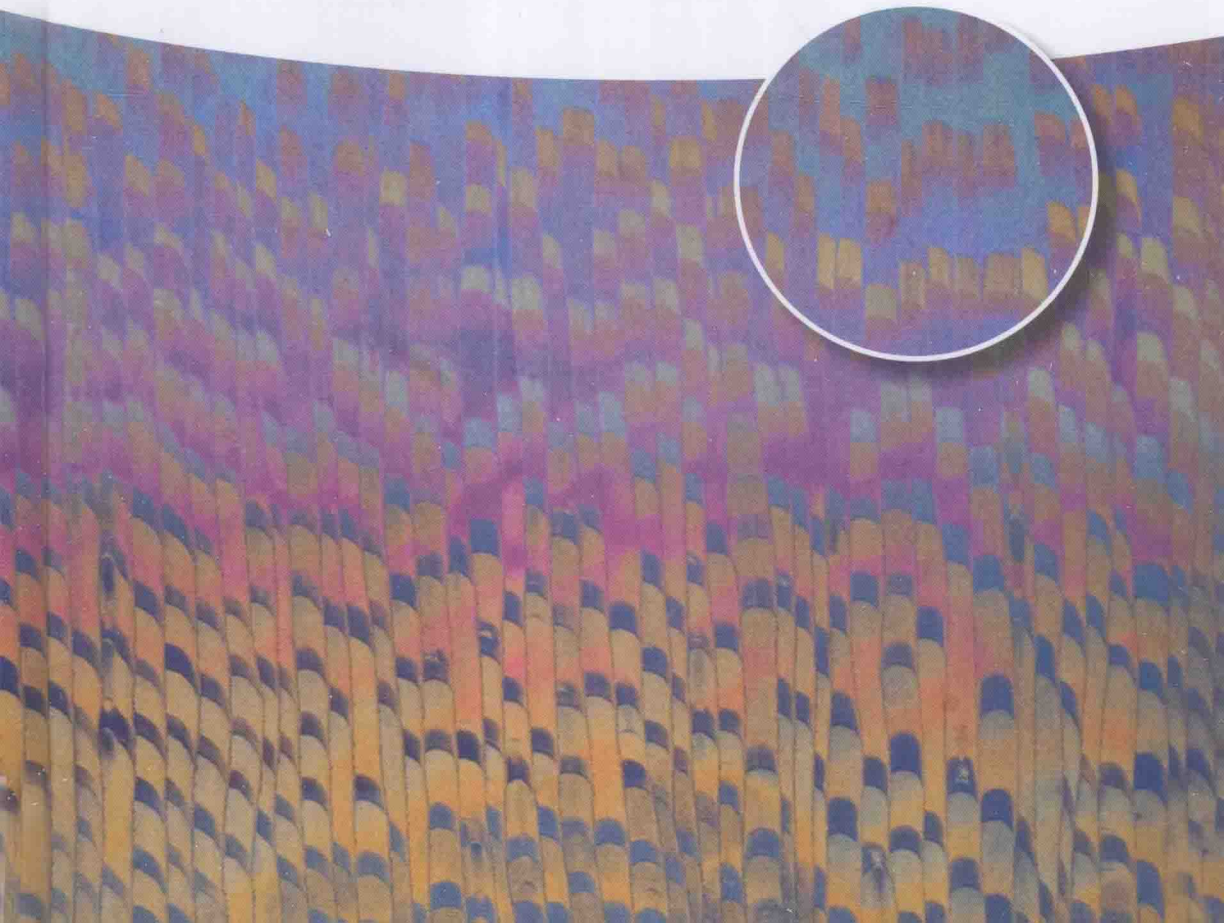


Luca Bertolini, Bernhard Elsener, Pietro Pedferri,
Elena Redaelli, Rob Polder

Corrosion of Steel in Concrete

Prevention, Diagnosis, Repair

Second, Completely Revised
and Enlarged Edition



*Luca Bertolini, Bernhard Elsener, Pietro Pedeferra,
Elena Redaelli, and Rob Polder*

