

Corrosion and Green Chemistry

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FROM RESEARCH TO INDUSTRY

cea den



CORRUSION & GREEN CHEMISTRY

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Green workshop "The perspectives on sustainable building and products - challenges and opportunities. Anticorrosion in sustainable building industry"

EUROCORR 2018

Wednesday 12, 2018 - KRAKOW, POLAND

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SYNOPSIS

Introduction

Green chemistry

Corrosion and green chemistry principles

Declination of the 12 principles

Conclusive remarks

Corrosion and green technologies



CORROSION …

The annual cost of corrosion is 3-4% of the world's Gross Domestic Product

One quarter of the steel annual production is destroyed by corrosion

Source: World Corrosion Organization (granted NGO by the United Nations)

Illustrations from the web



ERIKA (1999) "result of structural weakness caused by corrosion"



Mississippi Bridge, Minneapolis, August 1, 2007, 13 fatal structural weakness caused by corrosion



Pitting corrosion of an oil tank



Corrosion cracking of the fuselage of airplane (April 28, 1988 – 1 fatal over 95)



Sculpture by David E. Davis



Atmospheric corrosion in a chemical plant

GREEN CHEMISTRY…

The 12 principles of Green Chemistry

1. Prevention of waste & pollution
2. Atoms economy
3. Less hazardous conditions
4. Design safer chemicals
5. Benin solvents
6. Design for energy efficiency
7. Use of renewable feedstocks
8. Reduce derivatives
9. Catalysis
10. Design for innocuous degradation
11. Pollution prevention
12. Safer for accident prevention



From P.T. Anastas & J.C Warner, "Green Chemistry: theory & practice, 1998, Oxford University Press, New-York, USA & S. Sarrade, La chimie d'une planète durable, Editions Le Pommier, 2011.

Principle 1…

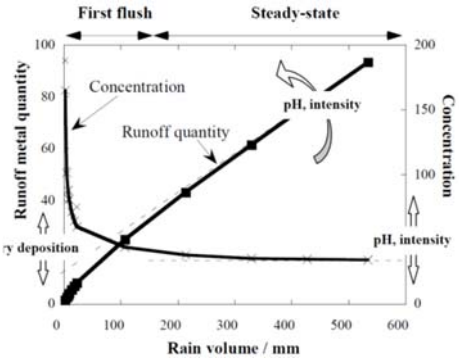
Prevention: it is better to prevent waste/pollution than to treat and clean up after it has been done



Illustration - Pollution linked to the copper roofs

In many cities, copper roofs are used since centuries, but with the recent requirements regarding the polluted waters, raining waters on these roofs are becoming too concentrated in metallic cations …





Solutions :

- More resistant alloys
- Pre-oxidized copper surfaces

C. Leygraf & al., Atmospheric corrosion, ECS series, 2000

Principle 2…

Atoms economy: economy of "raw materials"

Illustration – extension of exploitation time of industrial equipements

Initial nuclear power plants were planned for 30 years, new ones are planned for 60 years of operation and the exploitation of some old ones have been extended to 60 years or more, one reason being a very good corrosion resistance of the alloys.

Atoms economy:

7 000 tonnes for the confinement building,
550 tonnes for the steam generator,
330 à 510 tonnes for the vessel, ….



Beznau nuclear power plant (1969, 365 Mwe, initially planned for 40 years, the oldest nuclear power plant in operation today

Principle 3…

Less hazardous conditions: working and living in safer conditions with less hazardous chemicals

Illustration – the control of corrosion is needed for safe operation of plants and civil structures



Highway bridge over the Mississipi, Minesota, 2007 (40 years old, corrosion)



Viaduc de Polcevera, Genova, 2018 (09-1967)

Actions:

- In France 302 events are linked to corrosion and are analyzed on a governmental web site with the objective to inform and prevent

