Corrosion degradation

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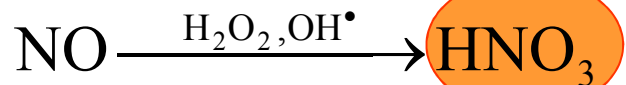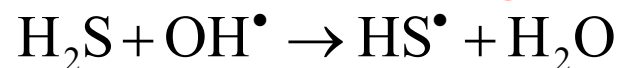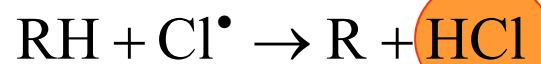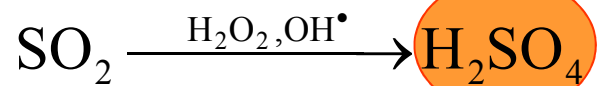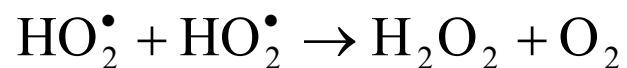**Department of General and Analytical Chemistry**

Atmospheric corrosion

Photoinduced creation of oxidants:

$$O_3 + hv \rightarrow O^* + O_2 \qquad \lambda < 310 \text{ nm}$$

$$O^* + H_2O \rightarrow 2OH^\bullet$$
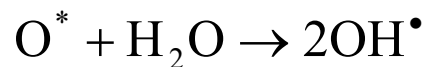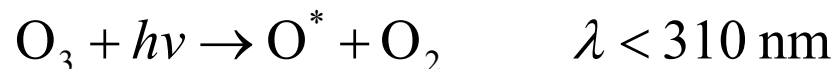
OH* radicals can oxidize several species such as SO_2, H_2S, and NO_2, a large fraction of radicals is consumed through reactions with hydrocarbon molecules, whereby one of the end products is the hydroperoxyl radical HO_2^*.

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$$

$$SO_2 \xrightarrow{H_2O_2, OH^\bullet} H_2SO_4$$

$$H_2S + OH^\bullet \rightarrow HS^\bullet + H_2O$$

$$HS^\bullet + 2O_2 \rightarrow HO_2^\bullet + SO_2$$

$$NO \xrightarrow{H_2O_2, OH^\bullet} HNO_3$$

$$Cl_2 + hv \rightarrow 2Cl^\bullet \qquad \lambda < 430nm$$

$$RH + Cl^\bullet \rightarrow R + HCl$$

Mechanism of atmospheric corrosion of carbon steels

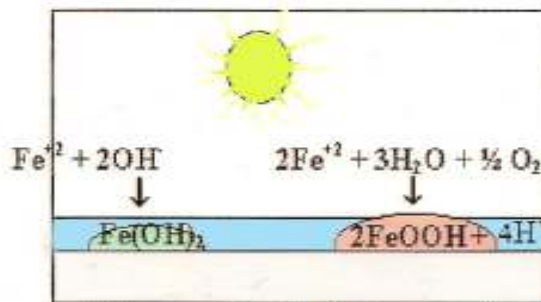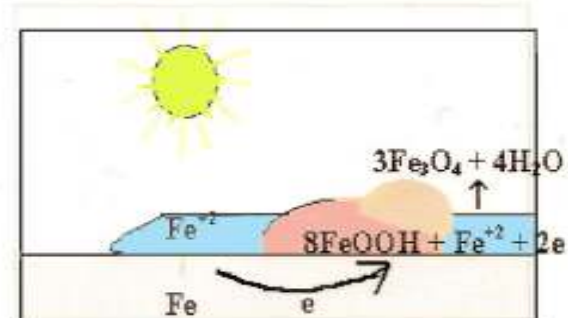a) formation of electrolyte layer
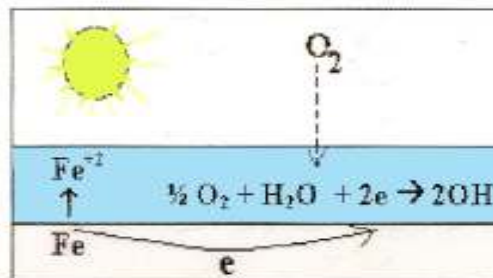
b) initiation of corrosion process

c) formation of insoluble corrosion products

d) formation of rust layer
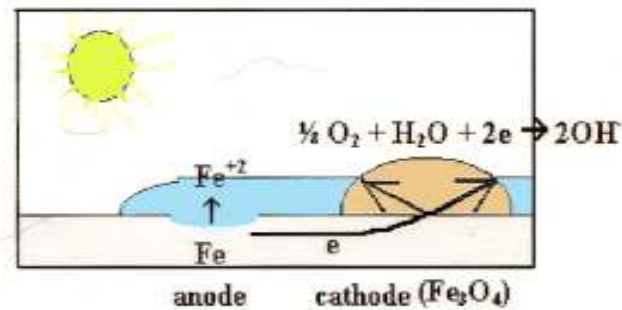
e) creation of galvanic cell
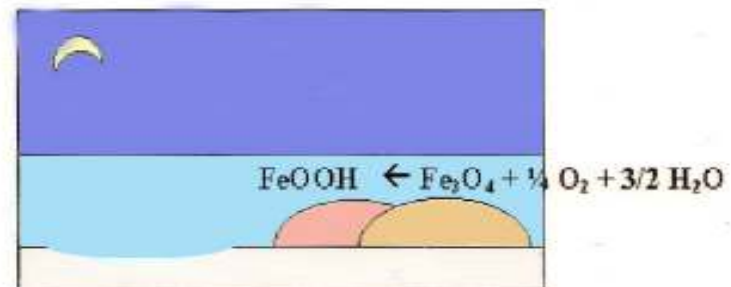
f) regeneration of FeOOH by oxidation of magnetite

Corrosion in water
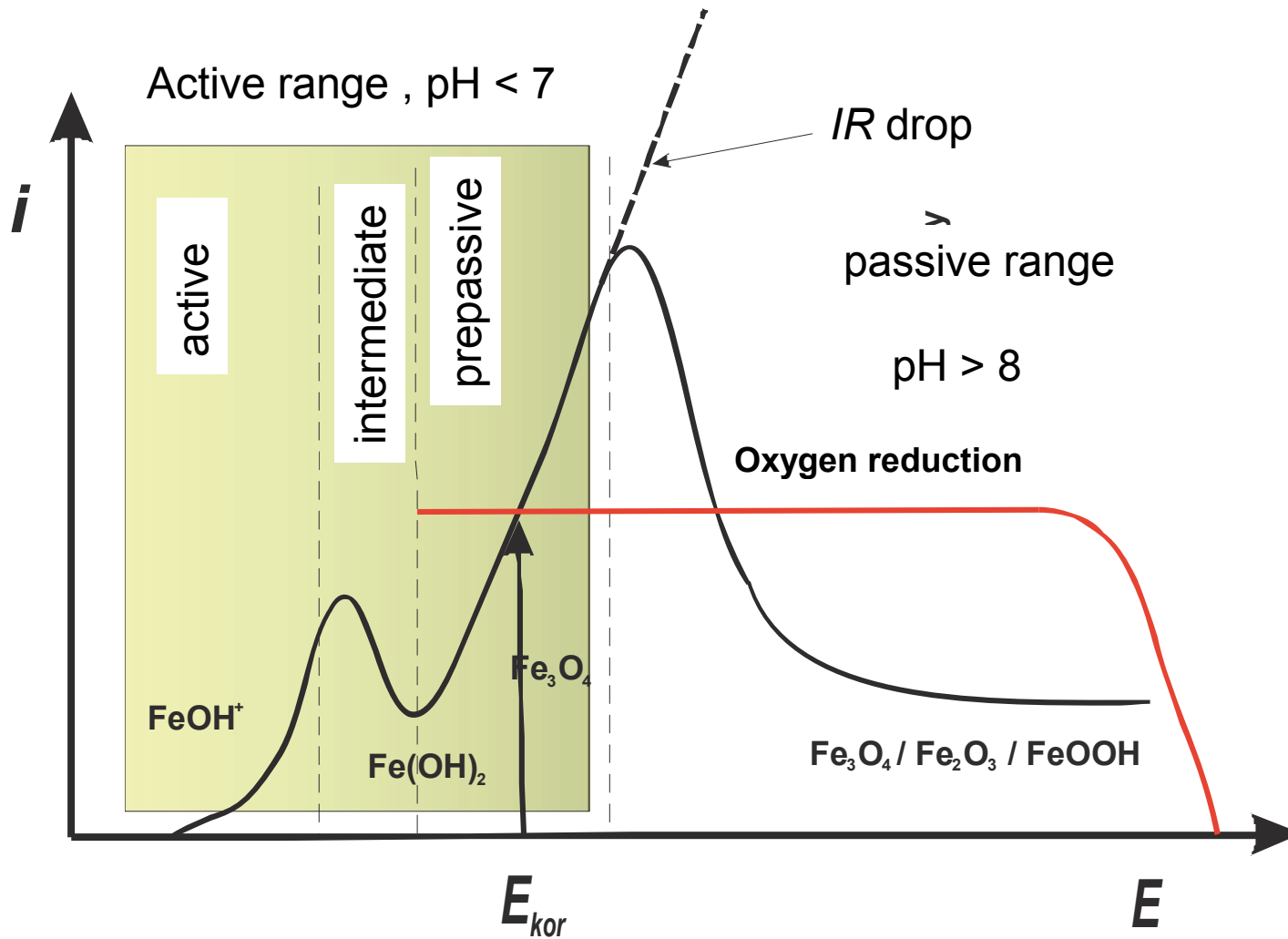
Polarisation diagram for iron – water system

Corrosion in water

próbka 1, woda surowa nasycona argonem

Legend:
- 1 V/min
- 3 V/min
- 5 V/min
- 20 V/min

Axes: i, mA / cm^2 versus $E_{Ag/AgCl}$, V
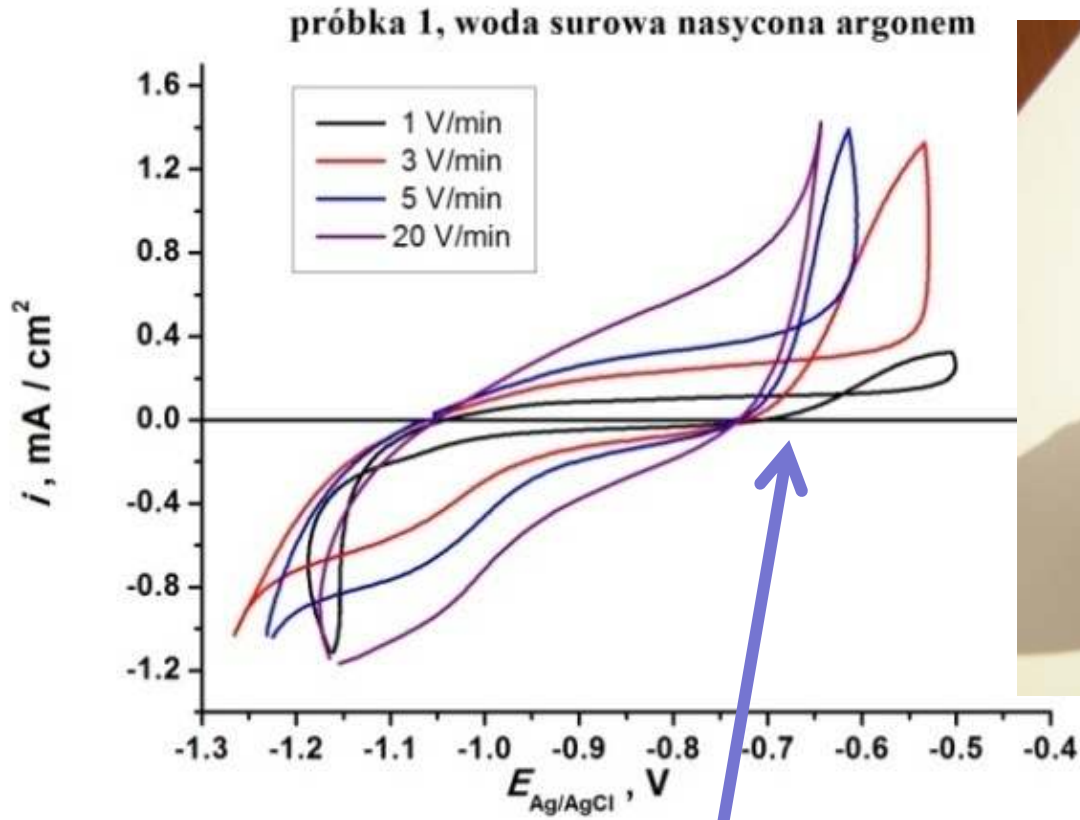
pH = 5.75, E_{corr} = -0.703

