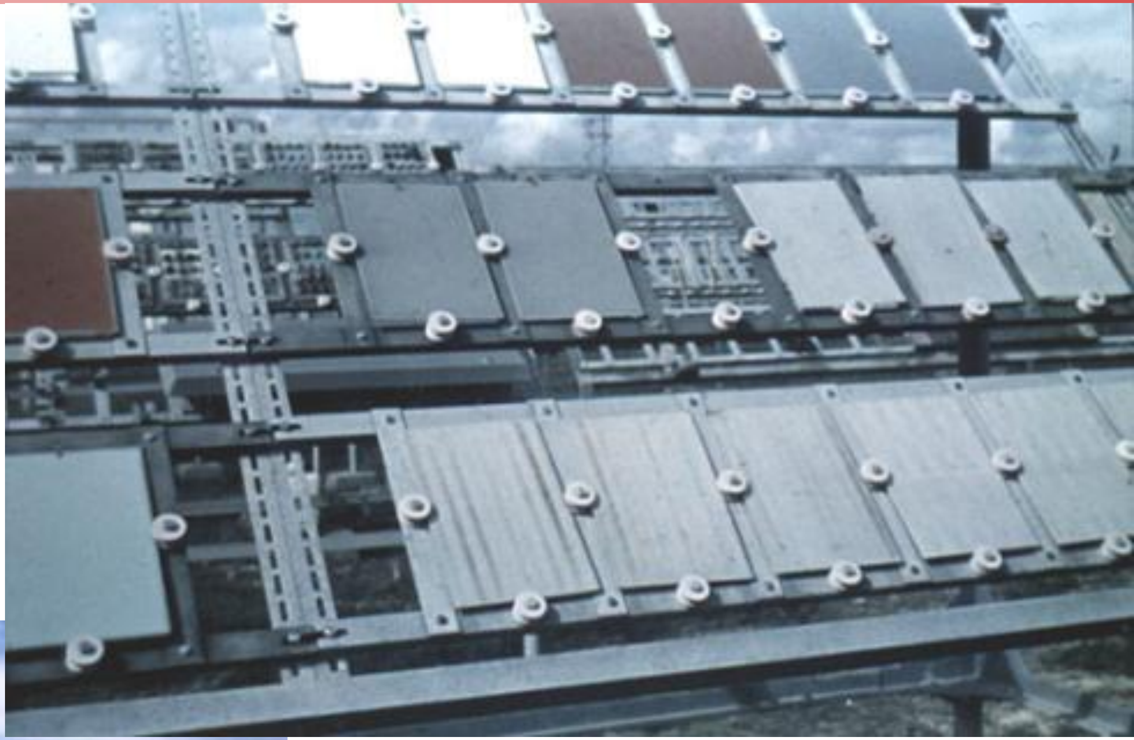
Coupons – Atmospheric Corrosion

- Corrosivity classes:
  - (ČSN) EN ISO 9223: Mass loss after 1 year of exposure
  - ISA-S71.04: Film thickness on copper after 30 days in industrial areas
  - ISO 11844-1: corrosion rate of silver and copper after 1 year of exposure
  - de Santoli et al.: Film thickness on copper and silver after 30 days of exposure



Coupons – Atmospheric Corrosion

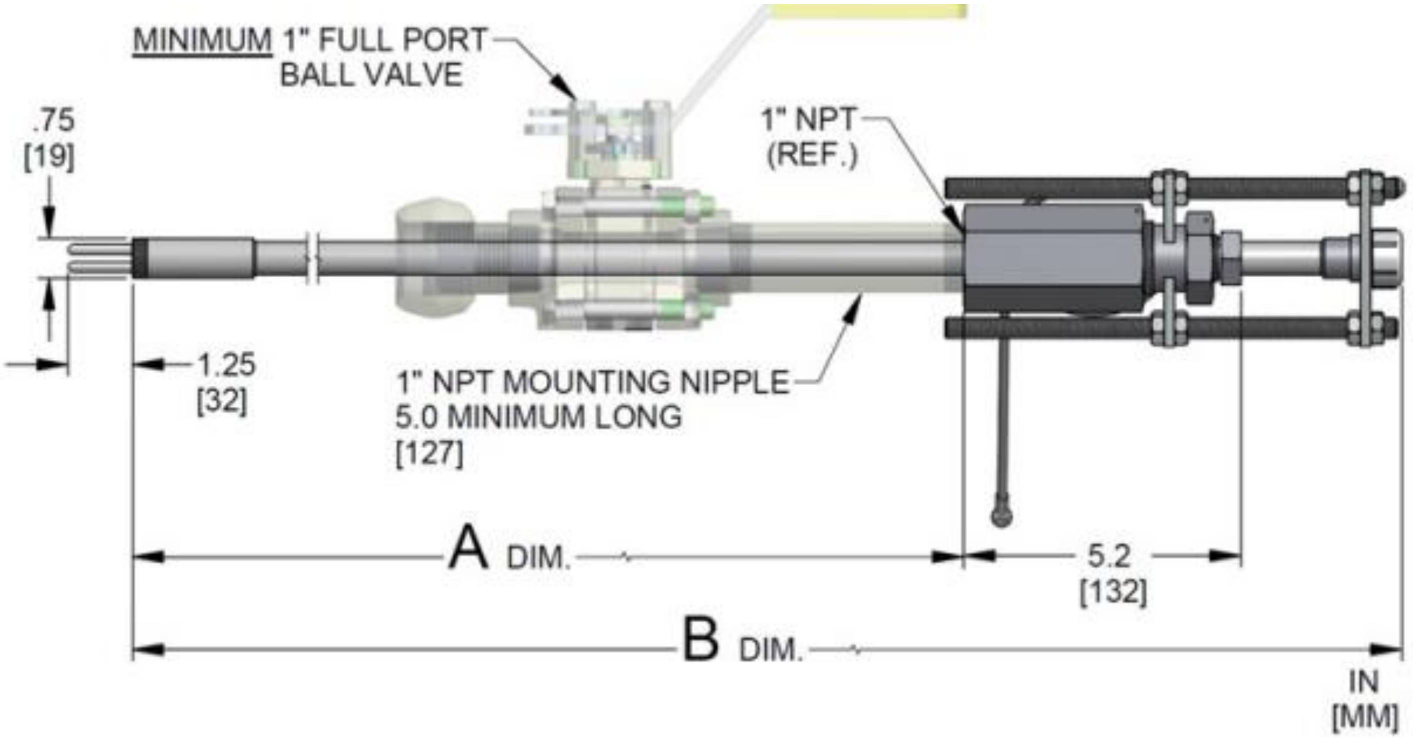
- (ČSN) EN ISO 9223: C1–C5, CX
- Corrosion rates at C3 (mm/a):
  - Steel < 10
  - Copper < 2
  - Zinc < 2
  - Aluminum < 0.2



Novák et al., Korozní inženýrství, UCT 2002

- **Polarization resistance – probe**
  - Fixed or removable, for chemical industry
    - Up to 150 °C, 10 MPa
    - Practically all materials available

