

Contents

Preface	VII
List of Authors	XIX

* * *

Chapter 1

Redox Potential Measurements in Natural Waters: Significance: Concepts and Problems

<i>L. Sigg</i>	I
1.1 Relevance of Redox Potential Measurements	1
1.2 Thermodynamic Definition of Redox Potential	2
1.3 Redox Potential Range in Natural Waters	5
1.4 Electrochemical Measurement of Redox Potential	6
1.5 Examples of Redox Potential Measurements	8
1.6 Redox Conditions in Natural Waters: Examples of Lack of Equilibrium	10
1.7 Conclusions	10
1.8 References	11

* * *

Chapter 2

Technique of Measurement, Electrode Processes and Electrode Treatment

<i>H. Galster</i>	13
2.1 Electron Transfers	13
2.1.1 Exchange Currents	13

2.1.2 MARCUS-Theory	15
2.1.3 Practical Rules	16
2.2 Electrodes.....	17
2.2.1 Platinum Electrodes	17
2.2.2 Oxygen.....	18
2.2.3 Mixed Potentials	19
2.2.4 Pre-Treatment	20
2.2.5 Design.....	21
2.2.6 Reference Electrodes	22
2.3 References	23

* * *

Chapter 3

Characterisation of the Redox State of Aqueous Systems: Towards a Problem-Oriented Approach

<i>S. Peiffer</i>	24
3.1 Introduction.....	24
3.2 pH and pε	25
3.3 Measurement of Redox Voltages at Redox Electrodes	27
3.4 New Perspectives	30
3.4.1 Hydrogen Concentration as a Master Variable to Characterise Metabolic Organic Matter Degradation	31
3.4.2 The Partial Equilibrium Approach	33
3.4.3 The Use of the pH ₂ S-Value to Quantify the Redox State of Sulfidic Systems	34
3.4.4 The Use of Probe Compounds to Characterise the Reactivity of a Solution.....	37
3.5 Summary and Conclusion	38
3.6 References	39

* * *

Chapter 4

Comparison of Different Methods for Redox Potential Determination in Natural Waters

<i>M. Kölling</i>	42
4.1 Introduction.....	42
4.2 Redox Potential Calculations	43
4.2.1 The H ₂ O/O ₂ -Couple	44
4.2.2 Fe-Species	45
4.2.3 As-Species	45
4.2.4 S-Species.....	46
4.2.5 N-Species.....	46
4.2.6 The CO ₂ /CH ₄ -Couple.....	47

4.3	Redox Potential Measurements	47
4.3.1	Metal Electrodes	48
4.3.2	Reference Electrodes	48
4.3.3	Calibration Solutions	48
4.4	Material and Methods	49
4.4.1	The Artesian Well "Schierensee"	49
4.4.2	Electrodes	49
4.4.3	Instruments	50
4.5	Results	50
4.5.1	Redox Potential Measurements	50
4.5.2	Calculation of Redox Potentials	51
4.6	Discussion	52
4.6.1	Redox Potential Measurements	52
4.6.2	Redox Potential Calculations	53
4.7	Conclusions	53
4.8	References	53

* * *

Chapter 5

A Novel Approach to the Presentation of $p\epsilon/pH$ -Diagrams

<i>M. Kölling, M. Ebert & H.D. Schulz</i>	55	
5.1	Introduction	55
5.2	Construction of $p\epsilon/pH$ -Diagrams	56
5.3	Disadvantages of Classical $p\epsilon/pH$ -Diagrams	60
5.4	New Presentation of $p\epsilon/pH$ -Diagrams	60
5.5	Conclusions	63
5.6	References	63

* * *

Chapter 6

The Couple As(V) – As(III) as a Redox Indicator

<i>T.R. Rüde & S. Wohnlich</i>	64	
6.1	Introduction	64
6.2	The Procedure	65
6.2.1	Sampling	66
6.2.2	Analysis	67
6.2.3	Analysing the Major Ions	69
6.2.4	Calculating the Ion Strength	70
6.2.5	Calculating the Activity Coefficients	71
6.2.6	Calculating the Activities of the As-Species	72
6.2.7	Drawing up a System of Thermodynamic Redox Equations	74
6.2.8	Solving the Thermodynamic Equations to get $p\epsilon$	77
6.3	Conclusions	77