Corrosion of cast iron in tap water

CORROSION OF IN H_2O – CO_2 – H_2S SYSTEM

Energetic systems and power plants,

oil–gas and petroleum industry,

geothermal systems,

high-level waste containers (HLW),

pressurized water reactors (PWR)

boiling water reactors (BWR),

heat exchangers,

tubing, pumps and armature

20.0kV   100X   100 um

CORROSION OF CARBON STEEL IN H_2O – CO_2 SYSTEM

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$
$$H_2CO_3 \Leftrightarrow H_2CO_{3\,ad}$$
$$H_2CO_{3\,ad} + e \rightarrow HCO_3^- + H_{ad}$$
$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$$
$$H_{ad} + H_{ad} \rightarrow H_2$$

Fe + H_2O

CO_2 H_2O

Fe_2O_3
Fe_3O_4
FeOOH

Fe^{2+}

$CO_2 + H_2O$

e

$H_2CO_{3\,ad}$ $\leftarrow$ H_2CO_3

H^+

$H_{ad} + HCO_3^-$
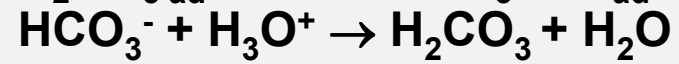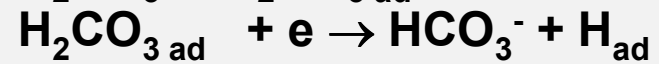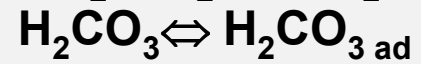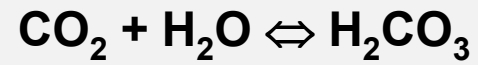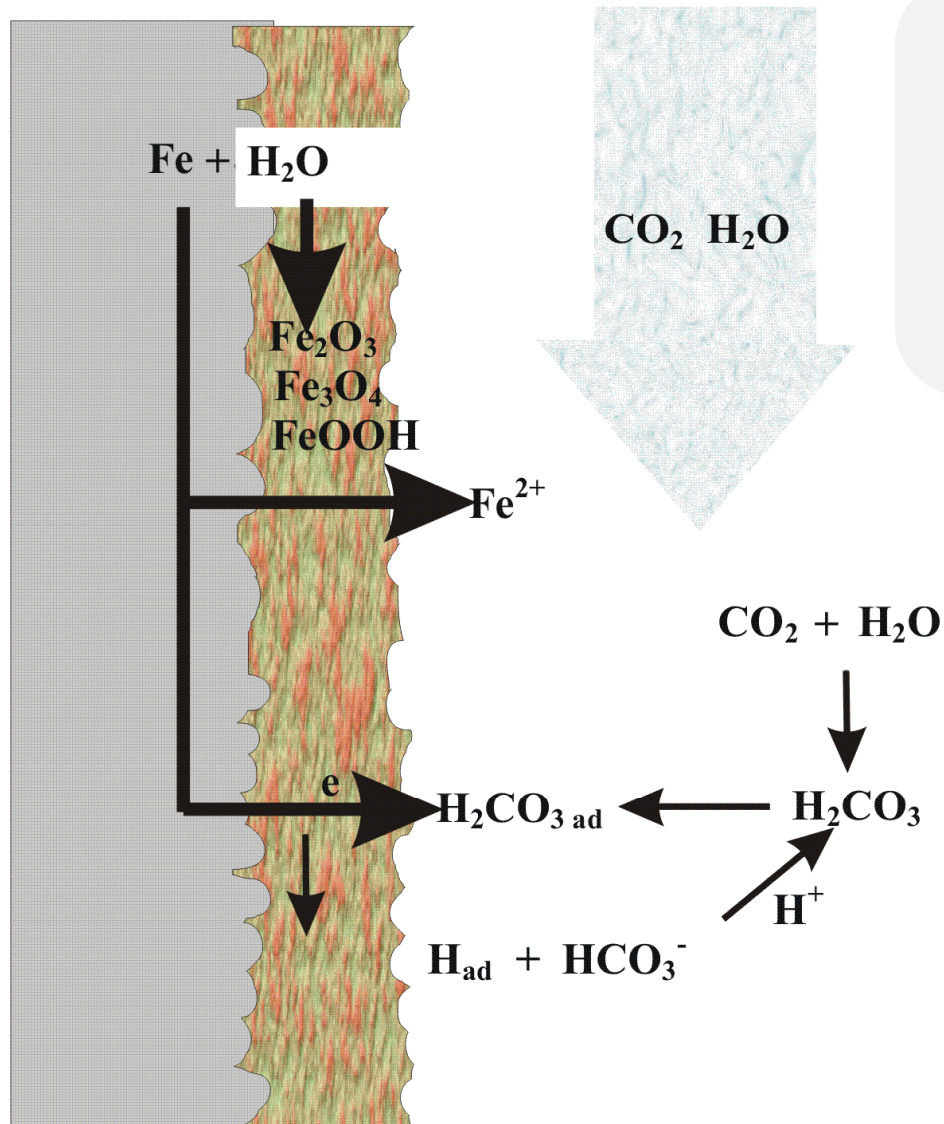
CORROSION OF CARBON STEEL IN $H_2O - CO_2 - H_2S$ SYSTEM

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

$$H_2CO_3$$

$$HCO_3^-$$

Cathodic reactions

$$H_{ab} \quad H_{ad} \longrightarrow \tfrac{1}{2} H_2 \uparrow$$

$$H^+ + HCO_3^- \Leftrightarrow H_2CO_3$$

$$H^+ + HS^- \Leftrightarrow H_2S$$

Anodic reaction

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

surface layer formation

$$FeCO_3$$

$$FeS$$

e

e

e
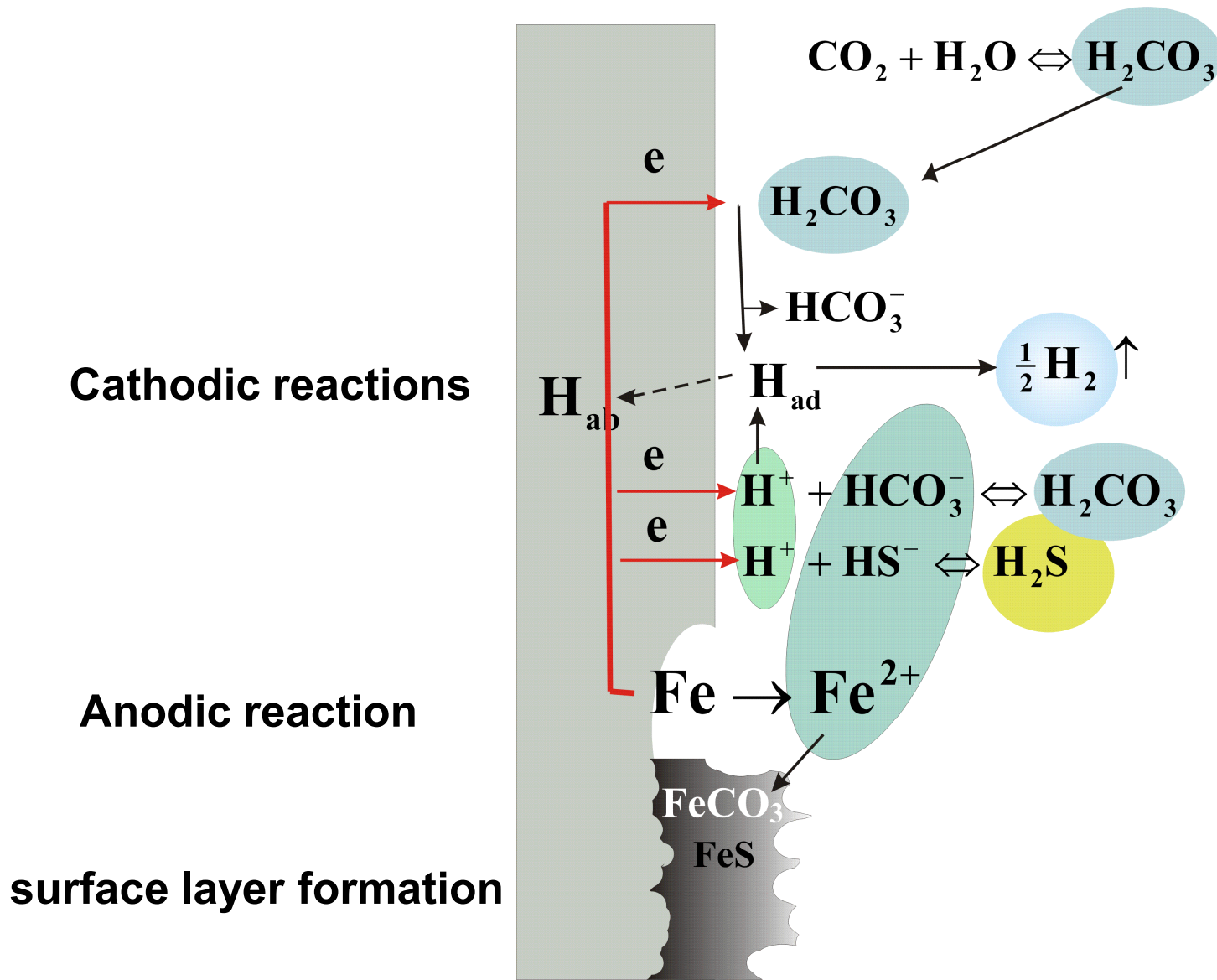
Corrosion in water (H_2O-CO_2-H_2S system)

Potential – pH diagram for Fe–thermal water system at the temperature of 80^0C (0.013M/dm^3 Cl-, 0.007M HCO$_3^-$, 0.0002M HS$^-$)

Activity of soluble products established as equal 10^{-6} M/dm^3, and solid products as one.
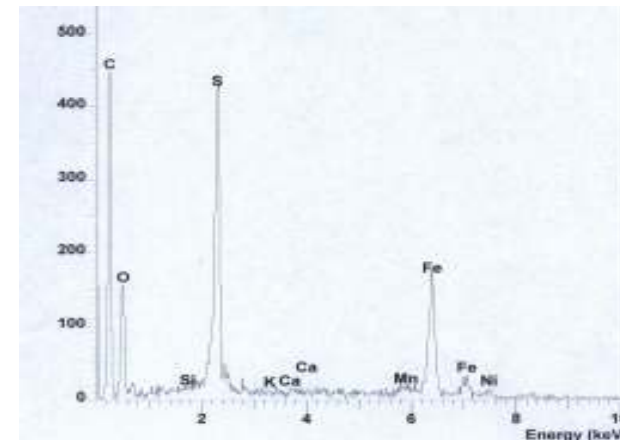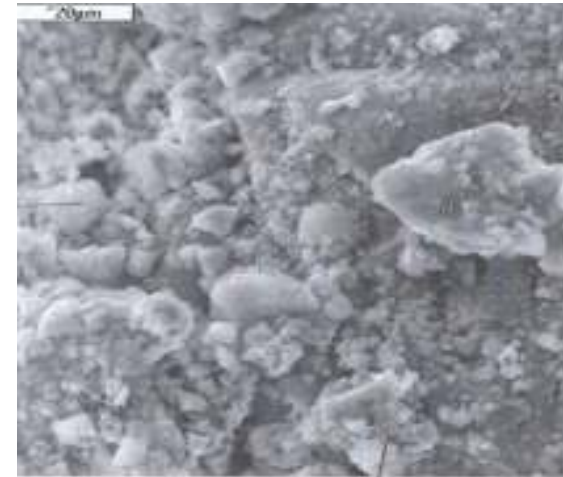
SEM image (a) and X ray analysis (b) of the corrosion products on the surface of ST3S steel exposed in thermal water in Geotermia Podhalańska S.A. (water flow rate = 10m/s, 80^0C).