Corrosion of Steel in Concrete

Prevention, Diagnosis, Repair

Second, completely revised and enlarged edition



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Luca Bertolini

Politecnico di Milano
Department of Chemistry,
Materials, and Chemical
Engineering "G. Natta"
Piazza Leonardo da Vinci 32
20133 Milano
Italy

Prof. Bernhard Elsener

ETH Zürich
Institute for Building Materials
ETH Hönggerberg
8093 Zürich
Switzerland

Dr. Elena Redaelli

Politecnico di Milano
Department of Chemistry,
Materials, and Chemical
Engineering "G. Natta"
Piazza Leonardo da Vinci 32
20133 Milano
Italy

Prof. Rob Polder

TNO Technical Sciences/
Built Environment
P.O. Box 49
2600 AA Delft
The Netherlands

Delft University of Technology
P.O. Box 5048
2600 CA Delft
The Netherlands

Cover:

The picture used on the cover is a painting on a titanium surface, created by Prof. Pietro Pedferri. We thank his heirs for the kind permission to use this work of art.

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form—by photoprinting, microfilm, or any other means—nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Toppan Best-set Premedia Ltd., Hong Kong

Printing and Binding Markono Print Media Pte Ltd, Singapore

Cover Design Blueseas Design, Simone Benjamin, McLeese Lake, Canada

Print ISBN: 978-3-527-33146-8

ePDF ISBN: 978-3-527-65172-6

ePub ISBN: 978-3-527-65171-9

mobi ISBN: 978-3-527-65170-2

oBook ISBN: 978-3-527-65169-6

Printed in Singapore

Printed on acid-free paper

*Luca Bertolini, Bernhard
Elsener, Pietro Pedferri,
Elena Redaelli, and
Rob Polder*

**Corrosion of Steel
in Concrete**

Related Titles

Sharma, S. K. (ed.)

Green Corrosion Chemistry and Engineering

Opportunities and Challenges With a
Foreword by Nabuk Okon Eddy

2012

ISBN: 978-3-527-32930-4

Kreysa, G., Schütze, M. (eds.)

Corrosion Handbook— Corrosive Agents and Their Interaction with Materials

13 Volume Set

2009

ISBN: 978-3-527-31217-7

Schütze, M., Wieser, D., Bender, R. (eds.)

Corrosion Resistance of Aluminium and Aluminium Alloys

2010

ISBN: 978-3-527-33001-0

Galambos, T. V., Surovek, A. E.

Structural Stability of Steel Concepts and Applications for Structural Engineers

2009

ISBN: 978-0-470-03778-2

Bernold, L. E., AbouRizk, S. M.

Managing Performance in Construction

2010

ISBN: 978-0-470-17164-6

Heimann, R. B.

Plasma Spray Coating Principles and Applications

2008

ISBN: 978-3-527-32050-9

Krzyzanowski, M., Beynon, J. H.,
Farrugia, D. C. J.

Oxide Scale Behavior in High Temperature Metal Processing

2010

ISBN: 978-3-527-32518-4

Geschwindner, L. F.

Unified Design of Steel Structures

2008

ISBN: 978-0-471-47558-3

Revie, R. W.

Corrosion and Corrosion Control, Fourth Edition

2010

ISBN: 978-0-470-65366-1

Roberge, P. R., Revie, R. W.

Corrosion Inspection and Monitoring

2007

ISBN: 978-0-471-74248-7

Preface to the Second Edition

Since this book was first published, durability of reinforced concrete structures has continued to receive worldwide interest of materials scientists and designing engineers. Although some of the open questions raised in the preface of the first edition have found reasonable explanations in the past decade, others are still unanswered and new issues have arisen. For example, the need for sustainability has, on the one hand, increased the demand for durable structures and, on the other hand, promoted the development and use of new materials with lower environmental impact whose durability properties need to be verified. The increased demand for maintaining large numbers of existing structures and prolonging their service life poses technical and economical challenges of a larger scale. At the same time, increased experience with regard to repair techniques and materials must be incorporated in asset management on the scale of, for example, road networks. Challenges for the next decade are science-based models for the prediction of service life of new and existing structures and reliable accelerated tests that are able to provide durability-related design parameters both for concrete (e.g., with regard to resistance to carbonation or chloride penetration) and for steel (e.g., relating to the chloride threshold for corrosion initiation).

