Fundamental aspects of atmosperic corrosion

Important parameters and mechanisms

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Rust in history: an early conclusion.

Pliny the Elder (AD 23-79)

At the time of the Roman empire, the great philosopher Pliny the Elder asked:

"why should iron corrode more easily than other metals?"

Since the metal was used for swords and other war purposes, Pliny came to the conclusion that the rusting of iron was a punishment of the gods.

German portal figure made of sandstone from 1702.
Left picture taken 1908, right picture taken 1969.

MOS(metal-oxide-semiconductor)circuit


Dust
H_2S
Time-of-wetness
Radiation
Sun
SO_2
Temperature
NO_x
pH
Rain
Wind velocity
Relative humidity
O_3
Soot
Chlorides

Atmosperic corrosion: Important prerequisites

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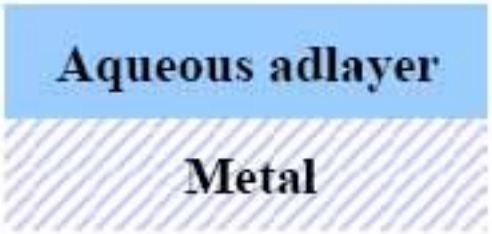
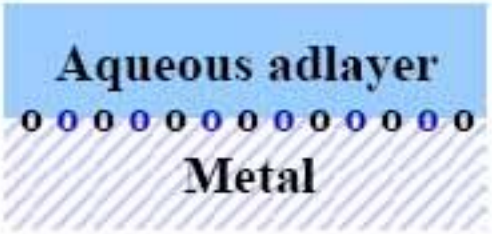
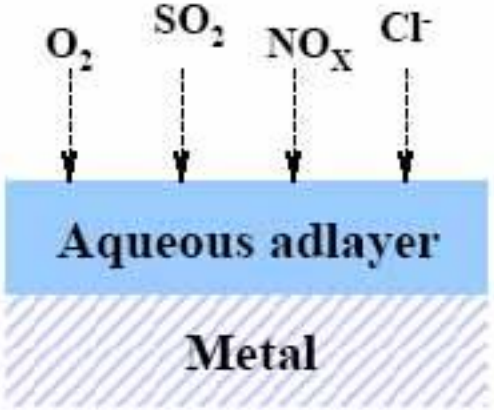
1. Thin water adlayer



2. Electrochemical reactions

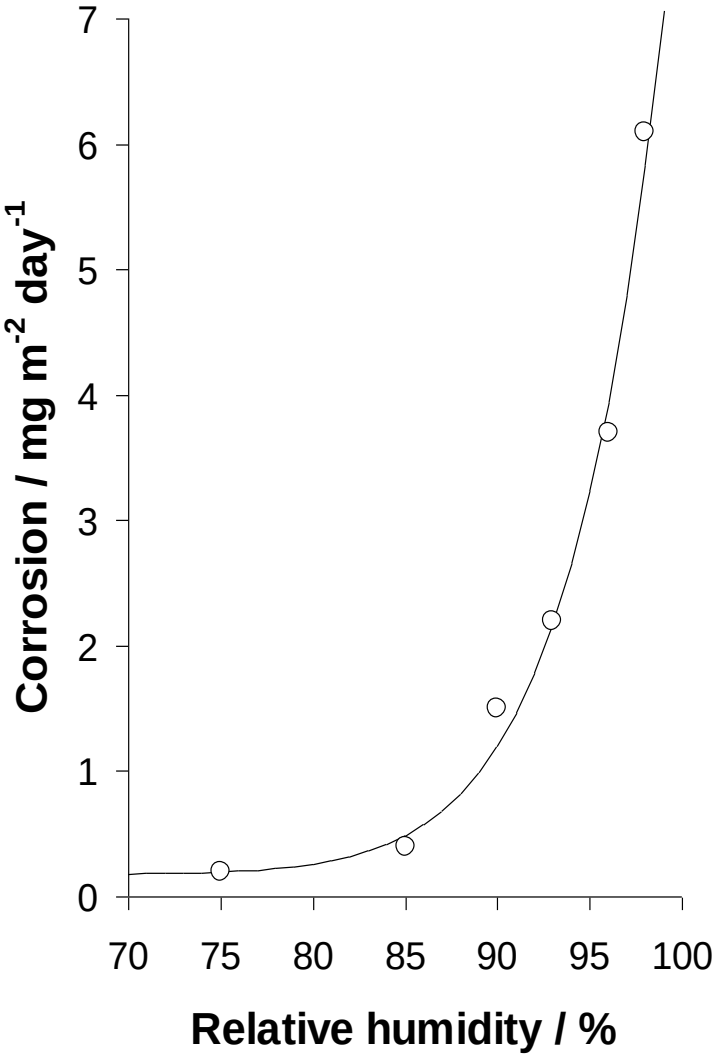


3. Atmospheric constituents



- Anode reaction : $Me \rightarrow Me^{2+} + 2e^-$
- Cathode reaction, e.g : $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2\ OH^-$

Corrosion rate of carbon steel



Interaction of water with metal surfaces, cont.

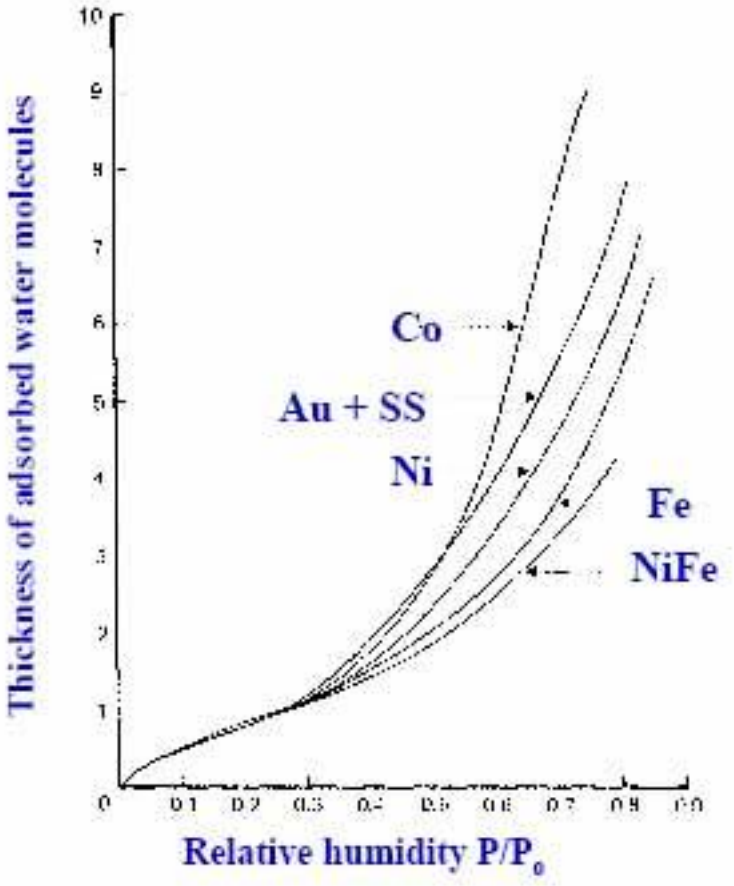
This initially formed film is relatively protective and reduces the reaction rate of water with the hydroxylated surface. Subsequent water with a vapour pressure of 10 torr requires of the order of tens of hours to produce one monolayer of reactions products.

The quantity of reversibly adsorbed water increases with relative humidity and with time. At 25C and steady state conditions, the following approximate number of monolayers are obtiande, irrespective of metal substrate:

Relative humidity (%)	Number of water monolayers
20	1
40	1.5-2
60	2-5
80	5-10

Interaction of water with metal surfaces, cont.