Effect of CO_2 pressure on corrosion of carbon steel in H_2O – CO_2 system

de Waard – Milliamsa equation:

$$\log V \text{ (mm/y)} = 5.8 - 1710/T + 0.67 \log (p_{CO_2})$$

p_{CO_2} – partial pressure in bar.

at high pressure the equation can be present in the form:

$$\log V \text{(mm/y)} = 5.8 - 1710/T + 0.67 \log (f_{CO_2})$$

$f_{CO_2} = a * p_{CO_2}$, where " f" is the fungicity and „a" is the activity of CO_2

Effect of CO$_2$ pressure on the corrosion of carbon steel in the thermal water from Bańska (laboratory experiments)
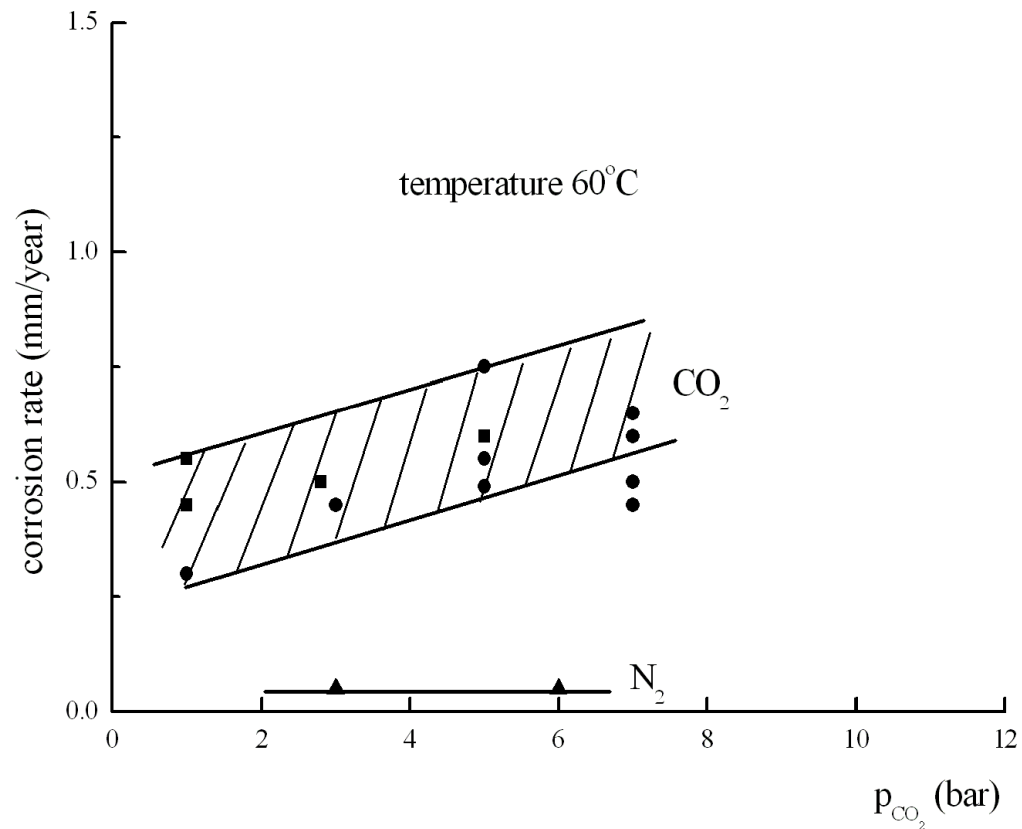
J. Banaś, K. Banaś, B. Stypuła: *Ochhrona przed Korozją* **6**, *136 (1991)*,
J. Banaś, J. Głownia, B. Stypuła, D. Walusiak: *in: Atlas of the Geothermal Waters of Polish Lowland, ed. by Institute of Fossil Fuels, AGH, Cracow Poland 1990*

Corrosion condition in H$_2$O-CO$_2$-H$_2$S system
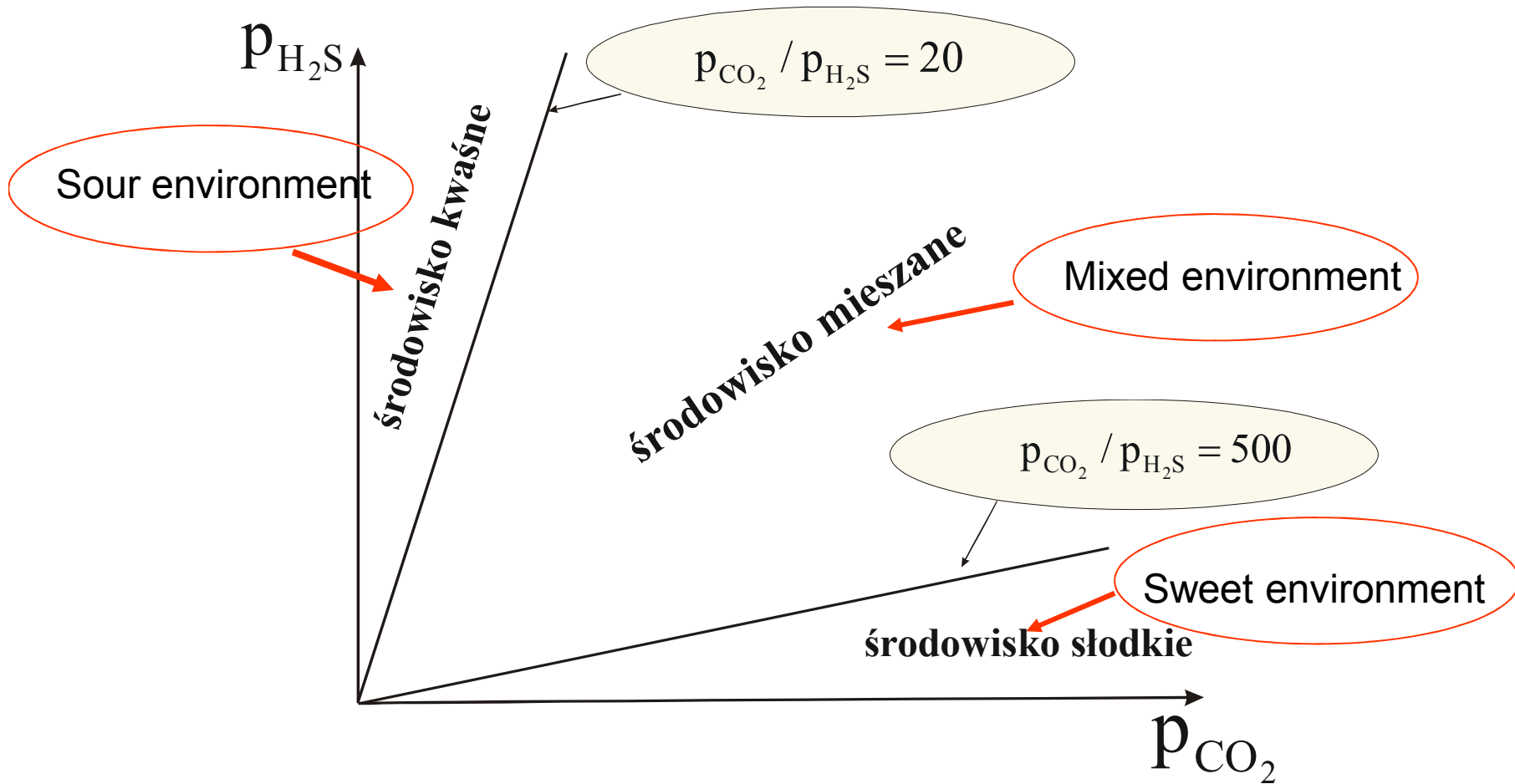
Corrosion condition in H$_2$O-CO$_2$-H$_2$S system defined by Post

Corrosion in water (H$_2$O-CO$_2$-H$_2$S system)
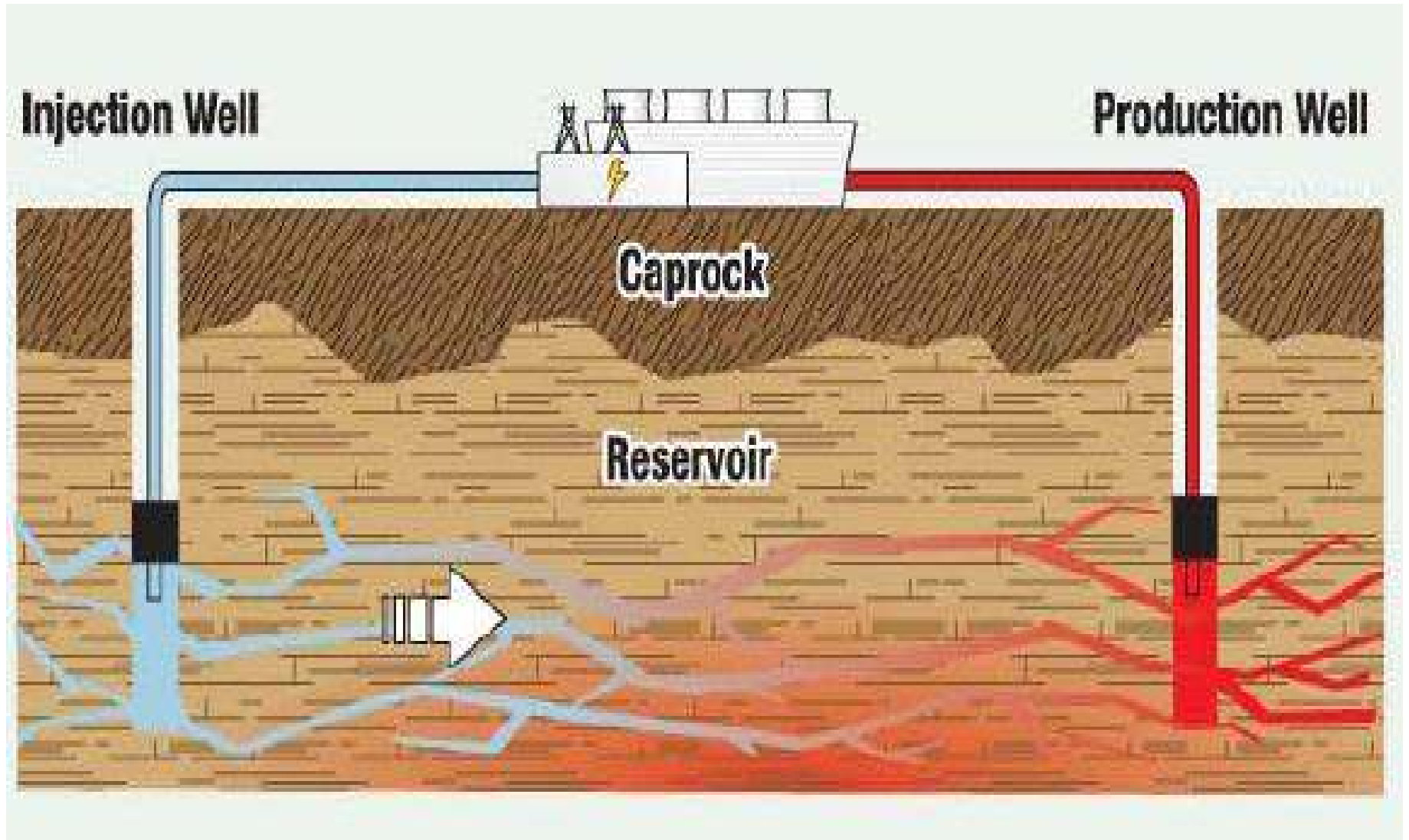
Polish geothermal power plants

