

Contents

Preface to the Second Edition XIII

Preface to the First Edition XV

Introduction 1

Part I Ozone in Overview

1 Toxicology 5

1.1 Background 5

1.2 Ozone in Gas 7

1.2.1 Inhalation 7

1.2.2 Skin Contact 7

1.2.3 Eye Contact 7

1.3 Ozone in Liquid 8

1.4 By-products 9

References 11

2 Reaction Mechanism 13

2.1 Ozonation 13

2.1.1 Indirect Reaction 13

2.1.1.1 Initiation Step 14

2.1.1.2 Radical Chain Reaction 15

2.1.1.3 Termination Step 15

2.1.1.4 Overall Reaction 16

2.1.2 Direct Reaction 17

2.2 Advanced Oxidation Processes (AOP) 20

2.2.1 Ozone/Hydrogen Peroxide O_3/H_2O_2 20

2.2.2 Ozone/UV-Radiation O_3/UV 21

2.2.3 Hydrogen Peroxide/UV-Radiation UV/H_2O_2 22

References 24

3	Ozone Applications	27
3.1	Historical Development	27
3.2	Overview of Ozone Applications	31
3.2.1	Ozone in the Gas Phase	32
3.2.2	Ozone in the Liquid Phase	34
3.3	Ozone in Drinking-Water Treatment	36
3.3.1	Disinfection	38
3.3.2	Oxidation of Inorganic Compounds	40
3.3.3	Oxidation of Organic Compounds	42
3.3.3.1	Natural Organic Matter (NOM)	42
3.3.3.2	Organic Micropollutants	43
3.3.4	Particle-Removal Processes	44
3.4	Ozonation in Waste-Water Treatment	46
3.4.1	Disinfection	47
3.4.2	Oxidation of Inorganic Compounds	48
3.4.3	Oxidation of Organic Compounds	49
3.4.3.1	Landfill Leachates–Partial Mineralization	52
3.4.3.2	Textile Waste Waters–Color Removal and Partial Mineralization	53
3.4.3.3	Other Applications	54
3.4.4	Particle-Removal Processes	55
3.5	Economical Aspects of Ozonation	56
	References	59

Part II Ozone Applied

4	Experimental Design	69
4.1	Experimental Design Process	70
4.2	Experimental Design Steps	73
4.2.1	Define Goals	73
4.2.2	Define System	74
4.2.3	Select Analytical Methods and Methods of Data Evaluation	81
4.2.3.1	Ozone	83
4.2.3.2	Target Compound M	83
4.2.4	Determine Experimental Procedure	85
4.2.5	Evaluate Data	88
4.2.6	Assess Results	89
4.3	Reactor Design	94
4.3.1	Reactor Types	94
4.3.1.1	Operating Mode	94
4.3.1.2	Mixing	95
4.3.2	Comparison of Reactor Types	97
4.3.3	Design of Chemical Oxidation Reactors	100
4.3.3.1	Reaction System	102
4.3.3.2	Ancillary Systems	103
4.3.3.3	Process Integration	103

4.3.3.4	Controllability	104
4.3.3.5	Site Integration	104
4.4	Checklists for Experimental Design	104
4.4.1	Checklists for Each Experimental Design Step	105
4.5	Ozone Data Sheet	108
	References	111
5	Experimental Equipment and Analytical Methods	113
5.1	Materials in Contact with Ozone	113
5.1.1	Materials in Pilot- or Full-Scale Applications	116
5.1.1.1	Reactors	116
5.1.1.2	Piping	116
5.1.2	Materials in Lab-Scale Experiments	117
5.1.2.1	Reactors	117
5.1.2.2	Piping	118
5.2	Ozone Generation	118
5.2.1	Electrical Discharge Ozone Generators (EDOGs)	120
5.2.1.1	Chemistry	121
5.2.1.2	Engineering and Operation	123
5.2.1.3	Type of Feed Gas and its Preparation	125
5.2.1.4	Ozone Concentration, Production Capacity and Specific Energy Consumption	126
5.2.1.5	Use of EDOGs in Laboratory Experiments	126
5.2.2	Electrolytic Ozone Generators (ELOGs)	127
5.2.2.1	Use of ELOGs in Laboratory Experiments	130
5.3	Reactors Used for Ozonation	130
5.3.1	Overview of Hydrodynamic Behavior and Mass Transfer	131
5.3.2	Directly Gassed Reactors	135
5.3.2.1	Bubble Columns and Similar Reactors	135
5.3.2.2	Stirred-Tank Reactors	136
5.3.3	Indirectly and Nongassed Reactors	138
5.3.3.1	Tube Reactors	138
5.3.3.2	Membrane Reactors	139
5.3.4	Types of Gas Contactors	141
5.3.5	Mode of Operation	144
5.3.6	Experimental Procedure	145
5.3.6.1	Batch Experiments	145
5.3.6.2	Continuous-Flow Experiments	146
5.3.6.3	Process Combinations	146
5.4	Ozone Measurement	147
5.4.1	Methods	147
5.4.1.1	Iodometric Method (Gas and Liquid)	147
5.4.1.2	UV Absorption (Gas and Liquid)	147
5.4.1.3	Visible-Light Absorption (Gas and Liquid)	149
5.4.1.4	Indigo Method (Liquid)	149