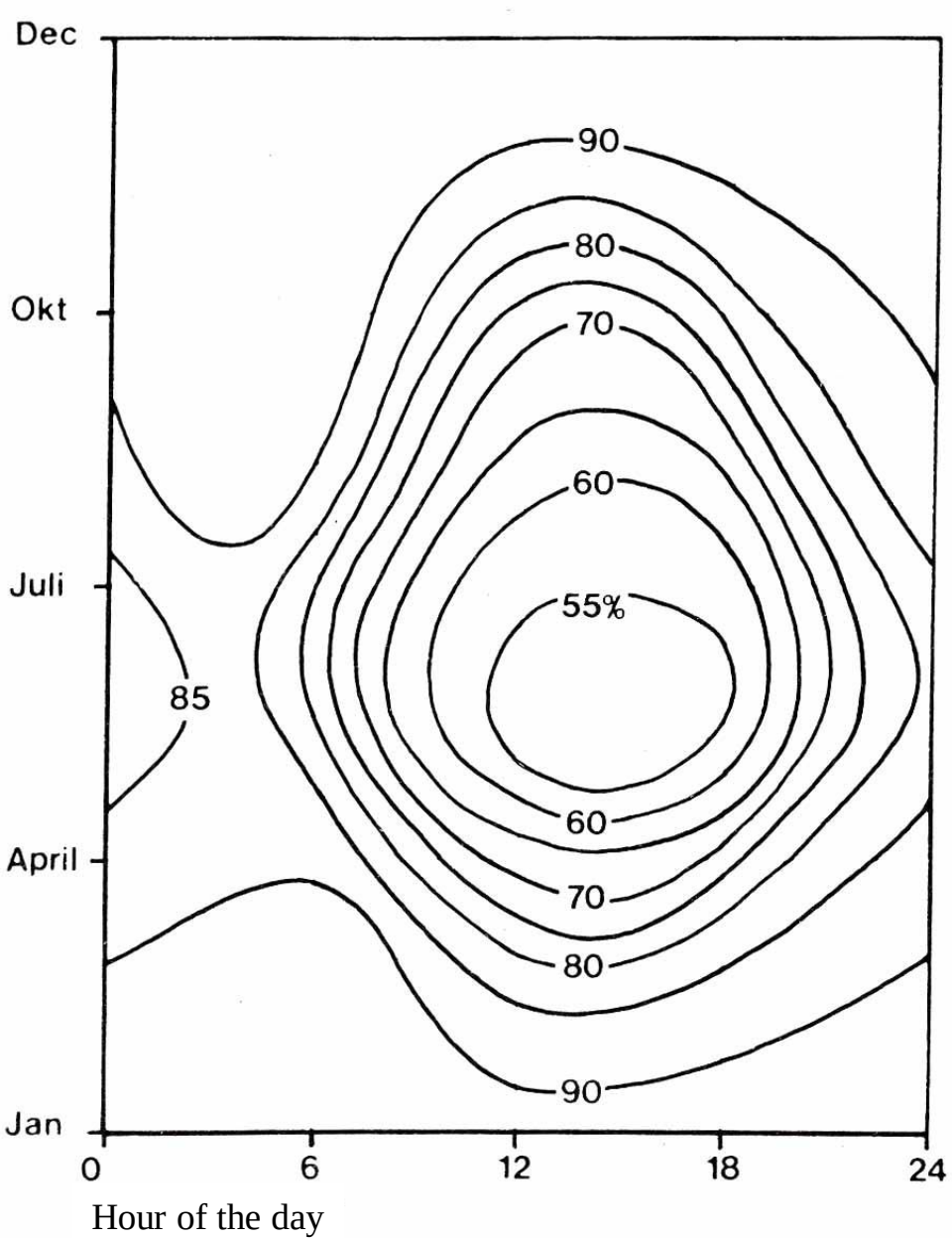
The adsorption characteristics of water is strikingly similar for many different metals. It seems that the exact nature of the hydroxylated metal oxide surface only has minor influence on the reversible adsorption phenomena.



More humid conditions

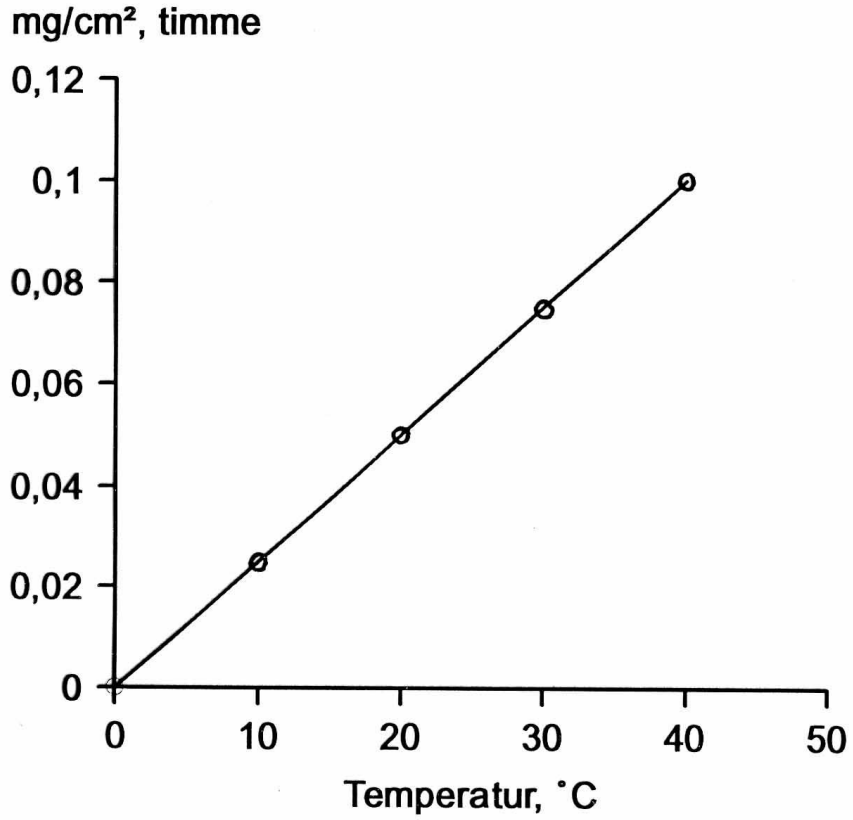
Condition	Amount of water, μm
Critical relative humidity	0.01
100 % relative humidity	1
Dew	10
Rain	100

