

Corrosion

Course contents:

Corrosion is the destructive attack of a metal by its reaction with environment. Thus corrosion refers to the degradation of a metal by its environment. The course in corrosion science is intended for master students. The course emphasizes basic principles of corrosion and describes challenges for today's corrosion science.

Subjects covered by the lectures are

- Societal aspects of corrosion
- Corrosion as a phenomenon
- A brief review of thermodynamics
- Thermodynamics of corrosion
- Kinetic of corrosion
- Passivity
- Mechanically Assisted Corrosion

Learning outcomes of the course :

Through a deep understanding of the theory and the realization of a project, the student will be able to describe and outline fundamental definitions and results of corrosion science and mechanical aspects of corrosion. He will be able to name the mechanisms of corrosion and tools to prevent corrosion in different environments. In particular:

- He will have a deep understanding of corrosion notions and aspects and will be able to summary, compare and explain them.
- He will have a deep understanding of the resolution methods of corrosion theories problems, and will be able to summary, compare and explain them. He will also know their application range.
- He will be able to apply the resolution methods to classical problems of corrosion theories.
- He will be able to analyze and to evaluate (justify and criticise) these methods.
- He will be able to analyze new problems.

Prerequisites and co-requisites/ Recommended optional programme components :

Basic knowledge in

- Differential Equations
- Elasticity Theory
- Plasticity Theory
- Creep Theory
- Thermodynamics
- Fracture Mechanics

Planned learning activities and teaching methods :

Exercises with professor assistance and personal project.

Mode of delivery (face-to-face ; distance-learning) :

Face-to-Face

Required readings :

- Groysman A. Corrosion for Everybody. New York: Springer, 2010. 377 p.
- McCafferty E. Introduction to Corrosion Science. New York, Dordrecht, Heidelberg, London: Springer, 2010. 574 p.
- Revie, R.W. (Ed.) Uhlig's Corrosion Handbook, Second Edition, Wiley-Interscience, 2006, pp. 305–328, 515–528, 569–580.

Assessment methods and criteria :

Evaluation is based on the realization of a project related to the use / development of numerical methods specific to corrosion mechanics and on an examination.

The examination is based on the whole content of the class. Problems similar to the ones studied during the classes, and new problems will be part of the questions. Justification using the theoretical content is also asked.

Participation to the examination and achievement of the project are mandatory.

Socratic Teaching Method: Class participation is mandatory. Everyone is expected to participate in discussions relating to reading materials, homework, exams and lectures.

Guaranteed Recipe for Success:

- 1) Take notes during lecture and sections.
- 2) After each lecture but before the next lecture review your notes. Identify the parts you do not understand.
- 3) Come to each lecture and discussion section with specific questions.
- 4) Keep up with the reading so that you have some familiarity with each topic prior to hearing about it in the lecture.
- 5) Find at least one "partner" in the class with whom you can meet at least once or twice a week to discuss materials from the lectures, the reading assignments and the homework.
- 6) Take the homework assignment seriously. Do not try to do the whole assignment the night before it is due. Some version of the homework questions will appear on the exams.

Course Contents

Corrosion

1 Corrosion Mechanism and Corrosion Factors

1.1 Definition of Corrosion. 1.2 Metals and Non-Metals. 1.3 Prediction of Corrosion of Metals. 1.4 Corrosion Kinetics. 1.4.1 Measuring the Corrosion Rate. 1.4.2 Duration of Corrosion Test. 1.5 Corrosion Mechanisms. 1.5.1 Electrolytes and Non-Electrolytes. 1.5.2 Corrosion of Metals by Non-Electrolytes. 1.5.3 Corrosion of Metals in the Presence of Electrolytes. 1.5.4 Reference Electrodes. 1.5.5 Electromotive Force Series. 1.5.6 Electrochemical Corrosion Mechanism (Corrosion by Electrolytes). 1.5.7 Electrochemical Mechanism on a Single Whole Alloy or Metal. 1.6 Corrosion of Iron in Water and Aqueous Salt Solutions. 1.7 Corrosion of Iron and Carbon Steels in Acids. 1.8 Corrosion Factors. 1.8.1 Influence of pH. 1.8.2 Influence of Dissolved Salts in Water on Corrosion. 1.8.3 Influence of Electrical Conductance of Media. 1.8.4 The Influence of Dissolved Oxygen. 1.8.5 The Influence of Temperature. 1.9 Differential Aeration Cell.

