
PHYSICAL
and
CHEMICAL
HYDROGEOLOGY

Patrick A. Domenico
Franklin W. Schwartz

Physical and Chemical Hydrogeology

Patrick A. Domenico

***David B. Harris Professor of Geology
Texas A&M University***

Franklin W. Schwartz

***Ohio Eminent Scholar in Hydrogeology
The Ohio State University***



John Wiley & Sons

New York

Chichester

Brisbane

Toronto

Singapore

Copyright © 1990 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 and 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons.

Library of Congress Cataloging in Publication Data:

Domenico, P. A. (Patrick A.)

Physical and chemical hydrogeology / Patrick A. Domenico, Franklin W. Schwartz.

p. cm.

Includes bibliographical references and index.

ISBN 0-471-50744-X

1. Hydrogeology. I. Schwartz, F. W. (Franklin W.) II. Title.

GB1003.2.D66 1990

551.46—dc20

90-39772

CIP

Printed in the United States of America

Printed and bound by the Hamilton Printing Company.

10 9 8 7 6 5

***Physical and
Chemical Hydrogeology***

***To Diane and Cynthia
and
The Memory of Lucy and Phil***

Preface

We view *Physical and Chemical Hydrogeology* as a textbook rather than a reference volume or collection of facts and formulas with little underlying organization. The approach taken is process-oriented, and one of the goals is to provide an intuitive feeling for the total science so that the subject can be seen as a whole rather than a collection of unconnected pieces. However, we have not overlooked the value of reference material, and original and other sources are included in a rather extensive bibliography. We recognize further that there is great interest in the practice of hydrogeology. To this end we include chapters or sections that deal exclusively with state-of-the-art applications, including a significant number of worked examples of computational procedures and a problem set for most of the chapters. We also recognize that in the absence of theory there can be no practice, only chaos. As some of the mathematical ideas in hydrogeology are among the most abstract that beginning students in the physical sciences will ever encounter, we have attempted a reader-friendly style of exposition so that the mathematics can at least be understood conceptually. The price one pays for this style of exposition is increased length and a fair amount of redundancy, some of which may hopefully reinforce the more difficult concepts.

Physical and Chemical Hydrogeology is divided into three sections. After presenting preliminary information on the hydrologic cycle and the porosity and permeability of porous material, the sections deal with fluid, energy, and mass transport in porous media. We believe these sections will serve a diversity of interests, including those of geologists, practicing hydrogeologists and engineers, geochemists, and geophysicists interested in fluid dynamics. We claim little originality in the basic content of the book, but we are pleased with the manner in which it is organized and treated. Whoever the reader, the book is intended as an introduction to hydrogeology, either at the

advanced undergraduate or beginning graduate level. We have assumed the reader knows something about calculus, basic physics, chemistry, and geology.

The consideration of notation and units is always a central one in textbooks. Because of the integration of ideas from a variety of disciplines, it is difficult to employ a consistently familiar system of symbols. Whenever one symbol is generally accepted for two different quantities, choices have to be made. The question of units is equally perplexing. The SI system is used to some degree within the United States and more or less universally everywhere else. In the United States, some units are derived from the English system, some from the metric system, and some are best regarded as “field” units because their use is so common in field practice. In this text, we generally use SI metric units but will also provide an equivalent measure in field units where the use of such units is common practice.

For us the work was truly a collaborative effort with each of us contributing equally to the book. We would like to express our thanks to others who contributed directly and indirectly, in particular Alan Fryar, who prepared Section 15.4, and Vic Palciauskas, who commented on most of the theoretical developments through Chapter 9. Large parts of the manuscript were reviewed by Dick Jackson, Darrell Leap, Gary Robbins, and Don Siegel. Jim Hendry, Les Smith, Rob Schincariol, John Tinker, Jr., and Hans-Olaf Pfannkuch reviewed sections of the manuscript. Their helpful comments and suggestions helped us shape the final draft. We are also indebted to other colleagues and friends, and students who have influenced us through the years.