68 000 mg Cl^- / dm^3

Geotermia Stargard 14 MJ/s

Geotermia Pyrzyce 50 MJ/s

70 – 80⁰C

40⁰C

68⁰C

Geotermia Mazowiecka S.A. 7.3 MJ/s

9.4 mg Cl^- / dm^3

Geotermia Uniejów 2.6 MJ/s

80-90⁰C

Geotermia Podhalańska S.A. 70 MJ/s

480 mg Cl^- / dm^3
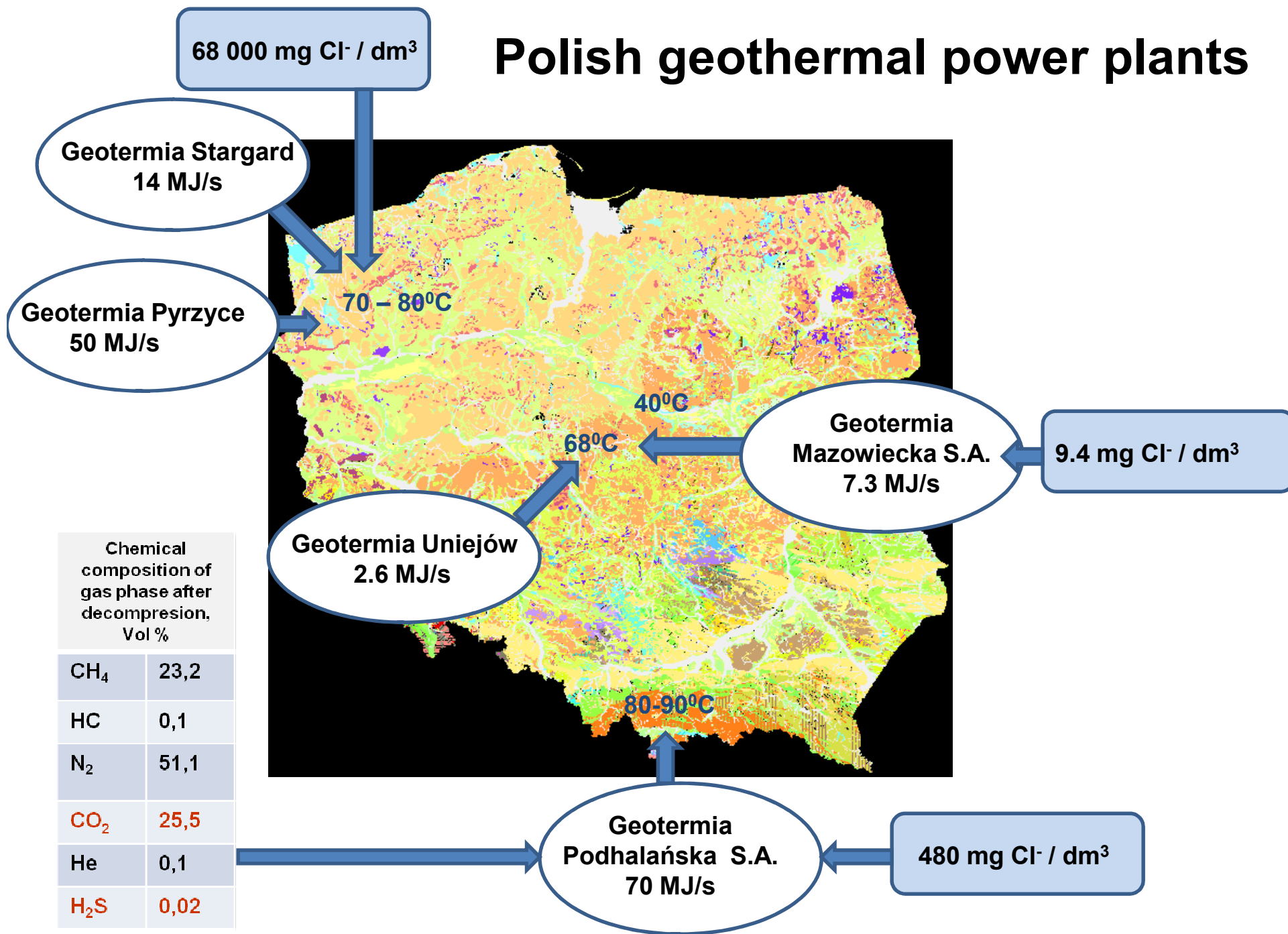
Chemical composition of gas phase after decompresion, Vol %	
CH_4	23,2
HC	0,1
N_2	51,1
CO_2	25,5
He	0,1
H_2S	0,02

Corrosion in acid environments

Anodic current in the passive range as a function of acid concentration.
Fe, Cr and Ni in H_2SO_4-H_2O system

Reductive behaviour:

$$H_2SO_4 + H_2O = H^+ + HSO_4^-$$
$$MO_{x/2} + xH^+ = M^{x+} + x/2H_2O$$
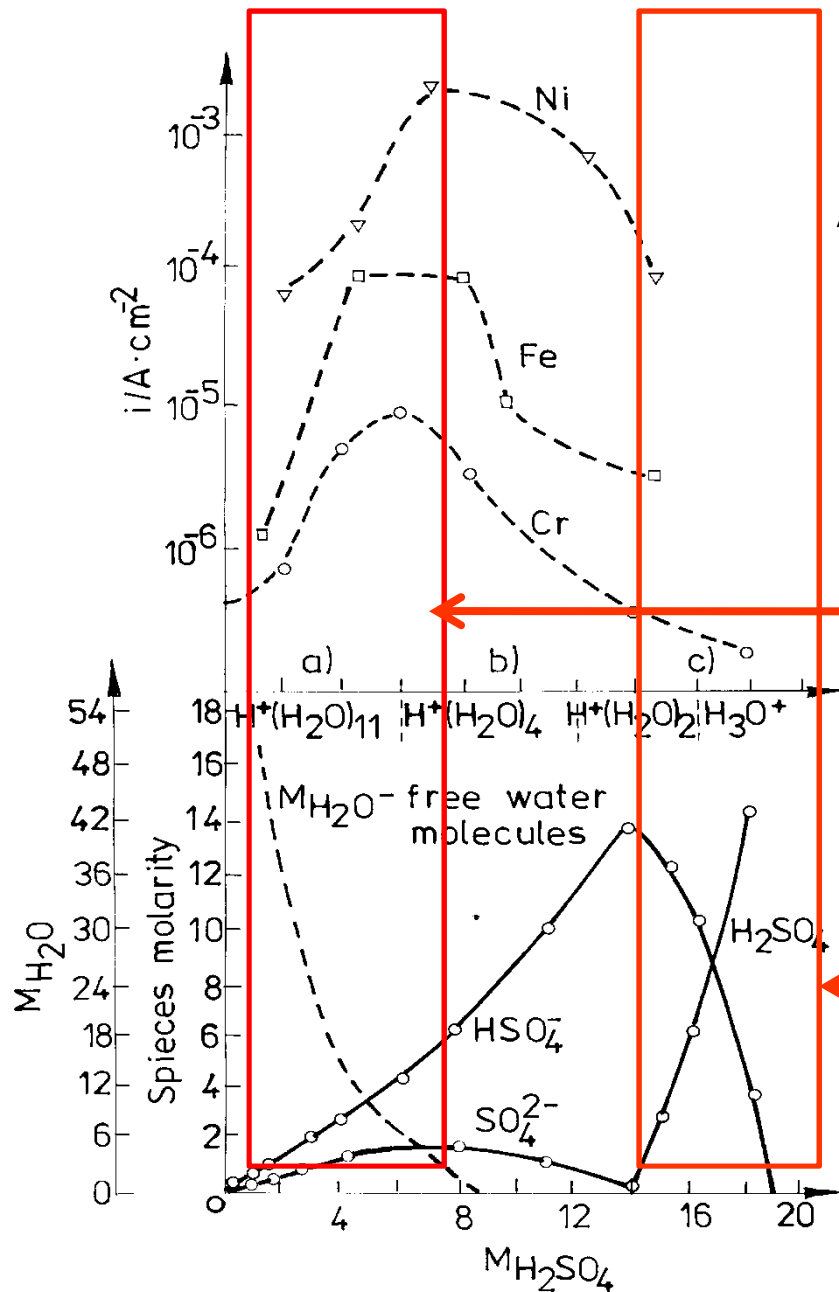
$$\frac{H^+}{H_2O} > \frac{1}{4}$$

Oxidative behaviour:

$$M + x/2H_2SO_4 = MO_{x/2} + x/2SO_2 + x/2H_2O$$
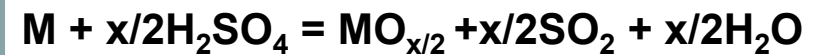
$$\frac{H^+}{H_2O} \triangleleft \frac{1}{4}$$

Metal corrosion in anhydrous organic media

The absence of water in the solution excludes the oxide formation on metal surface. The passivation process is possible only at the presence of the water or undissociated oxy-acid molecules.
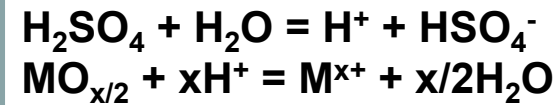
Stability of low valency anodic product (Zn^+, Cu^+) is always greater in organic environment than in aqueous medium.

Low dielectric permeability favours the formation of insoluble anodic product on the metals surface.

Frequently the strong inhibition of metal dissolution is observed at low anodic overvoltage and stationary polarization curve shows characteristic "S" - shape.

Corrosion of metals proceeds very often locally on the defects of metal surface (kink, steps, grain boundaries). This effect is very good known in the metallographic praxis.

Passivation in mixed aqueous-organic solvents

The dependence of passivation potential of some metals on water activity in mixed aqueous-organic or concentrated electrolytes fulfils the Nernst equation for the reaction:

$$Me + n/2H_2O = MeO_{n/2} + nH^+ + ne$$
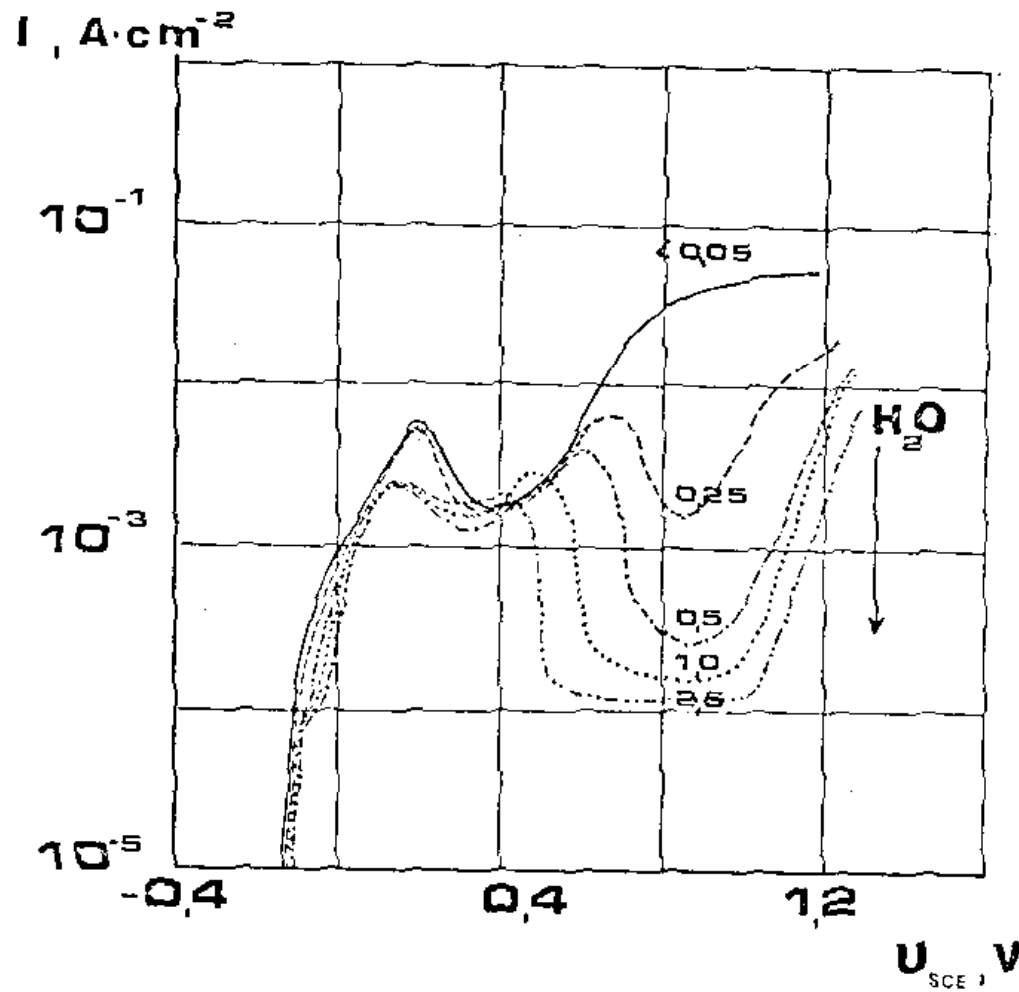
$$E = E^0 + \frac{RT}{nF}\ln[H_2O]$$

The passivation of metals proceeds according to the above mentioned reaction in electrolytes with the molar ratio of hydrogen ions to water :

$$\frac{H^+}{H_2O} \vartriangleleft \frac{1}{4}$$

At the higher ratio the water molecules are bound in hydration shell of hydrogen ions and do not take part in anodic reaction as a source of oxygen ions

Passivation in mixed aqueous-organic solvents

Effect of water concentration on passivity of nickel

in $CH_3OH - 1M\ H_2SO_4$

Is the oxide formation possible in completely anhydrous electrolytes?

Yes! At the presence other oxygen containing species, undergoing decomposition (reduction) on metal surface.

