Contents

Chapter 1
Introduction 1

1.1 What Is Hydrogeology? 1
Physical Hydrogeology Before the Early 1940s 2
Chemical Hydrogeology Before the Early 1960s 3
Post-1960 Hydrogeology 4

1.2 The Relationship Between Hydrogeology and Other Fields of Geology 4

1.3 Hydrologic Cycle 5
Components of the Hydrologic Cycle 5
Evapotranspiration and Potential Evapotranspiration 7
Infiltration and Recharge 8
Base Flow 8
Hydrologic Equation 10

Chapter 2
The Origin of Porosity and Permeability 13

2.1 Porosity and Permeability 13
Porosity and Effective Porosity 13
Permeability 15

2.2 Continental Environments 16
Weathering 16
Erosion, Transportation, and Deposition 17
Fluvial Deposits 17
Eolian Deposits 20
Lacustrine Deposits 20
Glacial Deposits 20

2.3 The Boundary Between Continental and Marine Environments 20

2.4 Marine Environments 21
Lateral and Vertical Succession of Strata 21
Ancestral Seas and Their Deposits 22
The Paleozoic Rock Group 23
The Mesozoic Rock Group 24
The Cenozoic Rock Group 24
Diagenesis in Marine Environments 24
Porosity Reduction: Compaction and Pressure Solution 24
Chemical Rock–Water Interactions: Secondary Porosity in Sandstones 26

2.5 Uplift, Diagenesis, and Erosion 27
The Style of Formations Associated with Uplift 27
Secondary Porosity Enhancement in Carbonate Rocks 29

2.6 Tectonism and the Formation of Fractures 29
Style of Fracturing 30
Fluid Pressure and Porosity 31
Connectivity 31

Chapter 3
Ground-Water Movement 33

3.1 Darcy's Experimental Law and Field Extensions 33
The Nature of Darcy's Velocity 34
Hydraulic Head: Hubbert's Force Potential 34
The Gradient and Ground-Water Flow 36
Physical Interpretation of Darcy's Proportionality Constant 36
Units and Dimensions 37

3.2 Hydraulic Conductivity and Permeability of Geologic Materials 37
Observed Range in Hydraulic Conductivity Values 37
Character of Hydraulic Conductivity Distribution 38
Anisotropicity and Heterogeneity Within Units 39
Heterogeneity Among Units and the Classification of Aquifers 41
Creating Hydraulic Conductivity Averages 42
Darcy's Law for Anisotropic Material 43
Measurement of Hydraulic Conductivity 44
Laboratory Testing 44
The Search for Empirical Correlations 44

3.3 Mapping Flow in Geological Systems 45
Hydrogeological Cross Sections 46
Potentiometric Surface and Water-Table Maps 47
Closing Statements 48
3.4 Flow in Fractured Rocks 48
Continuum Approach to Fluid Flow 48
Intergranular Porous Rocks 49
Fractured Rocks 49
3.5 Flow in the Unsaturated Zone 51
Hydraulic and Pressure Heads 51
Water Retention Curves 53
Darcy's Law for Variably Saturated Flow 54
Unsaturated Flow in Fractured Rocks 54

Chapter 4
Main Equations of Flow, Boundary Conditions, and Flow Nets **58**
4.1 Organizing the Study of Ground-Water Flow Equations 58
4.2 Conservation of Fluid Mass 59
Main Equations of Flow 60
4.3 The Storage Properties of Porous Media 62
Compressibility of Water and Its Relation to Specific Storage for Confined Aquifers 63
Compressibility of the Rock Matrix: Effective Stress Concept 64
Matrix Compressibility and Its Relation to Specific Storage of Confined Aquifers 65
Equation for Confined Flow in an Aquifer 67
Specific Yield of Aquifers 68
4.4 Boundary Conditions and Flow Nets 68
Graphic Flow Net Construction 71
4.5 Dimensional Analysis 72

Chapter 5
Ground Water in the Basin Hydrologic Cycle **75**
5.1 Topographic Driving Forces 75
The Early Field Studies 75
Conceptual, Graphical, and Mathematical Models of Unconfined Flow 76
Effects of Basin Geometry on Ground-Water Flow 78
Effects of Basin Geology on Ground-Water Flow 80
Ground Water in Mountainous Terrain 83
Ground Water in Carbonate Terrain 87
Ground Water in Coastal Regions 88
The Fresh Water–Salt Water Interface in Coastal Regions 89
The Ghyben-Herzberg Relation 89
The Shape of the Interface with a Submerged Seepage Surface 90
Upconing of the Interface Caused by Pumping Wells 91
5.2 Surface Features of Ground-Water Flow 91
Recharge–Discharge Relations 91
Ground Water–Lake Interactions 93
Ground Water–Surface Water Interactions 95
5.3 Some Engineering and Geologic Implications of Topographic Drive Systems 97
Large Reservoir Impoundments 97
Excavations: Inflows and Stability 98
The Sea-Level Canal 98
Ground-Water Inflows into Excavations 99
The Stability of Excavations in Ground-Water Discharge Areas 99
Landslides and Slope Stability 101