In the second edition of this book, all chapters have been revised and updated with recent findings and new perspectives. The structure of the book has been maintained, so that it may serve as a reference for students and materials scientists, who may learn from the explanation of corrosion and degradation mechanisms, as well as people involved in the design, execution, and management of reinforced concrete structures, who may concentrate on the parts of the book dealing with practical aspects of assessment, monitoring, prevention, and protection techniques.

With this second edition we also have a new co-author, Elena Redaelli, but, sadly, we lost Pietro Pedferri, who passed away on 3 December 2008. Pietro strongly wanted the first edition of this book, and he was the driving force for its realization. He dedicated his life to the study of electrochemistry and corrosion science and technology, making important contributions to several aspects of corrosion and protection techniques, such as localized corrosion of stainless steels, cathodic protection, corrosion in the human body, corrosion in the oil industry, surface treatments of titanium, and corrosion and protection of steel in concrete. Corrosion of steel in concrete became a major field of interest for him in the 1980s.

Looking for a durable solution to prevent corrosion of reinforcing steel in motorway bridges exposed to chloride contamination due to de-icing salt application, he proposed the technique of *cathodic prevention*, and in explaining the advantages of cathodic prevention over cathodic protection, he developed the graph shown in Figure 20.4, now internationally acknowledged as *Pedferri's diagram*. This graph definitely expresses Pietro's spirit as a researcher as well as a teacher, showing that he was able to transfer in a simple, although rigorous, manner a complex matter as the way of dealing with depassivation and repassivation of steel in chloride-contaminated concrete. Pietro Pedeferrri contributed to the understanding of several mechanisms involved in the corrosion behavior of steel reinforcement in concrete, and his knowledge permeates the whole book, even in this new edition.

The front cover is a tribute to Pietro Pedeferrri as an artist. In fact, he was able to conjugate his research studies on the anodic oxidation of titanium with his creativity, and he developed a unique technique for electrochemical painting of titanium. Mixing acids, electrical currents, flow of liquids, and his poetic inspiration, he generated beautiful and colorful drawings.

The Authors, January 2013

Preface to the First Edition

Over the millennia, concrete prepared by the Romans using lime, pozzolana and aggregates has survived the elements, giving proof of its durability. Prestigious concrete works have been handed down to us: buildings such as the Pantheon in Rome, whose current structure was completed in 125 A.D., and also structures in marine environments have survived for over two thousand years. This provides a clear demonstration that concrete can be as durable as natural stone, provided that specific causes of degradation, such as acids or sulphates, freeze–thaw cycles, or reactive aggregates, are not present.

Today, thanks to progress made over the past few decades in the chemistry of cement and in the technology of concrete, even these causes of deterioration can be fought effectively. With an appropriate choice of materials and careful, adequately controlled preparation and placement of the mixture, it is possible to obtain concrete structures which will last in time, under a wide variety of operative conditions.

The case of reinforced concrete is somewhat different. These structures are not eternal, or nearly eternal, as was generally supposed up until the 1970s. Instead, their service life is limited precisely because of the corrosion of reinforcement. Actually, concrete provides the ideal environment for protecting embedded steel because of its alkalinity. If the design of a structure, choice of materials, composition of the mixture, and placement, compaction and curing are carried out in compliance with current standards, then concrete is, under most environmental conditions, capable of providing protection beyond the 50 years typical of the required service life of many ordinary structures, at least in temperate regions. In fact, cases of corrosion that have been identified in numerous structures within periods much shorter than those just mentioned can almost always be traced to a failure to comply to current standards or to trivial errors in manufacturing of the concrete. However, under environmental conditions of high aggressiveness (generally related to the presence of chlorides), even concrete which has been properly prepared and placed may lose its protective properties and allow corrosion of reinforcement long before 50 years have elapsed, sometimes resulting in very serious consequences.