Undissociated oxy-acids molecules can passivate metal surface according to the mechanism:

$$Me + nRO_{m/2} \rightarrow MeO_{n/2} + nRO^{+n/n}_{(m-n/n)/2} + ne$$

$$nRO^{+n/n}_{(m-n/n)/2} + ne \rightarrow nRO_{(m-n/n)/2}$$

_____

$$Me + nRO_{m/2} \rightarrow MeO_{n/2} + nRO_{(m-n/n)/2}$$

The $RO_{m/2}$ is a molecule containing oxygen, **R** means the nonmetal atom of **+m** valency (or the group of nonmetallic atoms with the exception of oxygen) and **"n"** is a stoichiometric number (the number of oxidant molecules)

Passivation of metals in anhydrous environments

In anhydrous solutions or in aqueous concentrated solutions the oxygen containing species - undissociated molecules of oxyacids (H_2SO_4, H_3PO_4, HNO_3, HCOOH) play role of source of oxygen .
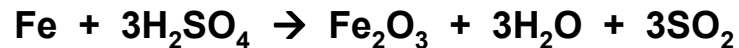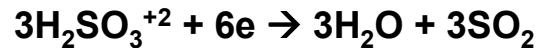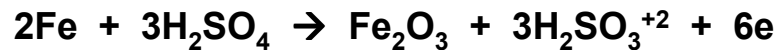
1) Passivation of chromium in anhydrous organic solutions of sulphuric acid:

$$Cr + H_2SO_4 \rightarrow CrHSO_{4\ ad} + H^+ + e$$
$$CrHSO_4 \rightarrow CrOOH + SO_2$$

2) Passivation of iron in anhydrous formic acid solutions:

$$Fe + 2HCOOH \rightarrow FeOOH + 2CO + 3H^+ + 2e$$

3) Passivation of iron in concentrated sulphuric acid:

$$2Fe + 3H_2SO_4 \rightarrow Fe_2O_3 + 3H_2SO_3^{+2} + 6e$$

$$3H_2SO_3^{+2} + 6e \rightarrow 3H_2O + 3SO_2$$

_____

$$Fe + 3H_2SO_4 \rightarrow Fe_2O_3 + 3H_2O + 3SO_2$$

Passivity of iron and nickel in anhydrous solution of H_2SO_4 in DMF and formamide.
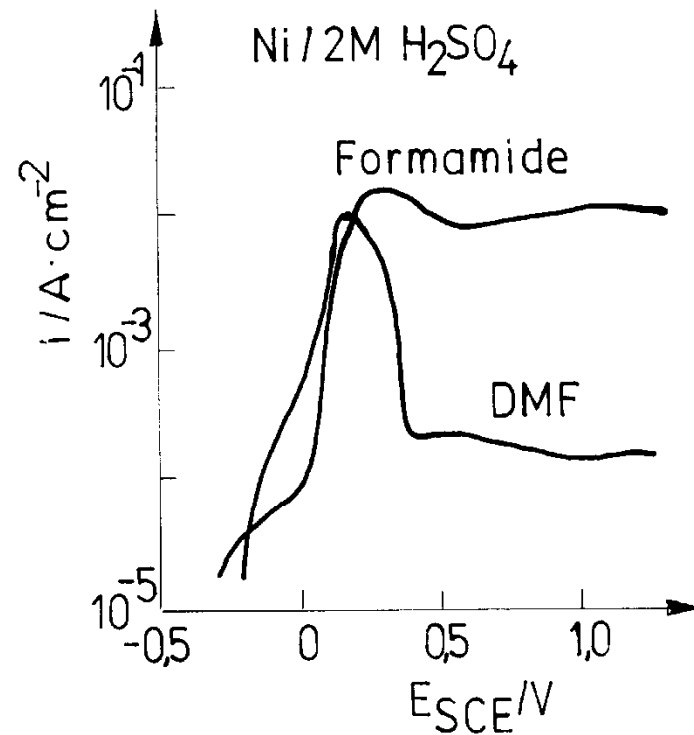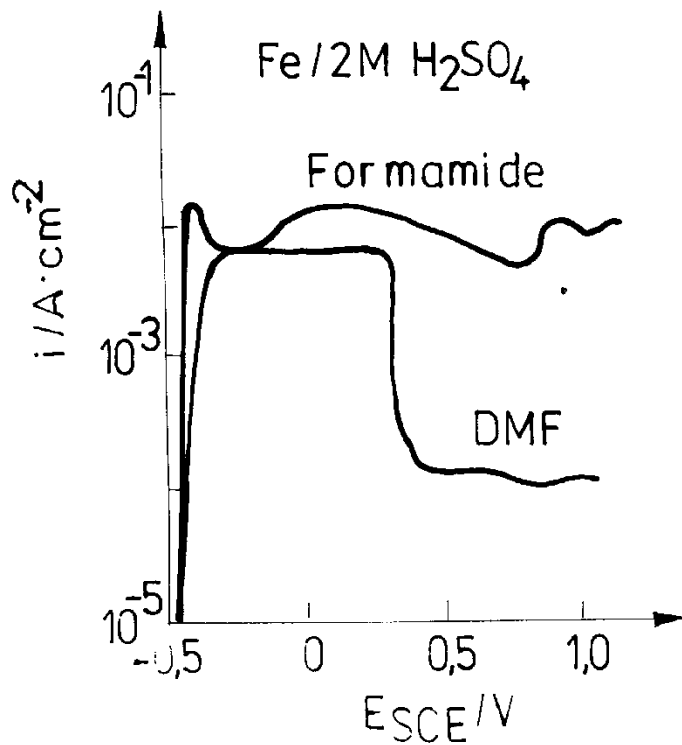
Corrosion of metals in anhydrous hydrocarbons

The rate of anodic dissolution of metals depends in these media on the structure and physicochemical properties of organic solvent.

Dielectric permittivity and donor or acceptor number determine the process of solvation and adsorption phenomena on metal surface.

Conductivity influences the action of corrosion microelements.

Corrosion of metals in hydrocarbons

The hydrocarbons, which are components of engine fuels and lubricants, are usually characterized by low permittivity and low conductivity. So, the process of corrosion in those media are proceeding at a very low rate.

The anodic reaction is strongly dependent on the structure of metal.

The lower is permittivity of the medium, the more is the anodic reaction dependent on the work done by the metal to free from crystal lattice.

The metals of low lattice energy (the low melting point metals),e.g. copper and zinc, dissolve much easier than metals characterized by a higher lattice energy, e.g. ferrous metals.

Corrosion of iron and zinc in N-dimethylformamide-formamide solvent
(DMF-FA, iron-80 days, zinc-5 days, 20C)
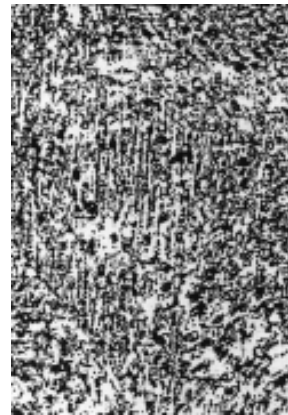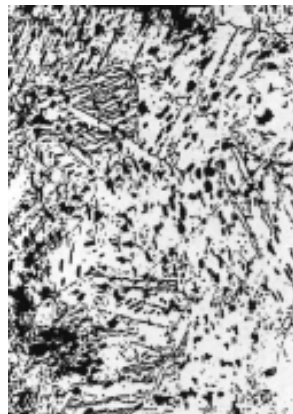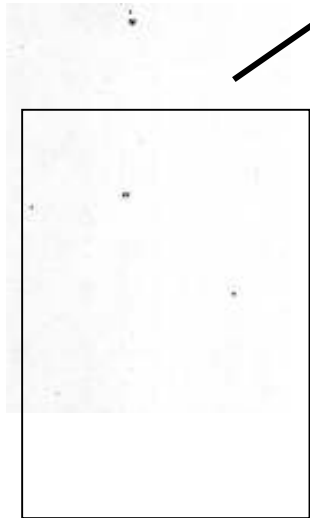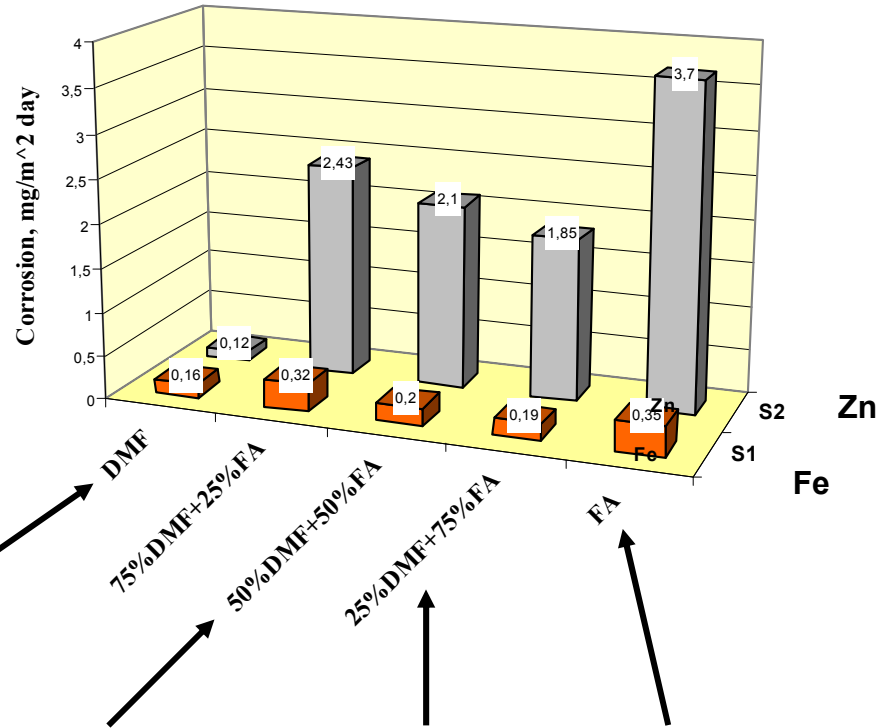
Surface morphology of Zn in N-dimethylformamide-formamide mixtures (20⁰C, 5 days)

Corrosion of Zn-4%Al in petrol

Petrol	Permittivity ε	Resistivity ρ, $\Omega \cdot cm$	Anodic current	Corrosion $\mu g /m^2 \cdot day$
Ref. petrol	2.27	$3.3 \cdot 10^9$	4 nA	5
Ethanol 3% Isobutanol 3% Water0,159% DAC 4303	3.31	$5.9 \cdot 10^7$	7 μA	302
Ethanol 5% Water 0,102%	3,68	$5.6 \cdot 10^5$	-	297
Methanol 3% Isobutanol 2% Water 0,03%	2,83	$5,9 \cdot 10^7$	25	666