July 1990

**PATRICK A. DOMENICO
FRANKLIN W. SCHWARTZ**

Contents

Chapter 1 ***Introduction / 1***

- 1.1 What Is Hydrogeology? / 2**
 - Physical Hydrogeology Before the Early 1940s / 3
 - Chemical Hydrogeology Before the Early 1960s / 5
 - Post 1960 Hydrogeology / 5
- 1.2 The Relationship Between Hydrogeology and Other Fields of Geology / 7**
- 1.3 How to Use This Book / 8**
- 1.4 The Hydrologic Cycle / 9**
 - Components Of the Hydrologic Cycle / 9
 - Evapotranspiration and Potential Evapotranspiration / 12
 - Infiltration and Recharge / 14
 - Baseflow / 14
 - Hydrologic Equation / 18

Chapter 2 ***The Origin of Porosity and Permeability*** / 23

2.1 Porosity and Permability / 24

Porosity and Effective Porosity / 24

Permeability / 27

2.2 Continental Environments / 28

Weathering / 28

Erosion, Transportation, and Deposition / 31

Fluvial Deposits / 32

Alluvial Valleys / 33

Alluvial Basins / 33

Eolian Deposits / 35

Lacustrine Deposits / 35

Glacial Deposits / 35

2.3 The Boundary Between Continental and Marine Environments / 36

2.4 Marine Environments / 38

Lateral and Vertical Succession of Strata / 38

Ancestral Seas and Their Deposits / 39

The Paleozoic Rock Group / 39

The Mesozoic Rock Group / 41

The Cenozoic Rock Group / 41

Diagenesis in Marine Environments / 42

Porosity Reduction: Compaction and Pressure Solution / 42

Chemical Rock-Water Interactions: Secondary Porosity in Sandstones / 44

2.5 Uplift, Diagenesis, and Erosion / 46

The Style of Formations Associated with Uplift / 47

Secondary Porosity Enhancement in Carbonate Rocks / 49

2.6 Tectonism and the Formation of Fractures / 50

Style of Fracturing / 51

Fluid Pressure and Porosity / 53

Connectivity / 53

Chapter 3 ***Ground Water Movement*** / 55

3.1 Darcy's Experimental Law and Field Extensions / 56

The Nature of Darcy's Velocity / 57

Hydraulic Head: Hubbert's Force Potential / 58

The Gradient: An Introduction to Field Theory / 60
 Physical Interpretation of Darcy's Proportionality Constant / 61
 Units and Dimensions / 63

3.2 Hydraulic Conductivity and Permeability of Geologic Materials / 63

Observed Range in Hydraulic Conductivity Values / 63
 Character of Hydraulic Conductivity Distribution / 66
 Anisotropy and Heterogeneity: Origin and Manifestations / 67
 Heterogeneity and the Classification of Aquifers / 70
 Darcy's Law for Anisotropic Material / 71
 Measurement of Hydraulic Conductivity / 74
 Laboratory Testing / 75
 The Search for Empirical Correlations / 75

3.3 Darcy's Law and the Field Mapping of Hydraulic Head / 77

3.4 Flow in Fractured Rocks / 83

Continuum Approach to Fluid Flow / 83
 Intergranular Porous Rocks / 83
 Fractured Rocks / 84
 The Cubic Law / 87

3.5 Flow in the Unsaturated Zone / 88

Unsaturated Flow in Fractured Rocks / 90

Chapter 4
Elastic Properties and Main Equations of Flow / 99

4.1 Conservation of Fluid Mass / 100

Main Equations of Flow / 102

4.2 The Storage Properties of Porous Media / 104

Compressibility of Water and Its Relation to Specific Storage / 105
 Compressibility of the Rock Matrix: Effective Stress Concept / 107
 Matrix Compressibility and Its Relation to Specific Storage / 109
 Equation for Confined Flow in an Aquifer / 115
 Specific Yield of Aquifers / 116