Relative humidity, Uppsala 1866-1945

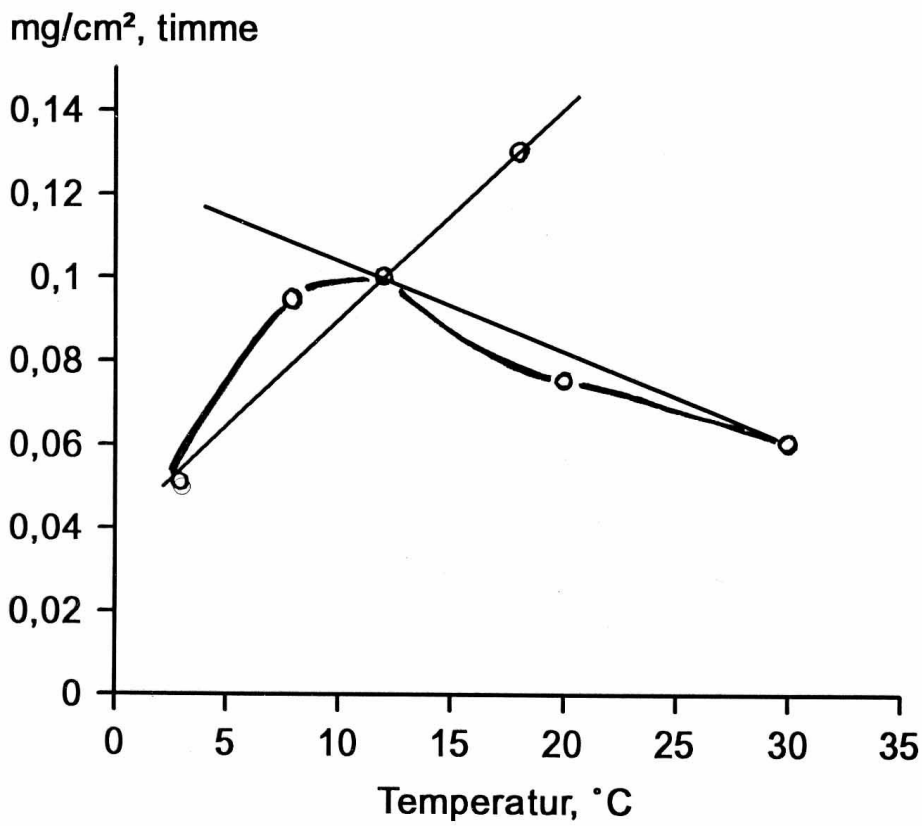


Influence of temperature, carbon steel

Rain



Drying of moisture film, 75% relative humidity



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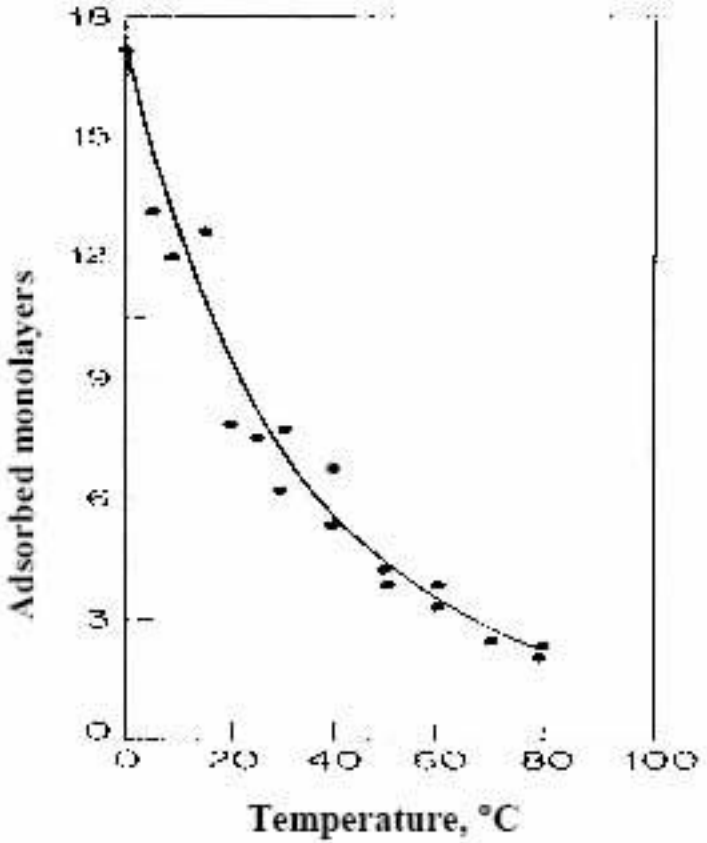
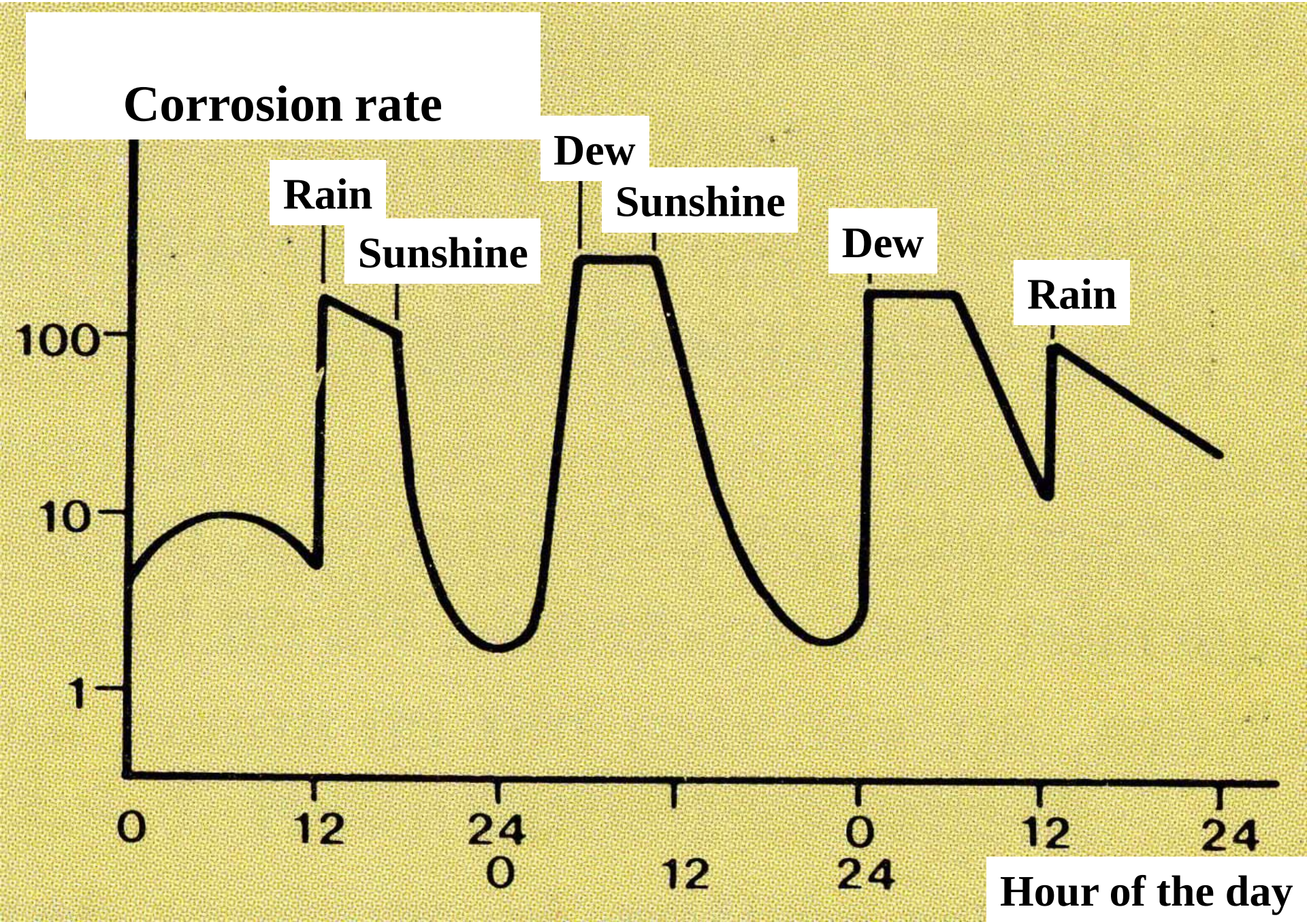
Temperature dependence of water adsorption.



The amount of physically adsorbed moisture on the surface of zinc at various temperatures and at a constant relative humidity of 93%.

