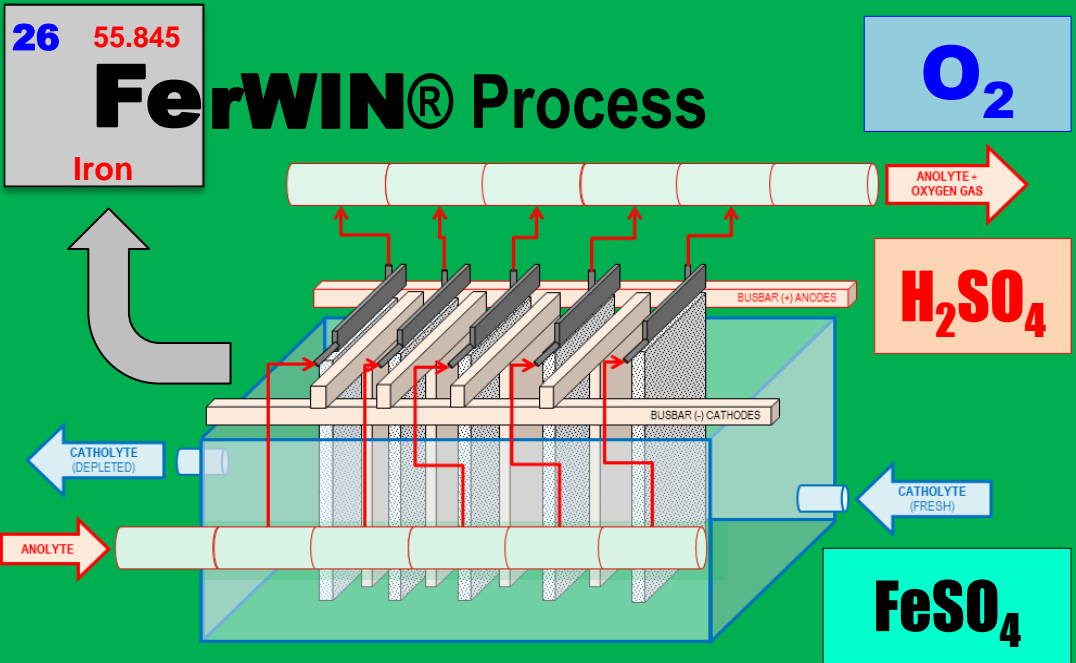


François Cardarelli

Electrowinning Iron and Recycling Sulfuric Acid from Iron Sulfates: A Zero-Carbon Iron-Making Process



François Cardarelli

**Electrowinning Iron and
Recycling Sulfuric Acid from Iron
Sulfates: a Zero-Carbon Iron-
Making Process**

Electrochem Technologies & Materials Inc.

François Cardarelli, President & Owner
Electrochem Technologies & Materials Inc.
2037 Aird Avenue, Suite 201
Montréal (QC) H1V 2V9, Canada
www.electrochem-technologies.com
Member of ACS, AIChE, CIC, ECS, MSA, OCQ, OS, and TMS

Email: contact@electrochem-technologies.com
contact@francoiscardarelli.ca

ISBN 978-1-7775769-3-6 (Softcover)

ISBN 978-1-7775769-5-0 (Hardcover)

ISBN 978-1-7775769-4-3 (eBook)

Copyright © Electrochem Technologies & Materials Inc., 2023

Legal deposit: Library and Archives Canada, Ottawa, 2023.

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use. The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editor give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper.

The Electrochem Technologies & Materials Inc. imprint is published by the Canadian corporation Electrochem Technologies & Materials Inc.

The registered company address is: 2037 Aird Avenue, Suite 201, Montréal (QC) H1V 2V9, Canada

Units Policy

In this monograph all the units of measure used for describing physical quantities and properties were those recommended by the *Système International d'Unités* (SI) except in some few instances where some units from the *US Customary System* (USCS) are used in conjunction. For accurate conversion factors between these units and the other non SI units (e.g., cgs, fps, Imperial, and US customary systems) please refer to the reference book of the same author:

CARDARELLI, F. (2005) *Encyclopaedia of Scientific Units, Weight and Measures. Their SI Equivalences and Origins*. Springer, New York, London, xxiv, 848 pages; ISBN 978-1-85233-682-0.

Books by the same author:

CARDARELLI, F. (2022) *Sulfuric Acid Digestion, Sulfuric Acid Baking, and Sulfation Roasting in Mineral and Chemical Processing, and Extractive Metallurgy*. Electrochem Technologies & Materials Inc., Montreal, Canada, xvi, 285 pages, 93 tables, 76 black and white figures. ISBN 978-1-7775769-0-5.

CARDARELLI, F. (2018) *Materials Handbook. A Concise Desktop Reference, Third edition*. Springer, Cham, London, New York. cxxxii, 2254 pages, 150 black and white figures, 25 illustrations in color in two volumes. ISBN 978-3-319-38923-3.

CARDARELLI, F. (2008) *Materials Handbook. A Concise Desktop Reference, Second edition*. Springer, London, xxxviii, 1340 pages, 55 figures; ISBN 978-1-84628-689 (Out-of-Print).

CARDARELLI, F. (2005) *Encyclopaedia of Scientific Units, Weight and Measures. Their SI Equivalences and Origins*. Springer, New York, London, xxiv, 848 pages; ISBN 978-1-85233-682-0.

CARDARELLI, F. (2000) *Materials Handbook. A Concise Desktop Reference*. Springer, London, New York, ix, 595 pages, 7 figures; ISBN 978-1-85233-168-2 (Out-of-Print).

CARDARELLI, F. (1999) *Scientific Unit Conversion. A Practical Guide to Metrication, Second edition*. Springer, London, New York, xvi, 488 pages; ISBN 978-1-85233-043-0 (Out-of-Print).

CARDARELLI, F. (1997) *Scientific Unit Conversion. A Practical Guide to Metrication*. Springer, London, Heidelberg, xvi, 456 pages, ISBN 978-3-540-76022-9 (Out-of-Print).

Author Biography

François Cardarelli
Canadian & French citizen

Academic Background

Ph.D. (Doctorat), Chemical Engineering (Université Paul Sabatier, Toulouse, 1996)
DEA in Electrochemistry (Université Pierre et Marie Curie, Paris, 1992)
M.Sc. (Maîtrise), Physical Chemistry (Université Pierre et Marie Curie, Paris, 1991)
B.Sc. (Licence), Physical Chemistry (Université Pierre et Marie Curie, Paris, 1990)
DEST (Credits) in Nuclear Sciences and Technologies (CNAM, Paris, 1988)
DEUG B in Geophysics and Geology (Université Pierre et Marie Curie, Paris, 1987)
Baccalauréat C (Mathematics, Physics, and Chemistry) (CNED, Versailles, France, 1985)

Working Areas

The author has worked in the following areas since 1990 until present:

2010-Present President and owner, Electrochem Technologies & Materials Inc., Montreal (Quebec), Canada, manufacturing industrial electrodes and electrolyzers, producing vanadium, tantalum, and tungsten chemicals, inventing, patenting, and commercializing electrochemical, chemical, and metallurgical processes for recycling by-products.

2008-2010 Recycling manager, 5N Plus Inc., Ville Saint-Laurent (Quebec), Canada, in charge of the recycling of end-of-life cadmium telluride (CdTe) thin-film photovoltaic solar panels and the hydrometallurgical recovery of tellurium and cadmium.

2007-2008 Principal electrochemist, Materials and Electrochemical Research (MER) Corp., Tuscon (Arizona), USA, working on the electrowinning of titanium metal powder from composite Ti_2OC anodes in molten salts, and other materials-related projects.

2000-2007 Principal chemist (materials), technology department, Quebec Iron and Titanium (QIT) now Rio Tinto, Sorel-Tracy (Quebec), Canada, invented the electrowinning of titanium metal from molten titanium slags and on other novel electrochemical processes.

1998-200 Materials expert and industrial electrochemist, lithium department, Avestor (now Blue Solutions), involved in the metallurgy and processing of lithium metal anodes and the recycling of spent lithium metal polymer batteries.

1997-1998 Battery product leader, technology department, Argotech Productions, Inc. (Avestor), Boucherville (Québec), Canada, in charge of electric-vehicle, stationary, and down-hole oil-drilling applications of lithium metal polymer batteries.

1996-1997 Registered consultant in chemical and electrochemical engineering (Toulouse, France) providing scientific advices on electrochemical processes and electrode materials.

1993-1996 Research scientist, Laboratory of Electrochemical Engineering (Université Paul Sabatier, Toulouse, France) for the electrodeposition of tantalum in molten salts and the preparation and characterization of iridium-based industrial electrodes for oxygen evolution in acidic media (sponsored by Electricité de France).

1992-1993 Design engineer, Institute of Marine Biogeochemistry (CNRS & École Normale Supérieure, Paris, France) for the environmental monitoring of heavy-metal pollution by electroanalytical techniques and by alpha spectrometry.

1990-1992 Research scientist, Laboratory of Electrochemistry (Université Pierre & Marie Curie, Paris, France) for the development of a beta nuclear scintillation detector used for electrochemical experiments involving radiolabelled compounds.

“Nothing is too wonderful to be true if it be consistent with the laws of nature.”

Michael Faraday (1791-1867)

“Il y a une analyse selon laquelle, d'une vérité compacte, on déduit des vérités plus simples.”

André-Marie Ampère (1775-1836)

“Ogni metallo ha un determinato potere, diverso da metallo a metallo, di mettere in moto il fluido elettrico.”

Alessandro Volta (1745-1827)

“Connaître, découvrir, publier, tel est le destin d'un scientifique.”