4.3 Boundary Conditions and Flow Nets / 118

4.4 Deformable Porous Media / 124

One-Dimensional Consolidation / 124
 Development of the Flow Equation / 124
 The Undrained Response of Water Levels to Natural Loading Events / 126
 The Drained Response of Water Levels to Natural Loading Events / 131

- Three-Dimensional Consolidation / 132
 - Elastic Properties in Deformational Problems / 132
 - Flow Equations for Deformable Media / 135

4.5 Dimensional Analysis / 136

Chapter 5
Hydraulic Testing: Models, Methods, and Applications / 141

5.1 Prototype Geologic Models in Hydraulic Testing / 142

5.2 Conventional Hydraulic Test Procedures and Analysis / 144

The Theis Nonequilibrium Pumping Test Method / 144

 The Curve Matching Procedure / 148

 Assumptions and Interpretations / 150

Modifications of the Nonequilibrium Equation / 151

 Time-Drawdown Method / 152

 Distance-Drawdown Method / 153

Steady State Behavior as a Terminal Case of the Transient Response / 155

The Hantush-Jacob Leaky Aquifer Method / 155

Water Table Aquifers / 159

5.3 Single Borehole Tests / 161

Recovery in a Pumped Well / 162

The Drill Stem Test / 163

Slug Injection or Withdrawal Tests / 164

Response at the Pumped Well: Specific Capacity / 168

Direct Determination of Ground Water Velocity: Borehole Dilution Tests / 171

**5.4 Partial Penetration, Superposition,
and Bounded Aquifers / 172**

Partial Penetration / 172

Principle of Superposition / 173

Bounded Aquifers / 175

**5.5 Hydraulic Testing in Fractured or Low
Permeability Rocks / 181**

Single Borehole Tests / 182

Multiple Borehole Tests / 182

5.6 Some Applications to Hydraulic Problems / 185

Planning a Pumping Test / 185

 Screen Diameter and Pumping Rates / 186

 Well Yield: The Step-Drawdown Test / 186

 Distance to the Observation Well(s) / 187

Planning a Dewatering Operation / 188

A Problem in Water Supply / 190

Chapter 6

Ground Water as a Resource / 199

6.1 Development of Ground Water Resources / 200

The Response of Aquifers to Pumping / 200

Yield Analysis / 202

Water Law / 203

Artificial Recharge and Conjunctive Use / 205

Artificial Recharge / 206

Conjunctive Use / 209

6.2 Simulation of Aquifer Response to Pumping / 210

Numerical Simulation / 211

The Method of Finite Differences / 211

Computational Techniques, Steady Flow / 214

Computational Techniques, Unsteady Flow / 216

The Method of Finite Elements / 216

On the Use of Numerical Models / 216

6.3 Land Subsidence and Sea Water Intrusion / 217

Land Subsidence / 217

Physical Properties of Sediments / 219

Mathematical Treatment of Land Subsidence / 224

Vertical Compression / 224

The Time Rate of Subsidence / 228

Simulation of Subsidence / 230

Salt Water Intrusion in Coastal Aquifers / 230

The Fresh Water–Salt Water Interface in Coastal Regions / 231

The Ghyben-Herzberg Relation / 232

The Shape of the Interface with a Submerged Seepage Surface / 233

Upconing of the Interface Caused by Pumping Wells / 235

6.4 Simulation-Optimization Concepts / 236

Chapter 7

Ground Water in the Basin Hydrologic Cycle / 241