Chapter 6
Hydraulic Testing: Models, Methods, and Applications **103**
6.1 Prototype Geologic Models in Hydraulic Testing 103
6.2 Conventional Hydraulic Test Procedures and Analysis 105
The Theis Nonequilibrium Pumping Test Method 105
The Curve-Matching Procedure 107
Assumptions and Interpretations 107
Modifications of the Nonequilibrium Equation 108
Time-Drawdown Method 108
Distance-Drawndown Method 109
Steady-State Behavior as a Terminal Case of the Transient Case 109
The Hantush-Jacob Leaky Aquifer Method 110
Water Table Aquifers 112
6.3 Single-Borehole Tests 114
Recovery in a Pumped Well 114
The Drill Stem Test 114
Slug Injection or Withdrawal Tests 115
Response at the Pumped Well: Specific Capacity and Well Efficiency 116
6.4 Partial Penetration, Superposition, and Bounded Aquifers 118
Partial Penetration 118
Principle of Superposition 118
Bounded Aquifers 120
6.5 Hydraulic Testing in Fractured or Low-Permeability Rocks 122
Single-Borehole Tests 123
Multiple-Borehole Tests 123
6.6 Some Applications to Hydraulic Problems 124
Screen Diameter and Pumping Rates 125
Well Yield: The Step-Drawdown Test 125
A Problem in Dewatering 125
A Problem in Water Supply 127

6.7 Computer-Based Calculations 128
Code Demonstration 131
Bounded Aquifers Revisited 131

Chapter 7
Ground Water as a Resource **136**
7.1 Development of Ground-Water Resources 136
The Response of Aquifers to Pumping 136
Yield Analysis 137
Case Study: The Upper Los Angeles River Area 137
Management Strategies 139
Artificial Recharge 139
Conjunctive Use 141
7.2 Introduction to Ground-Water Flow Simulation 142
Generalized Modeling Approach 142
Conceptual Model 142
Ground-Water Flow Simulation 143
Evaluation of Model Results 144
Model Verification 144
A Note of Caution 144
7.3 Formulating a Finite-Difference Equation for Flow 145
Description of the Finite-Difference Grid 145
Derivation of the Finite-Difference Equation 146
7.4 The MODFLOW Family of Codes 147
Solving Systems of Finite-Difference Equations 148
Modular Program Structure 148
Illustrative Example 148
Operational Issues 152
Time-Step Size 152
Drawdowns at "Pumping" Nodes 152
Water-Table Conditions 153
Boundary Conditions 153
7.5 Case Study in the Application of MODFLOW 154
Model Development 154
Data Preparation and Model Calibration 156

Chapter 8
Stress, Strain, and Pore Fluids **159**
8.1 Deformable Porous Media 159
One-Dimensional Consolidation 159
Development of the Flow Equation 159
The Undrained Response of Water Levels to Natural Loading Events 160
The Drained Response of Water Levels to Natural Loading Events 163
Land Subsidence as a One-Dimensional Drained Response 163
Mathematical Treatment of Land Subsidence 165
Three-Dimensional Consolidation 169
Elastic Properties in Deformational Problems 169
Flow Equations for Deformable Media 171
8.2 Abnormal Fluid Pressures in Active Depositional Environments 172
Origin and Distribution 172
Mathematical Formulation of the Problem 174
Isothermal Basin Loading and Tectonic Strain 175
One-Dimensional Basin Loading 176
Extensions of the One-Dimensional Loading Model 177
Thermal Expansion of Fluids 179
Fluid Pressures and Rock Fracture 182
Phase Transformations 183
Subnormal Pressure 184
Irreversible Processes 185
8.3 Pore Fluids in Tectonic Processes 185
Fluid Pressures and Thrust Faulting 185
Seismicity Induced by Fluid Injection 186
Seismicity Induced in the Vicinity of Reservoirs 187
Seismicity and Pore Fluids at Midcrustal Depths 188
The Phreatic Seismograph: Earthquakes and Dilatancy Models 188