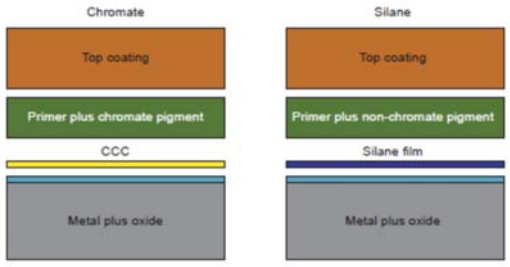
https://www.aria.developpement-durable.gouv.fr/wp-content/files_mf/SY_corrosion_JFM_FR_20052014.pdf

Principle 4…

Design safer chemicals: Chemical products should be designed to affect their design function while minimizing their toxicity

Illustration – Corrosion inhibitors (Directive REACH)

Chromium is a surprisingly common ingredient in anticorrosion coatings such as the paint pretreatment being sprayed on the airplane fuselage, but chromium ions are a serious health threat when inhaled or ingested





Solutions:

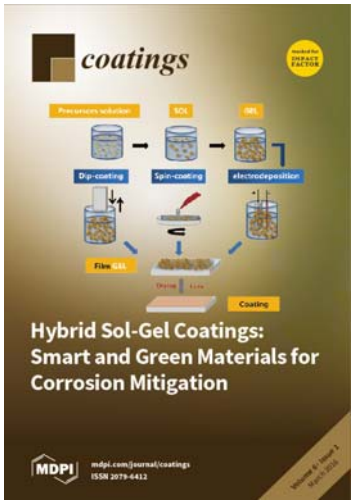
- Large developments for new and « green » inhibitors
  silane coatings for aerospace (?)

Principle 5…

Benin solvents: The use of auxiliary substances (e.g., solvents) should be made unnecessary wherever possible and, innocuous when used**.**

Illustration – protective coatings for anticorrosive purposes

International and national legislation aiming at reducing the emission of volatile organic compounds (VOCs) have caused significant changes in the anticorrosive coating industry



Solutions

- Solvent-free epoxy coatings are designed for long-term protection of steel & concrete structures against corrosion
- Water-borne anticorrosive paints are acquiring increasing relevance for the anticorrosive protection of steel surfaces exposed to the atmosphere…

Principle 6…

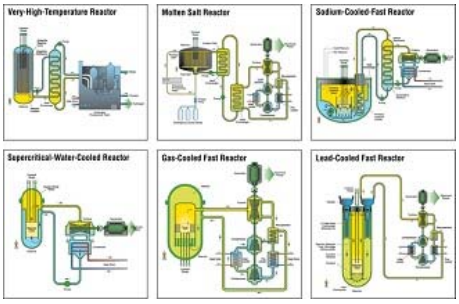
Design for energy efficiency

Illustration – Efficiency of electricity production

Thermal electricity generation process is limited by the Carnot efficiency = $(T_{source} - T_{sink}) / T_{source}$. High temperatures of T_{source} lead to a better efficiency, but corrosion is thermally activated.



A supercritical coal plant in Germany achieves thermal efficiency of 46%



Six nuclear energy systems for further development

Challenges:

- Thermally resistant alloys
- High temperature corrosion

https://www.gen-4.org
https://www.oecd.org/officialdocuments/

Principle 7…

Use of renewable feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Illustration – "Green Corrosion inhibitors", coming from plants, bacteria, fungi,…







Table 1: Green inhibitors used for corrosion inhibition of steel.

