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# CORROSION ENGINEERING

## Principles and Solved Problems

Branko N. Popov

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**BRANKO N. POPOV**
University of South Carolina,
301, Main Street
Department of Chemical Engineering
Swearingen Engineering Center
Columbia, SC 29208
popov@cec.sc.edu

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# PREFACE

**Corrosion Engineering–Principles and Solved Problems** is based on the author's experience teaching undergraduate and graduate corrosion courses entitled Corrosion Engineering, Advanced Corrosion Engineering, and Electrochemical and Corrosion Techniques at the University of South Carolina. The book provides an extensive and in-depth theoretical analysis of thermodynamics kinetics, mass transfer, potential theory, and passivation, creating a foundation for understanding the electrochemical nature of the corrosion process and corrosion protection strategies discussed in the book's second part. Around the world, the students who currently attend corrosion-engineering courses are enrolled in different engineering programs. This fact requires additional topics to be included in the book, and to this end, the book reviews the corrosion processes, protection strategies, and testing for civil-engineering structures; corrosion in chemical process engineering; mechanical and nuclear corrosion engineering; and metallurgy. The fundamental principles of corrosion and related protection strategies are explained through solved problems, exercises, and case studies, and the book helps upper-level undergraduate and graduate students learn the subject through an extensive theoretical description of corrosion theory, passivity, corrosion prevention strategies, and corrosion protection system design. The author has attempted to organize the book so the instructor can use it as the basis for a course in corrosion engineering for undergraduate students and also graduate students.

With a bibliography citing more than 1350 studies published in the last 10 years, the book is also designed to serve as a valuable scientific resource for professionals working in the fields of corrosion, electrochemical, chemical, metallurgical, mechanical, electrical, manufacturing, and nuclear engineering, as well as graduate students and material scientists.

Chapters 1 to 3 describe the theory of corrosion engineering and offer analyzed case studies and solved problems in the thermodynamics of corrosion processes, the relevance of electrochemical kinetics to corrosion, low field approximation theory, concentration polarization, the effects of polarization behavior on corrosion rate, the effect of mass transfer on electrode kinetics, and diffusion-limited corrosion rates.

Chapter 4 presents the fundamentals of passivity; the film and adsorption theories of passivity; criterion for passivation; methods for spontaneous passivation; factors affecting passivation, such as the effect of solution velocity and acid concentration; alloy evaluation; anodic protection systems; and design requirements. A full discussion on stainless steel composition and crystalline structure, oxidizer concentration, and alloy evaluation is included. The chapter also considers anodic protection to establish a basis for anodic protection systems and designs. By the end of the chapter, case studies, solved problems, and exercises illustrate passivation and anodic protection system design.

The basics of corrosion measurements are outlined in Chapter 5, which describes polarization methods for measuring corrosion rates, the oxidizing power of the environment, and corrosion protection effectiveness. The chapter starts by explaining corrosion measurement basics and corrosion rate determination by linear polarization using the Stern-Geary equation and Tafel extrapolation. The advantages of corrosion inhibitor evaluation, corrosion monitoring in process plants, and corrosion characteristics are also described, and the chapter considers potentiodynamic polarization for determining passivation and critical current density. At the end of the chapter, a detailed review of recent literature explains electrochemical impedance spectroscopy. Solved and exercise problems illustrate electrochemical techniques in corrosion rate measurements.

Chapter 6, which is on galvanic corrosion, describes theoretical galvanic corrosion aspects, mixed potential theory, galvanic series, and novel testing methods suggested by the literature. A detailed discussion on galvanic corrosion, polarization, and prevention provides information on materials, minimizing cathode-anode area ratio, coatings and inhibitors, and environmentally friendly sacrificial materials. A literature review also describes novel testing methods in galvanic corrosion, novel alloys for automotive applications, and galvanic corrosion inhibition in both concrete structures and dental magnetic attachments. Galvanic corrosion theory and evaluation are explained through case studies, solved problems, exercises, and numerical modeling.

In Chapter 7, the book addresses pitting potential analyses in connection with new alloys with low pitting corrosion susceptibility. In addition, the chapter considers the recent literature on pitting mechanisms and crevice corrosion evaluation as they relate to corrosion severity control, main variables, and experimental data consistency in particular systems. Electrochemical kinetics such as charge transfer, mass transport, and ohmic effects explain pit growth and arrest, and the discussion of pitting inhibition and crevice corrosion is focused on new alloys and alloy composition effects for decreased pitting corrosion susceptibility, conversion coating, inhibitor development, and cathodic and anodic protection. Crevice and filiform corrosion are also described via initiation and propagation processes, and the case study and exercise problems illustrate pitting and crevice mechanisms and corrosion protection strategies for inhibiting pitting corrosion.

Hydrogen permeation in metals is introduced for the first time in Chapter 8 of this book, which describes hydrogen permeation and hydrogen-induced damage and prevention in metals and alloys. To this end, the chapter discusses hydrogen evolution kinetics, theoretical diffusion solutions, and basic hydrogen permeation models. Models are used as a diagnostic tool for determining the effectiveness of various metals and alloys as hydrogen permeation inhibitors. Through case studies, the chapter then explains the experimental determination of atomic hydrogen permeation transients and the evaluation of hydrogen absorption rate constants and diffusivity into metals. A discussion on hydrogen embrittlement, hydrogen-induced cracking, hydrogen blistering, and hydrogen stress cracking then shows the relationship between hydrogen permeation and hydrogen-induced cracking mechanisms previously described in the chapter. The most recent research related to hydrogen kinetic parameters is also reviewed, and the case studies and solved problems illustrate models for developing alloys that reduce hydrogen ingress.