Dominique François Jean Arago (1786-1853)

Preface

This comprehensive monograph is primarily intended to describe the patented FerWIN® technology, a green and zero-carbon iron-making process, which consists to perform the electrowinning of iron metal and the recycling of sulfuric acid from iron sulfates that are by-produced at the million tonnes scale worldwide while releasing pure oxygen gas.

The information has been presented in such a form that industrial electrochemists, chemical engineers, metallurgists, and other practicing engineers, scientists, professors, and technologists will have access to relevant scientific and technical information supported by key experimental data that were obtained from extensive laboratory, prototype, and pilot testing. It also includes comprehensive electrochemical and engineering calculations, costs and benefits analysis, a financial and sensitivity analysis.

I hope this monograph will be of value also to men and women engaged in the traditional iron and steelmaking industries that want to understand this novel electrochemical approach outside their conventional blast furnace, direct reduced iron, and electric arc smelting processes.

Finally, the monograph may be of interest to persons in the steelmaking industries occupying managerial positions such as chief executives, chief operating officers, and V.P. of operations.

Montréal, Québec, Canada

François Cardarelli, November 2023

Dedication

I dedicate this monograph to my late mother Claudine, my father Antonio who together with my late uncle Consalvo supported me in the early 1980s in establishing a basic mineralogical, chemical, and metallurgical laboratory, and scientific library and to Louise St-Amour for her continuous support and understanding during all these years.

Acknowledgements

I want to express my deepest thanks to the companies in North America, South America, Europe, and Asia who tested and assessed the patented electrochemical process over the last decade and supplied various feedstocks originating from their commercial operations.

Table of Contents

1	Introduction	1
1.1	Background	1
1.2	Environmental Benefits.....	3
1.3	Sustainable Development Benefits	4
1.4	Regulatory Compliance and Environmental Liability	5
1.5	Economic Benefits.....	5
1.6	Implementation Strategy	6
1.7	The FerWIN® Patents.....	6
1.8	Road Map: How to Read this Book?	8
2	Markets	11
2.1	Titanium Dioxide Pigment Industries	12
2.1.1	Copperas from the Sulfate Process.....	12
2.1.2	Limited Commercial Applications	13
2.1.3	Thermal Roasting Issues.....	14
2.1.4	Oversupply of Copperas	15
2.2	Iron and Steel Making Industries	16
2.2.1	Acid Pickling of Iron and Steel.....	16
2.2.2	Spent Pickling Liquors Market	17
2.3	Hydrometallurgical Processing of Nonferrous Metals.....	18
2.4	Novel Hydrometallurgical Processing Routes.....	19
2.4.1	Processing of Bauxite Residues	19
2.4.2	Novel Processing of Titano-Magnetite and Hematite.....	21
2.5	World Production of Copperas.....	23
3	Prior Art.....	25
3.1	Electroplating Iron from Sulfates	25
3.1.1	Early Developments.....	26
3.1.2	The Ferrous Ammonium Sulfate Baths	28
3.2	Electrowinning Iron.....	35

3.2.1	Pyror Process.....	35
3.2.2	Rohm & Haas Process.....	37
3.2.3	Othmar Ruthner.....	40
3.2.4	Licencia Talalmanyokat Ertekesito Vallalat.....	41
3.2.5	Davis Walker Corp.....	44
3.2.6	Eddlemann.....	45
3.2.7	Oronzio De Nora Impianti Elettrochimici S.p.a.	47
3.2.8	Gewerkschaft Keramchemie	48
3.2.9	National Aeronautics and Space Administration (NASA)	49
3.3	Conclusions from the Prior Art.....	50
4	Electrochemical Definitions.....	53
4.1	Electrochemical Reaction	53
4.2	Electroactive Species	53
4.3	Electrodes	54
4.4	Sign Convention for the Electric Current	54
4.5	Separators.....	55
4.5.1	Diaphragms.....	55
4.5.2	Membranes.....	56
4.6	Electrolytes	56
4.6.1	Pure Electrolytes	56
4.6.2	Ionic Solutions.....	56
4.6.3	Solid Electrolytes.....	57
4.7	Electrochemical Cells	57
4.7.1	Galvanic Cells.....	57
4.7.2	Electrolytic Cells or Electrolyzers.....	58
4.8	Electric Potentials at the Electrode	59
4.8.1	Electromotive Force.....	59
4.8.2	Galvani or Inner Electric Potential.....	60
4.8.3	Volta or Outer Electric Potential.....	61
5	Thermochemistry of Electrochemical Reactions.....	63
5.1	Gibbs Enthalpy of Electrochemical Reactions.....	63
5.2	Ion Activity, and Mean Activity Coefficient	64
5.2.1	Ions in Aqueous Electrolytes.....	64
5.2.1.1	Ideal Solutions.....	64

5.2.1.2	Actual Solutions and Non-ideality.....	65
5.2.2	Debye-Hückel Equations.....	67
5.3	Thermochemical Data.....	68
5.4	Standard Molar Enthalpy, and Entropy of Reaction.....	70
5.5	Standard Molar Gibbs Enthalpy of Reaction.....	71
5.6	Standard Electrode Potential.....	73
5.7	Sign Convention for Standard Electrode Potentials.....	75
5.8	Standard Reversible Cell Voltage.....	76
5.9	Nernst Electrode Potential.....	77
5.10	Thermodynamic (Reversible) Cell Voltage.....	78
5.11	Standard Thermoneutral Potential.....	78
5.12	Thermoneutral Cell Voltage.....	79
5.13	Calculated Electrode Potentials vs. Temperature.....	80
5.14	Influence of pH.....	81
5.15	Reference Electrodes.....	82
5.15.1	Reference Electrode of the First Kind.....	83
5.15.1.1	Redox or Inert Electrode.....	83
5.15.1.2	Metallic Electrodes.....	84
5.15.1.3	Gas Electrodes.....	84
5.15.2	Reference Electrode of the Second Kind.....	85
5.15.3	Reference Electrode of the Third Kind.....	86
5.15.4	Standard Hydrogen Electrode.....	86
5.15.5	Silver-Silver Chloride Electrode.....	88
5.15.6	Standard Calomel Electrode.....	89
5.15.7	Mercury-Mercurous Sulfate Electrode.....	89
5.15.8	Silver-Silver Sulfate Electrode.....	90
5.15.9	Copper-Copper Sulfate Electrode.....	90
5.15.10	Temperature Coefficients of Reference Electrodes.....	91
5.16	Pourbaix Diagram for Iron.....	91
5.16.1	Hydrolysis, Complexation and Precipitation Reactions.....	92
5.16.2	Reduction and Oxidation Reactions.....	95

6 Transport Phenomena 107

6.1	Fluxes of Electroactive Species	107
6.2	Electro-Migration.....	108
6.3	Mass Diffusion	111
6.4	Natural and Forced Convection	112
6.5	Thermodiffusion	112
6.6	The Nernst-Planck's Equation.....	113
6.7	Liquid Junction Potential.....	113
6.7.1	Origins	113
6.7.2	Types of Liquid Junction Potentials	114
6.7.3	Planck Equation	114
6.7.4	Binary Electrolyte.....	116
6.7.5	Henderson Equation	117
6.8	Continuity Equations.....	119
6.9	The Nernst-Einstein's Equation.....	121
6.10	Electroneutrality.....	121
6.11	Current Density.....	122
6.12	Conservation of the Electric Charge.....	123
6.13	Electrical Conductivity	124
6.13.1	Electrolyte Electrical Conductivity.....	124
6.13.2	Molar Ionic Conductivity.....	124
6.13.3	Equivalent Ionic Conductivity	125
6.13.4	Limiting Equivalent Conductivity.....	127
6.13.5	Individual Equivalent Ionic Conductivity.....	127
6.13.6	Law of Independent Migration of Ions	127
6.13.7	Conductivity of Pure Water.....	129
6.13.8	Kohlrausch Equation	130
6.13.9	Onsager Equation	130
6.13.10	Influence of Temperature.....	131
6.13.11	Measurement of the Conductivity of Electrolytes.....	132
6.13.12	Transference Number of Ions	133
6.13.13	Role of a Supporting Electrolyte	134
7	Electrode Kinetics.....	135
7.1	Electrode Potential Measurements.....	135

7.2	Rest Potential.....	136
7.3	Overpotential (Overvoltage).....	136
7.4	Types of Overpotential.....	137
7.4.1	Concentration (Diffusion) Overpotential.....	138
7.4.2	Activation (Charge Transfer) Overpotential.....	138
7.4.3	Chemical Overpotential.....	138
7.4.4	Crystallization Overpotential.....	139
7.4.5	Passivation Overpotential.....	139
7.5	International Sign Convention.....	139
7.6	De Donder-Pourbaix Inequality.....	140
7.7	Reversible (Fast) Electrode Reaction.....	141
7.8	Irreversible (Slow) Electrode Reactions.....	142
7.9	Electrochemical Span.....	143
7.10	Concentration Overpotential.....	143
7.10.1	Nernst Diffusion Layer.....	144
7.10.2	Limiting Current.....	145
7.10.3	Electroreduction of Metal Cations.....	147
7.10.4	Diffusion Overpotential Equation.....	148
7.10.5	Diffusion Polarization Resistance.....	150
7.10.6	Mass Transfer Coefficient.....	151
7.10.6.1	Natural Convection and Laminar Flow.....	152
7.10.6.2	Forced Convection.....	153
7.11	Activation Overpotential.....	153
7.11.1	Butler-Volmer Equation.....	153
7.11.2	Generalized Butler-Volmer Equation.....	157
7.11.3	High Overpotentials.....	159
7.11.3.1	Anode Tafel's Coefficients.....	159
7.11.3.2	Cathode Tafel's Coefficients.....	161
7.11.4	Low Overpotentials.....	163
7.11.5	Low Activation Overpotentials.....	164
7.12	Electro-Crystallization Overpotential.....	164
7.13	Overall Overpotential.....	166
8	Electrochemical Figures of Merit.....	169
8.1	Faraday's Laws.....	169