7.1 Topographic Driving Forces / 242

The Early Field Studies / 242

Conceptual, Graphical, and Mathematical Models of Unconfined Flow / 243

Effect of Basin Geometry on Ground Water Flow / 247

Effect of Basin Geology on Ground Water Flow / 249

Ground Water in Mountainous Terrain / 255

7.2 Surface Features of Ground Water Flow / 260

Recharge-Discharge Relations / 260

Ground Water-Lake Interactions / 264

Ground Water-Surface Water Interactions / 266

**7.3 Some Engineering and Geologic Implications
of Topographic Drive Systems / 268**

Large Reservoir Impoundments / 268

Excavations and Tunnels: Inflows and Stability / 269

 The Sea Level Canal / 269

 Ground Water Inflow into Excavations / 271

 The Stability of Excavations in Ground Water Discharge Areas / 273

 Ground Water Inflows into Tunnels / 274

Landslides and Slope Stability / 278

Chapter 8

Ground Water in the Earth's Crust / 283

**8.1 Abnormal Fluid Pressures in Active
Depositional Environments / 284**

Origin and Distribution / 284

Mathematical Formulation of the Problem / 288

Isothermal Basin Loading and Tectonic Strain / 290

 One-Dimensional Basin Loading / 291

 Extensions of the One-Dimensional Loading Model / 294

 Vertical Compression with Compressible Components / 295

 Horizontal Extension and Compression / 295

 Tectonic Strain as a Pressure-Producing Mechanism / 297

Thermal Expansion of Fluids / 298

Fluid Pressures and Rock Fracture / 301

Phase Transformations / 304

Subnormal Pressure / 306

Irreversible Processes / 306

8.2 Pore Fluids in Tectonic Processes / 307

Fluid Pressures and Thrust Faulting / 308

Seismicity Induced by Fluid Injection / 309

Seismicity Induced in the Vicinity of Reservoirs / 312

Seismicity and Pore Fluids at Midcrustal Depths / 312

The Phreatic Seismograph: Earthquakes and Dilatancy Models / 313

Chapter 9
Heat Transport in Ground Water Flow / 317

- 9.1 Conduction, Convection, and Equations of Heat Transport / 319**
 - Fourier's Law / 319
 - Convective Transport / 321
 - Equations of Energy Transport / 323
 - The Heat Conduction Equation / 324
 - The Conductive-Convection Equation / 325
 - Dimensionless Groups / 326
- 9.2 Forced Convection / 327**
 - Temperature Profiles and Ground Water Velocity / 328
 - Heat Transport in Regional Ground Water Flow / 332
 - Heat Transport in Active Depositional Environments / 335
 - Heat Transport in Mountainous Terrain / 341
- 9.3 Free Convection / 343**
 - The Onset of Free Convection / 344
 - Sloping Layers / 345
 - Geologic Implications / 346
- 9.4 Energy Resources / 347**
 - Geothermal Energy / 347
 - Energy Storage in Aquifers / 348
- 9.5 Heat Transport and Geologic Repositories for Nuclear Waste Storage / 349**
 - The Nuclear Waste Program / 349
 - The Rock Types / 350
 - Thermohydrochemical Effects / 352
 - Thermomechanical Effects / 354

Chapter 10
Solute and Particle Transport / 357

- 10.1 Advection / 358**
- 10.2 Particle Transport / 360**
- 10.3 Basic Concepts of Dispersion / 362**
 - Diffusion / 366
 - Mechanical Dispersion / 369