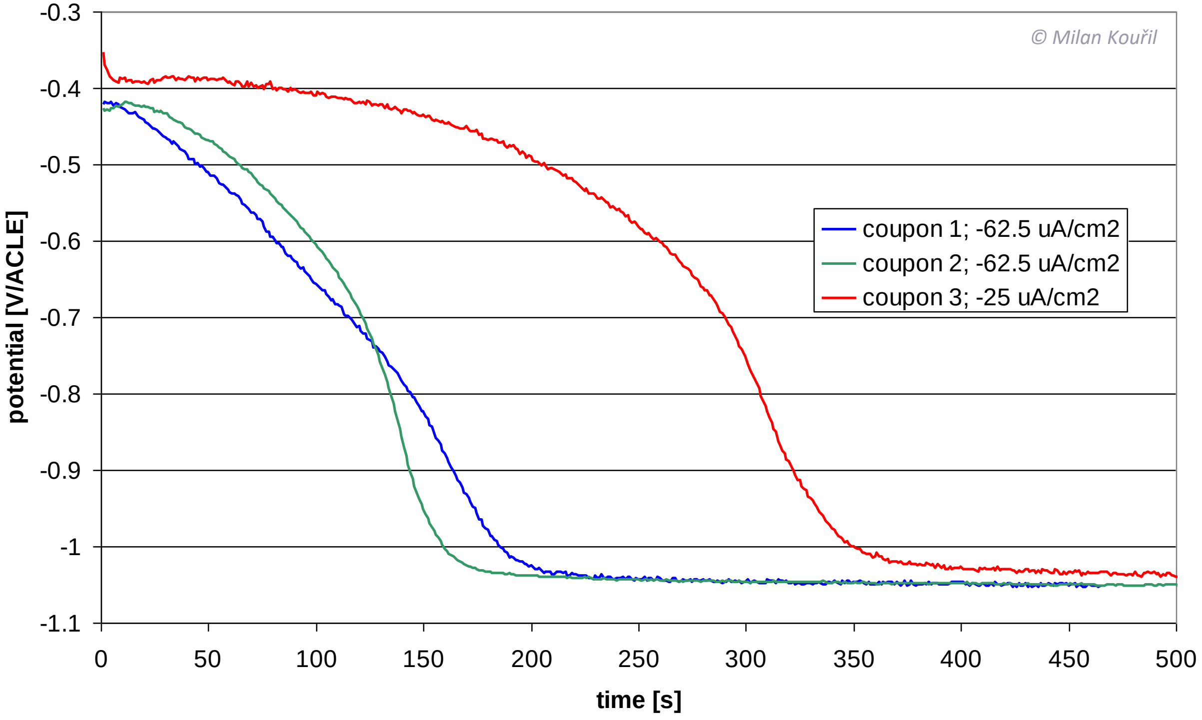
http://www.cosasco.com/images/two_electrode_lpr_adjustable_corrosion_probe.jpg

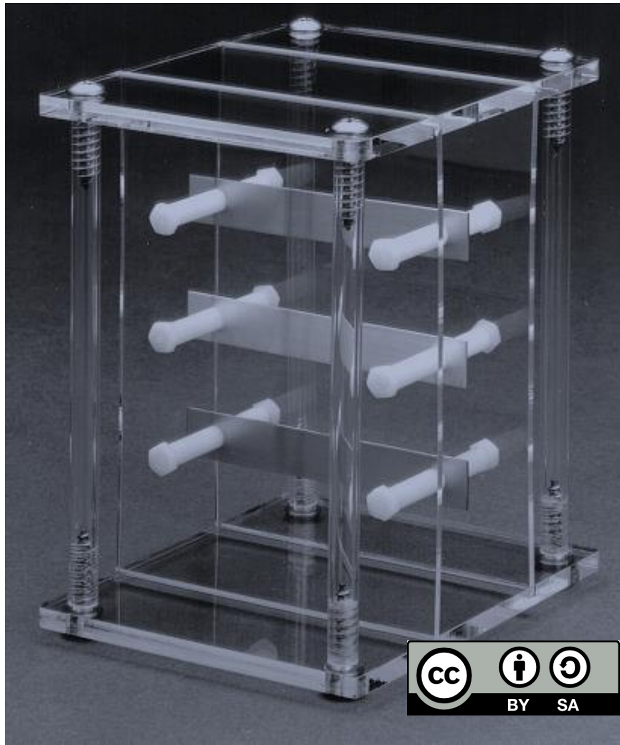


Coupons – Atmospheric corrosion

- Assessment of the amount of corrosion products from **electric charge** necessary for their reduction to metal
  - Well established for Cu and Ag
  - Exposure for at least 30 days
  - Real time monitoring impossible

Environmental Classification for Museums Silver Corrosion		
Class	Air Qualify Classification	Corrosion Rate (Å/30 Days)
S1	Extremely Pure	<40
S2	Pure	<100
S3	Clean	<200
S4	Slightly Contaminated	<300
S5	Polluted	≥300





Monitoring of Atmospheric Corr.

- Quartz crystal micro balance
  - Quartz crystal covered with metal film
  - Resonance frequency depends on mass:

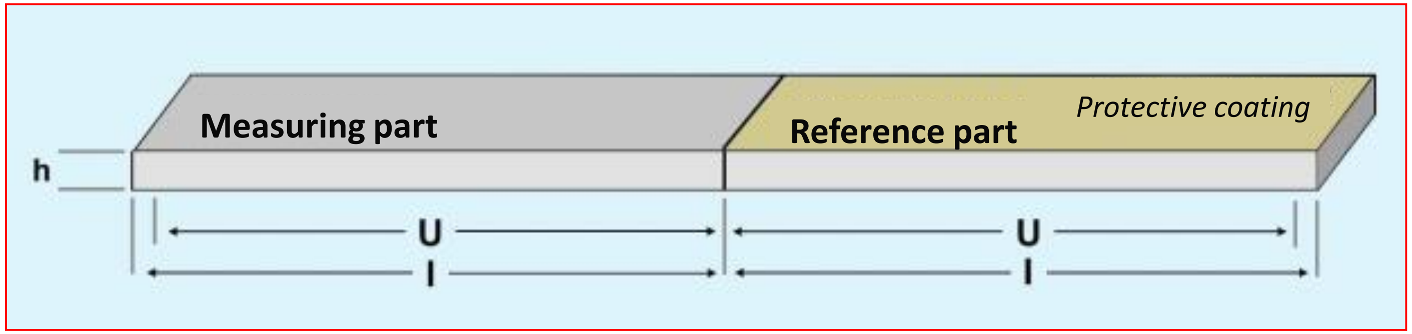
$$\Delta f = -\left(\frac{f_0^{\,2}}{N \cdot \rho_q}\right) \cdot \Delta m$$

Δf	Frequency change
N	Frequency constant
ρ	Density
Δm	Mass change

- High sensitivity
- Detection of whatever change in mass

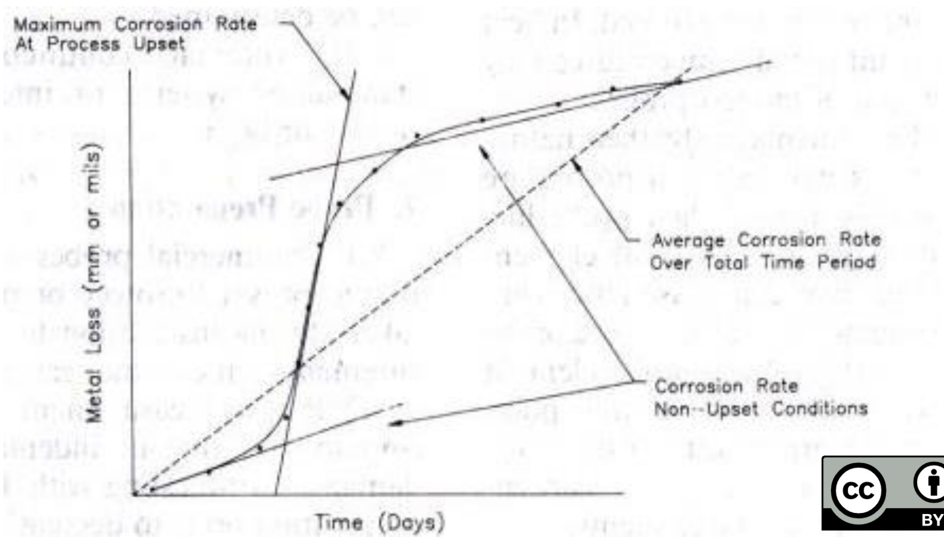
Resistometric Method

$$R = \rho \cdot \frac{l}{S} \qquad R = \rho \cdot \frac{l}{h.š}$$



- Corrosion probe – metallic sample with small size of one dimension (a small change in the dimension leads to a significant change in electric resistance)
- Change in ER with temperature:
  - Compensation necessary, measuring and reference parts

$$\Delta h = h_0 \cdot \left(1 - \frac{R_R}{R_M} \cdot \frac{R_{M,0}}{R_{R,0}}\right) \qquad \rho(T) = \rho(T_0) \cdot (1+\alpha)^{T-T_0}$$