8.1.1	First Faraday's Law	169
8.1.2	Second Faraday's Law	169
8.2	Electrochemical Equivalents	169
8.2.1	Gravimetric Electrochemical Equivalent.....	170
8.2.2	Volumetric Electrochemical Equivalent	170
8.3	Faradaic Current Efficiency.....	171
8.4	Overall Cell Voltage.....	173
8.5	Electrochemical Reaction Rates.....	174
8.5.1	Hourly Yield.....	174
8.5.2	Space Time Yield.....	174
8.6	Voltage, and Energy Efficiencies	175
8.6.1	Voltaic or Potential Efficiency	175
8.6.2	Energy Efficiency.....	175
8.7	Specific and Volumetric Energy Consumptions.....	176
9	Current Distributions.....	177
9.1	Primary Distribution.....	177
9.1.1	Laplace Equation.....	177
9.1.2	Cathode Edge Effects.....	179
9.2	Secondary Distribution.....	179
9.2.1	Haring-Blum Cell	179
9.2.2	Hull Cell.....	182
9.2.3	Wagner Number.....	185
9.2.4	Throwing Power.....	186
9.3	Tertiary Distribution.....	186
10	Electrochemical Reactors Design	189
10.1	Electrochemical Reactors Types	189
10.1.1	General Time Dependent Mass Balance Equation	189
10.1.2	Residence Time and Electrode Specific Surface Area	191
10.1.3	Fractional Conversion Rate	192
10.1.4	Batch Stirred Electrolyzer	192
10.1.4.1	Mass Transfer Limited Electrochemical Reaction	194
10.1.4.2	Electrolysis below Limiting Current Density.....	196
10.1.4.3	Galvanostatic Mode	198
10.1.5	Plug Flow Electrolyzer	200
10.1.5.1	Mass Transfer Limited Electrochemical Reaction	203

10.1.5.2	Electrolysis at Limiting Current (Potentiostatic)	204
10.1.5.3	Electrolysis below Limiting Current	205
10.1.5.4	Plug Flow Electrolyzer with Recirculation	206
10.1.5.5	Electrolysis at Limiting Current (Potentiostatic)	208
10.1.5.6	Cascade of Plug Flow Electrolyzers	209
10.1.6	Continuous Stirred Electrolyzer	210
10.1.6.1	Mass Transfer Limited Electrochemical Reaction	211
10.1.6.2	Electrolysis at Limiting Current (Potentiostatic)	211
10.1.6.3	Continuous Stirred Electrolyzer with Recirculation ...	213
10.1.6.4	Cascade of Continuous Stirred Electrolyzers	215
10.1.7	Models for Describing the Electrowinning of Iron	216
10.2	Mass and Energy Balances inside Electrolyzers	217
10.3	Heat Transfer Calculations	221
11	Electrolytes	223
11.1	Catholyte	223
11.1.1	Solubility of Ferrous Sulfate and Density of Solutions	223
11.1.2	Electrical Conductivity of Ferrous Sulfate Solutions	225
11.1.3	Specific Heat Capacity of Ferrous Sulfate Solutions	225
11.1.4	The Binary system: $\text{FeSO}_4\text{-H}_2\text{O}$	227
11.1.5	The Ternary System: $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$	228
11.1.6	Solubility of Metal Sulfates	230
11.1.7	Dissociation Constants of Metal Sulfates	232
11.1.8	Electrical Conductivity of Metal Sulfates	233
11.1.9	Influence of the pH and Precipitation	234
11.1.10	Supporting Electrolytes	237
11.1.10.1	Ammonium Sulfate	238
11.1.10.2	Sodium Sulfate	239
11.1.10.3	Potassium Sulfate	239
11.1.10.4	Magnesium Sulfate	239
11.1.10.5	Aluminum Sulfate	239
11.1.10.6	Lithium Sulfate	239
11.1.11	Additives	240
11.1.11.1	Buffering Agents	240
11.1.11.2	Surfactants	241
11.1.11.3	Levelling and Brightening Agents	241
11.1.11.4	Complexing Agents	241
11.1.12	Electroactive Impurities	242
11.1.13	Practical Catholyte Composition and Properties	243
11.1.14	Reducing and Dummying the Catholyte	245
11.1.14.1	Chemical Reduction	245
11.1.14.2	Electrochemical Reduction and Pre-electrolysis	246
11.2	Anolyte	250

11.2.1	Mass Density.....	250
11.2.2	Dynamic Viscosity	252
11.2.3	Specific Heat Capacity.....	252
11.2.4	Electrical Conductivity.....	254
11.2.5	Final Concentration of Sulfuric Acid	256
11.2.6	Selection of Construction Materials	259
11.2.7	Practical Anolyte Composition and Properties	261
12	Electrodes	263
12.1	Selection Criteria	263
12.2	Cathodes.....	263
12.2.1	Cathode Materials	264
12.2.2	Cathode Materials Physical Properties	266
12.2.3	Hydrogen Overvoltage.....	266
12.2.4	Cathode Tafel's Coefficients	267
12.2.4.1	Hydrogen Overpotential for Diluted Sulfuric Acid....	268
12.2.4.2	Hydrogen Overpotential for Concentrated Sulfuric Acid	270
12.2.5	Electro-crystallization Overvoltage	272
12.2.6	Cathode Polarization vs. Materials	274
12.2.7	Cathode Polarization vs. Temperature.....	277
12.2.8	Cathode Polarization vs. Concentration	277
12.2.9	Cathode Polarization vs. pH.....	277
12.2.10	Cathode Polarization vs. Surface Treatment.....	278
12.2.11	Cathode Overvoltage vs. Materials, and pH	278
12.2.12	Current Efficiency vs. Materials and Temperature.....	281
12.2.13	Cathode Current Efficiency vs. Initial pH and Time.....	282
12.2.14	Cathode Current Efficiency vs. pH and FeSO ₄	284
12.2.15	Cathode Current Efficiency at pH below 1.35	285
12.2.16	Cathode Current Efficiency vs. pH and Current Density.....	287
12.2.17	Cathode Current Efficiency vs. pH and Catholyte.....	288
12.2.18	Purity of Electrodeposited Iron	289
12.2.18.1	Electrolytic Iron Metal.....	289
12.2.18.2	Iron-rich Alloys.....	291
12.3	Anodes.....	293
12.3.1	Anode Materials	294
12.3.2	Oxygen Overvoltage.....	294
12.3.3	Impact of Sulfuric Acid Concentration.....	296
12.3.4	Impact of Catalyst Coating	297
12.3.5	Anode Tafel's Coefficients	297
12.3.6	Anode Current Efficiency vs. Sulfuric Acid in Catholyte..	299
12.3.7	Anode Current Efficiency vs. Impurities.....	300
12.4	Recommended Electrodes	300

13	Separators	301
13.1	Diaphragms.....	301
13.2	Anion Exchange Membranes (AEM).....	302
13.3	Commercial Brands.....	302
13.4	Ohmic Drop	303
	13.4.1 Low Current Density.....	304
	13.4.2 High Current Density	304
13.5	Transference Numbers.....	305
13.6	Membranes Protons Leakage and Rejection	309
13.7	Membranes Service Life.....	310
14	Electrochemical Calculations	313
14.1	Electrochemical Performances.....	313
	14.1.1 Minimizing the Specific Energy Consumption	313
	14.1.2 Increasing the Space Time Yield.....	314
14.2	Electrochemical Reactions.....	315
	14.2.1 Main Electrochemical Reactions.....	315
	14.2.2 Side Electrochemical Reactions.....	316
	14.2.3 Electrochemical Reactions Related to Impurities.....	317
14.3	Theoretical (Reversible) Cell Voltage	317
	14.3.1 Standard Electrode Potentials	318
	14.3.2 Standard Electrode Potentials vs. Temperature.....	319
	14.3.3 Standard Reversible Cell Voltage	319
	14.3.4 Nernst Electrode Potentials.....	322
	14.3.5 Nernst Electrode Potentials vs. Temperature	324
	14.3.6 Nernst Electrode Potentials vs. Temperature and pH.....	325
	14.3.7 Thermodynamic (Decomposition) Cell Voltage	326
14.4	Electrochemical Cell.....	327
14.5	Mass Transfer Coefficients	328
	14.5.1 Forced Convection and Turbulent Flow	329
	14.5.2 Laminar Flow between Cathode and Separator	329
14.6	Electrode Reactions Overpotentials.....	331
	14.6.1 Anode Overpotential.....	331
	14.6.2 Cathode Overpotentials.....	331

14.6.2.1	Electrodeposition of Metallic Iron.....	332
14.6.2.2	Iron Concentration Overpotential.....	332
14.6.2.3	Hydrogen Gas Evolution Reaction.....	332
14.7	Actual Electrode Potentials	334
14.8	Ohmic Drop Contributions.....	335
14.9	Liquid-Junction Potential.....	338
14.10	Overall Cell Voltage	339
14.11	Cell Potential Breakdown.....	339
14.12	Faradaic, Voltaic, and Energy Efficiencies.....	340
14.12.1	Faradaic Current Efficiency.....	340
14.12.2	Voltaic or Potential Efficiency.....	341
14.12.3	Energy Efficiency.....	341
14.13	Specific Energy Consumption	341
14.14	Hourly Space-Time Yield	342
15	Laboratory, Prototype, and Pilot Testing	343
15.1	Laboratory Electrolyzers.....	343
15.2	Prototype Electrolyzers.....	345
15.3	Semi-Pilot Electrolyzers.....	347
15.4	Production of Electrolytic Iron Powder.....	349
15.4.1	Plate and Frame Electrolyzers.....	349
15.4.2	Cylindrical and Tubular Electrolyzers	350
15.5	Single Pilot Electrolyzer.....	351
15.6	Electrolyzers Characteristics.....	352
15.7	Scale-up and Similarity Equations.....	352
15.8	Electrowinning Parameters.....	354
16	Electrowinning Plant Calculations	357
16.1	Fundamental.....	357