The discussion of stress corrosion in Chapter 9 begins with a definition and characteristics for stress corrosion cracking (SCC), testing methods common to SCC and hydrogen-induced cracking, principles and techniques of fracture mechanics, and corrosion fatigue testing. These methods have been updated with references published in the last 20 years. SCC metallurgy is explained through case studies on SCC variables such as solid solution composition, grain boundary segregation, alloy phase transformation and associated solute-depleted zones, duplex structures, and cold work. From 2000 to 2013, more than 200 published studies have analyzed electrochemical effects such as chloride-induced localized corrosion in stainless steels, SCC due to dealloying, and hydrogen-induced SCC in high-strength alloys. The chapter continues with corrosion fatigue cracking and detection. SCC failure prevention methods are discussed at the end of the chapter. In addition, the fundamental principles of SCC, the nature of the processes, and related protection strategies are explained through solved exercise problems from fracture mechanics and case studies published in the last decade.

Chapter 10 on atmospheric corrosion describes basic atmospheric corrosion principles resulting from metal exposure at ambient and near-ambient temperatures in humid air. It starts by presenting environment classification, common industrial pollutants, atmospheric corrosion factors, and atmospheric corrosion classifications according to the International Standard Organization. Atmospheric pollutants, such as sulfur-containing compounds, chlorine-containing compounds, and nitrates, are discussed in the chapter through a review of recent literature, and the chapter concludes by showing the role of industrial pollutants in controlling atmospheric corrosion, through a discussion of iron and low-alloy steel corrosion, as well as the atmospheric corrosion of nickel, magnesium alloys, zinc, and bare and anodized aluminum. The influence of alloying elements such as copper, tin, zinc, and lead on bronze corrosion and prevention is also explained through recent literature.

Chapter 11 introduces high-temperature corrosion, considering basic metal and alloy corrosion principles at elevated temperatures in air and other oxidizing gases. It starts by explaining high-temperature corrosion thermodynamics, the Pilling-Bedworth ratio, electrochemical oxidation processes, oxide-layer formation, microstructure, and oxidation kinetics. Parabolic, logarithmic, and linear rate equations and the combination of those equations also show the relationship between corrosion and oxide-layer formation at high temperatures. Hot metal-oxide corrosion is explained using molten halide, molten nitrite, and molten carbonate interactions. To further explain this interaction, a case study on molten halides is included. The chapter concludes by considering conventional and recently developed methods for hot corrosion protection and high-temperature vacuum plasma spraying (VPS), high-velocity oxy-fuel (HVOF) thermal spraying, platinum and aluminide coatings, silicon diffusion layers, chemical additions, ion implantation, and preformation of oxide layers. In addition, case studies, solved problems, and exercises on protective coatings illustrate engineered alloy protection designed for elevated temperature service.

Corrosion in concrete structures is addressed in Chapter 12, which starts by explaining engineering alloy composition and heterogeneity, steel reinforcement degradation in an alkaline environment, corrosion mechanisms, chloride-induced corrosion, and surface depassivation with carbon dioxide. The chapter describes electrochemical techniques used for concrete reinforcement corrosion evaluation, such as corrosion potential measurements, linear polarization, Tafel polarization, and electrochemical impedance spectroscopy, and it considers mineral admixtures, commercial coatings, calcium nitrite and organic inhibitors, pozzolans, sacrificial zinc coatings, durability assessments for internal chloride in corrosion control, and service life. Simulations using SimCorr™ then illustrate corrosion initiation time and crevice life prediction as a function of concrete structural and environmental parameters.

Chapters 13 to 15 describe corrosion protection methods. Chapter 13 introduces organic coating constituents, coating composition, underlying metal surface preparation, additives and fillers, metal surface prepainting treatments, and exposure testing. To this end, the chapter explains resins used in the paint industry, including vinyl resin, acrylics, alkyd (oil base), modified alkyds, chlorinated rubber, urethanes resin, and polyester resin, in the context of actual service life evaluation. The properties of paint pigments and their roles in providing color and opacity, mechanical and barrier properties, and water transport are discussed, as are the ASTM standards for pigment specification, surface preparation specifications, paint and paint material chemical analysis standards, paint application tool standards, and accelerated testing standards for coatings, with the information summarized in nine tables. The second part of the chapter discusses testing and coating evaluation, and a full discussion of physical and chemical aging mechanisms is included to show the relationship between corrosion and coating detachment or cracking, underlying metal degradation, and coating disintegration. In addition, the chapter provides a review of the recent literature on organic coatings.

Chapter 14 introduces corrosion inhibitor physicochemical and electrochemical properties. The chapter explains inhibitor classification according to mechanism, inhibitor application (pickling, acid cleaning, descaling, etc.), and inhibitor chemical nature (inorganic and organic). The chapter concludes by discussing the chemical and electrochemical properties related to anodic, passivating, and cathodic inhibitors (including cathodic poisons, cathodic precipitates, and oxygen scavengers), as well as adsorption of organic inhibitors, precipitation inhibitors, ohmic inhibitors, and vapor phase inhibitors. A literature review is provided for recent organic, inorganic, and green corrosion inhibitor development with "zero" environmental impact.

Chapter 15 outlines the fundamentals, criteria, field data, and design aspects of cathodic protection (CP), providing detailed descriptions for monitoring methods such as potential surveys, (PS), close interval potential surveys (CIPS), direct current voltage gradient surveys (DGVG), and corrosion rate measurement methods. The discussion of sacrificial protection system design illustrates total circuit resistance evaluation, anode output, number of anodes, and anode life. Impressed current systems (ICS) design is illustrated for a pipeline designed by the author, and anode, rectifier, and ground bed selection is explained, as is ground bed resistance calculation, rectifier output, number, and service life. Finally, case studies and solved problems illustrate sacrificial and impressed current cathodic protection system design.

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