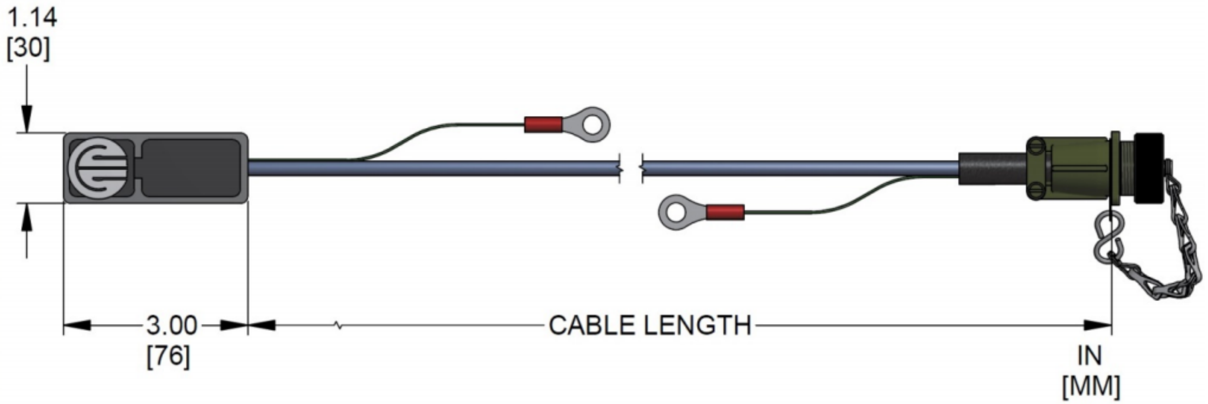


Resistometric Method

- **Resistometric probes**
  - Fixed or removable for chemical industry
    - Up to 520 °C, 27 MPa
    - Non-alloyed steel, stainless steel, nickel alloys

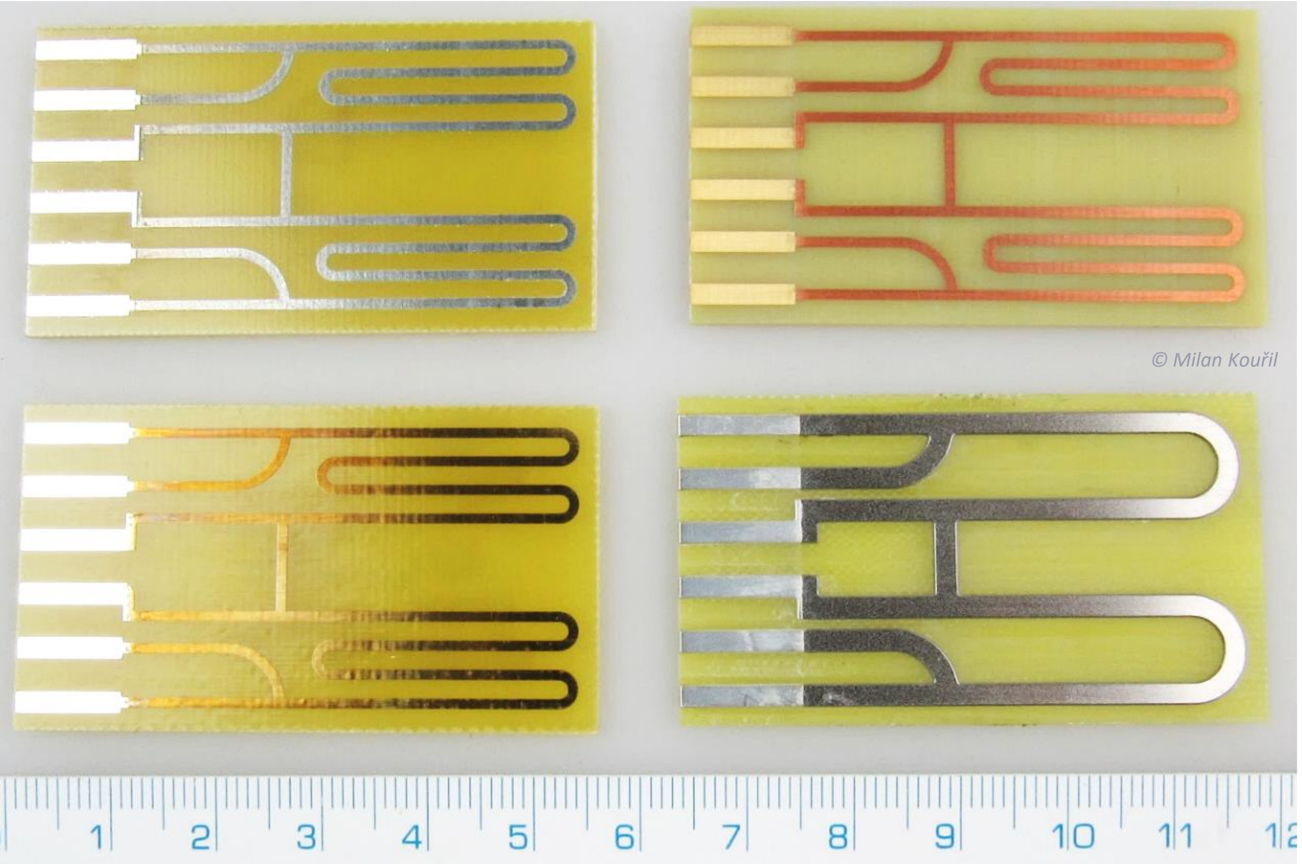
Resistometric Method

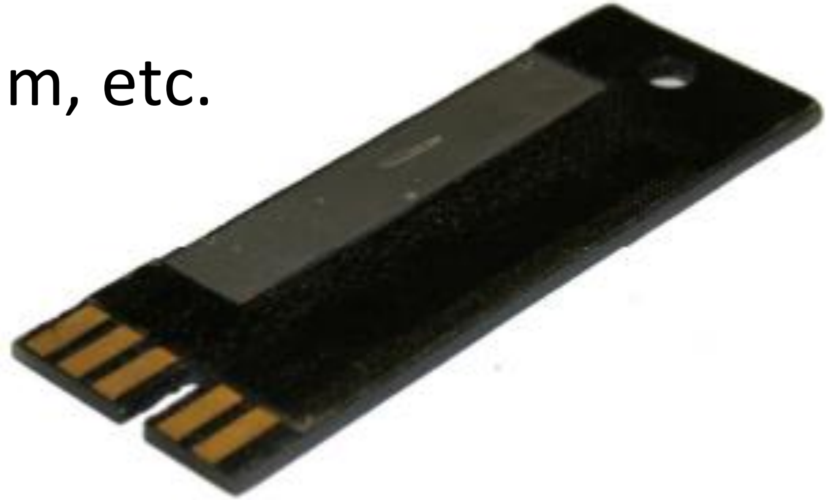
- **Resistometric probes**
  - For soil and concrete
    - Up to 520 °C, 27 MPa
    - Non-alloyed steel, stainless steel, nickel alloys