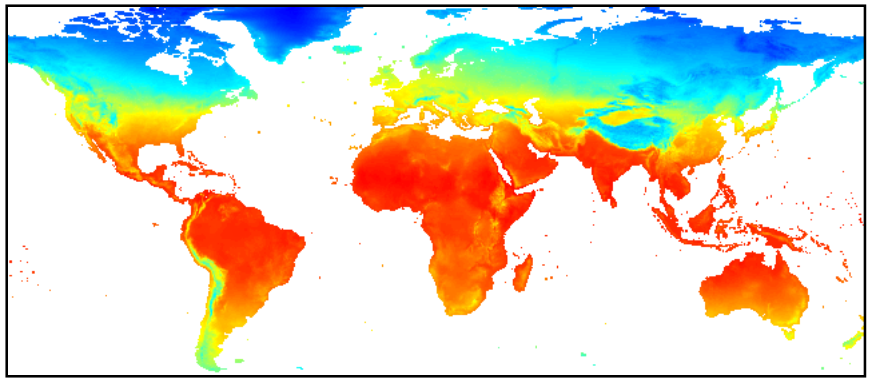

Corrosion rate
Rain
Sunshine
Dew
Sunshine
Dew
Rain
100
10
1
0
12
24
0
12
0
24
12
24
Hour of the day

Time of wetness
Rh>80% and T>0°C

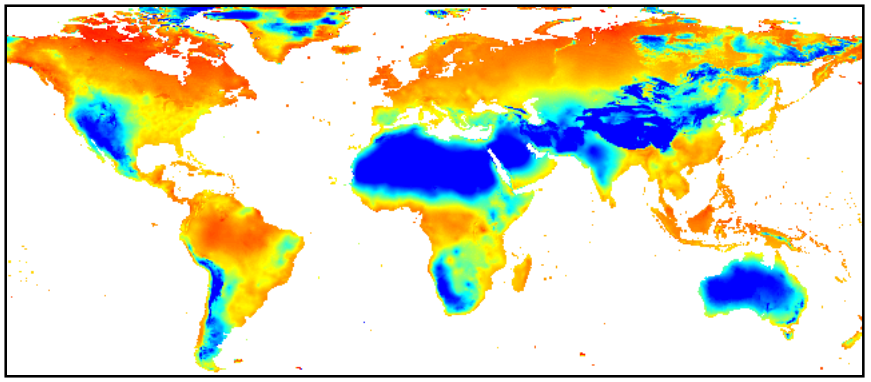
Place	Rh %	T °C	Tow h / year
Gällivare	76	-1,2	1600
Prag	77	8,3	2700
Beijing	60	11,5	840
Chengdu	83	16,4	6200
Maximum			8766

Climate maps

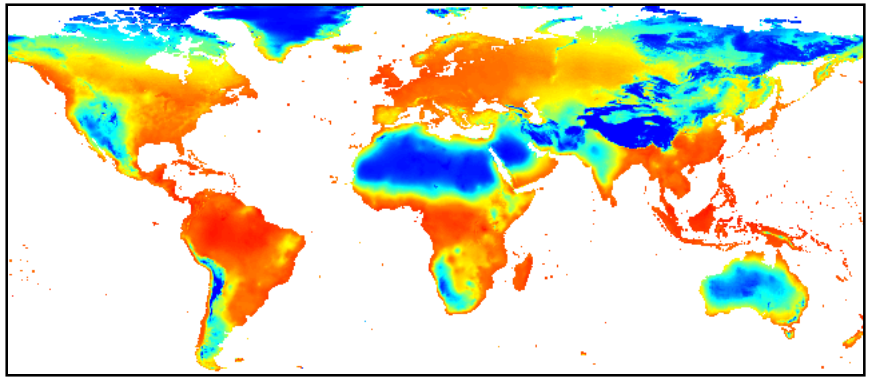
Temperature (T)



Relative humidity (Rh)



Time of wetness (Tow)



Tow
Rh>80% & T>0°C

Gaseous atmospheric corrosion stimulators.

Outdoor and indoor concentration ranges (in ppbv) of selected gaseous air constituents together with their solubilities in aqueous systems, expressed as Henry´s law constant (H, M/atm).

Species	Outdoor (ppbv)	Indoor (ppbv)	H (M/atm)
O_3	4-42	3-30	0,018
H_2O_2	10-30	5	240000
SO_2	1-65	0,3-14	1,4
H_2S	0.7-24	0,1-0,7	0.15
NO_2	9-78	1-29	0,007
HNO_3	1-10	3	91000
NH_3	7-16	13-260	1.0
HCl	0,2-3	0,05-0,2	2,0
HCHO	4-15	10	14000
HCOOH	4-20	20	3700

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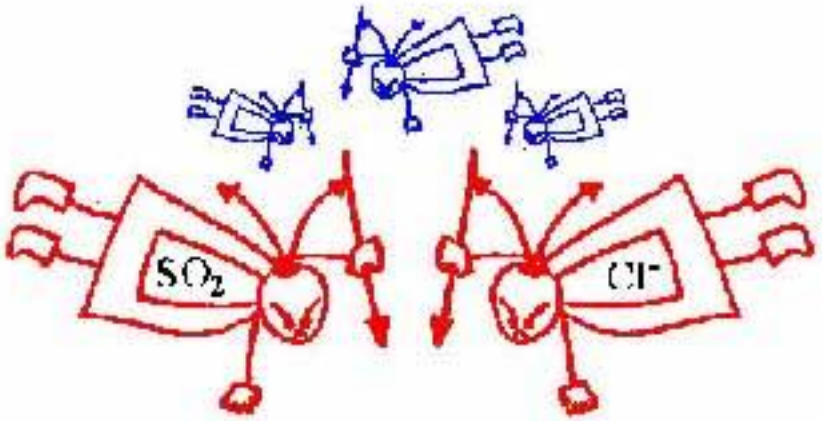
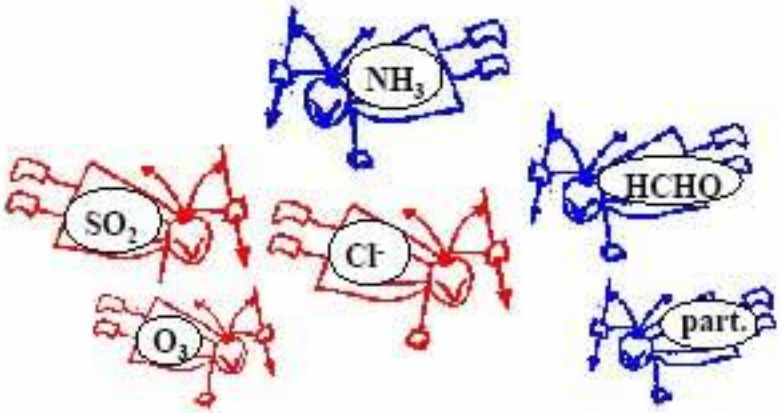
Corrosion effects outdoors vs. indoors.