Chapter 9
Heat Transport in Ground-Water Flow **191**
9.1 Conduction, Convection, and Equations of Heat Transport 191
Fourier's Law 192
Convective Transport 193
Equations of Energy Transport 194
The Heat Conduction Equation 195
The Conductive-Convective Equation 195
Dimensionless Groups 196
9.2 Forced Convection 197
Temperature Profiles and Ground-Water Velocity 197
Heat Transport in Regional Ground-Water Flow 199
Heat Transport in Active Depositional Environments 203
Heat Transport in Mountainous Terrain 205
9.3 Free Convection 207
The Onset of Free Convection 207
Sloping Layers 208
Geological Implications 208
9.4 Energy Resources 209
Geothermal Energy 209
Energy Storage in Aquifers 209
9.5 Heat Transport and Geologic Repositories for Nuclear Waste Storage 210
The Nuclear Waste Program 210
The Rock Types 210
Thermohydrochemical Effects 212
Thermomechanical Effects 213

Chapter 10
Solute Transport 215
10.1 **Advection 215**
10.2 **Basic Concepts of Dispersion 216**
Diffusion 218
Mechanical Dispersion 219
10.3 **Character of the Dispersion Coefficient 220**
Studies at the Microscopic Scale 220
Dispersivity as a Medium Property 221
Studies at Macroscopic and Larger Scales 221
10.4 **A Fickian Model of Dispersion 223**
10.5 **Mixing in Fractured Media 226**
10.6 **A Geostatistical Model of Dispersion 228**
Mean and Variance 228
Autocovariance and Autocorrelation Functions 229
Generation of Correlated Random Fields 230
Estimation of Dispersivity 230
10.7 **Tracers and Tracer Tests 231**
Field Tracer Experiments 232
Natural Gradient Test 232
Single Well Pulse Test 232
Two-Well Tracer Test 233
Single Well Injection or Withdrawal with Multiple Observation Wells 233
Estimates from Contaminant Plumes and Environmental Tracers 233
Massively Instrumented Field Tracer Tests 233
Borden Tracer Experiment 234
Validation of the Stochastic Model of Dispersion 235

Chapter 11
Principles of Aqueous Geochemistry 238
11.1 **Introduction to Aqueous Systems 238**
Concentration Scales 239
Gas and Solid Phases 240
11.2 **Structure of Water and the Occurrence of Mass in Water 240**
11.3 **Equilibrium Versus Kinetic Descriptions of Reactions 240**
Reaction Rates 241
11.4 **Equilibrium Models of Reaction 241**
Activity Models 242
11.5 **Deviations from Equilibrium 243**
11.6 **Kinetic Reactions 244**
11.7 **Organic Compounds 245**
11.8 **Ground-Water Composition 248**
The Routine Water Analysis 248
Specialized Analyses 249
11.9 **Describing Chemical Data 250**
Abundance or Relative Abundance 252
Abundance and Patterns of Change 253

Chapter 12
Chemical Reactions 255
12.1 **Acid–Base Reactions 255**
Natural Weak Acid-Base Systems 256
CO_2-Water System 256
Alkalinity 257
12.2 **Solution, Exsolution, Volatilization, and Precipitation 258**
Gas Solution and Exsolution 258
Solution of Organic Solutes in Water 258
Volatilization 259
Dissolution and Precipitation of Solids 262
Solid Solubility 262
12.3 **Complexation Reactions 263**
Stability of Complexes and Speciation Modeling 263
Major Ion Complexation and Equilibrium Calculations 264
Enhancing the Mobility of Metals 265
Organic Complexation 265
12.4 **Reactions on Surfaces 266**
Sorption Isotherms 266
Hydrophobic Sorption of Organic Compounds 267
K_d-based Approaches for Modeling the Sorption of Metals 269
Multiparameter Equilibrium Models 269
12.5 **Oxidation–Reduction Reactions 272**
Oxidation Numbers, Half-Reactions, Electron Activity, and Redox Potential 272
Kinetics and Dominant Couples 275
Control on the Mobility of Metals 276
Biotransformation of Organic Compounds 276
12.6 **Hydrolysis 277**
12.7 **Isotopic Processes 277**
Radioactive Decay 277
Isotopic Reactions 278
Deuterium and Oxygen-18 279