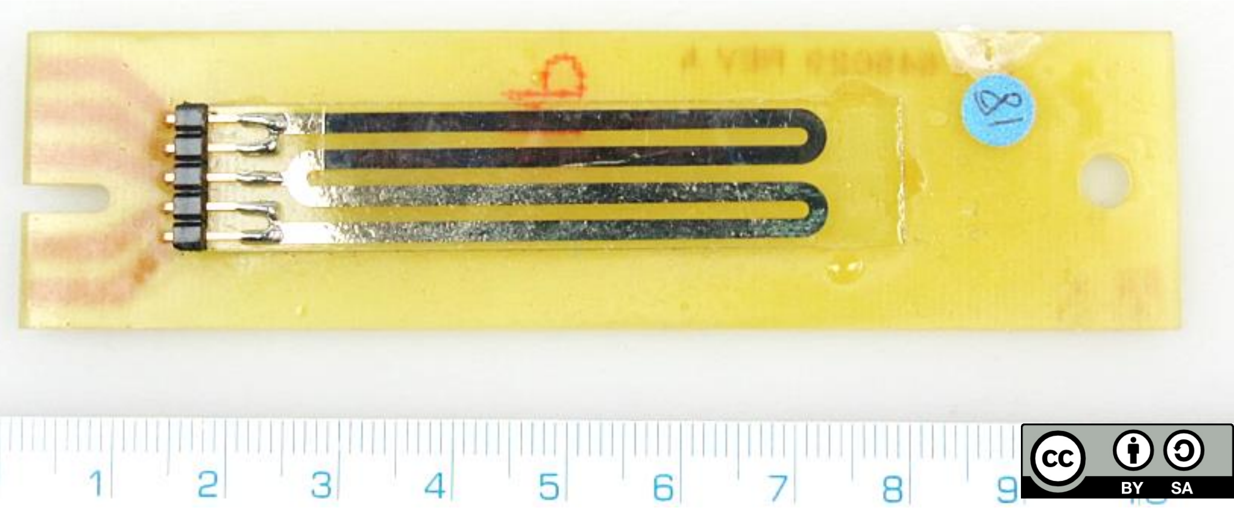


Resistometric Method

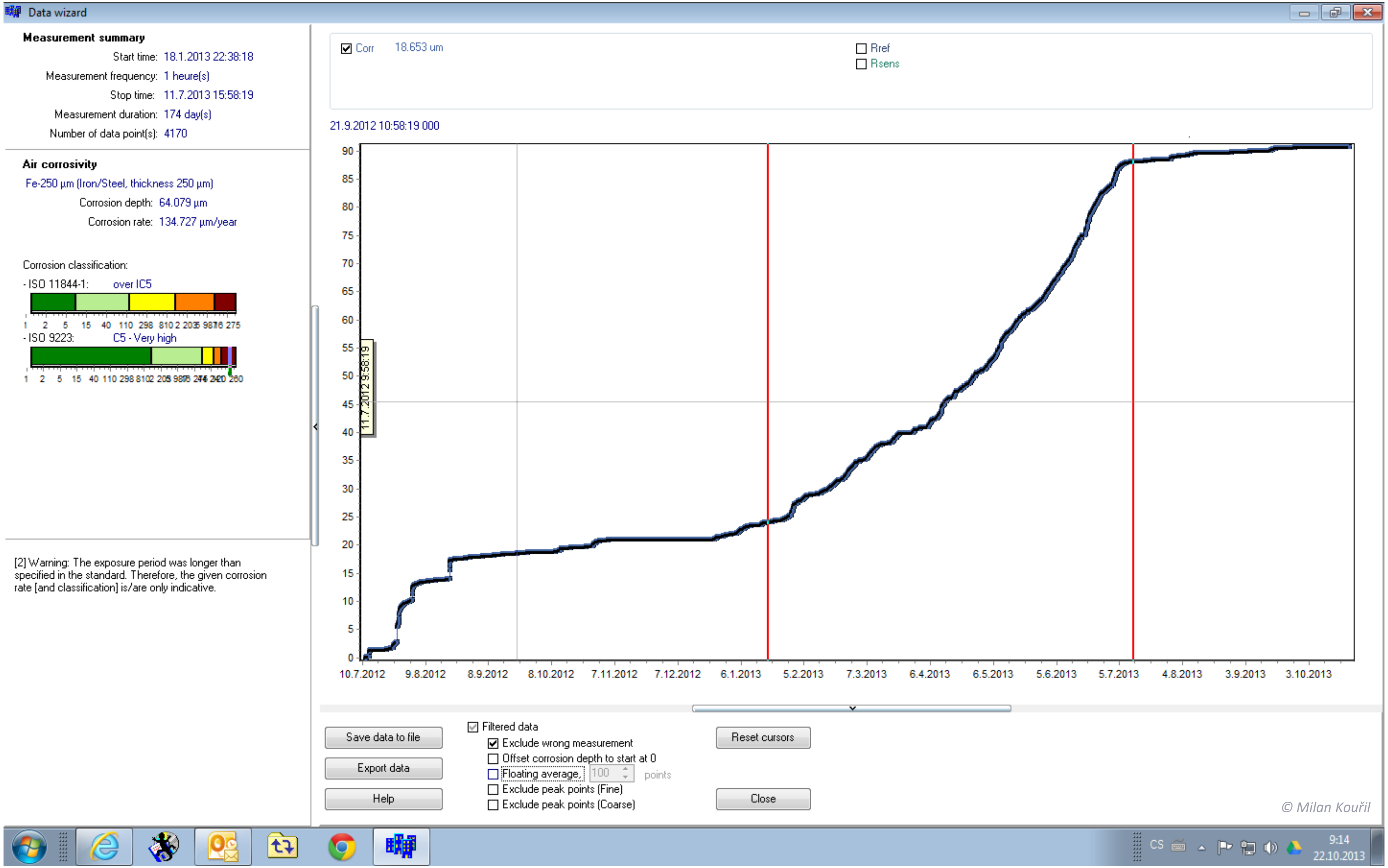
- **Resistometric probes**
  - For atmosphere
    - Copper and alloys, silver, steel, lead, aluminum, etc.