Outdoors

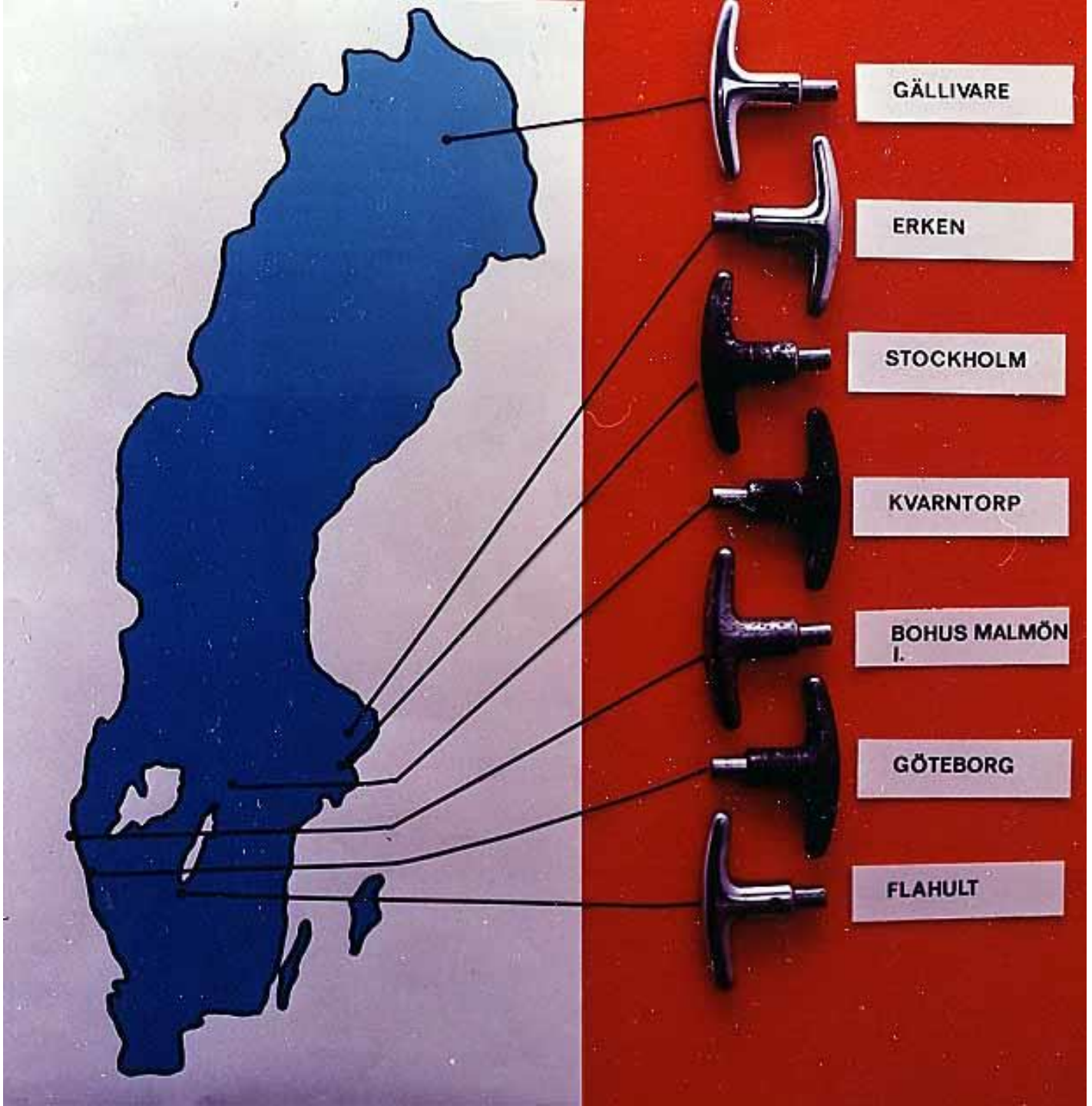


Metal

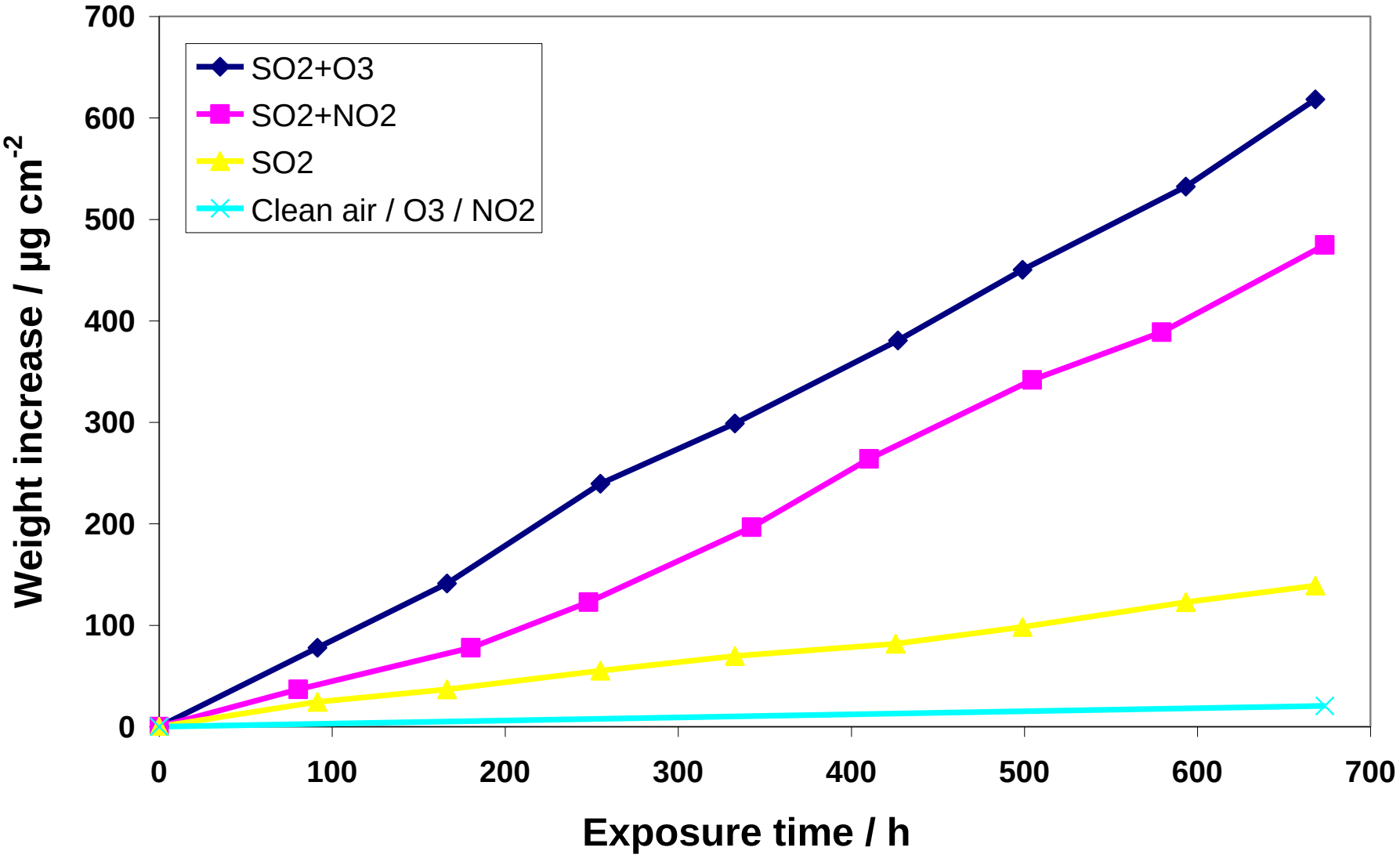
Indoors



Metal


GÄLLIVARE
ERKEN
STOCKHOLM
KVARNTORP
BOHUS MALMÖN I.
GÖTEBORG
FLAHULT

Synergistic effects, zinc