2 Corrosion Phenomena

2.1 Uniform, or General, Corrosion. 2.2 Non-Uniform, or Localized, Corrosion. 2.3 Pitting Corrosion. 2.3.1 Pitting Corrosion Caused by Factors Different from Chlorides. 2.4 Galvanic Corrosion. 2.4.1 Factors Influencing Galvanic Corrosion. 2.4.2 Galvanic Electromotive Force

Series. 2.4.3 Prediction of Galvanic Corrosion Rate by Means of Electrochemical Polarization Curves. 2.4.4 Interchange of Electrode Potentials between Dissimilar Metals. 2.4.5 Ratio between Anode and Cathode Areas. 2.4.6 The Distance between Anode and Cathode. 2.4.7 Galvanic Corrosion in the Presence of Corrosion Products on Metals. 2.4.8 Galvanic Corrosion Caused by the Presence of Metal Cations in Water. 2.4.9 Galvanic Corrosion in the Atmosphere. 2.4.10 Methods to Prevent Galvanic Corrosion. 2.5 Corrosion That Occurs with the Participation of Microorganisms. 2.5.1 Existence of Microorganisms. 2.5.2 Control of Microbiological Activity towards Metals. 2.5.3 The Prevention of MIC. 2.6 Erosion – Corrosion and Cavitation. 2.6.1 Mechanism of Erosion-Corrosion. 2.7 Other Corrosion Phenomena. 2.7.1 Fretting Corrosion. 2.7.2 Intergranular Corrosion. 2.7.3 Dealloying. 2.7.4 Stress Corrosion Cracking. 2.7.5 Hydrogen Damages. 2.7.6 Corrosion Fatigue.

3 Corrosion in Natural and Industrial Environments

3.1 Corrosion in Water. 3.1.1 Prediction of Corrosiveness of Water on the Basis of Chemical Content. 3.1.2 Methods of Prevention of Metallic Corrosion in Water. 3.2 Corrosion in the Atmosphere. 3.2.1 Factors Influencing the Corrosiveness of the Atmosphere. 3.2.2 Mechanism of Atmospheric Corrosion. 3.2.3 Methods of Prevention and Control of the Atmospheric Corrosion of Metals. 3.3 Dew point Corrosion. 3.4 Corrosion under Thermal Insulation. 3.4.1 Types of Insulation. 3.4.2 Corrosion Mechanism. 3.4.3 Prevention of Corrosion under Thermal Insulation. 3.5 Corrosion in Fuels. 3.5.1 Synthetic Chemicals in Gasoline, Polymers, and Ecology. 3.5.2 Change of Chemical and Physical Properties of Fuels Because of Metallic Corrosion. 3.6 Corrosion of Storage Tanks for Fuels and Their Corrosion Control. 3.6.1 Gasoline ASTs. 3.6.2 Gas Oil ASTs. 3.6.3 Heavy Fuel Oil Storage Tanks. 3.6.4 Crude Oil Storage Tanks. 3.6.5 Anti-Corrosion Techniques for ASTs. 3.7 Corrosion and Corrosion Control in the Presence of Naphthenic Acids. 3.7.1 Mitigation Measures.

4 Corrosion Control Measures

4.1 Use of Coatings. 4.1.1 Organic Coatings. 4.1.2 Surface Preparation. 4.1.3 Selection of Coating System. 4.1.4 Metallic Coatings. 4.2 Electrochemical Methods of Corrosion Control. 4.2.1 Cathodic Protection. 4.2.2 Criteria for Cathodic Protection. 4.2.3 Use of Organic Coatings Together with Cathodic Protection. 4.2.4 Limitations and Disadvantages of Cathodic Protection. 4.3 Change of Chemistry of the Environment. 4.3.1 Corrosion Inhibitors. 4.3.2 Corrosion Inhibitors in Water and Aqueous Solutions of Electrolytes. 4.3.3 Corrosion Inhibitors in Acidic Media (Pickling Inhibitors). 4.3.4 Mechanism of Corrosion Control with Inhibitors. 4.3.5 Factors Influencing Efficiency of Corrosion Inhibitors. 4.3.6 Inhibitor Efficiency. 4.3.7 Application of Corrosion Inhibitors and Some Recommendations. 4.3.8 Inhibitors and Ecology.

