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Pietro Pedeferri

# Corrosion Science and Engineering

Edited by Luciano Lazzari and MariaPia Pedeferri

In Cooperation with Marco Ormellese, Andrea Brenna, Silvia Beretta, Fabio Bolzoni, Maria Vittoria Diamanti

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# Preface

This Pedeferri's *Corrosion Science and Engineering* textbook is the English edition of Pietro Pedeferri's *Corrosione e Protezione dei Materiali*, Polipress, Milano (2007), with many integrations made by his collaborators of the PoliLaPP, the Laboratory of Corrosion of Materials that Pedeferri founded. The main goal while translating and integrating the original Italian book, so far very appreciated in Italy with about 2000 copies printed, is to give a modern and updated handbook on corrosion and corrosion prevention for a twofold use: as a teaching textbook and a modern, technical support for industrial applications. This textbook stands as an ideal learning resource for students of corrosion courses in chemical, mechanical, energy and materials engineering at graduate and advanced undergraduate levels, as well as a valuable reference for engineers.

This English edition, integrated and updated, contains 30 chapters, dealing with corrosion theory (9 chapters), forms of corrosion (7), corrosion control and prevention methods (3), applications in different environments as waters, air, soil, concrete (4), and industrial applications as petrochemical plants, refinery and high temperature (2) as well as corrosion of implants in the human body. Four chapters are dedicated to design, corrosion monitoring, laboratory tests and the statistical processing of corrosion data. Chapters dedicated to the on-field applications propose an overview of the most used metals and relevant case histories. Emphasis has been devoted to cathodic protection and corrosion of reinforced concrete to give merit to the pioneering works carried out by Pietro Pedeferri. Each chapter is enriched by pictures of corrosion case studies analysed by PoliLaPP; most of the samples are actually available at the "Corrosion Museum", where Pietro Pedeferri and his school have collected the most significant corrosion case studies.

The book offers the reader and the user many case histories and an important number of questions and exercises to help check the acquired knowledge. Questions and exercises included in each chapter represent the experience gathered by Pedeferri and his school over the last 50 years as a fruit of teaching, research, consultancy on material selection, failure analysis and corrosion engineering. Answers and solutions of exercises for readers will be available on PoliLaPP website (http://polilapp.chem.polimi.it).

Finally, a warm thank to all collaborators Andrea Brenna Silvia Beretta, Fabio Bolzoni, Maria Vittoria Diamanti for their hard, precious and tenacious work in contributing to the translation, integration and revision of the chapters and the effort spent on collecting more than 300 exercises. Special mention to Marco Ormellese for the unparalleled contribution. Thanks to Roberto Chiesa for reviewing the chapter related to corrosion in the human body, Giorgio Re for the suggestions on chapters dedicated to environmental-assisted cracking, Eleonora Faccioli for the drawing of figures and tables and Davide Prando for the collection of the original pictures.

Milan, Italy
June 2018

Luciano Lazzari
MariaPia Pedeferri

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# About the Author

*... 'I see that water, nay, I see*
*that fire and air and earth, and all their mixtures*
*become corrupt, and but a little while*
*endure; and yet created things were these!*
Dante, The Divine Comedy, Paradise VII

*Born "valtellinese", adopted "milanese", with heart*
*and spirit in Nestrelli*
Pietro Pedeferri

Pietro Pedeferri (1938–2008)

**Pietro Pedeferri** was a Full Professor in *Corrosion and Protection of Materials* at the School of Engineering at Politecnico di Milano, Italy.

He graduated in chemical engineering (cum laude) at Politecnico di Milano as Montecatini gold medal holder and won the De Nora Award with a thesis on electrochemistry under the supervision of Professor Roberto Piontelli. His career started and continued at Politecnico di Milano, as an Assistant Professor first and then Full Professor in electrochemistry and later in corrosion and protection of materials. In 1968, he was appointed as lecturer of the first ever course on corrosion and protection at an Italian university. He was a Visiting Professor at the University of Cambridge, UK, and the University of Connecticut, USA. From 1993 to 1999, he was Head of the Department of Applied Physical Chemistry at the Politecnico di Milano.

His first academic activity was electrochemistry research; then, in the 1963, he moved on to the corrosion field focusing on industrial and engineering aspects. His topics of study in electrochemistry were overvoltage in sulphamic solutions, anodic effects in Al production cells, anodic oxidation of Ti and so-called valve metals and relevant chromatic effects. His research in corrosion started with cold-worked stainless steels and continued with implanted metals in simulated physiological solutions, corrosion of bronze artefacts and cathodic protection. Since 1985, he dealt with corrosion of steel reinforcements in concrete, indicating factors and conditions for initiation and propagation. In 1991, he invented and proposed a new technique called *cathodic prevention* for concrete structures destined to be chloride contaminated, nowadays included in operative international standards. From the study of the corrosion behaviour of stainless steel reinforcements, he proposed a potential-to-chloride diagram for interpretation: this diagram is now called the *Pedeferri Diagram*.