The problem of corrosion in reinforced concrete structures is thus a very real one and must be given special consideration. It is, in fact, only since the early

1980s that research has devoted much attention to this problem. From those years on main physiological aspects related to behaviour of steel in concrete, such as the nature of the aqueous pore liquid present in the hardened concrete, the electrochemistry of steel in this environment, the mechanism of protection of steel by an oxide film, etc. have been established. Passing to the pathological side, research has explained the phenomenology and mechanisms of corrosion, established the conditions which give rise to it and the laws governing its evolution, and developed techniques for diagnosing and controlling it. In particular, it has been shown that the only circumstances that can give rise to corrosion are those when both depassivation occurs (e.g., due to carbonation or chlorides) and oxygen and humidity are present.

Several points still need to be clarified. For example: the atlas of pathological anatomy has been defined clearly with regard to corroding reinforcement, but only sketchily in relation to the surrounding concrete; the body of diagnostics allows the state of corrosion in a structure to be evaluated for the more common forms of corrosion, but is still incomplete in the case of hydrogen embrittlement in high-strength steels of prestressed structures or corrosion caused by stray current; the handbook of anticorrosionistic pharmacology includes a long list of methodologies of prevention (from inhibitors to coatings, to corrosion resistant reinforcement, to electrochemical techniques); however, their long-term effects or their possible negative side-effects are not always clearly known. Probably, the greatest shortcomings have to do with the basic aspects of corrosion. For instance, in the area of physiopathology: the species around the passive reinforcement in concrete are known, but those around corroding reinforcement are not; the influence of species on the passivity or corrosion of steel is known in qualitative terms, but very little is known of the entity of their interaction with the constituents of cement paste, and thus of their mobility in electrical fields or in various concentration gradients, in relation to the type of cement or to the characteristics of the concrete, etc.

In the field of construction, notable progress has also been achieved: the problem of corrosion, and more in general of the durability of structures in reinforced concrete, is very seriously taken into consideration; new laws are in place and new technologies and products are available.

But the above must not lull us into a false sense of security. It is true that today there is greater sensitivity to this problem, often being the subject of conferences, seminars and publications. New rules and standards do exist, though they are perceived as compulsory, being the result of legislation. Finally, new technologies and sophisticated products are being adopted, for example in the field of repair of structures damaged by corrosion. All these aspects do not, however, in themselves eliminate the errors, often trivial, that are at the basis of most failures today, and even less are they able to solve those cases where structures operate under conditions of high aggressiveness. Substantial progress will be made, also with regard to durability, only when our current technology, based on empiricism and common sense, evolves into a technology based on a thorough knowledge of degradation processes and of methods for their control.

Education, and thus teaching in particular, has a very important role to play, not only by making professionals sensitive to the durability problem, but also by giving them the tools necessary to solve it.

We hope that this text may be useful for those who work in the field of civil and construction engineering, as well as for those involved in the area of maintenance and management of reinforced concrete structures. Its aim is to provide the knowledge, tools and methods to understand the phenomena of deterioration and to prevent or control them. In some sections of the text, because of our professional background, we have gone into details of some electrochemical aspects. These explanations go beyond what is strictly required in civil and construction engineering and are not essential to an understanding of the other sections.

Finally, we wish to thank the European commissions that, by promoting the cooperative actions COST 509, 521 and recently 534, gave to several European researchers the opportunity to meet, collaborate and exchange views in the field of corrosion of steel in concrete. This book was born from that cooperation. We gratefully acknowledge all friends and colleagues on COST Actions, RILEM technical committees and European Federation of Corrosion working groups for providing data, papers and, most of all, for stimulating discussion.