The addition of components increasing conductivity of organic medium, or components facilitating the solvation of metal cations increase the rate of corrosion.
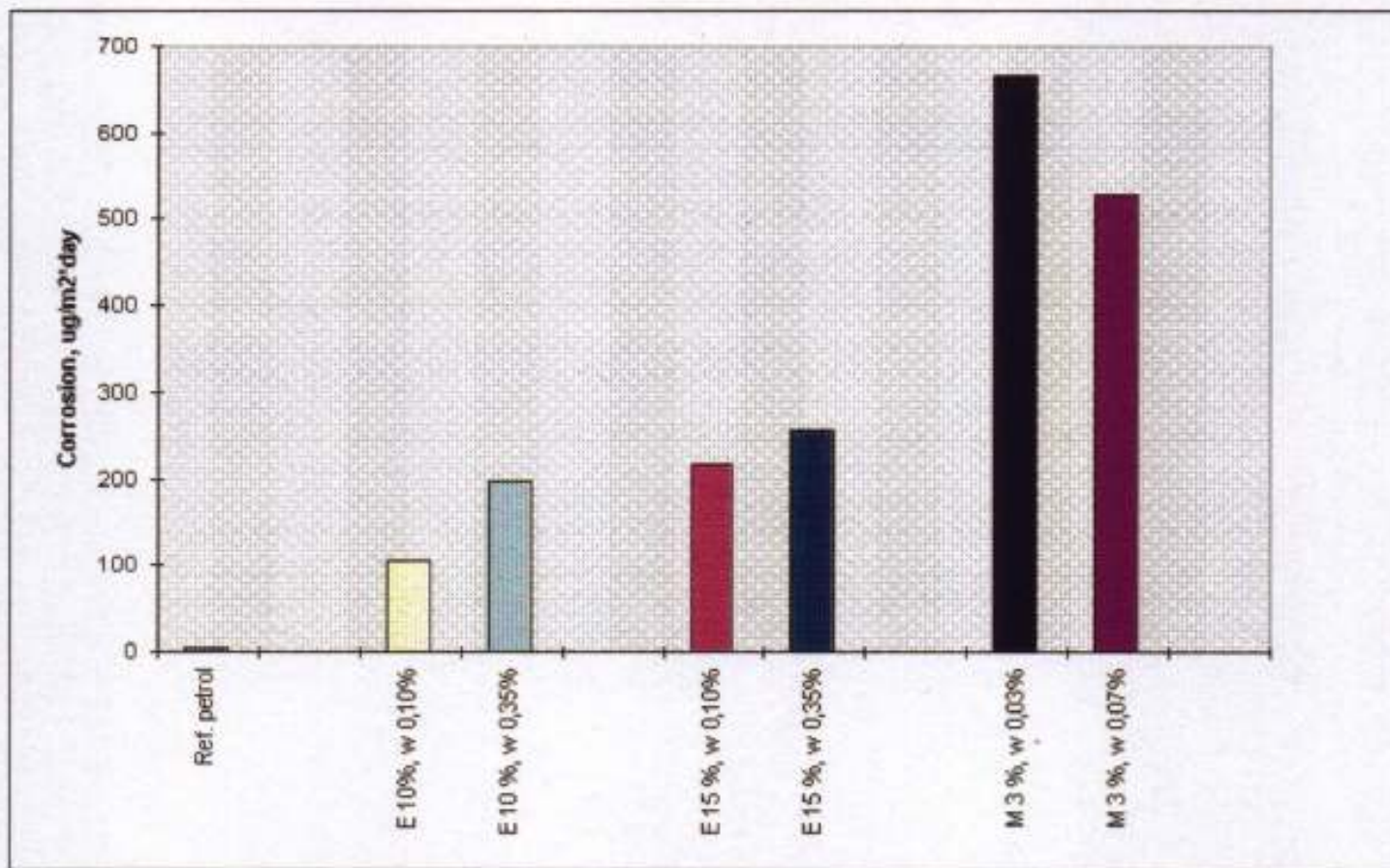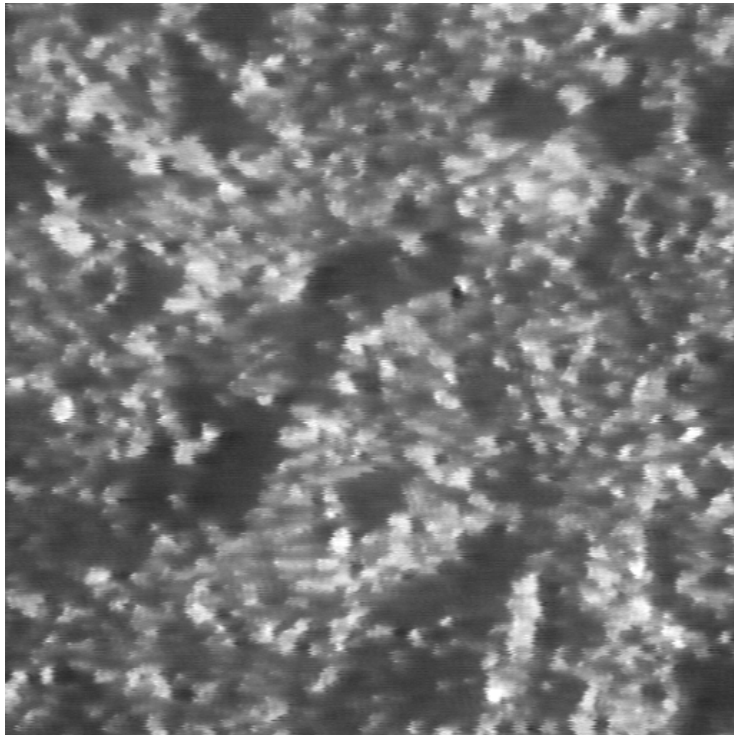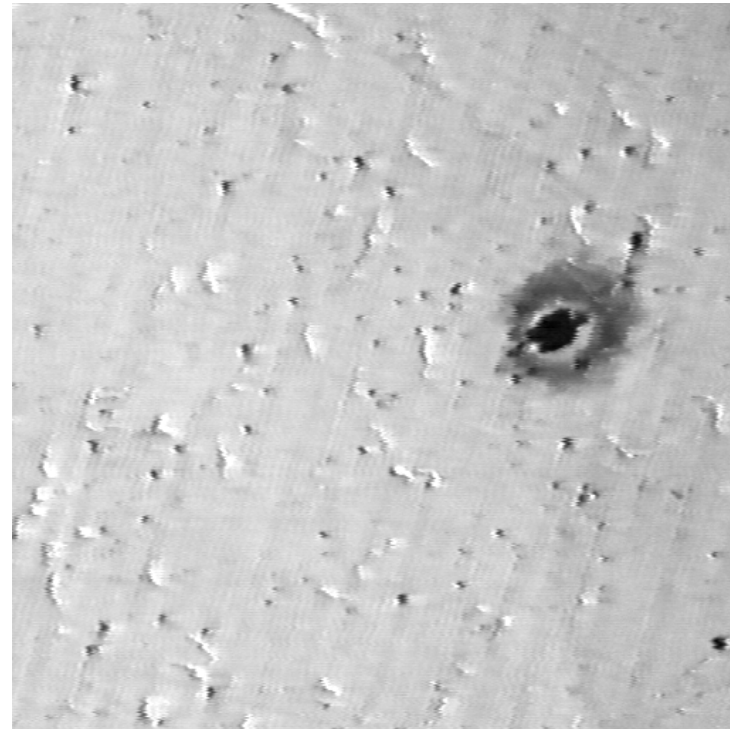

Fig.3. Effect of water concentration and of methanol and ethanol on corrosion rate of Zn - 4 % Al alloy in petrol. M - methanol, E - ethanol, W - water.

Corrosion morphology of zinc and carbon steel in gasoline
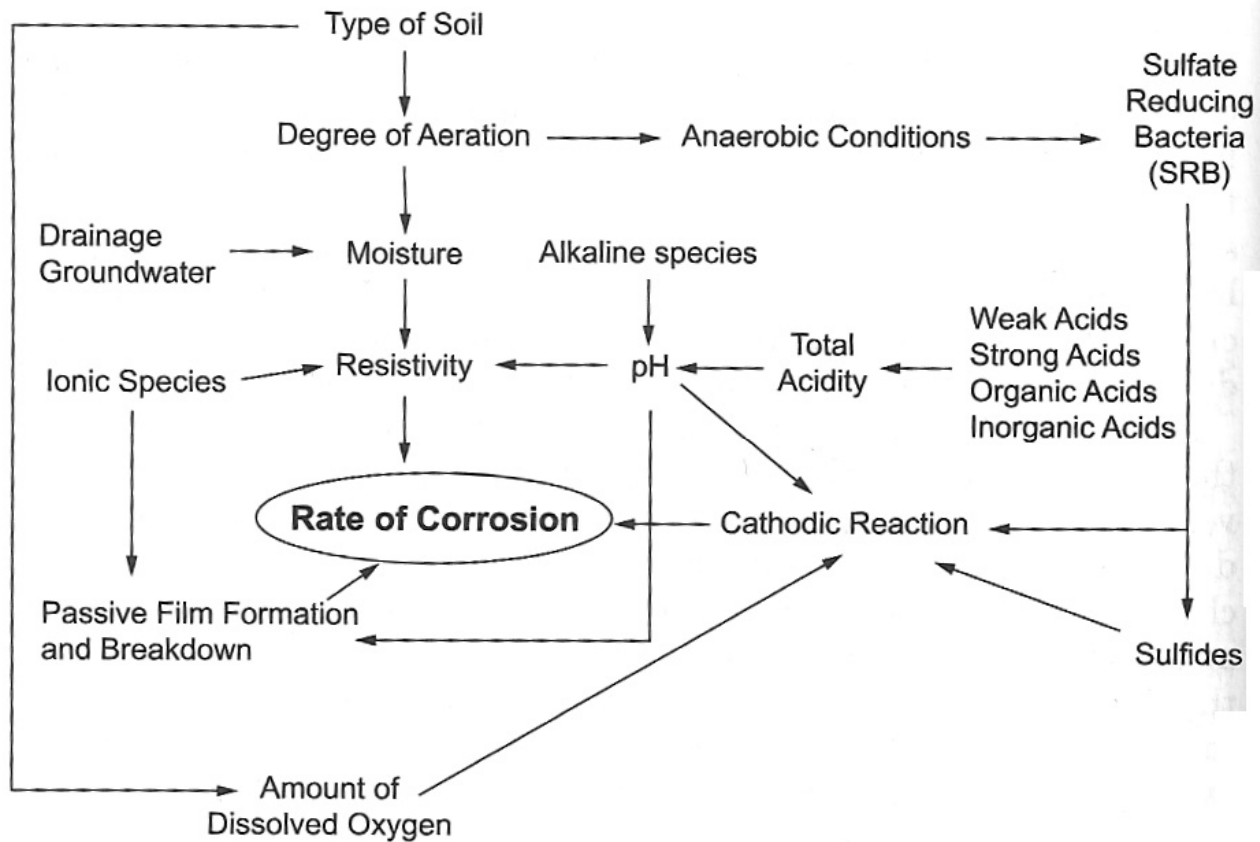

**Surface morfology of zinc
after corrosion in gasoline
(30 days)**

**Surface morfology of carbon
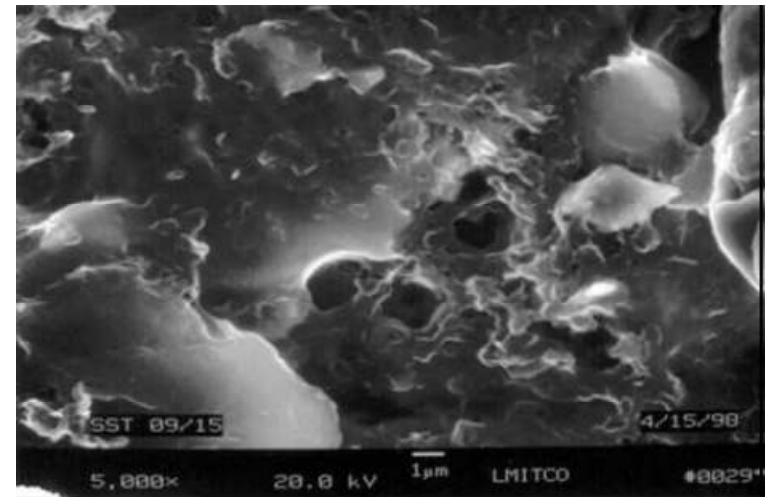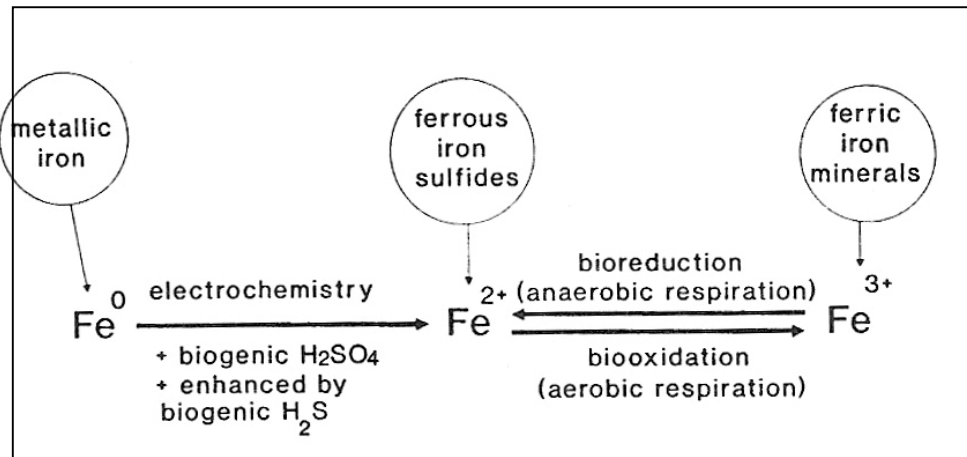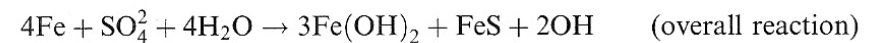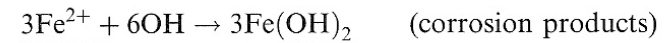steel after corrosion in gasoline
(30 days)**

Corrosion in soil

Relationship of variables affecting the rate of corrosion in soil

Point system for predicting soil corrosivity according to AWWA C-105 standard (American Water Works Association)