16.2	Process Flow Diagrams	358
16.3	Electrowinning Plant Schedule.....	361
16.4	Electrowinning Plant Nameplate Capacity	361
16.5	Mass Balances	363
16.5.1	Catholyte Mass Balance Equations	364
16.5.2	Anolyte Mass Balance Equations	366
16.6	Electrochemical Performances and Figures of Merit.....	369
16.7	Electrolytes Flows and Conversion Rates.....	370
16.7.1	Catholyte Fractional Conversion Rate.....	370
16.7.2	Catholyte Circulation Mode.....	370
16.7.3	Catholyte Volume Flow Rate.....	370
16.7.4	Anolyte Fractional Conversion Rate.....	372
16.7.5	Anolyte Circulation Modes	372
16.7.5.1	Continuous Increase of the Acid Concentration.....	372
16.7.5.2	Constant Concentration Operation.....	372
16.7.6	Anolyte Mass and Volume Flow Rates	373
16.8	Electrolyzer Design.....	373
16.8.1	Cathodes	373
16.8.1.1	Cathode Materials	373
16.8.1.2	Total Number of Cathodes per Electrolyzer	374
16.8.1.3	Rectangular Cathode Shape and Dimensions	374
16.8.1.4	Shape and Dimensions of Hanger Bar	376
16.8.1.5	Overall T-Shape Cathode Mass	376
16.8.1.6	Insulating Edge Strips or Slotted Plastic Edges.....	376
16.8.1.7	Actual Immersed Cathode Characteristics	377
16.8.1.8	Cathode Buttons	377
16.8.1.9	Cathode Active Surface Area	378
16.8.1.10	Cathode Specific Active Surface Area	378
16.8.1.11	Cathode Surface Velocity	378
16.8.2	Anodes	379
16.8.2.1	Anode Materials	379
16.8.2.2	Total Number of Anodes per Electrolyzer	379
16.8.2.3	Cathode-Anode Overlap.....	380
16.8.2.4	Anode Shape and Dimensions.....	380
16.8.2.5	Anode Specific Active Surface Area	383
16.8.2.6	Anode Surface Velocity	383
16.8.3	Membranes.....	384
16.8.4	Anode Compartment.....	384
16.8.5	Electrolyzer	386
16.8.5.1	Polymer Concrete Electrolyzer	387
16.8.5.2	Electrolyzer Design and Dimensions.....	388

16.8.5.3	Electrical Requirements.....	390
16.9	Cell House.....	391
16.9.1	Total Cathode Surface Area.....	391
16.9.2	Total Number of Electrolyzers.....	391
16.9.3	Number of Harvesting Cycles.....	392
16.9.4	Rectifier Specifications.....	393
16.9.5	Busbars Ampacities and Design.....	395
16.9.5.1	Ampacity.....	395
16.9.5.2	Busbars and Contact Ohmic Drop.....	396
16.9.6	Electrolytes Pumping and Manifolding.....	398
16.9.6.1	Catholyte Flow.....	398
16.9.6.2	Anolyte and Oxygen Gas Flow.....	399
16.9.7	Electrolyzer Elevation.....	399
16.9.8	Mist Suppression.....	400
16.9.8.1	Anolyte.....	400
16.9.8.2	Catholyte.....	400
16.9.9	Oxygen-gases Scrubber.....	400
16.9.10	Catholyte Continuous Filtration.....	400
16.9.11	Temperature Management and Control.....	401
16.9.12	Cathodes Harvesting Machinery.....	401
16.9.13	Cathode Two-stage Rinsing and Passivation.....	402
16.9.14	Cathodes Stripping Machine.....	404
16.9.15	Cell House Layout.....	404
17	Costs and Benefits Analysis.....	407
17.1	Business Case.....	407
17.1.1	Targeted Geographical Locations.....	407
17.1.2	Electrowinning Plant Nameplate Capacity.....	408
17.1.3	Plant History.....	408
17.2	Capital Expenses (CAPEX).....	408
17.2.1	CAPEX Cost Estimation Categories.....	409
17.2.2	Costs Estimates Types and Accuracy.....	409
17.2.3	The Six-tenth Rule.....	410
17.2.4	The "n" exponent.....	410
17.2.5	Plant Location Adjustment.....	411
17.2.6	Determination of the Present Costs.....	411
17.2.6.1	Price Deflator.....	412
17.2.6.2	Cost Indices.....	412
17.3	Fixed Capital Investment.....	413
17.3.1	Direct Costs.....	413
17.3.1.1	Purchased Equipment Costs.....	413
17.3.1.2	Equipment Installation Costs.....	413
17.3.1.3	Piping Costs.....	414

17.3.1.4	Instrumentation and Controls.....	414
17.3.1.5	Insulation Costs	414
17.3.1.6	Electrical Installation Costs.....	415
17.3.1.7	Building Costs	415
17.3.1.8	Yard Improvements	415
17.3.1.9	Services Facilities	415
17.3.1.10	Land.....	416
17.3.2	Indirect Costs.....	418
17.3.2.1	Engineering and Supervision Costs.....	418
17.3.2.2	Construction Expenses	419
17.3.2.3	Contractor's fee.....	419
17.3.2.4	Contingency.....	419
17.4	Working Capital.....	420
17.5	Operation Costs (OPEX).....	422
17.5.1	OPEX Cost Estimation Categories	422
17.5.2	Variable Costs.....	422
17.5.2.1	Raw Materials	423
17.5.2.2	Process Materials	423
17.5.2.3	Utilities, Energy and Fuels.....	423
17.5.3	Fixed Costs.....	424
17.5.4	Allotment of Workers and Staff.....	424
17.5.5	Labor Costs	425
17.5.6	Maintenance	426
17.5.7	Indirect Costs.....	426
17.5.8	Contingencies.....	426
17.5.9	Administration and Overhead Costs	426

18 Financial Analysis 429

18.1	Basis of Evaluation	429
18.1.1	Operating Life or Useful Life	429
18.1.2	Sales Revenue.....	429
18.1.3	Operating and Production Costs.....	429
18.1.4	Fixed-Capital Investment	430
18.1.5	Working Capital.....	430
18.1.6	Total Capital Investment.....	430
18.1.7	Gross Profit.....	430
18.1.8	Gross Profit margin	430
18.1.9	Net Profit Margin.....	431
18.1.10	Interest Rate or Discount Rate.....	431
18.1.11	Income Tax Rate	431
18.1.12	Salvage Value	431
18.1.13	Annual Depreciation.....	431
18.1.14	EBITDA.....	432
18.1.15	Taxable Income.....	432

18.1.16	Annual Cash Flow Equivalent	432
18.1.17	Net Profit.....	432
18.1.18	Present and Net Present Value	432
18.1.19	Internal Rate of Return	433
18.1.20	Return-on-Investment.....	433
18.1.21	Payback Time	433
18.1.22	Selling Prices of Metallic Iron and Sulfuric Acid.....	433
18.1.23	Taxation, Duties and Royalties	433
18.1.24	Project Discount Rate	433
18.1.25	Minimum Acceptable Rate of Return	434
18.1.26	Other Assumptions	434
18.2	Discounted Cash Flow Analysis	434
18.3	Key Financial Indicators	436
19	Sensitivity Analysis.....	437
19.1	Plant Nameplate Capacity.....	437
19.2	Price of Electrolytic Iron Metal	438
19.3	Price of Copperas.....	438
19.4	Price and Oversupply of Sulfuric Acid	439
19.5	“What if” Analysis	439
19.6	Fluctuation of the Price of Iridium.....	440
20	Bibliography.....	443
20.1	Electrochemical Data	443
20.2	Electrochemistry and Electrode Kinetics	444
20.3	Electrochemical Engineering.....	445
20.4	Industrial Electrochemistry and Electrosynthesis	446
20.5	Electroplating and Electrodeposition.....	446
20.6	Plant Economics and Financial Analysis	447
21	Appendices	449
21.1	Scientific and Technical Acronyms	449

21.2	Economic and Financial Acronyms.....	450
21.3	Latin and Greek Symbols.....	451
21.4	Selected Universal Constants (CODATA, 2018).....	455
21.5	Conversion Factors.....	457
21.6	Standard Relative Atomic Masses	460
21.7	Periodic Table of the Elements.....	461
21.8	Selected Oxidation-Reduction Potentials.....	462
22	Index	463