Meanwhile, he continued his studies on Ti colouring, winning an award in 1988 in Paris, within the international event *Science pour l'art*, and displaying his work in the *Fondazione Corrente Gallery* in Milan, Italy. He revisited the publications of Alessandro Volta and Leopoldo Nobili and then rewrote several chapters of the history of electrochemistry. Some of the Pedeferri's findings on Volta priorities in corrosion are reported in this book.

He published 388 papers and 34 books, and took out 8 patents.

# Symbols and Abbreviations

| | |
|---|---|
| $a_{M^{z+}}$ | Activity (or concentration) of ions of metal M in a solution (mol/L) |
| $\alpha$ | Coefficient (adimensional) |
| $b$ | Tafel slope (module) (V/decade) |
| $b_a$ | Tafel slope of the anodic curve (module) (V/decade) |
| $b_c$ | Tafel slope of the cathodic curve (module) (V/decade) |
| $b_{Fe}$ | Tafel slope of iron dissolution reaction (V/decade) |
| $b_{H_2}$ | Tafel slope of hydrogen evolution reaction (V/decade) |
| $b_{O_2}$ | Tafel slope of oxygen reduction reaction (V/decade) |
| $C$ | Concentration (mol/L) |
| $C_{rate}$ | Corrosion rate (mm/y) |
| $C_{rate,m}$ | Mass loss rate (mdd) |
| CCGS | Critical crevice gap size (μm) |
| CCT | Critical crevice temperature (°C) |
| CIPP | Close interval potential profile |
| CP | Cathodic protection |
| CPrev | Cathodic prevention |
| CPCC | Critical pitting chloride concentration |
| CPT | Critical pitting temperature (°C) |
| CSE | Saturated copper sulphate electrode (+0.32 V SHE) |
| $d$ | Distance (m) |
| $d_{eq}$ | Diameter of the coating equivalent defect (m) |
| D | Diffusion coefficient ($m^2/s$) |
| DL | Design life |
| $\delta$ | Diffusion layer thickness (m) |
| $e^-$ | Electron |
| $E$ | Electrode potential (V) |
| $E^{XY}$ | Potential difference between electrode X and Y (V) |
| $E^0$ | Standard potential (V) |
| $E_a$ | Anodic potential (V) |
| $E_c$ | Cathodic potential (V) |

| | |
|---|---|
| $E_{corr}$ | Free corrosion potential (V) |
| $E_{eq}$ | Equilibrium potential given by Nernst equation (V) |
| $E_{IR\text{-}free}$ | Potential free of the ohmic drop in CP applications (V) |
| $E_{off}$ | Off-potential in CP applications (V) |
| $E_{on}$ | On-potential in CP applications (V) |
| $E_p$ | Passivation potential (V) |
| $E_{pit}$ | Pitting potential or passivity breakdown potential (V) |
| $E_{pp}$ | Primary passivation potential (V) |
| $E_{prot}$ | Protection potential (V) |
| $E_{rp}$ | Repassivation potential (V) |
| $E_{tr}$ | Transpassive potential (V) |
| EMF | Electromotive force (V) |
| $\Delta E$ | Driving voltage or potential difference (V) |
| $\varepsilon$ | Efficiency (unitary fraction) |
| F | Faraday constant (96,485 C) |
| FEM | Finite element method |
| $\phi$ | Diameter (m) |
| $G$ | Gibbs free energy (J/mol) |
| GACP | Galvanic anode cathodic protection |
| $\gamma$ | Mass density (g/cm$^3$) |
| $\Delta G^\circ$ | Standard Gibbs free energy variation (J/mol) |
| $H$ | Activation energy (J/mol) |
| HE | Hydrogen embrittlement |
| HIC | Hydrogen-induced cracking |
| HID | Hydrogen-induced damage |
| $\eta$ | Overvoltage (with respect to the equilibrium potential) (V) |
| $\eta_a$ | Anodic overvoltage (V) |
| $\eta_{act,O_2}$ | Activation overvoltage of oxygen reduction (V) |
| $\eta_c$ | Cathodic overvoltage (V) |
| $\eta_{conc,O_2}$ | Concentration overvoltage of oxygen reduction (V) |
| $\eta_{H_2}$ | Activation overvoltage of hydrogen evolution reaction (V) |
| $\eta_M$ | Activation overvoltage of metal dissolution reaction (V) |
| $\eta_{O_2}$ | Overvoltage of oxygen reduction (V) |
| $i$ | Current density (mA/m$^2$) |
| $i_a$ | Anodic current density (mA/m$^2$) |
| $i_c$ | Cathodic current density (mA/m$^2$) |
| $i_{corr}$ | Corrosion current density (mA/m$^2$) |
| $i_{cp}$ | Critical passivation current density (mA/m$^2$) |
| $i_{GC}$ | Current density in galvanic coupling (mA/m$^2$) |
| $i_L$ | Oxygen limiting current density (mA/m$^2$) |
| $i_0$ | Exchange current density (mA/m$^2$) |
| $i_{0,H_2}$ | Exchange current density of hydrogen evolution (mA/m$^2$) |
| $i_{0,M}$ | Exchange current density of metal M (mA/m$^2$) |