6.4 Acknowledgements	78
6.5 References	78

* * *

Chapter 7

In Situ Long-Term-Measurement of Redox Potential in Redoximorphic Soils

S. Fiedler	81
7.1 Introduction	81
7.2 Study Sites and Soils	82
7.3 Methods	83
7.3.1 Redox Measurements	83
7.3.2 Methane Measurements	84
7.3.3 Spatial and Temporal Variability of E_H	85
7.4 Reasons for E_H -Variations in Soils	88
7.4.1 Temperature	88
7.4.2 Water Regime	89
7.4.2.1 Precipitation	89
7.4.2.2 Groundwater	91
7.5 Relationship Between Redox Conditions and Methane Flux	92
7.6 Conclusion	93
7.7 References	93

* * *

Chapter 8

Redox Measurements as a Qualitative Indicator of Spatial and Temporal Variability of Redox State in a Sandy Forest Soil

A. Teichert, J. Böttcher & W.H.M. Duijnisveld	95
8.1 Introduction	95
8.2 Material and Methods	97
8.2.1 Investigation Site	97
8.2.2 Transect Measurements	98
8.2.3 Electrodes	99
8.2.4 E_H - and $p\epsilon$ -Values	99
8.2.5 Statistical Data Analysis	100
8.3 Results and Discussion	101
8.3.1 E_H and pH at a Depth of 0.8 m and of 1.1 m	101
8.3.2 E_H at a Depth of 1.4 m	102
8.4 Conclusions	108
8.5 References	109

* * *

Chapter 9

Implementation of Redox Reactions in Groundwater Models

<i>W. Schäfer</i>	111
9.1 Introduction	111
9.2 The Redox Potential as Controlling Variable.....	112
9.2.1 Equilibrium Models	112
9.2.2 Combined Approach	114
9.3 Models that do not Explicitly Consider the Redox Potential	115
9.3.1 Superposition Models	115
9.3.2 Kinetic Models with Specified Reaction Rate Constants.....	116
9.3.3 Models with Variable Kinetics	117
9.4 Summary	118
9.5 References.....	119

* * *

Chapter 10

Variance of the Redox Potential Value in Two Anoxic Groundwater Systems

<i>M. Kofod</i>	120
10.1 Introduction	120
10.2 Groundwater in the River Marsh of the Elbe (Hamburg).....	121
10.2.1 Variation of the Measured E_H -Values	122
10.2.2 Spatial Distribution	124
10.2.3 Correlation Between the E_H -Value and the Chemical Composition of the Groundwater.....	124
10.3 Groundwater in the Oderbruch (Brandenburg).....	127
10.3.1 Variation of the Measured E_H -Values	128
10.3.2 Spatial Distribution	129
10.3.3 Correlation Between the E_H -Value and the Chemical Composition of the Groundwater	130
10.4 Interpretation and Conclusion	132
10.5 Acknowledgements	134
10.6 References	134

* * *

Chapter 11

Redox Fronts in Aquifer Systems and Parameters Controlling their Dimensions

<i>J. Schüring, M. Schlieker & J. Hencke</i>	135
11.1 Introduction	135
11.2 Regional Scales of Redox Fronts in Aquifer Systems.....	137
11.3 Investigating the Scales of Redox Fronts	139
11.3.1 Column Tests.....	139

11.3.1.1	Flow Rate versus Decomposition Rate	141
11.3.2	Lake Sediments	143
11.3.3	Bank Infiltration	147
11.4	Summary	149
11.5	References	150

* * *

Chapter 12

Redox Processes Active in Denitrification

<i>C.G.E.M. van Beek</i>	152
12.1	Introduction	152
12.2	Site and Methods	153
12.3	Geochemistry	153
12.3.1	Denitrification	155
12.3.2	Reduction Capacity	157
12.4	Conclusions	159
12.5	Acknowledgement	159
12.6	References	160