5 Corrosion Monitoring

5.1 Corrosion Allowance. 5.2 Corrosion Monitoring Methods. 5.2.1 Physical Methods of Corrosion Monitoring. 5.3 Controlling the Environment (Chemical Analytical, Physico-Chemical, Physical, and Microbiological Methods). 5.3.1 Monitoring of Microbiological Activity towards Metals. 5.3.2 Deposit Accumulation Test (Heat Transfer Resistance Method). 5.3.3 Hydrogen Monitoring. 5.4 Electrochemical Methods. 5.4.1 The Measurement of Oxidation/Reduction (Redox) Potential (ORP). 5.4.2 The Measurement of the Corrosion Potential of Metallic Equipment. 5.4.3 Linear Polarization Resistance (LPR) Method. 5.4.4 Electrochemical Noise Measurements (ENM). 5.4.5 Zero Resistance Ammetry (ZRA). 5.4.6 Electrochemical Impedance Spectroscopy (EIS). 5.4.7 Harmonic Distortion Analysis (HDA), or Harmonic Analysis (HA). 5.5 Monitoring of the Corrosiveness of the Atmosphere. 5.6 On-Line, Real-Time Corrosion Monitoring in Industrial Systems.

6 Humanitarian Aspects of Corrosion Science and Technology

6.1 History of the Evolution of Knowledge about Corrosion. 6.1.1 Ancient Times. 6.1.2 Metals and Mysticism. 6.1.3 The Alchemy Ages. 6.1.4 From Alchemy to Chemistry (1500–1791). 6.1.5 Discovery of New Metals. 6.1.6 Definition of “Corrosion”. 6.1.7 “Renaissance” Era (1791–1890). 6.1.8 “Baroque” Era (1890–1935). 6.1.9 “Classical” Period (1935–1960). 6.1.10 “Modern” Period (after 1960). 6.1.11 Conclusion. 6.2 Corrosion and Philosophy. 6.2.1 Duality and Uncertainty in Corrosion. 6.2.2 Dialectics of Corrosion. 6.2.3 Time in Corrosion, Philosophy and Art. 6.2.4

Corrosion and Entropy. 6.2.5 Beneficial Applications of Corrosion Phenomena. 6.3 Corrosion and Art. 6.3.1 Philosophy of Links between Corrosion and Art.

A Thermodynamics of Oxidation of Iron and Carbon Steels in Water

A.1 Reactions of Iron and Steels with Water.

A.2 Thermodynamics of Oxidation of Ferrous Ions with Oxygen in Aqueous Solutions.

A.3 Reaction of Pure Iron Fe with Ferric Cations Fe^{3+} in Aqueous Solutions

B Reversible and Irreversible Electrode Potential

B.1 Reversible Potential.

B.2 Corrosion Potential.

B.3 Distinction between Reversible and Corrosion Electrode Potential.

B.4 Influence of Temperature on Reversible Electrode Potential of Iron in Aqueous Solutions.

C Electrochemical Kinetics and Polarization Curves

C.1 Polarization.

C.2 The Causes of Polarization.

C.3 Polarization Curves.

Passivity.

Solubility of Oxygen in Water and Aqueous Solutions of Electrolytes

Influence of Temperature on Solubility of Oxygen in Water.

Influence of Pressure on Solubility of Oxygen in Water.

Influence of Type and Concentration of Electrolyte on Oxygen Solubility in Water.

Chemical Compositions of Alloys

Biocides Used in Industry

Physico-Chemical Properties of Crude Oil, Petroleum

Distillates/Fuels, Naphthenic, and Some Aliphatic Acids

Identification of Corrosion Products According to Their Colors

EXAMPLES.

See the examples of Corrosion (The authors of this programme thanks Alex Groysman and his wonderful book Groysmman A. Corrosion for Everybody. Springer, 2010. 377 p.)



Cracks in Admiralty brass tube.