| | |
|---|---|
| $i_{0,O_2}$ | Exchange current density of oxygen ($mA/m^2$) |
| $i_p$ | Passivity current density ($mA/m^2$) |
| $i_{prot}$ | Protection current density ($mA/m^2$) |
| $I$ | Current (A) |
| $I_a$ | Anodic current (A) |
| $I_c$ | Cathodic current (A) |
| $I_e$ | External current (A) |
| $I_{el}$ | Current in the electrolyte (A) |
| $I_{interf}$ | Interference current (A) |
| $I_{prot}$ | Protection current (A) |
| ICCP | Impressed current cathodic protection |
| $k$ | Constant (generic) |
| $\kappa$ | Conductivity of an electrolyte (S/m) |
| $K_s$ | Complex stability constant |
| $L$ | Length (m) |
| $L_{max}$ | Throwing power (m) |
| *LSI* | Langelier saturation index |
| $m$ | Mass (g) |
| M | Generic metal, less noble metal in a coupling |
| $M^{z+}$ | Oxidised metal species |
| MIC | Microbiologically influenced corrosion |
| MOB | Manganese oxidising bacteria |
| MMO | Mixed metal oxides (of noble metals Ir, Rh, Ru) |
| MW | Atomic or molecular weight (g/mol) |
| N | More noble metal in a coupling |
| $N_a$ | Anode number |
| $p$ | Porosity of a scale (unitary fraction) |
| $p_{CO_2}$ | Partial pressure of $CO_2$ (bar) |
| $p_{H_2S}$ | Partial pressure of $H_2S$ (bar) |
| $P$ | Pressure of a gas (bar) |
| PREN | Pitting resistance equivalent number |
| $Q$ | Flux of electrical charges (C) |
| $R$ | Generic ohmic resistance (Ω) |
| R | Gas constant (1.987 cal/mol K = 8.314 J/mol K) |
| $R_0$ | Coating insulation resistance ($\Omega\ m^2$) |
| $R_a$ | Anode resistance (Ω) |
| $R_c$ | Cathode resistance (Ω) |
| $R_{cable}$ | Resistance of feeding cables (Ω) |
| $R_{tot}$ | Total resistance (Ω) |
| *RH* | Relative humidity |
| *RSI* | Ryznar saturation index |
| $\rho$ | Resistivity (Ω m) |
| $\rho_{el}$ | Electrolyte resistivity (Ω m) |
| $\rho_{met}$ | Metal resistivity (Ω m) |

| | |
|---|---|
| $s$ | Thickness (m) |
| $S$ | Surface ($m^2$) |
| $S_a$ | Anodic surface ($m^2$) |
| $S_c$ | Cathodic surface ($m^2$) |
| $S_M$ | Surface of the less noble metal in a coupling ($m^2$) |
| $S_N$ | Surface of the more noble metal in a coupling ($m^2$) |
| SHE | Standard hydrogen electrode |
| SCC | Stress corrosion cracking |
| SCE | Saturated calomel electrode (+0.24 V SHE) |
| SOHIC | Stress-oriented hydrogen-induced cracking |
| SRB | Sulphate-reducing bacteria |
| SSC | Silver/silver chloride reference electrode (+0.25 V SHE) |
| SSC | Sulphide stress cracking |
| $\sigma$ | Conductivity (S/m) |
| $t$ | Time (s) |
| $T$ | Temperature (°C; K) |
| T/R | Transformer/rectifier |
| *TDS* | Total dissolved solids or salinity (g/L or mg/L) |
| $v$ | Velocity (m/s) |
| $V$ | Voltage or feeding voltage (V) |
| $\Delta V$ | Voltage drop or ohmic drop (V) |
| $\xi$ | Coating efficiency (unitary fraction) |
| $w$ | Anode consumption (kg/A y) |
| $\psi$ | Polarisation or potential shift from the free corrosion potential (V) |
| $\psi^*$ | Thermodynamic and kinetic contribution of electrode reactions (V) |
| $z$ | Valence, number of electrons in an electrodic reaction (adimensional) |
| ZN | Zinc/sea water reference electrode (−0.8 V SHE) |

## Units

| | |
|---|---|
| A | Ampere |
| cal | Calorie |
| C | Coulomb |
| °C | Degree centigrade |
| h | Hour |
| J | Joule |
| K | Degree Kelvin |
| L | Litre |
| m | Metre |
| M | Molar |
| mol | Mole |
| Ω | Ohm |
| s | Second |

| | |
|---|---|
| S | Siemens |
| V | Volt |
| W | Watt |