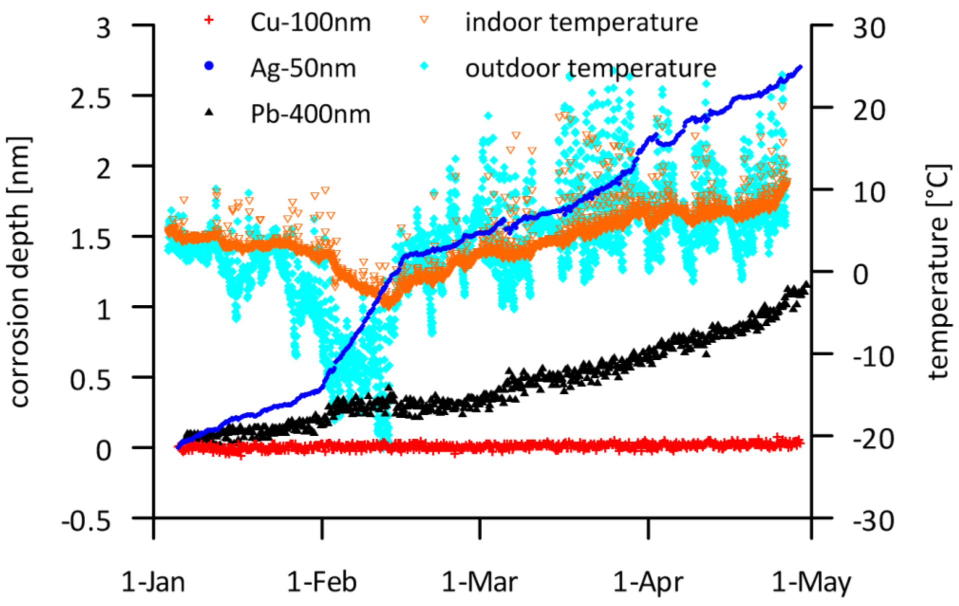


Resistometric Method

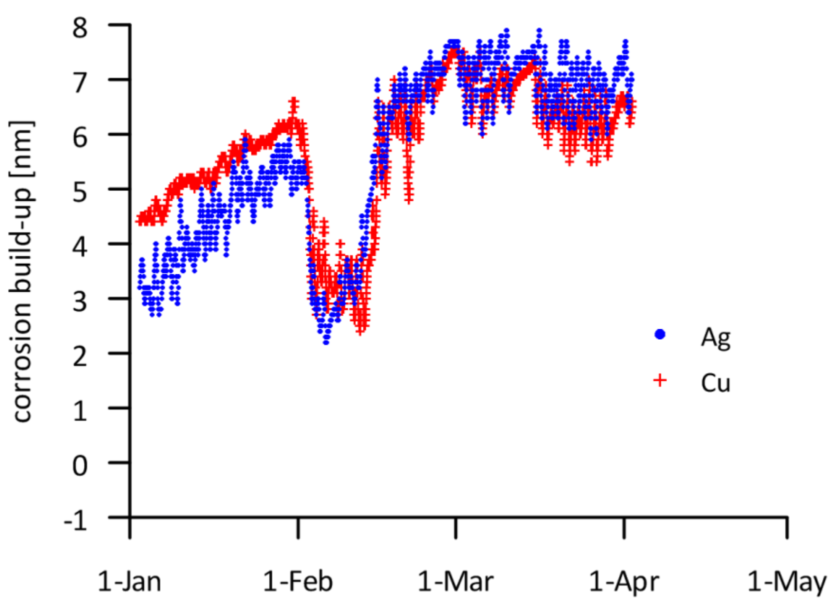


Resistometric Method

Resistometric method

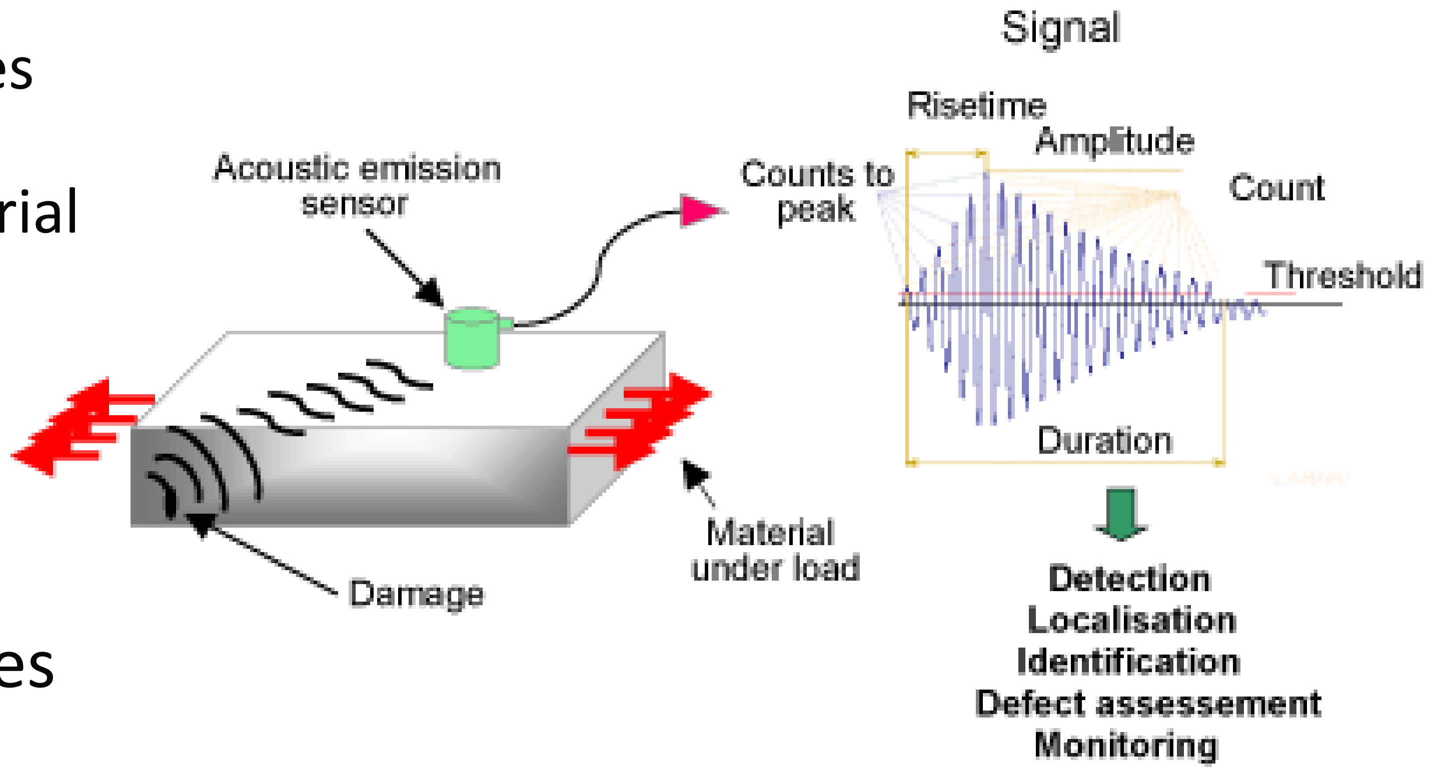


Quartz crystal micro balance



Acoustic Emission

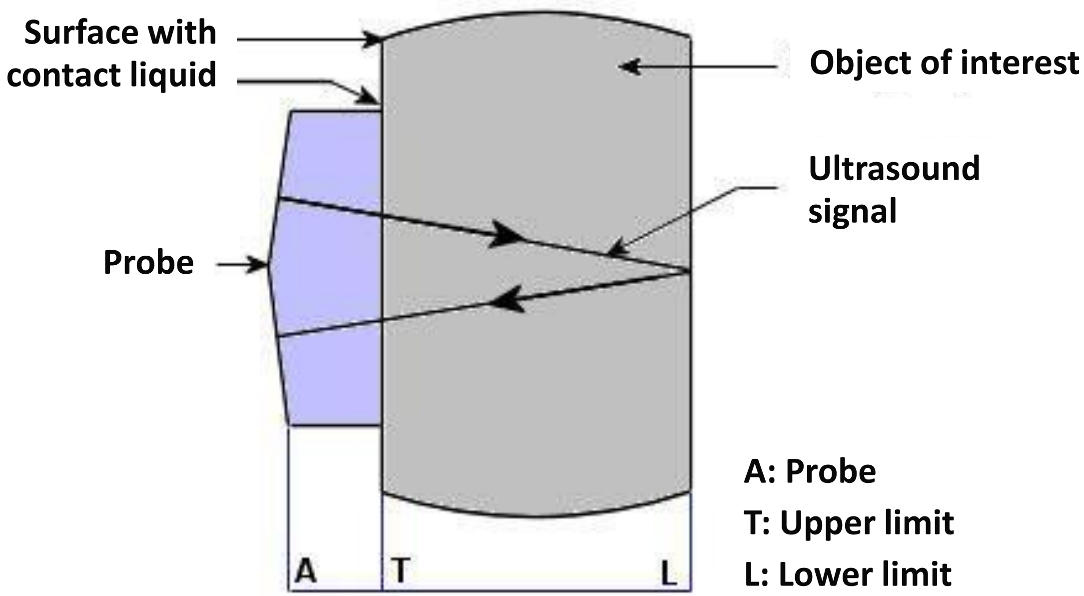
- Detection of defect formation
  - Measurement of acoustic pulses emitted during initiation and propagation of defects in material
- Suitable for non-uniform corrosion, mainly SCC
- Sensitive piezoelectric sound sensors
- Placement close to critical zones (welds, tension)
- Qualitative information
- Disturbance needs to be eliminated

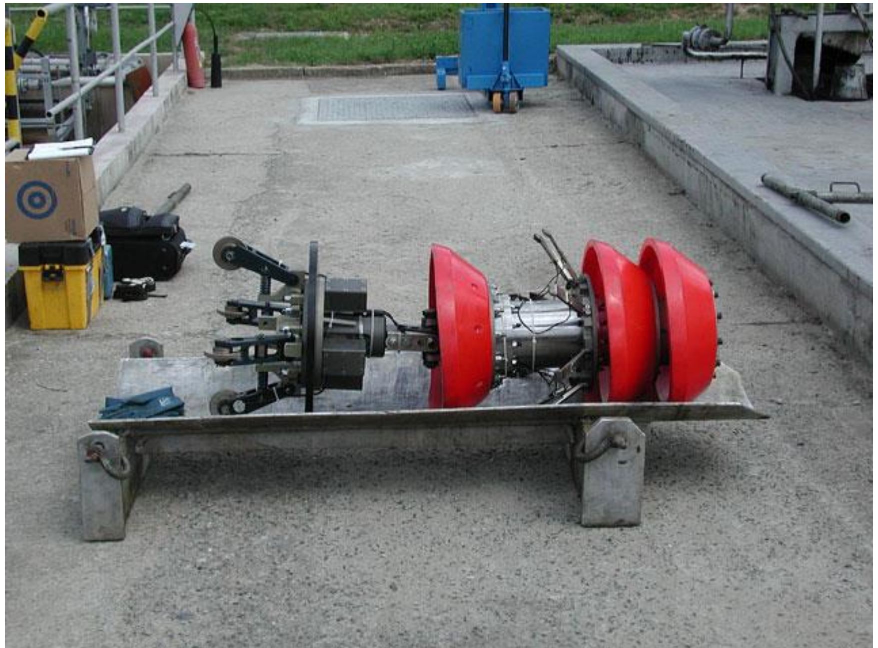


Ultrasound Sensors

Thickness measurement by ultrasound

- Measurement directly in the facility of interest
- Inspection of the inner, non-visible surface
- Sensitivity in micro meters
- Measurement of time until the impulse returns back from the opposite surface