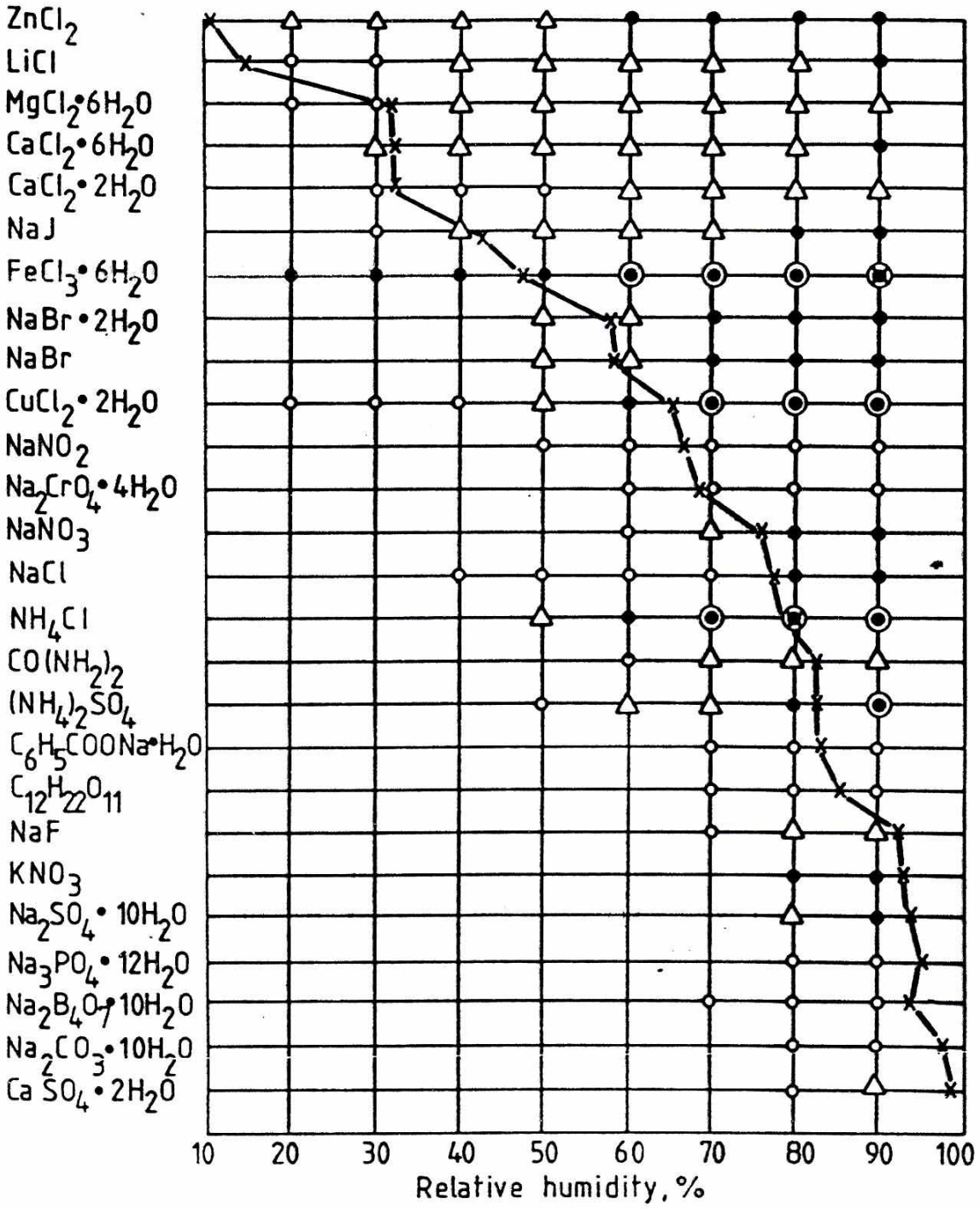
Source: J.-E. Svensson et al, Chalmers, Göteborg

Particulate matter

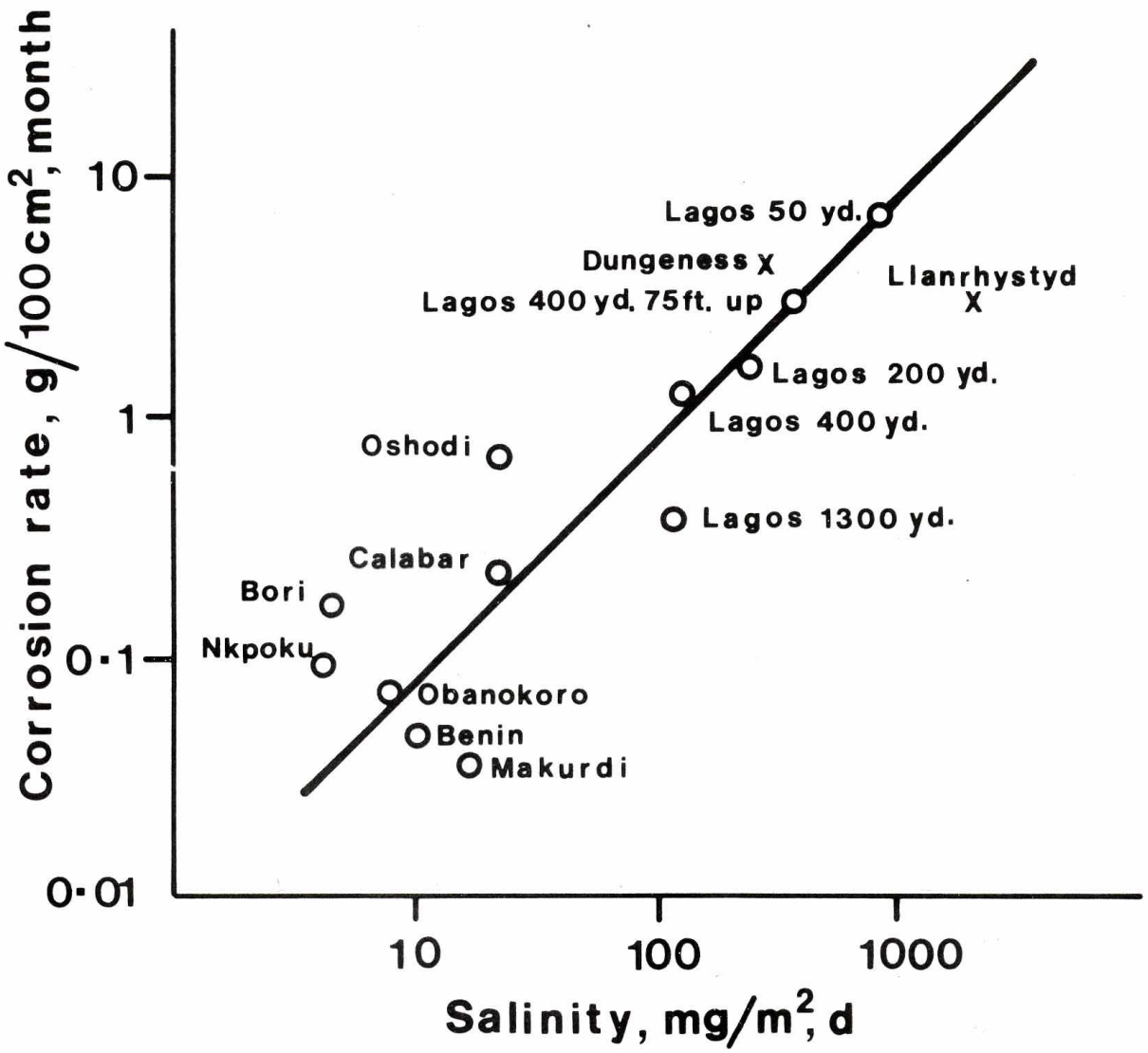
Corrosion of carbon steel due to different salts