The Authors, November 2003

Contents

Preface to the Second Edition XV

Preface to the First Edition XVII

1	Cements and Cement Paste	1
1.1	Portland Cement and Hydration Reactions	1
1.2	Porosity and Transport Processes	3
1.2.1	Water/Cement Ratio and Curing	4
1.2.2	Porosity, Permeability and Percolation	7
1.3	Blended Cements	8
1.3.1	Pozzolanic Materials	9
	Natural Pozzolana	9
	Fly Ash	10
	Silica Fume	10
1.3.2	Ground Granulated Blast Furnace Slag	10
1.3.3	Ground Limestone	11
1.3.4	Other Additions	11
1.3.5	Properties of Blended Cements	11
1.4	Common Cements	13
1.5	Other Types of Cement	15
	High Alumina Cement (HAC)	18
	Calcium Sulfoaluminate Cements (CSA)	19
	References	19
2	Transport Processes in Concrete	21
2.1	Composition of Pore Solution and Water Content	22
2.1.1	Composition of Pore Solution	22
2.1.2	Water in Concrete	23
	Capillary Water	23
	Adsorbed Water	26
	Interlayer Water	26
	Chemically Combined Water	26
2.1.3	Water Content and Transport Processes	26

2.2	Diffusion	27
2.2.1	Stationary Diffusion	28
2.2.2	Nonstationary Diffusion	29
2.2.3	Diffusion and Binding	30
2.3	Capillary Suction	32
2.4	Permeation	33
2.4.1	Water Permeability Coefficient	34
2.4.2	Gas Permeability Coefficient	35
2.5	Migration	35
2.5.1	Ion Transport in Solution	35
2.5.2	Ion Transport in Concrete	36
2.5.3	Resistivity of Concrete	37
	Temperature Dependence	38
	Concrete Resistivity and Corrosion Rate	39
	Measuring Concrete Resistivity	39
2.6	Mechanisms and Significant Parameters	40
	Correlations	40
	Presence of More Than One Transport Mechanism	43
	References	45
3	Degradation of Concrete	49
3.1	Freeze–Thaw Attack	50
3.1.1	Mechanism	51
3.1.2	Factors Influencing Frost Resistance	52
3.1.3	Air-Entrained Concrete	53
3.2	Attack by Acids and Pure Water	54
3.2.1	Acid Attack	54
3.2.2	Biogenic Sulfuric Acid Attack	56
3.2.3	Attack by Pure Water	58
3.2.4	Ammonium Attack	58
3.3	Sulfate Attack	59
3.3.1	External Sulfate Attack	59
	Protection	60
3.3.2	Internal Sulfate Attack	60
	Prevention	61
3.4	Alkali Silica Reaction	61
3.4.1	Alkali Content in Cement and Pore Solution	62
3.4.2	Alkali Silica Reaction (ASR)	63
	Presence and Quantity of Reactive Aggregate	64
	Alkali Content in the Pore Liquid of Concrete	64
	Type and Quantity of Cement	64
	Environment	65
	Prevention	65
3.5	Attack by Seawater	66
	References	67

4	General Aspects	71
4.1	Initiation and Propagation of Corrosion	71
4.1.1	Initiation Phase	71
4.1.2	Propagation Phase	73
4.2	Corrosion Rate	73
4.3	Consequences	74
4.4	Behavior of Other Metals	75
	References	77
5	Carbonation-Induced Corrosion	79
5.1	Carbonation of Concrete	79
5.1.1	Penetration of Carbonation	80
5.1.2	Factors That Influence the Carbonation Rate	81
	Humidity	81
	CO ₂ Concentration	83
	Temperature	84
	Concrete Composition	84
5.2	Initiation Time	85
5.2.1	Parabolic Formula	86
5.2.2	Other Formulas	86
5.3	Corrosion Rate	87
5.3.1	Carbonated Concrete without Chlorides	87
5.3.2	Carbonated and Chloride-Contaminated Concrete	90
	References	91
6	Chloride-Induced Corrosion	93
6.1	Pitting Corrosion	94
6.2	Corrosion Initiation	96
6.2.1	Chloride Threshold	96
	Chloride Binding	98
	Atmospherically Exposed Structures	100
	Submerged Structures	100
6.2.2	Chloride Penetration	101
6.2.3	Surface Content (C_s)	103
6.2.4	Apparent Diffusion Coefficient	106
6.3	Corrosion Rate	108
	Exceptions	109
	References	109
7	Electrochemical Aspects	113
7.1	Electrochemical Mechanism of Corrosion	113
	Polarization Curves	115
7.2	Noncarbonated Concrete without Chlorides	116
7.2.1	Anodic Polarization Curve	116
7.2.2	Cathodic Polarization Curve	118