List of Tables

Table 1 – Worldwide patents and patents applications	7
Table 2 – World sources for copperas (tonnes per year)	23
Table 3 – First commercial electroplating of iron in Russia (Russian Mint)	27
Table 4 – First commercial electroplating of iron in Germany (Schlötter)	28
Table 5 – Electroplating of iron from mixed sulfates (Hoepner and Klic)	29
Table 6 – Commercial electroplating in the US (Burgess and Hambuechen)	30
Table 7 – Commercial electroplating in the UK (MacFadyen).....	31
Table 8 – Commercial electroplating in the UK (Westinghouse)	32
Table 9 – Production of iron powder (Plastic Metals).....	33
Table 10 – Production of iron powder (SCM Corp.).....	34
Table 11 – Electrowinning iron from pregnant leach solutions (Pyror)	36
Table 12 – Electrowinning of iron from spent pickling liquors (Rohm & Haas Co.)	39
Table 13 – Electrowinning of iron from spent pickling liquors (Hungary).....	42
Table 14 – Electrowinning of iron from spent pickling liquors (Davis Walker)	45
Table 15 – Electrowinning of iron from spent pickling liquors (Keramchemie)	49
Table 16 – International convention of electrochemical cells	58
Table 17 – Thermochemical data for selected inorganic substances at 298.15 K	69
Table 18 – Temperature dependence of molar and Gibbs enthalpies of reaction	73
Table 19 – Selected electrochemical reactions involving metal sulfates.....	75
Table 20 – Standard electrode potential for selected redox couples	76
Table 21 – Standard thermoneutral potential for selected redox couples	79
Table 22 – Standard reversible and thermoneutral cell voltages for water and FeSO ₄	80
Table 23 – Thermodynamic functions of relevant reactions in sulfate medium	80
Table 24 – Standard electrode potential vs. pH and temperature.....	82
Table 25 – Potential of silver-silver chloride electrodes	88
Table 26 – Potential of calomel electrodes.....	89
Table 27 – Potential of mercury sulfate electrodes	90
Table 28 – Potential of silver-silver sulfate Electrodes.....	90
Table 29 – Potential of copper sulfate electrode	91
Table 30 – Potential of selected reference electrodes vs. temperature (V/SHE).....	91
Table 31 – Names, symbols and SI units of various fluxes	108
Table 32 – Ionic mobility of selected cations and anions	110
Table 33 – Equivalent ionic conductivities of selected electrolytes at 18°C	126
Table 34 – Limiting equivalent ionic conductivities of salts with anions in common	128
Table 35 – Equivalent ionic conductivity and diffusion coefficients at infinite dilution.....	129
Table 36 – Diffusion overpotential vs. ratio of current densities and electrons exchanged	150
Table 37 – Correlations for mass transfer coefficients with plane parallel vertical plates....	153
Table 38 – Electrochemical equivalents for selected redox couples.....	171
Table 39 – Hull cell cathode current density vs. cathode abscissa.....	185
Table 40 – Basic equations for various electrochemical reactors	216
Table 41 – Mass and energy balances for the iron electrowinning cell	220
Table 42 – Counter and parallel crossflow HX	222
Table 43 – Solubility of FeSO ₄ in water and mass density of solution vs. temperature	224
Table 44 – Specific heat capacity of solutions of ferrous sulfate vs. temperature	227
Table 45 – Solubility of ferrous sulfate vs. concentration of sulfuric acid.....	230
Table 46 – Solubility of metal sulfates vs. temperature	231
Table 47 – Dissociation constant and degree of dissociation of metal sulfates	233
Table 48 – Electrical conductivity of solutions metal sulfates in S/m at 20°C.....	234
Table 49 – Precipitation pH of selected metal hydroxides	236
Table 50 – Proposed buffering agents and additives to improve deposition	242
Table 51 – Half electrochemical reactions related to impurities	243

Table 52 – Composition and selected properties of the catholyte vs. temperature	244
Table 53 – Specific consumption of reducing agents	246
Table 54 – Mass density of sulfuric acid solutions	251
Table 55 – Dynamic viscosity of sulfuric acid solutions.....	252
Table 56 – Specific heat capacity of sulfuric acid vs. mass percentage and temperature	254
Table 57 – Electrical conductivity of sulfuric acid vs. percentage and temperature	255
Table 58 – Mass percentage of sulfuric acid vs. anolyte and catholyte compositions.....	259
Table 59 – Plastics compatibility with cold and hot sulfuric acid (30 wt.% H ₂ SO ₄).....	260
Table 60 – Recommended plastics and elastomers for piping and gaskets	261
Table 61 – Selected properties of anolyte vs. temperature.....	262
Table 62 – Industrial cathode materials	265
Table 63 – Mass density and electrical resistivity of selected cathode materials	266
Table 64 – Cathode overpotential for H ₂ evolution in 1 N sulfuric acid at 20°C	269
Table 65 – Cathode Tafel's coefficients in 1 N sulfuric acid at 20°C.....	270
Table 66 – Cathode overpotential for H ₂ evolution in 31 wt.% sulfuric acid at 20°C.....	271
Table 67 – Cathode Tafel's coefficients in 31 wt.% sulfuric acid at 20°C.....	272
Table 68 – Electrode kinetics data for anode and cathode electrode reactions	273
Table 69 – Cathode polarization vs. cathode current density (saturated)	276
Table 70 – Cathode polarization vs. cathode current density (concentrated)	276
Table 71 – Cathode polarization vs. temperature.....	277
Table 72 – Cathode polarization vs. catholyte saturation.....	277
Table 73 – Cathode Polarization vs. pH.....	278
Table 74 – Selected surface finishing techniques.....	278
Table 75 – Potentials for iron deposition and hydrogen evolution (pH 1.0, -500 A/m ²)....	279
Table 76 – Potentials for iron deposition and hydrogen evolution (pH 1.0, -1500 A/m ²)..	280
Table 77 – Potentials for iron deposition and hydrogen evolution (pH 3.0, -750 A/m ²)....	281
Table 78 – Cathode current efficiency vs. materials and temperature.....	282
Table 79 – Cathode current efficiencies at pH below 1.4 vs. cathode current densities	286
Table 80 – Chemical composition of an electrolytic iron deposit from copperas.....	289
Table 81 – Macro- and micro-photographs of iron and iron-rich alloys	292
Table 82 – Composition of electrodeposited iron-rich alloys from pickling liquors	293
Table 83 – Selected anode materials and suppliers.....	294
Table 84 – Oxygen evolution overpotentials for various MMO anodes	296
Table 85 – Tafel's coefficients for anode materials in 10 and 30 wt.% H ₂ SO ₄	299
Table 86 – Recommended electrode materials	300
Table 87 – Measured dry density, thickness, and swelling	303
Table 88 – Specifications and physical properties of anion-exchange membranes	303
Table 89 – Ions transport equations inside the membrane electrolyzer	308
Table 90 – Measured ASI, and ohmic drop of anion exchange membranes.....	308
Table 91 – Main, side, and overall electrochemical reactions	316
Table 92 – Standard electrode potentials at 298.15 K and 101.325 kPa	318
Table 93 – Standard electrode potentials of reducible metallic impurities	318
Table 94 – Standard electrode potentials vs. temperature.....	319
Table 95 – Main standard reversible cell voltage vs. temperature.....	320
Table 96 – Main standard thermoneutral cell voltage vs. temperature.....	321
Table 97 – Standard potential, reversible, and thermoneutral voltage vs. temperature	322
Table 98 – Nernst potential, reversible, and thermoneutral voltage vs. temperature	324
Table 99 – Nernst electrode potentials vs. temperature and pH.....	326
Table 100 – Thermodynamic and thermoneutral cell voltage vs. temperature.....	327
Table 101 – Electrolyzer single cell size and dimensions	328
Table 102 – Mass transfer coefficients for the anode and cathode at 60°C.....	330
Table 103 – Mass transfer coefficients for the cathode vs. temperature	330
Table 104 – Mass transfer coefficients for the anode vs. temperature.....	331

Table 105 – Electrode overpotentials at 500 A/m ² and 60°C.....	333
Table 106 – Overpotentials for activation, diffusion and crystallization vs. temperature....	334
Table 107 – Electrode potential and cell voltage vs. temperature at 500 A/m ²	334
Table 108 – Composition and properties of anolyte and catholyte at 20°C.....	335
Table 109 – Properties of electrodes and membrane materials.....	337
Table 110 – Ohmic drop contributions at 60°C and 500 A.m ⁻²	337
Table 111 – Breakdown of ohmic drop contributions vs. temperature.....	338
Table 112 – Contributions to the ohmic drop with and without supporting electrolyte	338
Table 113 – Liquid junction potentials vs. temperature	339
Table 114 – Overall cell voltage of three-compartment cell vs. temperature	339
Table 115 – Specific energy consumptions at 500 A.m ⁻²	342
Table 116 – Space time yield at 500 A.m ⁻²	342
Table 117 – Figures of merit and indices of performances vs. temperature	342
Table 118 – Pilot and prototype electrolyzer configurations.....	348
Table 119 – Rectangular electrolyzer characteristics	352
Table 120 – Cell voltage similarity equations between electrolyzers	354
Table 121 – Electrowinning operating conditions	355
Table 122 – Main and side electrochemical reactions.....	358
Table 123 – Iron electrowinning plant schedule.....	361
Table 124 – Theoretical mass equivalence factors (100% current efficiency).....	362
Table 125 – Iron electrowinning plant nameplate capacity.....	363
Table 126 – Electrochemical performances and figures of merit	369
Table 127 – Inlet and outlet catholyte composition and properties	372
Table 128 – Inlet and outlet anolyte composition and properties	373
Table 129 – Total number of cathodes per cell vs. annual tonnage of iron	374
Table 130 – Cathode hanger bar dimensions and characteristics	376
Table 131 – Cathodes characteristics, sizes and dimensions	379
Table 132 – MMO coated-titanium anodes characteristics, sizes and dimensions.....	383
Table 133 – Anion exchange membrane characteristics	384
Table 134 – Dimensions of the anode compartment	386
Table 135 – Characteristics of the parallelepiped electrolyzer.....	389
Table 136 – Electrical requirement vs. electrodes arrangement.....	390
Table 137 – Electrolyzer electrical requirements	391
Table 138 – Cell house	392
Table 139 – Harvesting cycle.....	392
Table 140 – Bank electrical requirements vs. electrolyzer arrangement.....	393
Table 141 – Rectifiers specifications	395
Table 142 – Main busbars design and characteristics	396
Table 143 – Drag-out of the catholyte at various temperatures.....	402
Table 144 – Two-stage rinsing of cathodes.....	404
Table 145 – Vendors for cathode stripping machines	404
Table 146 – CAPEX costs estimation categories	409
Table 147 – Cost estimate classification (AACE).....	409
Table 148 – Geographical adjustment factor for electrowinning plants	411
Table 149 – Cost index sources	412
Table 150 – Installation costs	414
Table 151 – Piping costs	414
Table 152 – Instrumentation costs	414
Table 153 – Buildings with services costs.....	415
Table 154 – Land and site preparation costs.....	416
Table 155 – Fixed capital investment calculations (Direct costs)	417
Table 156 – Direct costs.....	418
Table 157 – Fixed capital investment calculations (Indirect costs).....	419