○ 0-1 mg
△ 2-5 mg
● 6-20 mg
⊙21-100 mg

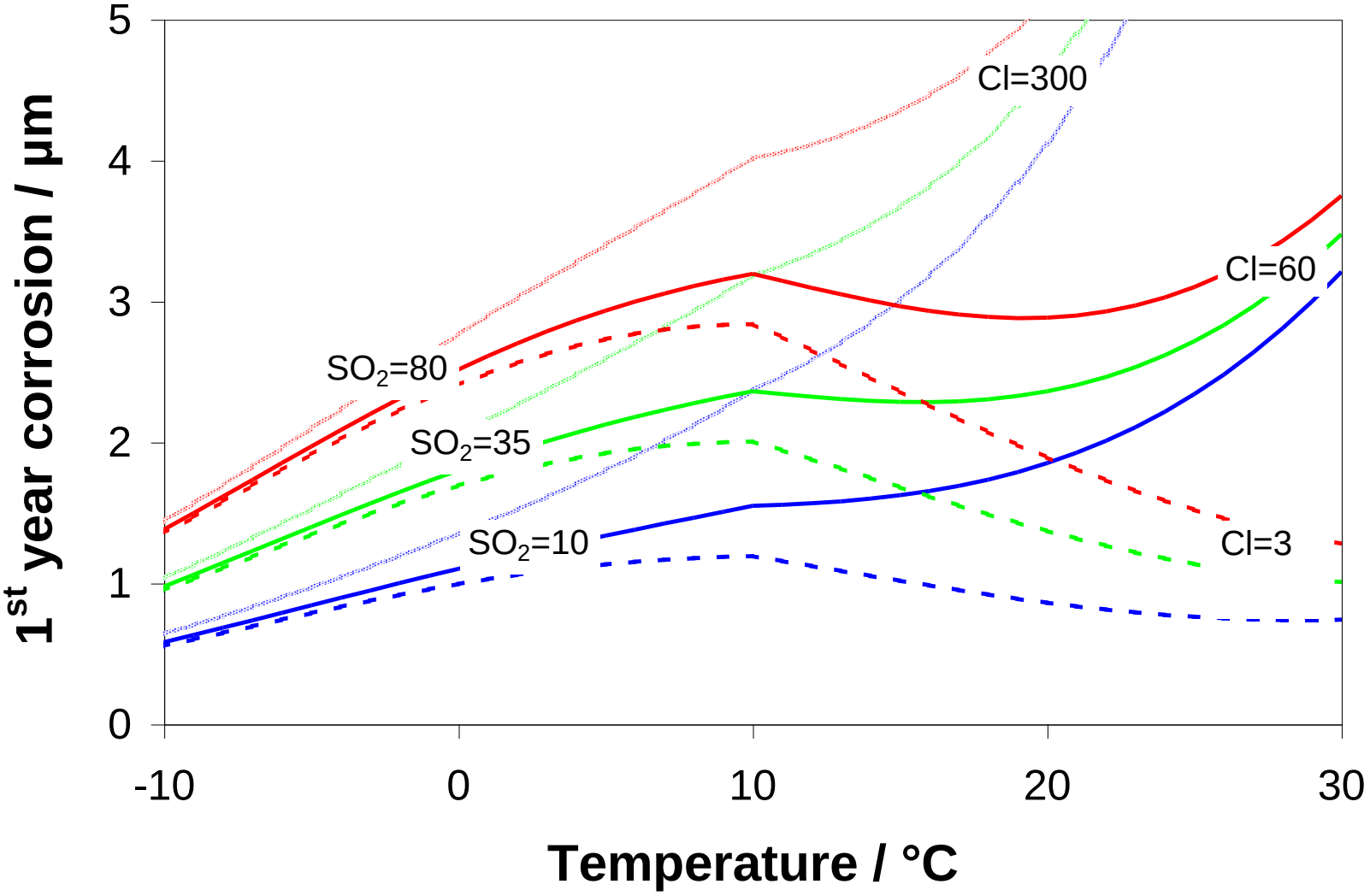
x (solid line) is Rh at equilibrium with a saturated solution