Electrochemical Methods

- **Potential – qualitative assessment**
  - Free corrosion potential – passivity vs. activity
  - Protection potential – setting the cathodic and anodic protection
  - Redox potential – amount of oxidation agent in environment (oxymeter, Pt – inert metal)
  - Potential of ion-selective electrode – amount of aggressive ions
  - pH electrode potential
- **Rate – corrosion current (density)**
  - Corrosion rate from polarization resistance
  - Galvanic current

$$m = \frac{M}{z} \cdot \frac{I.t}{F}$$

$$v_k [mm/a] = j_{kor} \cdot \frac{M}{z.\rho.F} \cdot 60 \cdot 60 \cdot 24 \cdot 365$$

Electrochemical Methods

- **Polarization resistance**

$$R_p \approx \frac{1}{v_k}$$

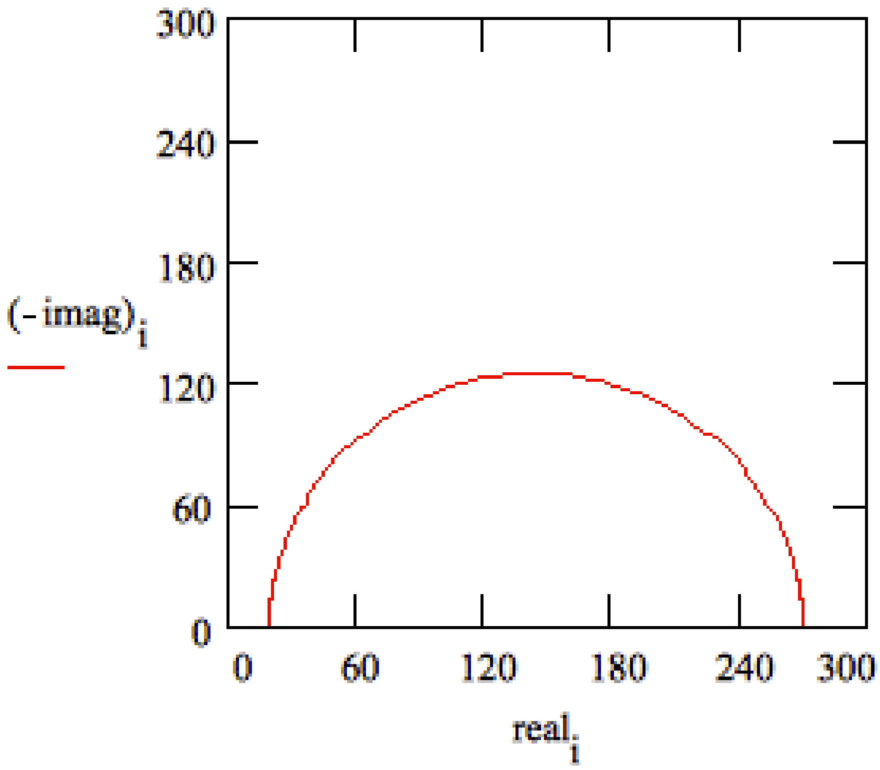
$$R_p = \frac{B}{j_{kor}}$$

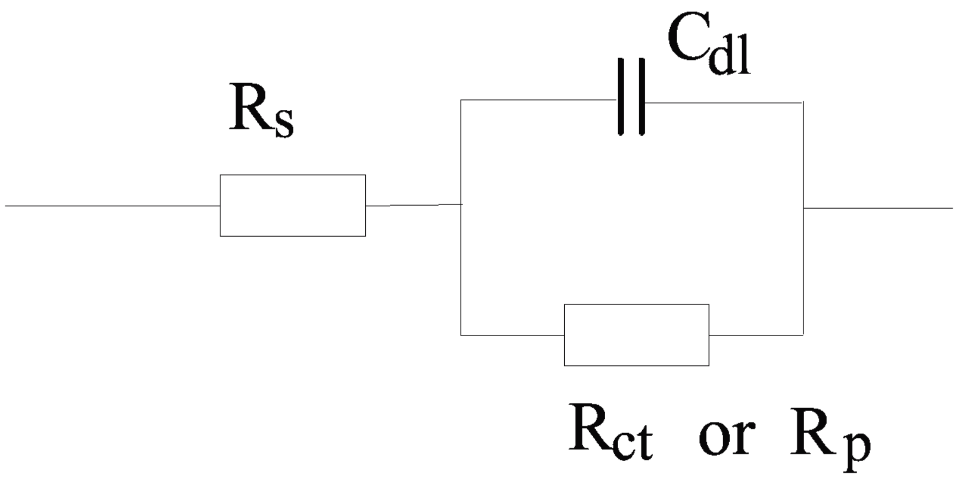
http://www.cosasco.com/images/two_electrode_lpr_corrosion_probe.gif

$$R_p = \frac{\Delta E}{I}$$

- B often unknown, but change of R_p in order of magnitude is equal to a similar change in corrosion rate
- Response: Minutes, actual corrosion rate
- Limited to conductive environments
- Calculation of corrosion rate of uniform corrosion

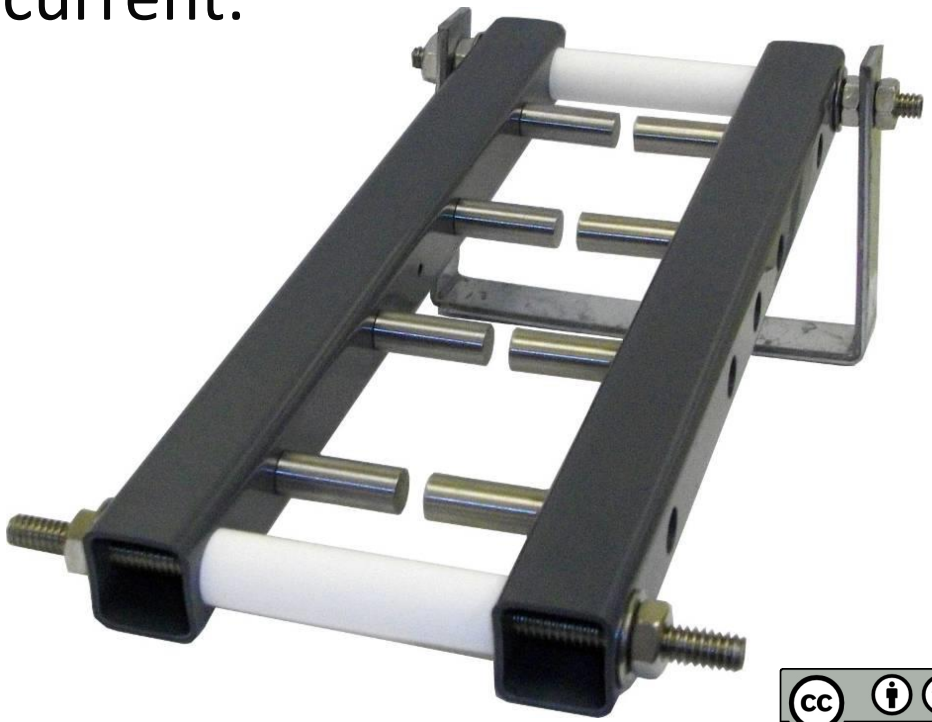
- **Electrochemical impedance spectroscopy**
  - Excitation by alternating current