7.2.3	Corrosion Conditions	119
7.3	Carbonated Concrete	120
7.4	Concrete Containing Chlorides	122
7.4.1	Corrosion Initiation and Pitting Potential	122
7.4.2	Propagation	124
7.4.3	Repassivation	125
7.5	Structures under Cathodic or Anodic Polarization	126
	References	127
8	Macrocells	129
8.1	Structures Exposed to the Atmosphere	129
	Coated Reinforcement	130
	Protection Effect	130
	Presence of Different Metals	130
	Other Macrocell Effects	131
8.2	Buried Structures and Immersed Structures	131
	Differential Aeration in Buried Structures	131
	Structures Immersed in Seawater	132
	Rebars Not Entirely Embedded in Concrete	133
	Buried Structures Connected with Ground Systems	133
8.3	Electrochemical Aspects	134
8.4	Modeling of Macrocells	137
	References	138
9	Stray-Current-Induced Corrosion	141
9.1	DC Stray Current	142
9.1.1	Alkaline and Chloride-Free Concrete	142
	First Precondition	144
	Second Precondition	146
9.1.2	Passive Steel in Chloride-Contaminated Concrete	147
	Interruptions in the Stray Current	148
9.1.3	Corroding Steel	148
9.2	AC Stray Current	149
9.3	High-Strength Steel	150
9.4	Fiber-Reinforced Concrete	151
9.5	Inspection	151
9.6	Protection from Stray Current	152
	References	153
10	Hydrogen-Induced Stress Corrosion Cracking	155
10.1	Stress Corrosion Cracking (SCC)	156
	Anodic Stress Corrosion Cracking	156
	Hydrogen-Induced Stress Corrosion Cracking (HI-SCC)	156
10.2	Failure under Service of High-Strength Steel	157
10.2.1	Crack Initiation	158

10.2.2	Crack Propagation	158
	σ_s and K_{ISCC}	159
10.2.3	Fast Propagation	159
10.2.4	Critical Conditions	160
10.2.5	Fracture Surface	162
10.3	Metallurgical, Mechanical and Load Conditions	162
10.3.1	Susceptibility of Steel to <i>HI-SCC</i>	164
10.4	Environmental Conditions	165
	Critical Intervals of Potential and pH	166
10.5	Hydrogen Generated during Operation	166
	Noncarbonated and Chloride-Free Concrete	167
	Carbonated Concrete	167
	Concrete Containing Chlorides	167
	Cathodically Protected Structures	168
10.6	Hydrogen Generated before Ducts Are Filled	169
10.7	Protection of Prestressing Steel	169
	References	170
11	Design for Durability	171
11.1	Factors Affecting Durability	172
11.1.1	Conditions of Aggressiveness	172
11.1.2	Concrete Quality	173
11.1.3	Cracking	173
11.1.4	Thickness of the Concrete Cover	175
11.1.5	Inspection and Maintenance	176
11.2	Approaches to Service-Life Modeling	177
11.2.1	Prescriptive Approaches	178
11.2.2	Performance-Based Approaches	179
	Limit States and Design Equation	181
	Variability	181
11.3	The Approach of the European Standards	183
11.4	The <i>fib</i> Model Code for Service-Life Design for Chloride-Induced Corrosion	189
11.5	Other Methods	194
11.6	Additional Protection Measures	197
11.7	Costs	198
	References	200
12	Concrete Technology for Corrosion Prevention	203
12.1	Constituents of Concrete	203
12.1.1	Cement	203
12.1.2	Aggregates	204
12.1.3	Mixing Water	205
12.1.4	Admixtures	205
	Water Reducers and Superplasticizers	206