10.4 Character of the Dispersion Coefficient / 371

Studies at the Microscopic Scale / 371

Dispersivity as a Medium Property / 372

Studies at Macroscopic and Larger Scales / 372

10.5 A Geostatistical Model of Dispersion / 377

Mean and Variance / 378

Autocovariance and Autocorrelation Functions / 378

Estimation of Dispersivity / 379

10.6 Mixing in Fractured Media / 381

Chapter 11

Principles of Aqueous Geochemistry / 387

11.1 Introduction to Aqueous Systems / 388

Aqueous Solution Phase / 389

Gas and Solid Phases / 391

**11.2 Structure of Water and the Occurrence
of Mass in Water / 391**

**11.3 Equilibrium Versus Kinetic Descriptions
of Reactions / 392**

Reaction Rates / 393

11.4 Equilibrium Models of Reaction / 394

Activity Models / 395

11.5 Deviations from Equilibrium / 398

11.6 Kinetic Reactions / 399

11.7 Organic Compounds / 402

11.8 Ground Water Composition / 408

The Routine Water Analysis / 408

Specialized Analyses / 410

11.9 Describing Chemical Data / 411

Abundance or Relative Abundance / 411

Abundance and Patterns of Change / 414

Chapter 12

Chemical Reactions / 421

12.1 Acid-Base Reactions / 422

Natural Weak Acid-Base Systems / 423

CO₂-Water Systems / 424

- Alkalinity / 425
- 12.2 Solution, Exsolution, Volatilization, and Precipitation / 427**
 - Gas Solution and Exsolution / 427
 - Solution of Organic Solutes in Water / 428
 - Volatilization / 430
 - Dissolution and Precipitation of Solids / 432
 - Solid Solubility / 432
- 12.3 Complexation Reactions / 434**
 - Stability of Complexes and Speciation Modeling / 434
 - Major Ion Complexation and Equilibrium Calculations / 437
 - Enhancing the Mobility of Metals / 438
 - Organic Complexation / 438
- 12.4 Reactions on Surfaces / 440**
 - Sorption Isotherms / 440
 - Hydrophobic Sorption of Organic Compounds / 443
 - Multiparameter Equilibrium Models / 446
- 12.5 Oxidation-Reduction Reactions / 450**
 - Oxidation Numbers, Half-Reactions, Electron Activity, and Redox Potential / 450
 - Kinetics and Dominant Couples / 455
 - Control on the Mobility of Metals / 455
 - Biotransformation of Organic Compounds / 457
 - Rates Limited by Substrate Availability / 458
 - Rates Limited by Availability of Electron Acceptors / 459
- 12.6 Hydrolysis / 460**
- 12.7 Isotopic Processes / 462**
 - Radioactive Decay / 462
 - Isotopic Reactions / 464
 - Deuterium and Oxygen-18 / 465
 - Carbon-13 and Sulfur-34 / 467

Chapter 13

The Mathematics of Mass Transport / 471

- 13.1 Mass Transport Equations / 472**
 - The Diffusion Equation / 472
 - The Advection-Diffusion Equation / 473
 - The Advection-Dispersion Equation / 475

13.2 Mass Transport with Reaction / 475

First-Order Kinetic Reactions / 476

Equilibrium Sorption Reactions / 476

Heterogeneous Kinetic Reactions / 478

13.3 Boundary and Initial Conditions / 480

Chapter 14

***Mass Transport in Ground Water Flow:
Aqueous Systems / 483***

14.1 Mixing as an Agent for Chemical Change / 484

The Mixing of Meteoric and Original Formation Waters / 485

Diffusion in Deep Sedimentary Environments / 487

14.2 Inorganic Reactions in the Unsaturated Zone / 492

(1) Gas Dissolution and Redistribution / 492

(2) Weak Acid-Strong Base Reactions / 494

(3) Sulfide Oxidation / 497

(4) Gypsum Precipitation and Dissolution / 497

(5) Cation Exchange / 497

14.3 Organic Reactions in the Unsaturated Zone / 498

(1) Dissolution of Organic Litter / 499

(2) Complexation of Fe and Al / 499

(3) Sorption of Organic-Metal Complexes / 499

(4) Oxidation of Organic Compounds / 499

14.4 Inorganic Reactions in the Saturated Zone / 500

(1) Weak Acid-Strong Base Reactions / 500

(2) Dissolution of Soluble Salts / 504

(3) Redox Reactions / 504

(4) Cation Exchange / 509

14.5 Case Study of the Milk River Aquifer / 510

**14.6 Quantitative Approaches for Evaluating
Chemical Patterns / 515**

Homogeneous and Heterogeneous Equilibrium Models / 515

Mass Balance Models / 520

Reaction Path Models / 523

14.7 Age Dating of Ground Water / 525

Tritium / 526

Carbon-14 / 527

Chlorine-36 / 530