* * *

Chapter 13

Measurement of Redox Potentials at the Test Site "Insel Hengsen"

<i>U. Schulte-Ebbert & T. Hofmann</i>	161
13.1	Introduction	161
13.2	The Test Site	162
13.3	Observed Redox Conditions	163
13.4	Interpretation Problems	165
13.5	Groundwater Sampling and Redox Measurement	167
13.6	Kinetics of Redox Measurements	169
13.7	Conclusions and Recommendations	172
13.8	Acknowledgements	173
13.9	References	173

* * *

Chapter 14

Redox Reactions, Multi-Component Stability Diagrams and Isotopic Investigations in Sulfur- and Iron-Dominated Groundwater Systems

<i>F. Wisotzky</i>	175
14.1	Introduction	175

14.2	Methods	176
14.2.1	Locations of the Study Area	176
14.2.2	Sediment and Water Analyses	176
14.2.3	Analysis of Isotopes	177
14.2.4	Multi-Component Stability Diagrams (pH-p ϵ -Diagrams)	177
14.3	Results	178
14.3.1	Mobilising Reactions of Sulfur and Iron	178
14.3.2	Immobilising Reactions of Sulfur and Iron	181
14.4	Summary	186
14.5	References	187

* * *

Chapter 15

Redox Buffer Capacity Concept as a Tool for the Assessment of Long-Term Effects in Natural Attenuation / Intrinsic Remediation

F. von der Kammer, J. Thöming & U. Förstner	189	
15.1	Introduction	189
15.1.1	Natural Attenuation	189
15.1.1.1	Redox Processes in the Natural Attenuation Concept	190
15.1.1.2	Practical Experience and Priority Parameters	191
15.1.2	Contaminant Plumes in Groundwater	192
15.1.3	Redox Buffer Capacity	193
15.2	Redox Buffer Capacities: Conceptual Approach	194
15.3	Analytical Approach and Application	195
15.3.1	Overview	195
15.3.1.1	OXC	195
15.3.1.2	TRC	196
15.3.2	Case Study: Simplified Illustration of a Groundwater Plume's Redox Activities by Common Sequential Extraction	196
15.3.2.1	Determination of the Total Reduction Capacity (TRC)	196
15.3.2.2	Soil Sample and Extraction Scheme	197
15.3.2.3	Results and Discussion of the Case Study	198
15.4	Conclusions	200
15.5	References	201

* * *

Chapter 16**Redox Zones in the Plume of a Previously Operating Gas Plant**

*K. Weber, N. Brandsch, B. Reichert, M. Eiswirth, H. Hötzl,
O. Hümmel & A. Dahmke.....* 203

16.1	Introduction	203
16.2	Geology and Hydrology	205
16.3	Methods and Materials	207
16.4	Results and Discussion	208
16.5	Summary and Conclusions	215
16.6	References	215

* * *

Chapter 17**Degradation of Organic Groundwater Contaminants:
Redox Processes and E_H-Values**

M. Ebert, O. Hümmel, M. Mayer, O. Schlicker & A. Dahmke..... 217

17.1	Introduction	217
17.2	Degradation of BTX in the Underground of a Former Gas Plant	219
17.3	Reductive Dehalogenation of Chlorinated Hydrocarbons	222
17.4	Conclusions	225
17.5	References	226

* * *

Chapter 18**Microbial Metabolism of Iron Species in Freshwater Lake Sediments**

B. Schink & M. Benz..... 228

18.1	Introduction	228
18.2	Iron Compounds in Lake Constance Sediments	230
18.3	Microbial Oxidation of Iron Compounds	231
18.4	Reduction of Ferric Iron Hydroxides	232
18.5	Conclusions	233
18.6	Acknowledgements	234
18.7	References	234

* * *

Chapter 19**Redox Measurements in Marine Sediments**

<i>H.D. Schulz</i>	235
19.1 The Scope of Redox Measurements	235
19.2 How Measurements are Performed	238
19.3 Typical E _H -Profiles and their Interpretation	239
19.4 Precision and Reproducibility	243
19.5 Relevance of the Results	245
19.6 References	246
* * *	
Subject Index	248