Electrochemical Methods

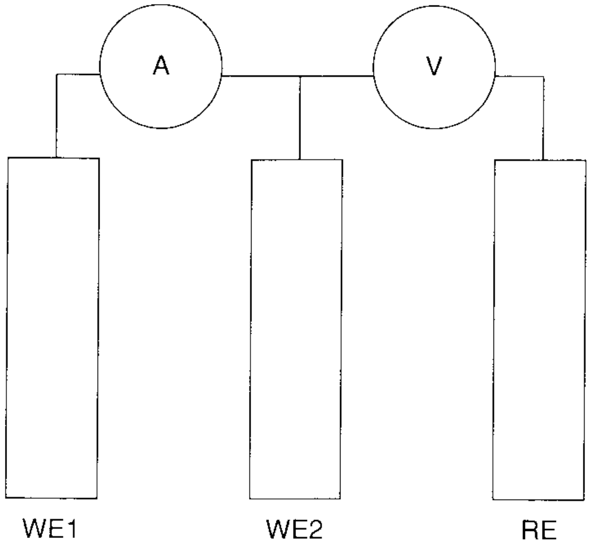
- **Current in galvanic couple**
  - Higher corrosivity of the environment leads to an increase in galvanic current between dissimilar metals
  - Current between such metals correlates to i_{corr}
  - Measurement of galvanic current:
    - Current recorder
    - Bypass potential



http://www.intertek.com/uploadedImages/Blocks/Images/Divisions/Industry_Assurance/EP/IMG_1456%20LATEST%20M4%20PROBE.jpg?n=2005

Electrochemical Methods

- **Electrochemical noise**
  - Recording of immediate changes in the potential or current
    - Instant damage of passive film – anodic process
      - Small changes in the potential in anodic direction – potential noise
      - Current flowing between two identical samples – current noise



4.1 Three-electrode method of EN measurement.

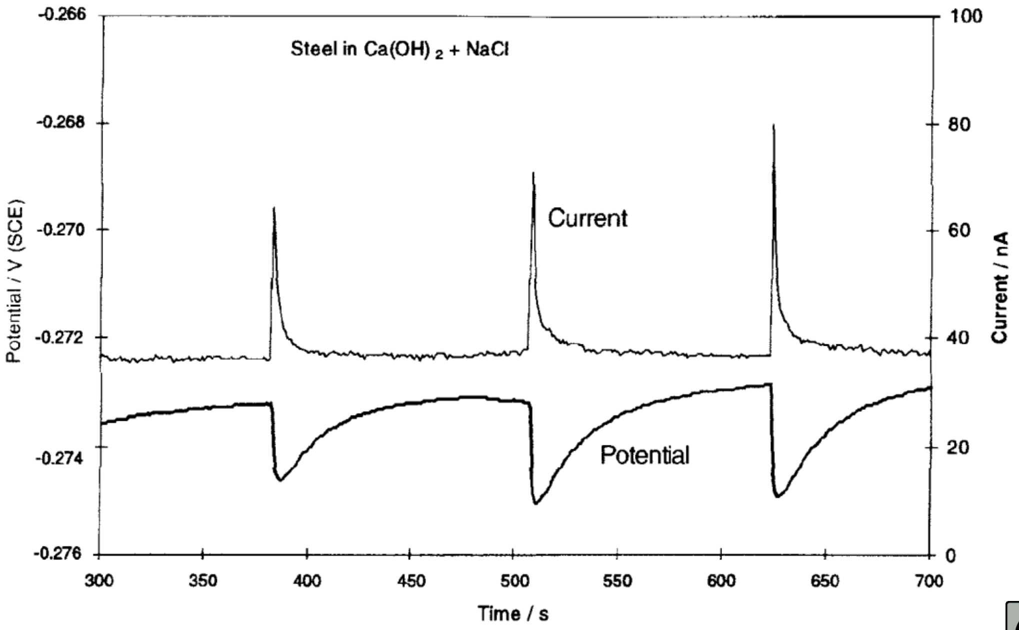


FIGURE 7.1. Current and potential time records for a steel sample in 0.05M $Ca(OH)_2$ + 0.025M NaCl solution, showing

Electrochemical Methods

- **Data acquisition**
  - Portable recorders, data loggers, distant monitoring

Copyright & Contact

Tomáš Prošek, Ph.D.

University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

Corrosion Engineering

Exercises

Šárka Msallamová

Tomáš Prošek, Ph.D.
University of Chemistry and Technology Prague
Technická 5, 166 28 Praha 6, Czech Republic
tomas.prosek@vscht.cz
+420 220 446 104, +420 723 242 413

Lesson 1

a) Calculation of corrosion rates from the current density; derivation of units ($mm.a^{-1}$, $kg.m^2.s^{-1}$).
b) Calculation of Fe corrosion rate in the closed water system.

Example 1

Calculate corrosion rates for:

a) **Fe**, M_{Fe} = 55.85 $g.mol^{-1}$, ρ_{Fe} = 7.86 $g.cm^{-3}$
b) **Zn**, M_{Zn} = 65.39 $g.mol^{-1}$, ρ_{Zn} = 7.13 $g.cm^{-3}$
c) **Al**, M_{Al} = 26.98 $g.mol^{-1}$, ρ_{Al} = 2.7 $g.cm^{-3}$
d) **Cu**, M_{CU} = 63.55 $g.mol^{-1}$, ρ_{Cu} = 8.96 $g.cm^{-3}$

The current density is j = 1 $A.m^{-2}$. Specify units in [$mm.a^{-1}$] and [$g.m^{-2}.h^{-1}$].

Example 2

Calculate a decrease in the thickness of steel pipes and heaters after every filling of the heating system with aerated water; calculate a change of pH of the electrolyte. The volume of water in the system is 150 litres. The heating system consists of 12 pieces of steel heaters and 60 meters of supply steel pipes. The surface of each heater is 4.5 m^2 and the surface of supply pipes is 4.5 m^2.

M_{Fe} = 55.85 $g.mol^{-1}$

Lesson 2

a) Nernst equation.
b) E-pH diagrams.

Example 1

Construction of E-pH diagram for Cu-H_2O

$c_{Cu} = 10^{-6}$ mol.l^{-1}, t = 25 °C, p = 101 325 Pa

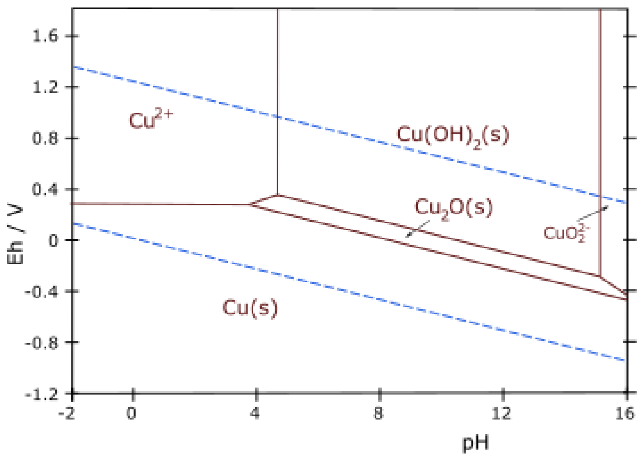


Fig. 1 E-pH diagram Cu-H_2O

Lesson 3

a) Construction of j-E diagrams.
b) Construction of log j – E diagrams.

- Equilibrium potential, mixed potential
- Bimetallic couple
- Concentration cell

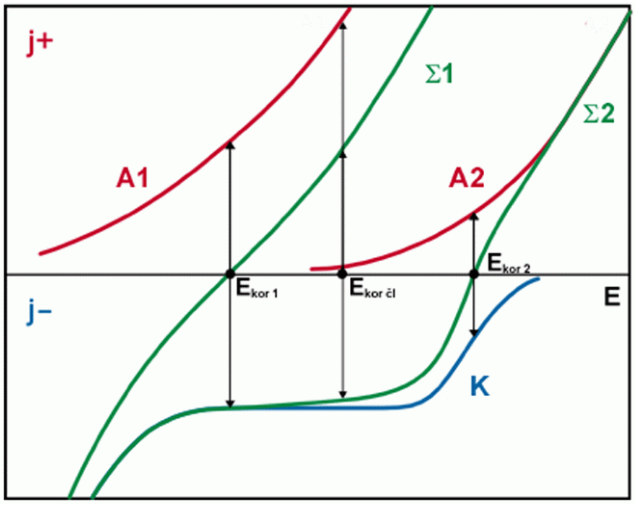


Fig. 2 Principle of bimetallic couple

Lesson 4

a) Kinetics of corrosion reactions.
b) Butler – Volmer equation.