Sl. no.	Metal	Inhibitor source	Active ingredient	References
(1)	Steel	Tamarind		[39]
(2)	Steel	Tea leaves		[40]
(3)	Steel	Pomegranate juice and peels		[41]
(4)	Steel	*Emblica officinalis*		[42]
(5)	Steel	*Terminalia bellerica*		[43]
(6)	Steel	Eucalyptus oil	Monomtrene 1,8-cineole	[44]
(7)		Rosemary		[45]
(8)	C-steel, Ni, Zn	Lawsonia extract (Henna)	Lawsone (2-hydroxy-1, 4-napthoquinone resin and tannin, coumarine, Gallic, acid, and sterols)	[46]
(9)	Mild steel	Gum exudate	Hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and nonreducing sugars	[47]
(10)	Mild steel	*Musa sapientum* peels (Banana peels)		[48]
(11)	Carbon steel	Natural amino acids—alanine, glycine, and leucine		[48]
(12)	Steel	Natural amino acids		[15]
(13)	Mild steel	*Garcinia kola* seed	Primary and secondary amines Unsaturated fatty acids and biflavnone	[49]
(14)	Steel	*Auforpio turkiale*	Protein hydrolysis	[50]
(15)	Steel	*Azydracta indica*	Protein hydrolysis	[51]
(16)	Steel	Aloe leaves		[52]
(17)	Steel	Mango/orange peels		[53]
(18)	Steel	*Hibiscus sabdariffa* (*Calyx extract*) in 1 M H_2SO_4 and 2 M HCl solutions, Stock 10–50%	Molecular protonated organic species in the extract. Ascorbic acid, amino acids, flavonoids, Pigments and carotene	[54]

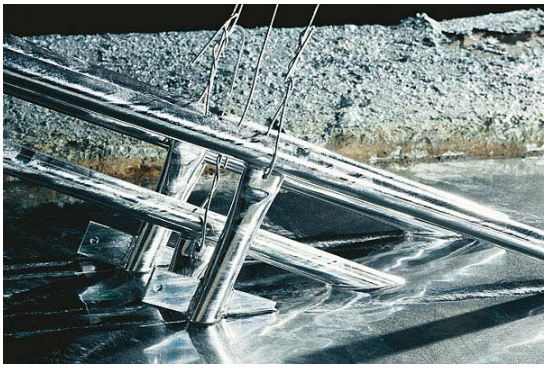
B. E. Amitha Rani and Bharathi Bai J. Basu, Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview, International Journal of Corrosion, 2012,

Principle 8…

Reduce derivatives: Try not to have too many steps in the reaction because this means more reagents are needed and it can generate waste

Illustration – galvanizing

- Galvanization is the process of coating iron and steel with zinc is widely used in applications where corrosion resistance is needed.
- Electro- galvanization used high chemical electrolytes (cyanides, caustic or acid solutions with several types of preparation)
- Hot-dip galvanization is used more and more during which the steel is dipped into molten zinc and so less chemical reagents are used.

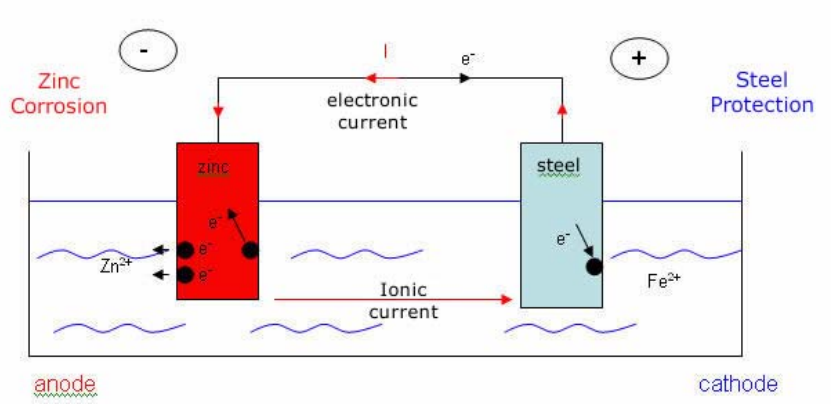


Références à ajouter

Principle 9…

Catalysis

Illustration – cathodic protection



- Anodic reaction is increased on the « anode »
- Cathodic reaction is increased on the « cathode », the metal to protect
- To avoid cationic metallic pollution, imposed current is used