Corrosion of carbon steel at different levels of salinity

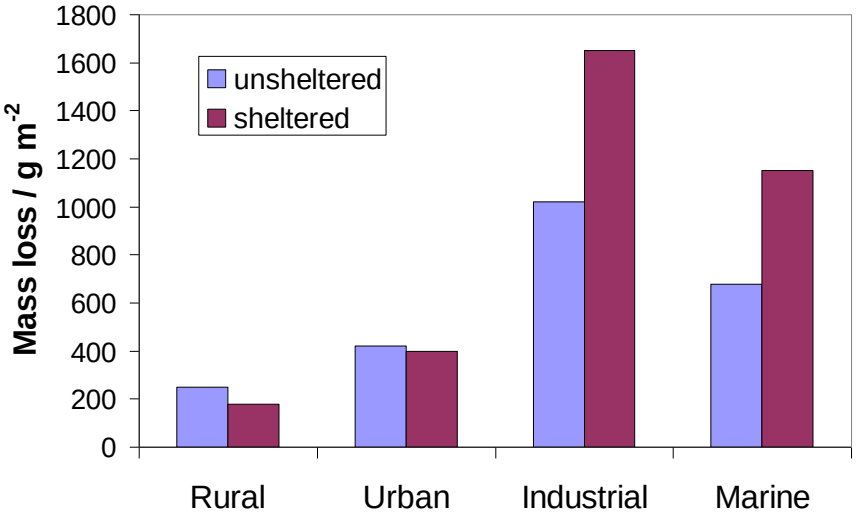


Zinc corrosion temperature dependence

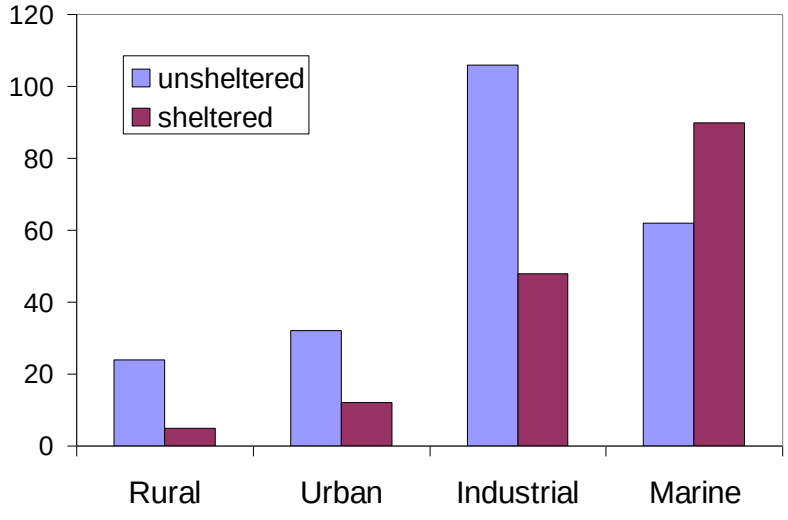


Effect of rain

Carbon steel



Zinc



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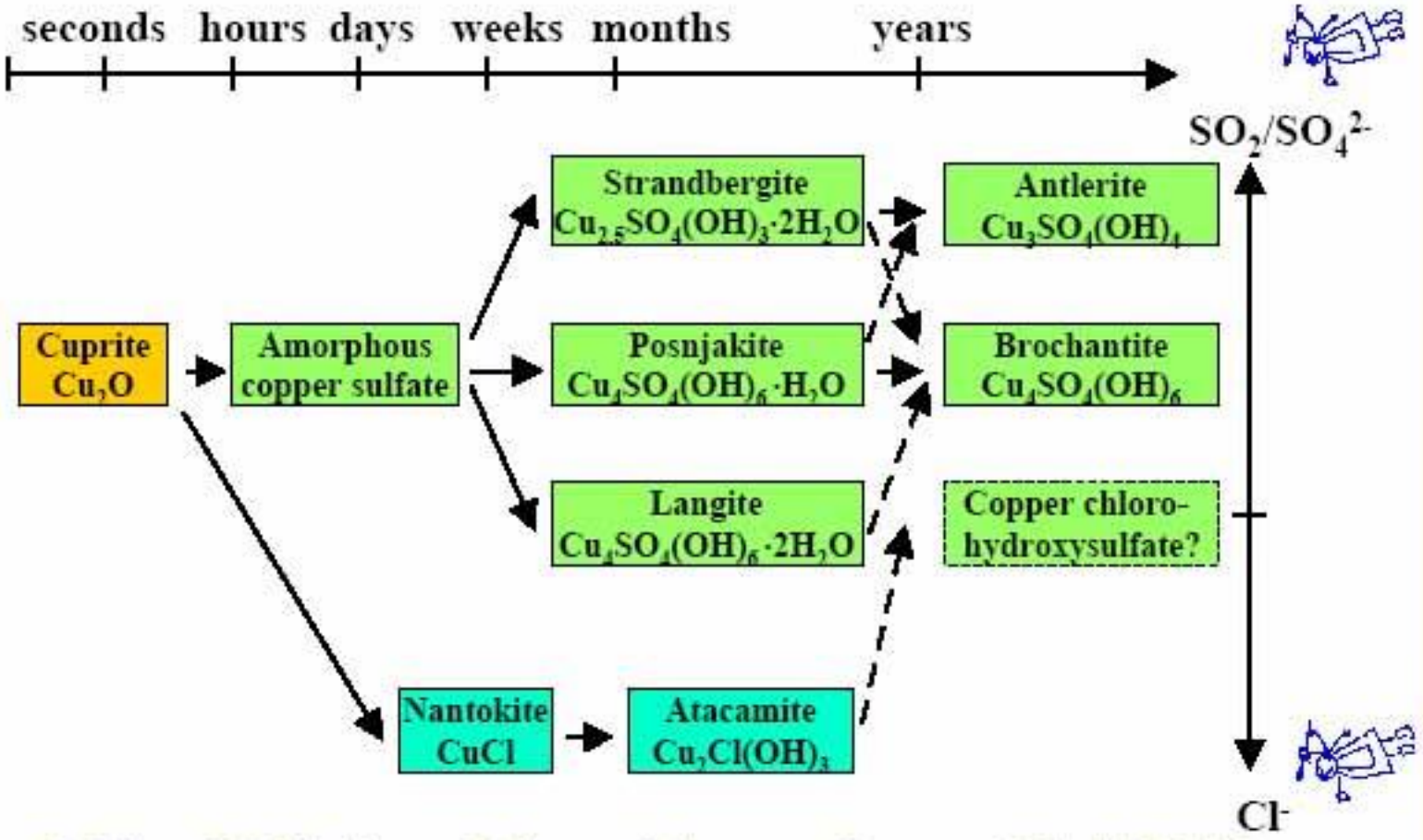
The evolution of copper patina.



A. Krätschmer, I. Odnevall Wallinder and C. Leygraf, Corrosion Science, 44(3), 425 (2001)

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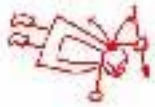
The evolution of zinc patina.

$Zn_4SO_4(OH)_6 \cdot nH_2O$ → $Zn_4Cl_2(OH)_4SO_4 \cdot 5H_2O$

SO_2/SO_4^{2-}



ZnO / $Zn(OH)_2$ → $Zn_5(CO_3)_2(OH)_6$

$NaCl/Cl^-$

$Zn_5(OH)_8Cl_2 \cdot H_2O$ → $NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$

seconds *hours* *days* *weeks* *months* *years*

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The cycle of metals.

Metal

Corrosion & Wear

Complex Compound Ion

(Me-EDTA) ($Me_4SO_4(OH)_6$) ($Me(H_2O)_6^{2+}$)

Mineralization

Mineral

Metal extraction

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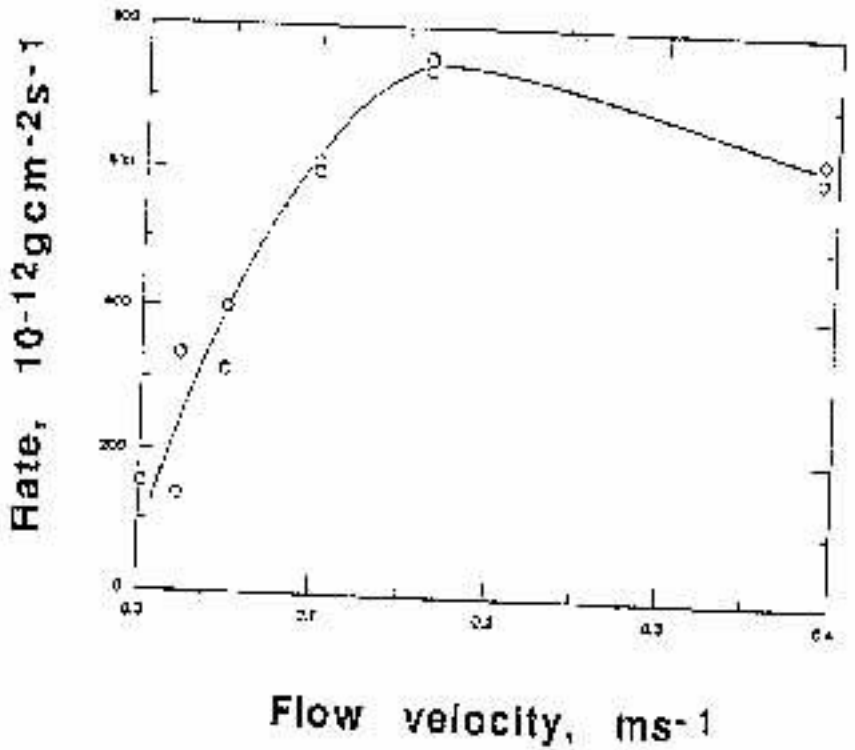
Air flow velocity dependence on atmospheric corrosion rate of copper.



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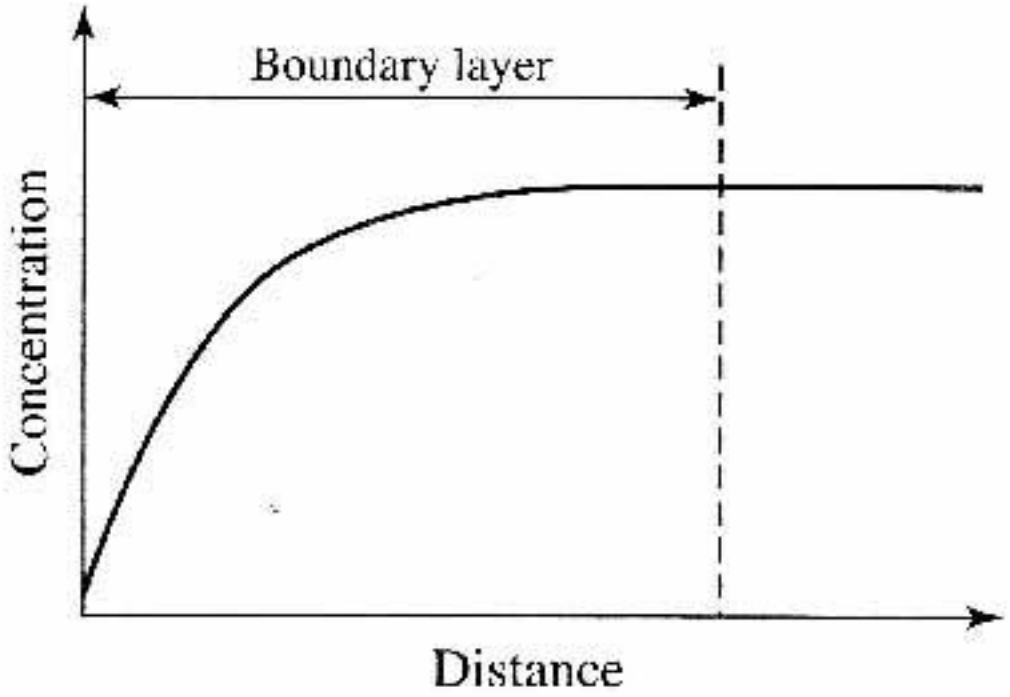
The boundary layer in the gas phase next to the solid phase.



Summary of important parameters for atmospheric corrosion

- Climate
- Air pollutants (gases and particles)
- Other aggressive substances (clorides)
- Acid rain
- wind