Soil parameter	Assigned points
Resistivity, $\Omega \cdot$cm	
< 700	10
700–1000	8
1000–1200	5
1200–1500	2
1500–2000	1
> 2000	0
pH	
0–2	5
2–4	3
4–6.5	0
6.5–7.5	0
7.5–8.5	0
> 8.5	3
Redox potential, mV	
> 100	0
50–100	3.5
0–50	4
< 0	5
Sulfides	
Positive	3.5
Trace	2
Negative	0
Moisture	
Poor drainage, continuously wet	2
Fair drainage, generally moist	1
Good drainage, generally dry	0

>10 points – protection of steel is recommended (cathodic protection, coatings)

Microbiological induced corrosion (MIC)

$4Fe \rightarrow 4Fe^{2+} + 8e$ (anodic reaction)

$8H_2O \rightarrow 8H^+ + 8OH$ (dissociation of water)

$8H^+ + 8e \rightarrow 8H_{ad}$ (cathodic reaction)

$SO_4^2 + 8H_{ad} \rightarrow S^2 + 4H_2O$
    (cathodic depolarization by sulfate-reducing bacteria)

$Fe^{2+} + S^2 \rightarrow FeS$ (corrosion products)

$\underline{3Fe^{2+} + 6OH \rightarrow 3Fe(OH)_2}$ (corrosion products)

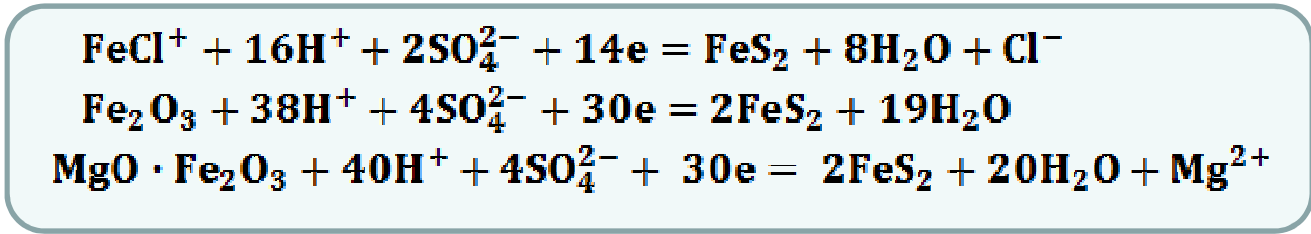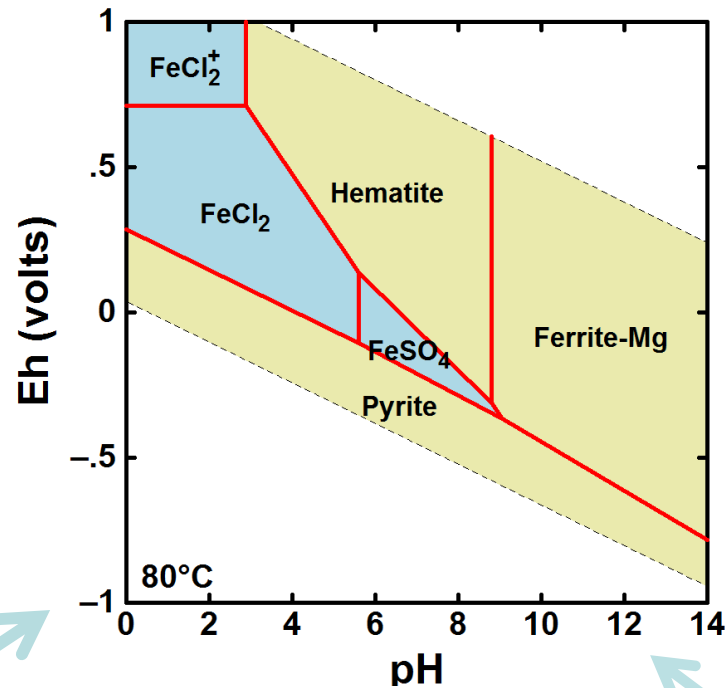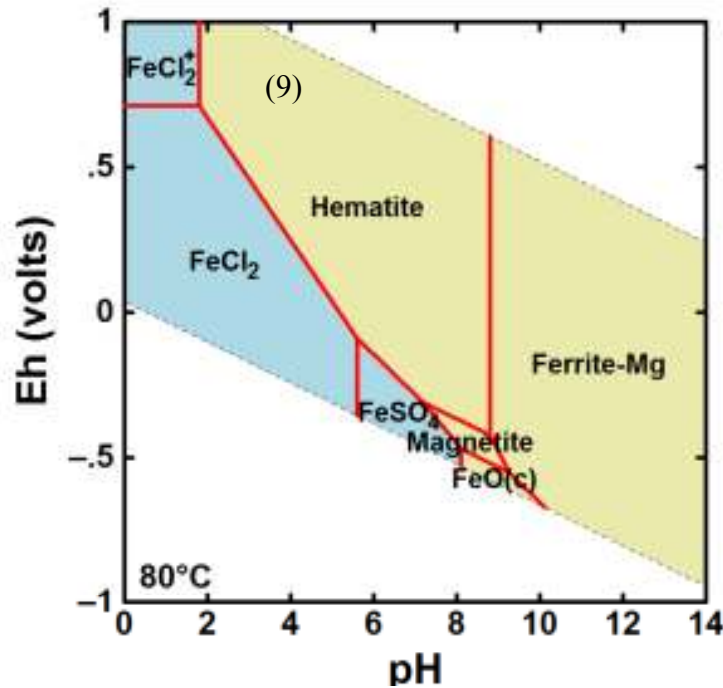$4Fe + SO_4^2 + 4H_2O \rightarrow 3Fe(OH)_2 + FeS + 2OH$ (overall reaction)
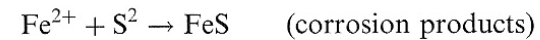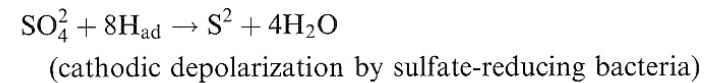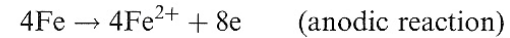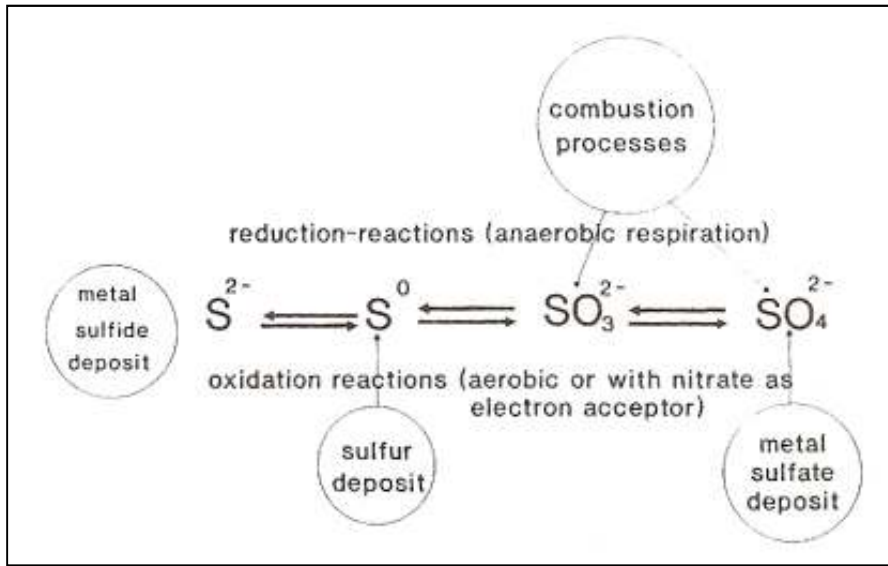
SEM image of biofilm on steel coupons exposed in geothermal water (one month)

Microbiological induced corrosion (MIC)

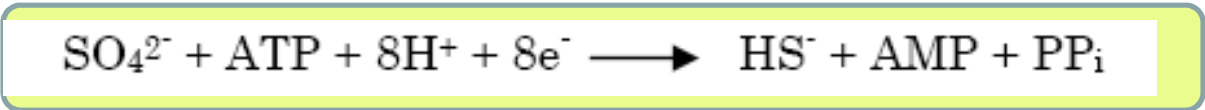| Industry	Problem areas
Chemical processing industries	Stainless steel tanks, pipelines, and flanged joints, particularly in welded areas after hydrotesting with natural river or well waters
Nuclear power generation	Carbon and stainless steel piping and tanks; copper-nickel, stainless, brass, and aluminum-bronze cooling water pipes and tubes, especially during construction, hydrotest, and outage periods
Onshore and offshore oil and gas industries	Mothballed and waterflood systems, oil and gas handling systems, particularly in environments sourced by sulfate-reducing bacteria (SRB)–produced sulfides
Underground pipeline industry	Water-saturated clay-type oils of near-neutral pH with decaying organic matter and a source of SRB
Water treatment industry	Heat exchangers and piping
Seawage handling and treatment industry	Concrete and reinforced concrete structures
Highway maintenance industry	Culvert piping
Aviation industry	Aluminum integral wing tanks and fuel storage tanks
Metalworking industry	Increased wear from breakdown of machining oils and emulsions

Thermodynamics of sulphate reduction

$$FeCl^+ + 16H^+ + 2SO_4^{2-} + 14e = FeS_2 + 8H_2O + Cl^-$$

$$Fe_2O_3 + 38H^+ + 4SO_4^{2-} + 30e = 2FeS_2 + 19H_2O$$

$$MgO \cdot Fe_2O_3 + 40H^+ + 4SO_4^{2-} + 30e = 2FeS_2 + 20H_2O + Mg^{2+}$$

Kryspinów, pH = 5 - 5.5
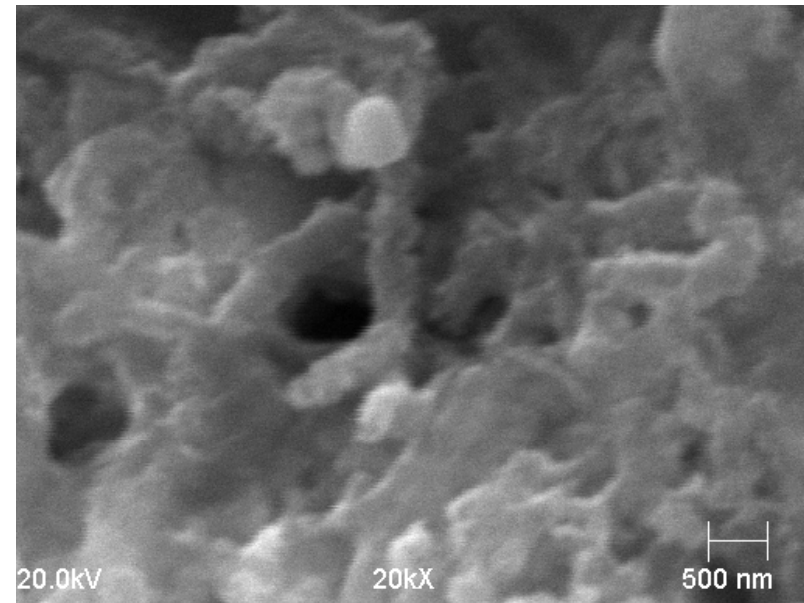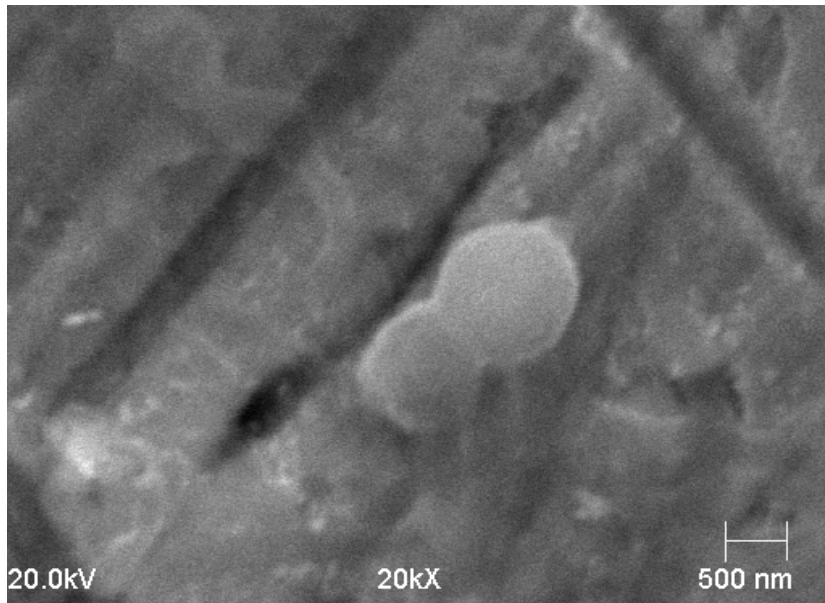
diagram Fe+++ on Eh vs pH
log activity main = -4.523
log activity Ca++ = -1.599
log activity Mg++ = -2.78
log activity Na+ = -1.256
log activity Cl- = -2.301
log activity HCO3- = -2.229
log activity HSO4- = -3.201