Table 158 – Indirect and fixed costs	420
Table 159 – Fixed capital investment calculations (Working capital)	421
Table 160 – Working capital	421
Table 161 – Total capital expenditures (CAPEX)	422
Table 162 – OPEX costs estimation categories	422
Table 163 – Costs of raw materials, process materials, and utilities	423
Table 164 – Other costs	424
Table 165 – Allotment of workers and staff	425
Table 166 – Labor costs	426
Table 167 – Operating expenditures (OPEX)	427
Table 168 – OPEX breakdown	428
Table 169 – Assumptions	434
Table 170 – Discounted cash flow analysis	435
Table 171 – Key financial indicators	436
Table 172 – Financial indicators vs. production cost and nameplate capacity	437
Table 173 – Sensitivity analysis	439
Table 174 – List of scientific and technical acronyms	449
Table 175 – List of economic and financial acronyms	450
Table 176 – Latin symbols	451
Table 177 – Greek symbols	454
Table 178 – Selected universal constants (CODATA, 2018)	455
Table 179 – Selected conversion factors	457
Table 180 – Standard Relative Atomic Masses	460
Table 181 – Selected oxidation-reduction potentials	462

List of Figures

Figure 1 – Schematic of the FerWIN® process (Two-compartment electrolyzer).....	2
Figure 2 – Schematic of the FerWIN® process (Three-compartment electrolyzer)	3
Figure 3 – Road map for navigating through this book	9
Figure 4 – Vertical integration of FerWIN® with the sulfation bauxite residues	21
Figure 5 – Vertical integration of the FerWIN® process with the VEPT	22
Figure 6 – Schematic of the Pyror process.....	37
Figure 7 – Schematic of the Rohm & Haas process	40
Figure 8 – Schematic of the Hungarian process	43
Figure 9 – Schematic of the Davis Walker process.....	44
Figure 10 – Schematic of the Eddleman process	46
Figure 11 – Sign convention for the electric current (Power source).....	55
Figure 12 – Sign convention for the electric current (Electrolyzer)	55
Figure 13 – Galvanic cell.....	59
Figure 14 – Electrochemical cell	60
Figure 15 – Theoretical galvanic cell	61
Figure 16 – Volta potential	62
Figure 17 – Simplified Pourbaix (<i>E</i> -pH) diagram for iron.....	106
Figure 18 – Interphase.....	114
Figure 19 – Electrical resistance of an electrolytic cell	132
Figure 20 – Wheatstone bridge.....	133
Figure 21 – Kohlrausch bridge.....	133
Figure 22 – Piontelli's three-electrode system.....	135
Figure 23 – Schematic of an electrochemical reaction pathway.....	137
Figure 24 – Plot of the current density vs. electrode potential.....	140
Figure 25 – Plot of the absolute value of current density vs. electrode potential.....	140
Figure 26 – DeDonder-Pourbaix quadrants.....	141
Figure 27 – Polarization plots for reversible and irreversible electrode reactions	142
Figure 28 – Electrochemical span of the solvent	143
Figure 29 – Nernst diffusion layer	145
Figure 30 – Polarization plot due to concentration overvoltage.....	149
Figure 31 – Pure activation current-potential plot	157
Figure 32 – Mixed activation-diffusion current-potential plot.....	159
Figure 33 – Horiuti plot showing the anode and cathode Tafel's parameters	163
Figure 34 – Schematic of the steps occurring during electro-crystallization	165
Figure 35 – Breakdown of the electrode overpotential vs. current density.....	167
Figure 36 – Primary current distribution with equipotential and electric field lines	178
Figure 37 – Schematic of the Haring-Blum cell.....	180
Figure 38 – Schematic of the 267-mL type Hull cell	183
Figure 39 – Sturdy construction of a 267-mL type Hull cell with single use copper foil	183
Figure 40 – Cut strips of the iron-plated copper foil used as cathode	184
Figure 41 – Primary, secondary, and tertiary current distributions.....	187
Figure 42 – Schematic of the batch stirred electrolyzer (BSE).....	193
Figure 43 – Concentration of electroactive species vs. time inside the BSE.....	193
Figure 44 – Schematic of the plug flow electrolyzer (PFE)	201
Figure 45 – Concentration of electroactive species vs. distance from the entrance.....	201
Figure 46 – Differential volume for concentric electrodes	202
Figure 47 – Differential volume for parallel electrodes.....	202
Figure 48 – Schematic of the plug flow electrolyzer with recirculation (PFE-R).....	207
Figure 49 – Cascade of <i>N</i> cells of plug flow electrolyzer in series.....	209
Figure 50 – Schematic of the continuous stirred electrolyzer (CSE).....	210
Figure 51 – Concentration vs. distance from the entrance	210

Figure 52 – Schematic of the continuously stirred electrolyzer with recirculation (CSE-R)	213
Figure 53 – Cascade of N continuously stirred electrolyzers in series	215
Figure 54 – Energy and mass flow rates inside a divided electrolyzer	219
Figure 55 – Counter flow configuration	221
Figure 56 – Parallel flow configuration	221
Figure 57 – Phase diagram of the binary $\text{FeSO}_4\text{-H}_2\text{O}$ system	228
Figure 58 – Phase diagram of the ternary system: $\text{FeSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$	229
Figure 59 – Solubility of FeSO_4 in water vs. $(\text{NH}_4)_2\text{SO}_4$	238
Figure 60 – Solubility of FeSO_4 in water vs. Li_2SO_4	240
Figure 61 – Schematic P&ID diagram for the electrochemical reduction	248
Figure 62 – Electrochemical reduction plots with various cathode materials	249
Figure 63 – Electrochemical reduction of a pregnant leach solution	250
Figure 64 – Electrical conductivity vs. mass percentage of sulfuric acid	256
Figure 65 – Cathode polarization vs. current density for 1 N H_2SO_4	268
Figure 66 – Cathode overpotential vs. current density in 31 wt.% H_2SO_4	271
Figure 67 – Cathode potential vs. cathode current density in FeSO_4 (pH = 1.0)	275
Figure 68 – Cathode potential vs. cathode current density in FeSO_4 (pH = 2.0)	275
Figure 69 – Cathode current efficiency vs. cathode current density, pH and duration	283
Figure 70 – Cathode current efficiency vs. pH and concentration of FeSO_4	284
Figure 71 – Cathode current efficiency vs. pH and cathode current density	287
Figure 72 – Cathode current efficiency vs. supporting electrolyte, pH and CCD	288
Figure 73 – Microphotographs and EPMA of electrolytic alpha-iron deposits	290
Figure 74 – Polarization of MMO anode in 30 percent sulfuric acid	297
Figure 75 – Polarization of MMO anodes with various catalysts coatings	297
Figure 76 – Experimental setup for measuring of the ohmic drop across a membrane	304
Figure 77 – Ohmic drop vs. membrane current density below 3500 A/m^2	305
Figure 78 – Ohmic drop vs. membrane current density up to 8000 A/m^2	305
Figure 79 – Anion exchange membranes after accelerated service life testing	311
Figure 80 – Schematic of the electrolyzer with electrochemical reactions	315
Figure 81 – Standard electrode potential of various redox couples vs. temperature	321
Figure 82 – Breakdown of the overall cell voltage for a current density of 500 A/m^2	340
Figure 83 – Three-compartment laboratory electrolyzer RECTLAB II (2010)	344
Figure 84 – Three-compartment laboratory electrolyzer RECTLAB III (2011)	344
Figure 85 – Setup with RECTLAB III (2011)	344
Figure 86 – RECTLAB III with recirculation of anolyte and catholyte (2011)	344
Figure 87 – Sketch of pump heads with recirculation of electrolyte (2011)	344
Figure 88 – Two-compartment laboratory electrolyzer RECTLAB IV (2012)	345
Figure 89 – Setup laboratory electrolyzer RECTLAB V (2013)	345
Figure 90 – Two-compartment laboratory electrolyzer RECTLAB V (2013)	345
Figure 91 – Hull cell (2014)	345
Figure 92 – Plate heat exchanger for RECTLAB cells	345
Figure 93 – PROTOTYPE I electrolyzer (2011)	346
Figure 94 – PROTOTYPE II electrolyzer (2012)	346
Figure 95 – PROTOTYPE II electrolyzer with catholyte recirculation (2013)	346
Figure 96 – Close view of PROTOTYPE II electrolyzer (2013)	346
Figure 97 – FLOWPRO I electrolyzers for electrochemical reduction (2015)	346
Figure 98 – FLOWPRO II electrolyzer for electrochemical reduction (2016)	346
Figure 99 – Prototype mild steel starter sheet	347
Figure 100 – Prototype titanium cathode blank	347
Figure 101 – Copper busbars	347
Figure 102 – Mixed metal oxides (MMO) anode	347
Figure 103 – Prototype MMO anode (Corrugated)	347
Figure 104 – Copper cathode	347