Chapter 13
Colloids and Microorganisms 282
13.1 **A Conceptual Model of Colloidal Transport 282**
Occurrence of Colloidal Material 283
Stabilization 283
Transport and Filtration 284
13.2 **Colloidal Transport in Ground Water 284**
Sampling and Measuring 284
Studies at Cape Cod 285
13.3 **Microbiological Systems 285**
Biofilms 287
Sampling and Enumerating Microbial Populations 287
Plate Counts 288
Direct Counting Procedures 288
Biochemical Techniques 288
Rates of Microbial Reactions 288
Microbial Ecology of the Subsurface 290
13.4 **Microbial Processes 291**
Issues in Biodegradation 292
Biofilm Kinetics 292
13.5 **Biotransformation of Common Contaminants 293**
Hydrocarbons and Derivatives 293
Halogenated Aliphatic Compounds 294
Halogenated Aromatic Compounds 294
Polychlorinated Biphenyls (PCBs) 295
Complex Transformation Pathways 295

Chapter 14
The Equations of Mass Transport 296
14.1 **Mass Transport Equations 296**
The Diffusion Equation 296
The Advection-Diffusion Equation 297
The Advection-Dispersion Equation 297
14.2 **Mass Transport with Reaction 298**
First-Order Kinetic Reactions 298
Equilibrium Sorption Reactions 299
Heterogeneous Kinetic Reactions 299
14.3 **Boundary and Initial Conditions 300**

Chapter 15
Mass Transport in Natural Ground-Water Systems 303
15.1 **Mixing as an Agent for Chemical Change 303**
The Mixing of Meteoric and Original Formation Waters 303
Diffusion in Deep Sedimentary Environments 305
15.2 **Chemical Reactions in the Unsaturated Zone 306**
Gas Dissolution and Redistribution 306
Weak Acid-Strong Base Reactions 307
Sulfide Oxidation 309
Gypsum Precipitation and Dissolution 309
Cation Exchange 309
Organic Reactions 309
15.3 **Chemical Reactions in the Saturated Zone 310**
Weak Acid-Strong Base Reactions 310
Dissolution of Soluble Salts 312
Redox Reactions 312
Cation Exchange 315
15.4 **Case Study of the Milk River Aquifer 316**
15.5 **Age Dating of Ground Water 319**
Direct Methods 319
Tritium 319
Carbon-14 320
Chlorine-36 322
Indirect Methods 322
$\delta^{18}O$ and δD 322
Chlorofluorocarbons 322

Chapter 16
Mass Transport in Ground-Water Flow: Geologic Systems 326
16.1 **Mass Transport in Carbonate Rocks 326**
The Approach Toward Chemical Equilibrium in Carbonate Sediments 327
The Problem of Undersaturation 329
Dolomitization 330
16.2 **Economic Mineralization 330**
Origin of Ore Deposits 331
Roll-Front Uranium Deposits 331
Mississippi Valley-Type Lead-Zinc Deposits 332
Noncommercial Mineralization: Saline Soils and Evaporites 337
16.3 **Migration and Entrapment of Hydrocarbons 337**
Displacement and Entrapment 337
Basin Migration Models 339
16.4 **Self-Organization in Hydrogeologic Systems 341**
Patterning Associated with Dissolution 341
Patterning Associated with Precipitation and Mixed Phenomena 341

Chapter 17
Introduction to Contaminant Hydrogeology 344
17.1 **Sources of Ground-Water Contamination 344**
Radioactive Contaminants 346
Trace Metals 347
Nutrients 349
Other Inorganic Species 349
Organic Contaminants 349
Petroleum Hydrocarbons and Derivatives 349
Halogenated Aliphatic Compounds 350
Halogenated Aromatic Compounds 350
Polychlorinated Biphenyls 350
Health Effects 350
Biological Contaminants 350
17.2 **Solute Plumes as a Manifestation of Processes 352**
Fractured and Karst Systems 357
Babylon, New York, Case Study 357
Alkali Lake, Oregon, Case Study 359
17.3 **Design and Quality Assurance Issues in Solute Sampling 360**
Design of Sampling Networks 360
Assuring the Quality of Chemical Data 362

17.4 Sampling Methods 362
Conventional Wells or Piezometers 362
Multilevel Samplers 363
Solid and Fluid Sampling 364
Cone Penetrometry 365
Other Sampling Methods 367
Dissolved Contaminants in the Unsaturated Zone 367

17.5 Indirect Methods for Detecting Contamination 367
Soil-Gas Characterization 367
Geophysical Methods 368
Electrical Methods 369
Ground-Penetrating Radar 370
Magnetometry 371
Seismic Methods 371