Corroded anchor made of carbon steel



Heat exchanger: tubes made of titanium and baffles made of carbon steel (cooling water, 4 years)



Carbon steel tubes used in contact with water



Scale (calcium and magnesium carbonates) formed inside of heat exchanger with cooling water after 4 years



Metallic structures and equipment in the atmosphere



Natural patina formed on a bronze statue



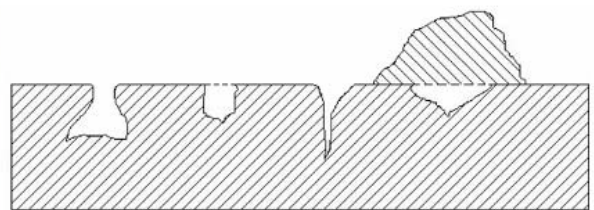
Sculpture "Sun - Man" (1998) made of *weathering steel* (CORTEN) by Jorge Vieira (Lisbon, Portugal).



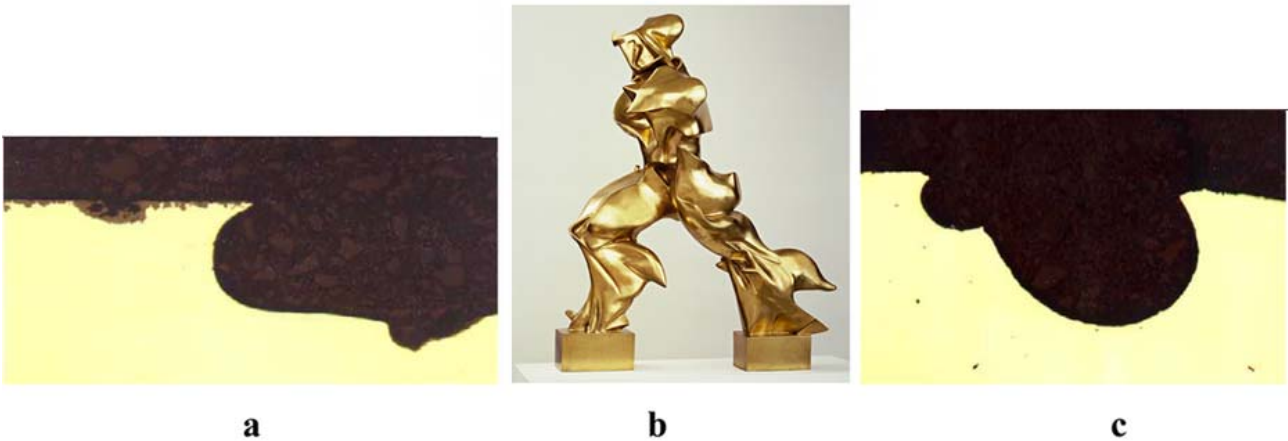
The exhaust system of a vehicle after dewpoint corrosion.



Alberto Giacometti (1901–1966) “Tall Figure” (1949, painted bronze), resembles uniform corrosion. © Photo Scala, Florence, The Museum of Modern Art, New York/Scala Florence, 2009.



Philip Guston “Pit” (1976) National Gallery of Australia, Canberra. The Estate of Philip Guston. Pitting corrosion – severe local corrosion. Reprinted with permission.



a **b** **c**
 Umberto Boccioni (1882–1916) “Unique Forms of Continuity in Space” (1913) or “Erosion”. (a, c) Erosion inside brass tube; (b) the sculpture of Umberto Boccioni. Photo Scala, Florence, The Museum of Modern Art, New York/Scala, Florence, 2009.



Corrosion of vintage US automobiles



A view on the storage, recycling and reclamation of used automobiles (from McCafferty E. Introduction to Corrosion Science. New York, Dordrecht, Heidelberg, London: Springer, 2010. 574 p.).

Recommended Literature

1. Revie, R.W. (Ed.), *Uhlig's Corrosion Handbook*, Second Edition, Wiley-Interscience, 2006, pp. 305–328, 515–528, 569–580.
2. Borenstein, S.B., *Microbiologically Influenced Corrosion Handbook*, Industrial Press, New York, 1994.
3. Charaklis, W.G. and Marshall, K.C. (Eds.), *Biofilms*, John Wiley & Sons, New York, 1990.
4. Flemming, H.C. and Geesey, G.G. (Eds.), *Biofouling and Biocorrosion in Industrial Water Systems*, Springer-Verlag, Berlin, 1991, 220 pp.