Figure 105 – Semi-pilot electrolyzer (2016).....	348
Figure 106 – 10-square foot tank electrolyzer (2016)	348
Figure 107 – Two-square foot slot electrolyzer (2016).....	348
Figure 108 – Cylindrical electrolyzers with coaxial design (2016).....	348
Figure 109 – FLOWPRO IV for producing iron powder (2016) and Fe-filter cake	349
Figure 110 – FLOWPRO III electrolyzer for producing iron powder (2016).....	350
Figure 111 – Tubular electrolyzer for the production of electrolytic iron powder	350
Figure 112 – MMO mesh anode.....	351
Figure 113 – Sketch anode compartment.....	351
Figure 114 – Schematic P&ID for the pilot electrowinning plant.....	351
Figure 115 – Schematic of iron electrowinning with electrochemical reactions.....	357
Figure 116 – Flow diagram of the FerWIN® process for electrowinning iron.....	359
Figure 117 – Flow diagram of the FerWIN® process for electrowinning with APU unit..	360
Figure 118 – Mass balance flow diagram for the catholyte stream (CCE 100%)	364
Figure 119 – Mass balance flow diagram for the anolyte stream (ACE 100%)	366
Figure 120 – Daily mass balance per single electrolyzer for electrowinning iron.....	368
Figure 121 – Titanium cathode blank shape and dimensions with edge strips.....	375
Figure 122 – MMO plate anode shape and dimensions with inclined bottom	381
Figure 123 – MMO mesh anode shape and dimensions with inclined top and bottom	382
Figure 124 – Cut-off view of anode compartment with membranes and frames	385
Figure 125 – Anode compartment with MMO mesh anode	385
Figure 126 – Schematic of the iron electrowinning electrolyzer	387
Figure 127 – Sketch of polymer concrete cell.....	388
Figure 128 – Electrolyzer with anode and cathodes connected in parallel.....	390
Figure 129 – Cell house with electrolyzers connected in parallel and series	394
Figure 130 – Contact resistance in busbars	397
Figure 131 – Iron electrowinning cell with anolyte and catholyte flows.....	399
Figure 132 – Oxygen-gas scrubber	400
Figure 133 – Harvesting cathodes	401
Figure 134 – Schematic of the two-stage rinsing of the harvested cathode	403
Figure 135 – Schematic block diagram for the electrowinning	405
Figure 136 – Breakdown of the operating expenses	428
Figure 137 – Prices of selected iron product vs. purity and quality.....	438
Figure 138 – Sensitivity analysis of the net present worth	440
Figure 139 – Prices of iridium metal from 1992 to 2023	441
Figure 140 – Periodic chart of the elements.....	461

22 Index

“what-if” analysis	437	Cathode	54
Absolute electric mobility	110	Cathode current efficiency	340
Acid pickling	16	cathode first Tafel’s coefficient	162
Activation overpotential	138, 173, 314	Cathode surface velocity	378
activation resistance of polarization	164	Cathode Tafel’s slope	162
Activation resistance of polarization	298	Cathode transfer coefficient	155
Active sign convention	54	Cathode-anode overlap	380
Activity coefficient	65	Catholyte	55
Adatom	164	<i>CE plant Cost Index</i>	412
Adatoms	139	<i>Celanese Corporation</i>	46
Additional capital investments	430	Cell constant	132
Adion	164	Cell house	391
Ammonium sulfate hexahydrate	28	Cell potential drift	173, 314
Ampacity	395	Charge transfer overpotential	138
Annual cash flow equivalent	432	<i>Chemical Engineering</i>	412
Annual depreciation	431	Chemical overpotential	138
Annual income	429	Chemical potentials	64
Annual shut down	361	<i>Comité International de Corrosion et</i>	
Anode	54	<i>Technologie Electrochimique</i>	139
Anode surface velocity	383	Concentration overpotential	138, 173,
Anode Tafel’s intercept	298	314	
Anode Tafel’s slope	160, 298	<i>Conservatoire National des Arts et Métiers</i>	34
Anode transfer coefficient	155	Construction expenses	419
Anolyte	55	Contingency charges	419
Antoine’s equation	323	Continuity equation	119
Apparent proton transference	306	Continuous stirred electrolyzer	189
Apparent standard electrode potential	97,	Contractor’s fee	419
147		Copper reference electrode	90
Area specific impedance	303	Copperas	11
<i>Armco Steel Corporation</i>	274	Correction factor	221
<i>Asahi Glass Co Ltd</i>	247	<i>Corrosion Technology International Group</i>	387
Asymmetric electrolytes	57	Cost indices	412
Auto-protolysis constant of water,	92, 94	Counter electrode	135
Base electrolyte	237	Crude steel	16
Basic oxygen furnace	4	Crystallization overpotential	139
Batch recirculation	372	<i>CTI Ancor</i>	387
Batch stirred electrolyzer	189, 192	Current efficiency	171
Bauxite residues	19	Current safety factor	394
Blank cathodes	373	Current-potential curves	135
Blast furnace process	4	<i>Davis Walker Corp</i>	44
Bottom edge strip	377	De Donder-Pourbaix inequality	141
Bruggeman equation	336	Debye-Hückel equation	68
Bubble overvoltage	137	Debye-Hückel-Onsager equation	130
Building costs	415	Decomposition cell voltage	326

Decomposition voltage	136	Electrolytic cell	58
Degree of ionization	232	Electrolyzer	54, 58
Depolarizer	53	Electro-migration	107, 108
Depolarizing substance	53	Electromotive force	59
Diaphragms	55	Electron work function	60
Diffusion	107, 111	Electro-oxidizable	54
Diffusion coefficient	111	Electroplating	25
Diffusion overpotential	138	Electroplating tape	377
Digester	12	Electro-reducible	53
Dimensionally stable anodes	47	Empirical correlations	152
Dimensionless current density	197, 206	Energy efficiency	175, 341
Direct costs	413	Engineering and supervision costs	418
Discounted cash flow analysis	434	Equilibrium constants	64
Dissociation constant	232	Equivalent conductivity at infinite dilution	127
Dogbone busbars	397	Equivalent ionic conductance	125
Double contacts busbars	398	Equivalent ionic conductivity	125
DSA®	47	Exchange current density	156
Dühring plot	323	<i>Faculté des Sciences de Paris</i>	34
Dummying	245	Faradaic cathode efficiency	340
Dynamic viscosity	252	Faradaic current efficiency	176, 313, 314
Earnings, before income tax, depreciation, and amortization	432	Faradaic efficiency	171
Edge strips	376	Faradaic process	169
<i>E-j</i> curves	135	Fermi energy	62
Electric current	173, 313	Ferrate anions	96
Electric current density	122	Ferrous sulfate heptahydrate	11
Electrical conductivity	124, 254	FerWIN® process	1
Electrical installation costs	415	Fick's first law	111
Electrical mobility	109	Fick's second law	120
Electroactive species	53	Fixed-capital investment	430
Electroactivity domain	143	Flux of the electroactive species	107
<i>Electrochem Technologies & Materials Inc.</i>	20, 21	Forced convection	107
Electrochemical batch stirred tank reactor	189, 192	Fractional conversion rate	192, 370
Electrochemical cell	57	Galvani potential	60
Electrochemical continuous stirred tank reactor	189	Galvanic cell	57, 59
Electrochemical plug flow reactor	189	Galvanostatic mode	180
Electrochemical potential	62	Gassing overvoltage	137
Electrochemical reaction	53	General continuity equation	120
Electrochemical reactor time constant	197	General Debye-Hückel equation	67
Electrochemical Society	139	Generalized Butler-Volmer equation	158
Electrochemical span	143	<i>Genverkschaft Keramchemie</i>	48
Electrochemically inert	143	Gibbs enthalpy	63
Electrode	53, 54	Gibbs free energy	63
Electrode kinetics	135	Gibbs molar enthalpy	71
Electrode potential	59	Gibbs-Ostwald sign convention	75
Electrode specific surface area	191	Good manufacturing and processing practices	361
Electrodeposition	25	Grashof number	152
Electrolyte	53	Gravimetric electrochemical equivalent	170
Electrolytes	56	Green vitriol	11
		<i>Gross Profit</i>	430
		Gross profit margin	430

Grotthus mechanism	309	Latent molar entropies	71
Gulden-Waage law of mass action	235	Latimer's rule	96
Haber-Luggin capillary	135	Law of electroneutrality for electrolytes	121
Haring-Blum cell	179	Limiting current density	146
Harvesting cycle time	392	Limiting equivalent conductivity	127
Heat capacity coefficients	71	Liquid junction	113
Hematite	16	Liquid junction potential	113, 314
Henderson equation	117	Logarithmic mean temperature difference	221
Henderson's equation	338	Ludwig-Soret effect	112
Heterogeneous ion exchange membranes	302	Macrokinetic models	189
Homogeneous membranes	302	Magnetite	16
Horiuti diagram	160, 161	Manufacturing costs	422
Hourly yield	174	<i>Marshall & Swift Equipment Cost Index</i>	412
Hull cell	182	Mass diffusivity	111
<i>Hunstman Pigments</i>	47	Mass equivalence factors	361
hypoferrite anions	95	Mass transfer coefficient	146, 151
Ideally polarized	143	Mass transfer polarization resistance	151
Income tax rate	431	Maximum carrying current	395
Indifferent electrolyte	237	Maximum current density	146
Indirect costs	418	Mean activity coefficient	66
Individual ionic conductivity	127	Melanterite	11
Infinite dilution	65	Membrane-electrode gaps	174, 314
Inner electric potential	60	Membranes	56
Installation costs	413	Mercury-mercurous sulfate electrode	89
Instrumentation costs	414	Microscopic electrical mobility	306
Insulation costs	414	Midlyte	40
Inter electrode gap	174, 314	Migration number	133
Interest rate	431	Millennium <i>Inorganic Chemicals SA</i>	247
Internal rate of return	433	Minimum acceptable rate of return	434
<i>International Electrotechnical Commission</i>	139	Mixed activation-diffusion regime	158
Internationally adopted sign convention	139	Mohr's salt	28
Ion selective	56	Mohr's salt	238
Ionic conductors	56	Molar conductance	125
Ionic mobility	109	Molar heat capacity	71
Ionic strength	67	Molar ionic conductivity	125
<i>Ionics Incorporated</i>	38	<i>Montecatini</i>	47
Ionophores	56	<i>Montedison</i>	47
Ions	56	<i>National Aeronautics and Space Administration (NASA)</i>	49
Ion-selective electrode	85	<i>National U.S. Radiator Corp.</i>	32
Iron-rich alloy	242	Natrojarosite	19
Irreversible electrochemical system	142	Natural convection	107
Junk value	431	Navier-Stokes equation	112
Kohlrausch bridge	133	Nernst's layer	144
Kohlrausch's law of independent ionic migration	128	Nernstian system	141
Kohlrausch equation	130	Nernst-Lewis-Latimer sign convention	75
<i>Kronos NL</i>	15	Nernst-Planck's equation	113
Laplace equation	177	Net present value	433
Laplace's equation	123	Net present worth	433
<i>Larox</i>	400	Net profit	432
Latent molar enthalpies	71		