12.2	Properties of Fresh and Hardened Concrete	206
12.2.1	Workability	207
	Measurement of Workability	207
12.2.2	Strength	208
	Compressive Strength and Strength Class	210
	Tensile Strength	210
12.2.3	Deformation	212
12.2.4	Shrinkage and Cracking	212
12.3	Requirements for Concrete and Mix Design	212
12.4	Concrete Production	215
12.4.1	Mixing, Handling, Placement and Compaction	215
12.4.2	Curing	217
12.5	Design Details	219
12.6	Concrete with Special Properties	219
12.6.1	Concrete with Mineral Additions	221
12.6.2	High-Performance Concrete (HPC)	223
12.6.3	Self-Compacting Concrete (SCC)	223
	References	225
13	Corrosion Inhibitors	227
13.1	Mechanism of Corrosion Inhibitors	228
13.2	Mode of Action of Corrosion Inhibitors	228
13.3	Corrosion Inhibitors to Prevent or Delay Corrosion Initiation	229
13.4	Corrosion Inhibitors to Reduce the Propagation Rate of Corrosion	234
13.5	Transport of the Inhibitor into Mortar or Concrete	236
13.6	Field Tests and Experience with Corrosion Inhibitors	238
13.7	Critical Evaluation of Corrosion Inhibitors	238
	Concentration Dependence	239
	Measurement and Control of Inhibitor Action	240
13.8	Effectiveness of Corrosion Inhibitors	240
	References	240
14	Surface Protection Systems	243
14.1	General Remarks	243
14.2	Organic Coatings	245
14.2.1	Properties and Testing	248
14.2.2	Performance	250
14.3	Hydrophobic Treatment	251
14.3.1	Properties and Testing	253
14.3.2	Performance	255
14.4	Treatments That Block Pores	257
14.5	Cementitious Coatings and Layers	258
14.6	Concluding Remarks on Effectiveness and Durability of Surface Protection Systems	259
	References	260

15	Corrosion-Resistant Reinforcement	263
15.1	Steel for Reinforced and Prestressed Concrete	263
15.1.1	Reinforcing Bars	263
15.1.2	Prestressing Steel	264
15.1.3	Corrosion Behavior	266
15.2	Stainless Steel Rebars	266
15.2.1	Properties of Stainless Steel Rebars	267
	Chemical Composition and Microstructure	267
	Mechanical Properties	268
	Weldability	268
	Other Properties	268
15.2.2	Corrosion Resistance	269
	Resistance to Pitting Corrosion	269
	Fields of Applicability	271
15.2.3	Coupling with Carbon Steel	273
15.2.4	Applications and Cost	275
15.2.5	High-Strength Stainless Steels	276
15.3	Galvanized Steel Rebars	276
15.3.1	Properties of Galvanized Steel Bars	277
15.3.2	Corrosion Resistance	279
15.3.3	Galvanized Steel Tendons	280
15.4	Epoxy-Coated Rebars	280
15.4.1	Properties of the Coating	280
15.4.2	Corrosion Resistance	281
15.4.3	Practical Aspects	282
15.4.4	Effectiveness	282
	References	283
16	Inspection and Condition Assessment	287
16.1	Visual Inspection and Cover Depth	288
16.2	Electrochemical Inspection Techniques	291
16.2.1	Half-Cell Potential Mapping	291
	Principle	292
	Procedure	292
	Data Collection and Representation	294
	Interpretation	295
16.2.2	Resistivity Measurements	298
	Measurements at the Concrete Surface	300
	Procedure	301
	Interpretation	301
16.2.3	Corrosion Rate	302
	Determination of the Polarization Resistance	304
	Execution of the Measurements	305
	Corrosion Rate Measurements Onsite	305
	Interpretation of the Results	306