5. Geesey, G.G., Lewandowski, Z. and Flemming, H.C. (Eds.), *Biofouling and Biocorrosion in Industrial Water Systems*, Lewis Publishers, CRC Press, USA, 1994, 297 pp.
6. Videla, H.A., *Manual of Biocorrosion*, Lewis Publishers, CRC Press, USA, 1996, 273 pp.
7. Korb, L.J. and Sprowls, D.O., *Metals Handbook, Vol. 13: Corrosion*, Ninth Edition, ASM International, USA, 1987, pp. 114–122, 314–315, 492–494.
8. Gaylarde, C.C., Bentom, F.M. and Kelly, J., Microbial Contamination of Stored Hydrocarbon Fuels and Its Control, *Revista de Microbiologia* **30**, 1999, pp. 1–10.
9. Groysman A. *Corrosion for Everybody*. New York: Springer, 2010. 377 p.
10. Davis, J.R. (Ed.), *Corrosion. Understanding the Basics*, ASM International, USA, 2000, pp. 180–189.
11. McCafferty E. *Introduction to Corrosion Science*. New York, Dordrecht, Heidelberg, London: Springer, 2010. 574 p.

Questions.

- What is Corrosion? Give Definition of Corrosion.
- Describe Corrosion Mechanism and Corrosion Factors.
- Why do some elements and molecules react under particular conditions and others do not?
- Emphasize several points related to the prediction of corrosion of metals by means of thermodynamic Gibbs energy values.
- What do we mean by “mechanism of corrosion reaction”?
- Describe Corrosion of Iron in Water and Aqueous Salt Solutions.
- All metals may be divided into five groups according to their relationship (corrosion resistance) to pH values. Describe the groups.
- We may sum up that electrical conductance of media is very important factor in corrosion processes. Why?
- Outline Factors Influencing the Corrosiveness of the Atmosphere.
- Describe Mechanism of Atmospheric Corrosion.
- Name Methods of Prevention and Control of the Atmospheric Corrosion of Metals.
- How to prevent Corrosion under Thermal Insulation.
- Describe Mechanical (physical) methods of Corrosion Control Measures.

Problems

1. Examples of corrosion can be found in every day life. Describe one example that you have seen. In this particular instance of corrosion primarily an example of wastage of materials, an economic loss, or a safety issue? Or is this a combination of several of these factors? Note: many photographs of corrosion can be found on the Internet. If you not familiar with an examples of corrosion, select one photograph from the Internet and then complete this problem.
2. Based on your everyday experience, name one method of corrosion protection which you have observed in use.
3. Ordinary garbage cans are often constructed from galvanized steel (a coating of zinc on steel). What direct costs and indirect costs of corrosion are involved if you need to replaced such a garbage can with a similar one because your old one is no longer usable due to severe corrosion?
4. Refer to Figures shown above which illustrate the interdisciplinary nature of corrosion. What additional formal disciplines of study would be useful in expanding our knowledge of corrosion?
5. Increasing the corrosion resistance of a metal part or structure so as to make the metal piece last longer is one way to conserve the earth’s supply of metals. What other practices can be undertaken to help stretch our natural supply of metals?
6. Are the following degradation processes strictly physical processes or do they also involve an environmentally assisted components?
 - a) The cleaning of a metal piece by sandblasting.

- b) Damage to the interior of a pipeline used to transport an abrasive slurry of coal.
 - c) The deterioration of steel reinforcing bars in concrete bridges.
 - d) The fracture of an artificial hip constructed of an alloy of cobalt and chromium when in service in the human body.
7. When pure zinc undergoes corrosion in aerated hydrochloric acid, what is the anodic half-cell reaction? Which cathodic half-cell reactions are possible? What is the overall reaction in each case?
 8. Type 430 stainless steel is an alloy of iron and chromium. Suppose that this alloy is used in flowing seawater (pH 8.0) which contains dissolved oxygen. Write the possible anodic half-cell reactions. What is the cathodic half-cell reaction?
 9. What qualitative statement can be made about the change in entropy when a metal atom in a crystalline lattice goes into solution to become a metal cation. Explain your answer.