MIC – cathalysed reduction of sulphates

Reduction proceeds in cytoplasma according to the reaction:

$$SO_4^{2-} + ATP + 8H^+ + 8e^- \longrightarrow HS^- + AMP + PP_i$$

Katalizatory redukcji siarczanów korozja mikrobiologiczna

Redukcja siarczanów jest możliwa dzięki ich aktywacji do czynnej formy jaką jest adenozyno-5-fosfosiarczan (APS). Redukcja jest procesem trójetapowym:

3'-Phosphoadenosine-5'-phosphosulfate (APS)

Adenosine-5'-triphosphate (ATP)

Adenosine monophosphate (AMP)

Pyrophosphate (PPi)
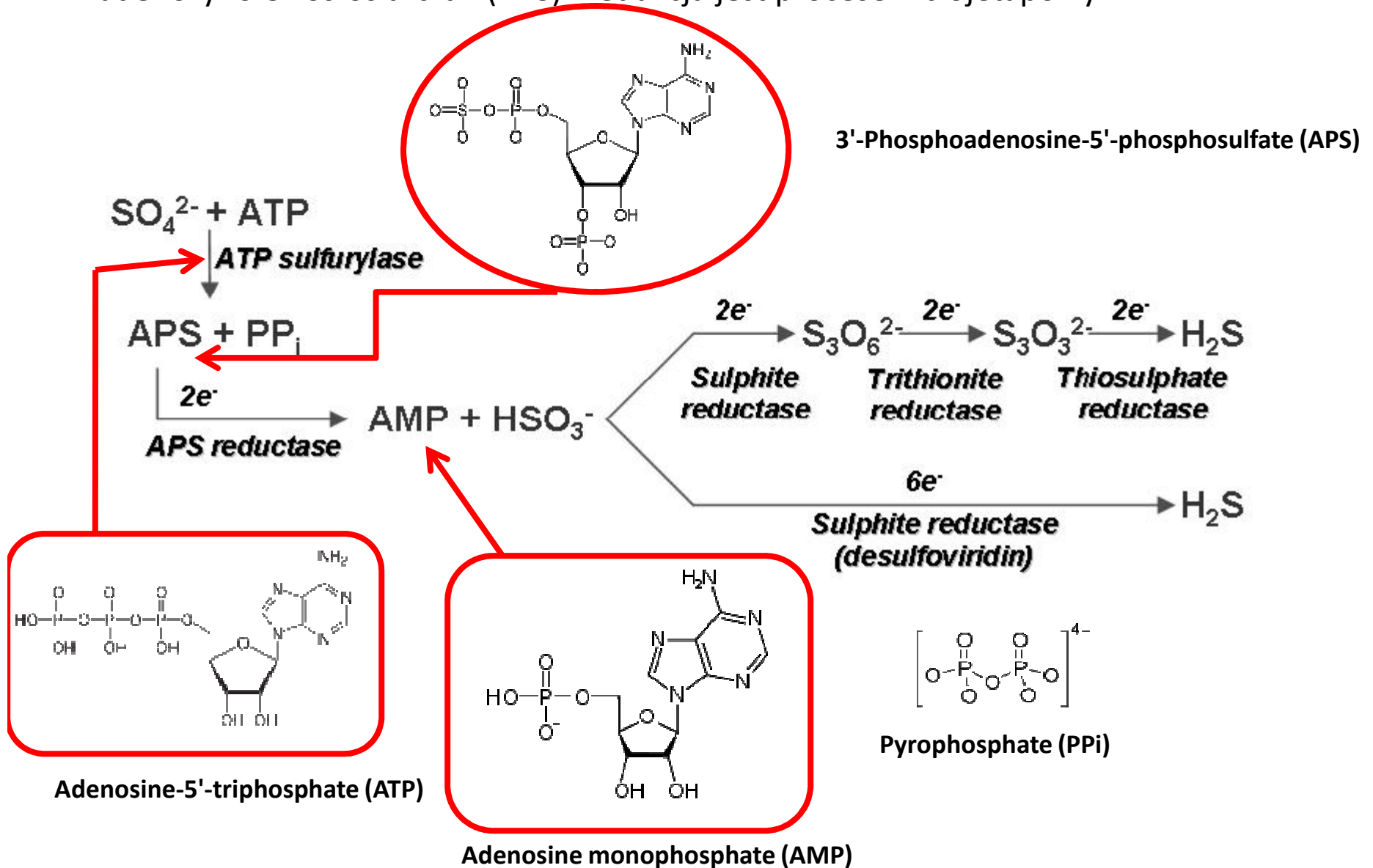
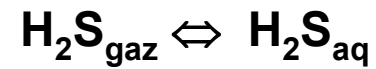# Microbiological induced corrosion (MIC)
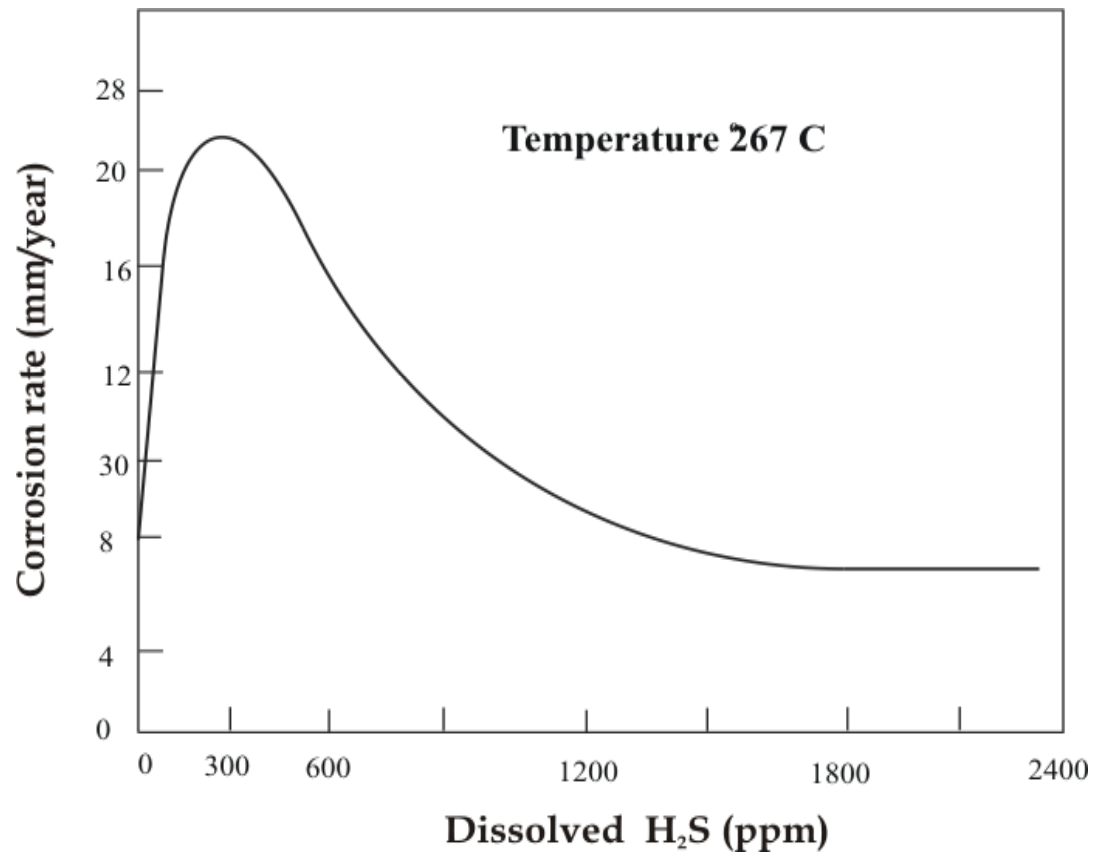

SEM image of biofilm on carbon steel exposed in geotehrmal water, in of Geotermia Stargard (salt water, 70C)

Microbiological induced corrosion (MIC)

Equilibrium H_2S – H_2O

$H_2S_{gaz} \Leftrightarrow H_2S_{aq}$

$H_2S_{aq} \Leftrightarrow H^+ + HS^-$

$HS^- \Leftrightarrow H^+ + S^{-2}$

The effect of hydrogen sulphide concentration in water on the corrosion rate of carbon steel.

The effect of H$_2$S on hydrogen embrittlement

HIC – hydrogen induced cracking,
occurs in low- and high-strength steels even without external stress.
Crack propagation proceeds paralell to surface.

SSCC – sulphide stress corrosion cracking,
occurs in high-strength steels.
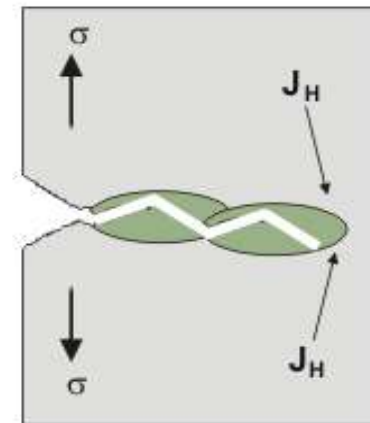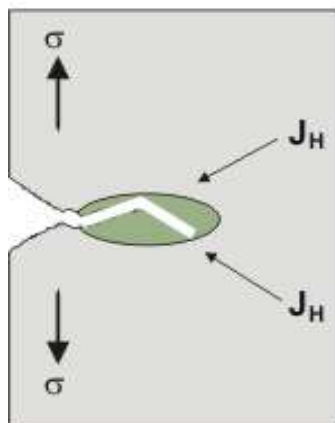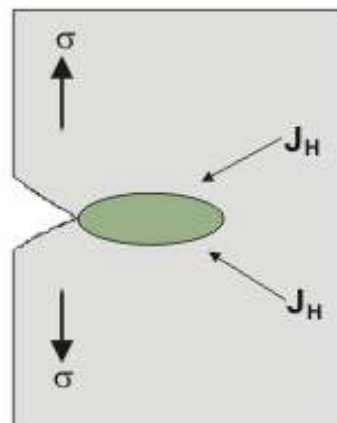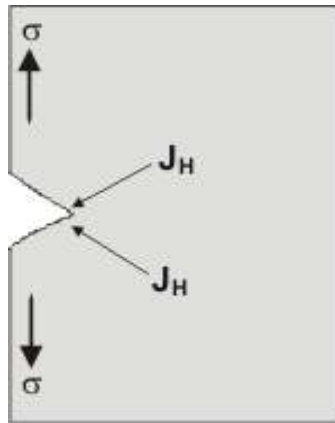**Crack propagation proceeds perpendicular to surface.**

Parallel to surface   **perpendicular to surface**

Hydrogen induced cracking (HIC) of carbon steel (pipelines after 10 years exploitation in natural gas containing 4.5% H_2S).

Mechanism of hydrogen embrittlement by stress iduced hydride formation.

Proposed mechanism for generalized embrittlement

Accumulation of hydrogen as a gas at internal defects.
The pressure developed by this precipitation is added to the applied stress and thus lowers the apparent fracture stress. Evidence to support this early theory continues to be developed, particular for hydrogen assisted cracking in H_2S gas, where crack formation involves hydrogen precipitation as molecular hydrogen at inclusion/matrix interfaces.

Interaction of dissolved hydrogen to reduce the cohesive strength of the lattice.

Adsorption of hydrogen to reduce the surface energy required to form a crack and thus lower the fracture stress.

Hydrogen embrittlement

Hydrogen absorption
$H_{ad} \rightarrow H_{Lattice}$ $\rightarrow$ **Crack initiation** $\rightarrow$ **Crack propagation**

$\uparrow$ $\downarrow$ $\downarrow$

Corrosion ($H^+ + e \rightarrow H_{ad}$) **Inclusions (elongated MnS)** **Anomalous structure Segregation of Mn and P**

$\uparrow$ $\uparrow$ $\uparrow$

•Alloy components
•Coatings
•Inhibitors

•Low content of S and P
•Spheroidization of inclusions

•Heat treatment
•Rolling conditions