Net profit margin	431	Processing losses	361
Non-faradaic process	169	Product recovery yield	361
Normal hydrogen electrode	86	Production costs	422, 429
Ohm's law	124	Proton leakage	309
Ohmic drops	173, 314	Proton rejection	309
Onsager equation	130	Purchased equipment costs	413
Open circuit voltage	59	<i>Pyror Limited</i>	35
Operating costs	429	Quasi-reference electrodes	84
Operating Income	430	Quasi-reversible	143
Operating plant life	429	Rate determining step	137
Optibar intercell busbars	398	Reaction time	193
<i>Orkla Grube AB</i>	35	Red mud	19
<i>Oronzio de Nora Impianti Elettrochimici</i>		Redox reactions	53
<i>S.p.A.</i>	247	Reducing	54
<i>Oronzio De Nora Impianti Elettrochimici</i>		Reduction	54
<i>S.p.a.</i>	47	Reference electrode	135
Ostwald equation	232	Reference electrode of the first kind	83
Outer electric potential	61	Residence time	191, 204
<i>Outokumpu Oy</i>	398	Residual value	431
<i>Outotec Oy</i>	398	Resistance of polarization	267
Overall cell voltage	176, 313	Rest potential	136
Overall heat transfer coefficient	221	Return-on-investment	433
Overall ohmic drop	335	Reversibility criterion	142
Overall resistance of polarization	163	Reversible cell voltage	78, 173, 314
Overpotential	136	Reversible electrochemical system	141
Overpotentials	173, 314	Reynolds number	152
Overvoltage	136	<i>Rhone-Poulenc Chimie</i>	247
Owner's costs	419	<i>Rohm & Haas Company</i>	37
Oxidation	54	Rule of six-tenths	410
Oxidation-reduction potential	105	<i>Russian Mint</i>	26
Oxidizing	53	Sales revenue	429
Passivation overpotential	139	Salvage value	431
Passive sign convention	55	Sand's equation	199
Payback time	433	Saturated calomel electrode	89
Permselective	56	Scheibler polishing filters	400
Piontelli's three-electrode system	135	Schmidt number	152
Piping costs	414	SCM Corporation	34
Piston-flow electrolyzer	200	Scrap value	431
Planck equation	116	Secondary current distribution	179
<i>Plastic Metals Inc.</i>	32	Sensitivity analysis	437
Plug flow electrolyzer	189, 200	Sherwood number	152
Poisson equation	177	Silver-silver chloride electrode	88
Poisson's law	121	Silver-silver sulfate electrode	90
Polarization	136	Slotted plastic edges	377
Polymer-concrete tank	387	Smut	17
Potential efficiency	175, 341	<i>Société d'Électrochimie, d'Électrometallurgie et</i>	
Pourbaix diagrams	91	<i>des Acières Électriques d'Ugine</i>	34
Power source	54	Solid electrolytes	57
Pregnant leach solutions	11, 18	Solubility	230
Present value	432	Solubility product	234
Present worth	432	Sørensen hydrogen potential	87
Pressure differential	310	Soret coefficient	112
Price deflator	412	Soret effect	112

Space-time	191, 204	Throwing power	179, 186
Space-time yield	174, 313, 314, 327	<i>Toxide Europe Srl</i>	47
Specific conductance	124	Toroidal conductivity probes	133
Specific electrochemical equivalent	170	Total capital investment	430
Specific energy consumption	176, 313	Total cathode surface area	391
Specific heat capacity	225	Total number of anodes per electrolyzer	379
Spent pickling liquors	11, 17	Total number of cathodes per electrolyzer	374
Standard exchange current density	156	Total number of electrolyzers	391
Standard exchange rate constant	156	Total number of membranes per electrolyzer	384
Standard hydrogen electrode	74, 86	Transference number	133
Standard molar enthalpy	70	Transient state	217
Standard molar entropy	70	Transport number	133
Standard reversible cell voltage	77, 319	Transport phenomena	107
Standard thermoneutral electrode potential	320	Triangular busbars	398
Starter sheets	373	Underpotential deposition	165
<i>Steuler GmbH</i>	387	Useful plant life	429
Stokes' law	109	<i>VanadiumCorp Resource Inc.</i>	21
Strong electrolytes	56	VanadiumCorp-Electrochem Process Technology (VEPT)	21
Sulfate process	12	Variable costs	422
Supporting electrolyte	134, 237	<i>Venator</i>	47
Symmetric electrolytes	57	Vertical edge strips	377
Tafel first anode coefficient	160	Volmer-Weber growth regime	165
Tafel's intercept	161, 162	Volta potential	61
Tafel's second anode coefficient	161	Voltage safety factor	394
Tafel's second coefficient	162	Voltaic efficiency	175, 341
Taxable income	432	Volumetric electrochemical equivalent	170
Tertiary current distribution	186	Volumetric energy consumption	176
Theory of absolute reaction rates	155	Wagner number	185
Theory of the activated complex	155	Wagner's ground	60, 61
Thermoelectrodiffusion	112	Weak electrolytes	57
Thermoelectrodiffusion coefficient	112	Wheatstone bridge	133
Thermoelectrodiffusion factor	112	working capital	6, 408
Thermodynamic activity	65	Working capital	420, 430
Thermodynamic cell voltage	78, 173, 314	Working electrode	135
Thermodynamic reversible cell voltage	326	Wustite	16
Thermodynamic sign convention	191	Yard improvements costs	415
Thermoneutral cell voltage	79		
Thermoneutral electrode potential	78		
Thermophoresis	112		

About the Author



Dr. François Cardarelli, President and Owner of the Canadian company *Electrochem Technologies & Materials Inc.*, is an industrial chemist with a strong physical-chemistry background and a doctorate in chemical engineering from the University Paul Sabatier (UPS) Toulouse III. He is the inventor and co-inventor of 16 patents, and the sole author of three reference handbooks published worldwide by Springer since 1996 and two monographs.

He has over 34 years of industrial experience in North America and Europe in developing electrochemical, chemical, and metallurgical processes for winning, refining or producing a variety of metals, alloys, and inorganic chemicals either from aqueous solutions or molten salts media.

A particular area of his professional expertise is the chemical, and electrochemical processing of mining residues, metallurgical wastes, and industrial effluents, the manufacture of industrial electrodes, the electrochemical production of vanadium electrolyte, the pyro- and hydrometallurgical production of vanadium, niobium, tantalum, and tungsten compounds and chemicals, and finally the manufacture of novel industrial materials. All these processes are covered by patents enforced in many jurisdictions.

Dr. François Cardarelli is a member in good standing of the following professional organizations and societies: *American Institute of Chemical Engineers* (AIChE) [Lifetime member], *American Chemical Society* (ACS), *Chemical Institute of Canada* (CIC), *Canadian Society for Chemical Engineering* (CSChE), *The Electrochemical Society* (ECS), *Mineralogical Society of America* (MSA), *Ordre des Chimistes du Québec* (OCQ), *The Oughtred Society* (OS), and *The Minerals, Metals and Materials Society* (TMS).

François Cardarelli

Electrowinning Iron and Recycling Sulfuric Acid from Iron Sulfates: A Zero-Carbon Iron-Making Process



This comprehensive monograph is primarily intended to describe the patented FerWIN® technology, a green and zero-carbon iron-making process, which consists to perform the electrowinning of iron metal and the recycling of sulfuric acid from iron sulfates that are by-produced at the million tons scale worldwide while releasing pure oxygen gas.

The information has been presented in such a form that industrial electrochemists, chemical engineers, metallurgists, and other practicing engineers, scientists, professors, and technologists will have access to relevant scientific and technical information supported by key experimental data that were obtained from extensive laboratory, prototype, and pilot testing. It also includes comprehensive electrochemical and engineering calculations, costs and benefits analysis, financial and sensitivity analysis.

This monograph will be of value also to men and women engaged in the traditional iron and steelmaking industries that want to understand this novel electrochemical technology outside their conventional blast furnace, direct reduced iron, and electric arc smelting processes.

Finally, the monograph may be of interest to persons in the steelmaking industries occupying managerial positions such as chief executives, chief operating officers, and V.P. of operations.

The following topics are covered:

- Background, markets, and prior art;
- Electrochemical calculations and figures of merit;
- Selection of industrial electrodes and membranes
- Electrochemical reactor design and performances;
- Industrial electrowinning plant calculations;
- Prototype and pilot testing;
- Costs and benefits analysis;
- Financial and sensitivity analysis;
- Implementation strategy;
- Bibliography;
- Appendices.