Chapter 18
***Modeling the Transport of Dissolved Contaminants* 372**

18.1 Analytical Approaches 372
Advection and Longitudinal Dispersion 372
The Retardation Equation 375
Radioactive Decay, Biodegradation, and Hydrolysis 376
Transverse Dispersion 377
Models for Multidimensional Transport 378
Continuous Sources 378
Numerical Integration of an Analytical Solution 380
The Instantaneous Point Source Model 380

18.2 Programming the Analytical Solutions for Computers 382

18.3 Numerical Approaches 384
A Generalized Modeling Approach 384
The Common Solution Techniques 385
Adding Chemical Reactions 386

18.4 Case Study in the Application of a Numerical Model 386

Chapter 19
***Multiphase Fluid Systems* 393**

19.1 Basic Concepts 393
Saturation and Wettability 393
Interfacial Tension and Capillary Forces 394
Imbibition and Drainage 394
Relative Permeability 395
Solubility and Effective Solubility 397

19.2 LNAPLs and DNAPLs 398
Conceptual Models for the Occurrence of LNAPLs 399
Occurrence of DNAPLs in Ground Water 401
Secondary Contamination Due to NAPLs 401
Conceptual Models and Quantitative Methods 403
A Case Study of Gasoline Leakage 404
Hyde Park Landfill Case Study 404

19.3 Partitioning 405

19.4 Fate of Organics in the Unsaturated Zone 406
Volatilization 406
Gas Transport by Diffusion 408
Equilibrium Calculations of Mass Distributions 409
Mass of VOC in Gas Phase 411
Mass of VOC in Aqueous Phase 411
Mass of VOC in Sorbed Phase 411
Mass of VOC in NAPL Phase 411

19.5 Fate of Organics in the Saturated Zone 411
Equilibrium Calculations of Mass Distribution 412

19.6 Air-Permeability Testing 412

19.7 Recognizing DNAPL Sites 413
Systematic Screening Procedure 414

Chapter 20
***Remediation: Overview and Removal Options* 417**

20.1 Containment 417
Slurry Walls 417
Sheet Pile Walls 418
Grouting 418
Surface Seals and Surface Drainage 418
Hydrodynamic Controls 419
Stabilization and Solidification 420

20.2 Management Options 420

20.3 Overview of Methods for Contaminant Removal 420
Excavation and Ex Situ Treatment 421
Pump and Treat 421
Interceptor Systems 421
Soil-Vapor Extraction 421

20.4 Pump and Treat 422
The Problem of Pump and Treat 422
Technical Considerations with Injection-Recovery Systems 423
Methods for Designing Pump-and-Treat Systems 425
Expanding Pilot-Scale Systems 425
Capture Zones 426
Analytical Approaches to Defining Capture Zones 426
Model-Based Approaches for the Design of Recovery Systems 429
Simulation-Optimization Techniques 429
Issues in the Design of Capture Zones 430

20.5 Interceptor Systems for NAPL Recovery 430

20.6 Soil-Vapor Extraction 431
Components of an SVE System 432

When Can SVE Systems Be Used? 433
Estimating Removal Rates 434
Removal Rate Calculations 435
Field Estimates of Soil Permeability 435
Heterogeneity and the Efficiency of SVE Systems 436

20.7 Air Sparging 437
Airflow and Channeling 437
Designing Air-Sparging Systems 438

20.8 Case Studies in Site Remediation 438
Oil Spill: Calgary, Alberta 438
Gilson Road: Nashua, New Hampshire 439
Hyde Park Landfill: Niagara Falls, New York 440
Groveland Wells Site, Massachusetts 441

Chapter 21
***In Situ Destruction and Risk Assessment* 443**

21.1 Intrinsic Bioremediation 443

21.2 Bioventing and Bioslurping 445
Applicability of the Technology to Contaminant Groups 446
Requirements for Success with Bioventing Systems 446
In Situ Respiration Testing 447
Progress in Solvent Bioremediation 448

21.3 Abiotic Chemical Destruction 449
Reactive Barrier Systems 450
Funnel-and-Gate Systems 450

21.4 Risk Assessment 450
Data Collection and Data Evaluation 451
Exposure Assessment 451
Toxicity Assessment 453
Health-Risk Assessment 454
Types of Risk Assessments 455
Environmental Risk Assessment 456

21.5 Fernald Case Study 456
Detailed Risk Assessment 457

***Answers to Problems* 461**

Appendix A
***Derivation of the Flow Equation in a Deforming Medium* 463**

Appendix B
***About the Computer Disk* 464**

Appendix C
***Table of Atomic Weights* 466**

***References* 468**

***Index* 494**