5.4.1.5	N,N-diethyl-1,4 Phenylenediammonium–DPD (Liquid)	150
5.4.1.6	Chemiluminescence–CL (Liquid)	150
5.4.1.7	Membrane Ozone Electrode (Liquid)	151
5.4.2	Practical Aspects of Ozone Measurement	152
5.5	Safety Aspects	152
5.5.1	Vent Ozone Gas Destruction	152
5.5.2	Ambient Air Ozone Monitoring	154
5.6	Common Questions, Problems and Pitfalls	154
	References	159
6	Mass Transfer	163
6.1	Theory of Mass Transfer	163
6.1.1	Mass Transfer in One Phase	164
6.1.2	Mass Transfer between Two Phases	166
6.1.3	Equilibrium Concentration for Ozone	167
6.1.4	Two-Film Theory	172
6.2	Parameters That Influence Mass Transfer	173
6.2.1	Mass Transfer with Simultaneous Chemical Reactions	175
6.2.1.1	Interdependence of Mass Transfer and Chemical Reaction	176
6.2.1.2	Effect of Kinetic Regime on Determination of Mass-Transfer Coefficients	180
6.2.2	Predicting the Mass-Transfer Coefficient	182
6.2.2.1	Theta Factor–Correction Factor for Temperature	183
6.2.2.2	Alpha Factor–Correction Factor for Water Composition	183
6.2.3	Influence of Water Constituents on Mass Transfer	184
6.2.3.1	Change in Bubble Coalescence	184
6.2.3.2	Changes in Surface Tension	185
6.3	Determination of Mass-Transfer Coefficients	186
6.3.1	Choice of Direct or Indirect Determination of $k_L a(\text{O}_3)$	187
6.3.2	General Experimental Considerations and Evaluation Methods	188
6.3.2.1	Equilibrium Concentration c_L^*	189
6.3.3	Nonsteady-State Methods Without Mass-Transfer Enhancement	191
6.3.3.1	Batch Model	191
6.3.3.2	Experimental Procedure	192
6.3.3.3	Continuous-Flow Model	192
6.3.3.4	Experimental Procedure	193
6.3.4	Steady-State Methods Without Mass-Transfer Enhancement	193
6.3.4.1	Semibatch and Continuous-Flow Models	194
6.3.4.2	Experimental Procedure	194
6.3.4.3	Simultaneous Determination of $k_L a$ and r_L	195
6.3.5	Methods with Mass-Transfer Enhancement	196
6.3.5.1	Experimental Procedure	197
6.3.6	Problems Inherent to the Determination of Mass-Transfer Coefficients	197