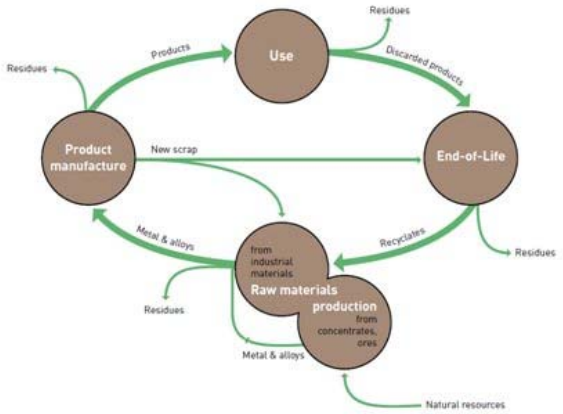
Principle 10…

Design for innocuous degradation: design a product including for its final degradation.

Illustration - recycling metals and alloys

Metal	Global recycling rate, %
Aluminum	40
Copper	38
Iron/steel	47
Lead	47
Nickel	34
Zinc	36

Table 1. Indicative global recycling rates of some metals – values depend on the measure used and should usually be defined as a range due to the complexity of recycling systems ([NOR] & [REU2])



Evolution

- Life cycle management
- Include other metals (Mo, Co, Sn, In…)

Challenges of metals recycling, Markus A. Reuter, Ilkka V. Kojo

Principle 11…

Pollution prevention: real-time, in-process monitoring and control prior to the formation of hazardous substances.

Illustration – corrosion monitoring

Metallic cations are pollutants for natural environments
Corrosion Monitoring is a process that evaluates and monitors equipment components, structures, process units, and facilities for signs of corrosion.
It is a way to know corrosion rates and releases of metallic ions in aqueous environments
It is a way to control structure integrity and environmental pollution



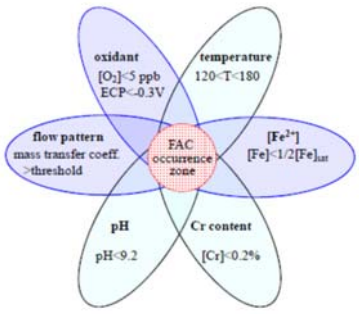


Principle 12…

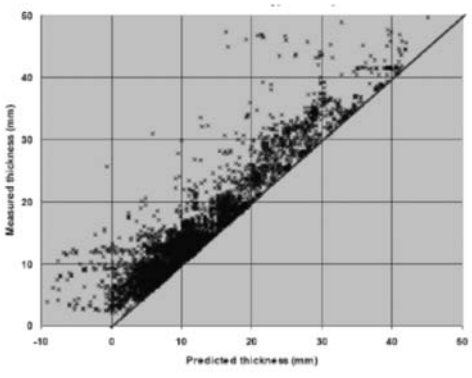
Safer for accident prevention: process should be chosen to minimize the potential for accidents, including chemical releases, explosions, and fires

Illustration - modelling of flow accelerated corrosion (FAC)

FAC leads to several accidents with causalities in all steam-water systems including nuclear power plants
In France BRT-Cicero code is used



Ajouter référence Cicero.



CONCLUSIVE COMMENTS

Corrosion follows the 12 principles of "green chemistry"

Design, inhibitors, coatings, monitoring, modelling…



Knowledge in corrosion is also needed for the development of "green" technologies

Windmills (coastal & offshore)

Supercritical water technologies (energy and waste destruction)

Supercritical CO_2 (solvent, energy & storage)



Corrosion of pipes in $SCCO_2$ storage system
from G. Schmitt, White paper, WCO, 2009



EUROPÄISCHE FÖDERATION KORROSION
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THE WORLD CORROSION ORGANIZATION

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Welcome to WCO – The World Corrosion Organization
a non-governmental organization (NGO) of the United Nations (UN)
April 24th is Corrosion Awareness Day







Thank You for your attention

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