Example 1

Calculate the corrosion rate of Zn and Fe in diluted hydrochloric acid. Construct the log j-E diagram. Compare the calculated value of corrosion current density $j_{corr(Zn)}$ and $j_{corr(Fe)}$ with the value of $j_{corr(Zn)}$ and $j_{corr(Fe)}$ from the constructed log j-E diagram. Explain the corrosion rate difference between both of the metals used in the measurement in diluted hydrochloric acid.

Zn:

$E_{r(Zn)} = –0.7$ V, $E_{(Zn)} = 0$ V, $j_{0\,(Zn)} = 10^{-7}$ A.cm^{-2}, $E_{r(H,\,Zn)} = 0$ V, $E_{(H,Zn)} = –0.7$ V, $j_{0(H)} = 10^{-10}$ A.cm^{-2},
$\beta_A = 0.1$ V.dec^{-1}, $\beta_c = –0.1$ V.dec^{-1}

Fe:

$E_{r(Fe)} = –0.44$ V, $E_{(Fe)} = 0$ V, $j_{0\,(Fe)} = 10^{-6}$ A.cm^{-2}, $E_{r(H,\,Fe)} = 0$ V, $E_{(H,Fe)} = –0.44$ V, $j_{0\,(H)} = 10^{-10}$ A.cm^{-2},
$\beta_A = 0.1$ V.dec^{-1}, $\beta_K = –0.1$ V.dec^{-1}

Lesson 5

Summary test I

Lesson 6

a) Explanation and correction of mistakes from summary test I.
b) Pitting corrosion and crevice corrosion.

Example 1

How long will it take for oxygen to be consumed in the crevice width of 10 µm? What is the critical parameter for the crevice corrosion initiation? Approximate the crevice by a cuboid. The corrosion rate of the metal is v_{corr} = 0.1 µm.a^{-1}.

M_{Fe} = 55.85 g.mol^{-1}, M_{O2} = 32 g.mol^{-1}, ρ_{Fe} = 7.86 g.cm^{-3}

Lesson 7

Revision, questions and answers

Lesson 8

a) Other types of uniform corrosion.
b) Corrosion caused by galvanic cells.

Example 1

Calculate the range of the galvanic cell when stainless steel (KO) and carbon steel (UO) are coupled together. The free corrosion potential values before coupling were $E_{(UO)}$ = –0.6 V/SCE and $E_{(KO)}$ = 0 V/SCE. Assume that the potential in the galvanic cell on the interface is equal to the potential of the carbon steel (UO) (with regard to the easiness of polarization of the stainless steel). Conductivity of the electrolyte is σ = 662 µS.cm^{-1}. The initial corrosion rate of the carbon steel is $v_{corr(UO)}$ = 0.3 mm.a^{-1}. It corresponds to the limiting current density of oxygen $j_{lim(O2).}$ Assume the same value of j_{lim} for the stainless steel.

Example 2

Calculate the concentration of OH^- in the solution given by the solubility equilibrium of $Fe(OH)_2$. What is the pH value of the solution? Assume that $Fe(OH)_2$ is completely dissociated.

$Ks_{(Fe(OH)2)} = 1.67.10^{-14}$

Lesson 9

a) Average and immediate corrosion rate dependency on time, bi-logarithmic dependency.
b) Estimation of mass loss from atmospheric parameters and classification of corrosivity.

Example 1

Carbon steel exposure at a seaside resulted in mass loss p = 130 µm after one year. After four years, the mass loss was p = 190 µm. Assume the validity of bi-logarithmic dependency.

Calculate:
a) the average corrosion rate in 40 years, on the assumption that the conditions are stable.
b) the immediate corrosion rate in the fifth, twenty-fifth and fortieth year of the exposure.

Example 2

Calculate the maximum concentration of Fe^{3+} for the passivation of stainless steel by ferric sulphate (Fe_2SO_4) in the aerated solution of 0.5 M H_2SO_4.

$[Fe^{2+}] = 10^{-3}$ mol.l^{-1}, E_p = 0.04 V (–0.2 V/SCE), $j_{corr} = 10^2$ µa.cm^{-2}, $j_{cp} = 10^4$ µa.cm^{-2}, j_p = 1 µa.cm^{-2},
$j_{Fe2+/Fe3+} = j_0$ = 0.1 µa.cm^{-2}, $E^0_{Fe3+/Fe2+}$ = 0.771 V, β_c = –0.1

Lesson 10

a) Formation of deposits in water, Langelier saturation index, Ryznar index of stability.

Example 1

Determine the quality and quantity of deposit of $CaCO_3$ (i.e., the saturation index of stability) on the surface of steel in solutions:

Solution A: t = 75 °C, saturation pHs = 6, current pH = 6
Solution B: t = 75 °C, saturation pHs = 10, current pH = 10.5

Example 2

Determine the quality and quantity of the deposit of $CaCO_3$ (i.e., the saturation index of stability) on the surface of steel in solutions:

Solution A: t = 40 °C, $c(HCO_3^-)$ = 120 mg/l, $c\ (Ca^{2+})$ = 28 mg/l
Solution B: t = 27 °C, $c(HCO_3^-)$ = 264 mg/l, $c\ (Ca^{2+})$ = 84 mg/l

Lesson 11

Summary test II

Lesson 12

a) Explanation and correction of mistakes from summary test II.
b) Cathodic and anodic protection.

Example 1

When the cathodic protection of steel is applied in a soil electrolyte, the resulting pH value depends on the intensity of the cathode reaction and on the concentration of the soil anions. What is the influence of the alkalization speed of the electrolyte in the close proximity of the cathodically protected surface at the concentration of HCO_3^- = 77 mg/l? The volume of the electrolyte is 120 ml and consumed charge Q = 392 C. The exposure time is 72 hours. $M(_{OH-})$ = 17 g.mol^{-1}.

Lesson 13

a) Stainless steels - PRE, ARE, CPT, CCT.
b) Corrosion of non-ferrous alloys.

Example 1

Calculate PRE and ARE for the following alloys and evaluate their resistance against pitting and crevice corrosion, and their resistance in acid solutions.

Corrosion-resistant steels

[wt.%]	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	N
304L	<0.03	<1	<2	<0.04	<0.03	17-20	-	10-12.5	-	-
316L	<0.03	<1	<2	<0.04	<0.03	16.5-18.5	2-2.5	11-14	-	-
317L	<0.03	<1	<2	<0.04	<0.03	18-20	3-4	11-15	-	-
AL-6XN*	<0.03	<1	<2	<0.04	<0.03	20-22	6-7	23.5-25.5	0.18-0.25	
1.4529**	<0.02	<1	<2	<0.04	<0.03	19-21	6-7	24-26	1.2-2	<0.15
*superaustenitic stainless steel, ** austenitic-feritic stainless steel										

Inconell Alloy 625

[wt.%]	C	Si	Mn	P	S	Cr	Mo	Fe	Co	Nb+Ta	Al	Ti
	0.1	0.5	0.5	<0.015	<0.015	20-23	8-10	5	<1	3.15-4.15	0.4	0.4

*the rest is Ni

Example 2

Determine if silver will corrode at the increase of H_2 in the deareated solution of KCN at pH = 7.

$E^0_{H2/H+} = 0$ V, $E^0_{Ag0/Ag+} = 0.799$ V, $K_{D(Ag(CN)2-)} = 1.5.10^{-19}$, $a_{(CN-)} = 1$, $a_{(Ag(CN)2-)} =$ 0001

Lesson 14

Revision/recycling, questions and answers