6.3.6.1 Nonsteady-State Method 197

6.3.6.2 Steady-State Method 199

References 200

7 Reaction Kinetics 205

7.1 Reaction Order 205

7.1.1 Experimental Procedure to Determine the Reaction Order n 209

7.1.1.1 Half-Life Method 210

7.1.1.2 Initial Reaction Rate Method 210

7.1.1.3 Trial and Error 210

7.2 Reaction Rate Constants 211

7.2.1 Determination of Rate Constants 213

7.3 Parameters That Influence the Reaction Rate 215

7.3.1 Concentration of Oxidants 216

7.3.1.1 Direct Reactions 216

7.3.1.2 Indirect or Hydroxyl Radical Reactions 216

7.3.2 Temperature Dependency 217

7.3.3 Influence of pH 217

7.3.4 Influence of Inorganic Carbon 218

7.3.5 Influence of Inorganic Salts 219

7.3.6 Influence of Organic Carbon on the Radical Chain-Reaction

Mechanism 220

References 221

8 Modeling of Ozonation Processes 225

8.1 Ozone Modeling 228

8.1.1 General Description of the Ozone Modeling Problem 228

8.1.2 Chemical Model of Ozonation 231

8.1.3 Mathematical Model of Ozonation 232

8.1.3.1 Mass Balances 232

8.1.3.2 Rate Equations 234

8.1.3.3 Solving the Model 235

8.1.4 Summary 236

8.2 Modeling of Drinking-Water Oxidation 237

8.2.1 Chemical and Mathematical Models 237

8.2.2 Methods to Determine the Hydroxyl-Radical Concentration 240

8.2.2.1 Indirect Measurement 241

8.2.2.2 Complete Radical-Chain-Reaction Mechanism 244

8.2.2.3 Semiempirical Method Based on Observable Parameters 245

8.2.2.4 Semiempirical Method Based on Observed Hydroxyl Radical Initiating Rate 246

8.2.2.5 Empirical Selectivity for Scavengers 247

8.2.2.6 Summary of Chemical and Mathematical Models for Drinking Water 249

8.2.3	Models Including Physical Processes	249
8.3	Modeling of Waste-Water Oxidation	250
8.3.1	Chemical and Mathematical Models	251
8.3.2	Empirical Models	260
8.3.3	Summary	261
8.4	Final Comments on Modeling	261
	References	263
9	Application of Ozone in Combined Processes	267
9.1	Advanced Oxidation Processes	268
9.1.1	Chemical AOPs	269
9.1.1.1	Principles and Goals	269
9.1.1.2	Existing Processes	269
9.1.1.3	Experimental Design	272
9.1.2	Catalytic Ozonation	273
9.1.2.1	Principles and Goals	273
9.1.2.2	Existing Processes and Current Research	275
9.1.2.3	Experimental Design	280
9.2	Three-Phase Systems	281
9.2.1	Principles and Goals	282
9.2.1.1	Gas / Water / Solvent Systems	283
9.2.1.2	Gas / Water / Solid Systems	284
9.2.2	Mass Transfer in Three-Phase Systems	284
9.2.3	Existing Processes and Current Research	287
9.2.3.1	Gas / Water / Solvent Systems	287
9.2.3.2	Gas / Water / Solid Systems	290
9.2.3.3	Change in the Solids	290
9.2.3.4	Change in Compounds Adsorbed on the Solids	292
9.2.3.5	Soil Ozonation	292
9.2.3.6	Regeneration of Adsorbents	293
9.2.4	Experimental Design	294
9.2.4.1	Define System	294
9.2.4.2	Select Analytical Methods	295
9.2.4.3	Determine Experimental Procedure	296
9.2.4.4	Evaluate Data and Assess Results	296
9.3	Chemical-Biological Processes (CBP)	297
9.3.1	Principles and Goals	297
9.3.2	Existing Processes and Current Research	301
9.3.2.1	Drinking-Water Applications	302
9.3.2.2	Waste-Water Applications	304
9.3.3	Experimental Design	314
9.3.3.1	Define System	315
9.3.3.2	Select Analytical Methods	318
9.3.3.3	Determine Experimental Procedure	320
9.3.3.4	Evaluate Data	323

9.3.3.5	Assess Results	324
9.4	Applications in the Semiconductor Industry	327
9.4.1	Production Sequence	327
9.4.2	Principles and Goals	329
9.4.3	Existing Processes for Cleaning and Oxidation	330
9.4.4	Process and / or Experimental Design	333
9.4.4.1	Define System	333
9.4.4.2	Select Analytical Methods	333
9.4.4.3	Determine Procedure	333
9.4.4.4	Evaluate Data and Assess Results	334
	References	334
	Glossary of Terms	345
	Index	353

