Contents

List of contributors xv
Preface xvii

1. Introduction 1
   Kevin R. Henke
   1.1 Arsenic origin, chemistry, and use 1
   1.2 Arsenic environmental impacts 2
   1.3 Arsenic toxicity 3
   1.4 Arsenic treatment and remediation 3
       1.4.1 Introduction 3
       1.4.2 Treatment and remediation of water 4
       1.4.3 Treatment and remediation of solid wastes, soils, and sediments 4
       1.4.4 Treatment of flue gases 5
   References 5

2. Arsenic Chemistry 9
   Kevin R. Henke and Aaron Hutchison
   2.1 Introduction 9
   2.2 Atomic structure and isotopes of arsenic 9
   2.3 Arsenic valence state and bonding 10
   2.4 Chemistry of arsenic solids 13
       2.4.1 Elemental arsenic 13
       2.4.2 Common arsenic minerals and other solid arsenic compounds 15
       2.4.3 Arsine and other volatile arsenic compounds 24
       2.4.4 Organoarsenicals 24
   2.5 Introduction to arsenic oxidation and reduction 26
       2.5.1 Arsenic oxidation 26
       2.5.2 Arsenic reduction 27
   2.6 Introduction to arsenic methylation and demethylation 28
   2.7 Arsenic in water 30
       2.7.1 Introduction 30
       2.7.2 Aqueous solubility of arsenic compounds and thermodynamics 31
       2.7.3 Dissolved arsenic species 40
       2.7.4 Dissociation of arsenious and arsenic acids 42
       2.7.5 Eh-pH diagrams, and their limitations 45
       2.7.6 Sorption, ion exchange, precipitation, and coprecipitation of arsenic in water 46
   2.8 Chemistry of gaseous arsenic emissions 57
   References 59

2.7.3 Dissolved arsenic species 40
3 Arsenic in Natural Environments

Kevin R. Henke

3.1 Introduction

3.2 Nucleosynthesis: the origin of arsenic
  3.2.1 The Big Bang
  3.2.2 Arsenic formation in stars

3.3 Arsenic in the universe as a whole

3.4 Arsenic chemistry of the solar system
  3.4.1 Arsenic in the Sun, Moon, and planets
  3.4.2 Arsenic in meteorites and tektites

3.5 Arsenic in the bulk Earth, crusts, and interior
  3.5.1 Estimating arsenic concentrations of the bulk Earth and the Earth’s core and mantle
  3.5.2 The core
  3.5.3 The mantle
  3.5.4 The Earth’s crusts

3.6 Arsenic in hydrothermal and geothermal fluids and their deposits
  3.6.1 Introduction
  3.6.2 Origins of hydrothermal fluids and their arsenic
  3.6.3 Arsenic chemistry of hydrothermal fluids
  3.6.4 Arsenic mineralogy of hydrothermal deposits
  3.6.5 Surface and near-surface oxidation of hydrothermal arsenic
  3.6.6 Arsenic chemistry in hot springs
  3.6.7 Arsenic in geothermal power plant scales
  3.6.8 Arsenic in volcanic gas emissions
  3.6.9 Environmental impacts of arsenic in hydrothermal and geothermal fluids

3.7 Oxidation of arsenic-bearing sulfides in geologic materials and mining wastes
  3.7.1 Oxidation of sulfide minerals
  3.7.2 Factors influencing the oxidation of arsenic-bearing sulfide minerals
  3.7.3 Environmental consequences of sulfide and arsenic oxidation
  3.7.4 Oxidation chemistry of major arsenic-bearing sulfides

3.8 Interactions between arsenic and natural organic matter (NOM)

3.9 Sorption and coprecipitation of arsenic with iron and other (oxy)(hydr)oxides
  3.9.1 Introduction
  3.9.2 Iron, aluminum, and manganese (oxy)(hydr)oxides
  3.9.3 Sulfate (oxy)(hydr)oxides and related compounds

3.10 Arsenate (inorganic As(V)) precipitation

3.11 Reductive dissolution of iron and manganese (oxy)(hydr)oxides

3.12 Arsenic and sulfide at < 50 °C

3.13 Arsenic and its chemistry in mined materials
  3.13.1 Environmental issues with arsenic-bearing sulfide minerals in coal and ore deposits
  3.13.2 Behavior of arsenic within mining wastes
  3.13.3 Movement of arsenic from mining wastes and into the environment

3.14 Marine waters and sediments
  3.14.1 Inorganic arsenic in seawater
  3.14.2 Marine arsenic cycle
  3.14.3 Arsenic methylation in marine environments
  3.14.4 Arsenic in marine sediments
Contents ix

3.15 Estuaries 122
  3.15.1 Arsenic in estuaries 122
  3.15.2 Seasonal effects on arsenic in estuaries 125
  3.15.3 Arsenic in pristine estuaries 125
  3.15.4 Arsenic in contaminated estuaries 126
3.16 Rivers and other streams 127
3.17 Lakes 136
3.18 Wetlands 145
3.19 Groundwater 146
  3.19.1 Subsurface water and groundwater 146
  3.19.2 Impacts of arsenic contamination in shallow (< 1 km deep) groundwaters 148
  3.19.3 ‘Dissolved’ and particulate arsenic in groundwater 148
  3.19.4 Arsenic mobility in groundwater 148
  3.19.5 Sources of arsenic contamination in groundwater 149
  3.19.6 Arsenic chemistry in groundwater 161
3.20 Glacial ice and related sediments 162
3.21 Arsenic in air and wind-blown sediments 163
  3.21.1 Arsenic emission sources 163
  3.21.2 Arsenic atmospheric chemistry 165
  3.21.3 Arsenic in precipitation 166
  3.21.4 Arsenic in atmospheric dust 166
  3.21.5 Arsenic in wind-blown sediment deposits (loess) 168
  3.21.6 Arsenic in soil and sediment gases 168
3.22 Petroleum 168
3.23 Soils 169
  3.23.1 Distinguishing between soils and sediments 169
  3.23.2 Arsenic chemistry in soils 171
  3.23.3 Soil porewater chemistry 178
3.24 Sedimentary rocks 178
  3.24.1 Diagenesis and sedimentary rocks 178
  3.24.2 Coal 180
  3.24.3 Shales and oil shales 190
  3.24.4 Other sedimentary rocks 195
3.25 Metamorphic rocks 196
References 198
Further reading 235

4 Toxicology and Epidemiology of Arsenic and its Compounds 237
  Michael F. Hughes, David J. Thomas, and Elaina M. Kenyon
  4.1 Introduction 237
  4.2 Physical and chemical properties of arsenic 238
  4.3 Exposure to arsenic 238
  4.4 Arsenic disposition and biotransformation in mammals 240
    4.4.1 Introduction 240
    4.4.2 Respiratory deposition and absorption 240
    4.4.3 Gastrointestinal absorption 241
    4.4.4 Dermal absorption 242
4.5 Systemic clearance of arsenic and binding to blood components 243
4.6 Tissue distribution 244
4.7 Placental transfer and distribution in the fetus 246
4.8 Arsenic biotransformation 247
  4.8.1 Introduction 247
  4.8.2 Arsenic methylation in humans and other mammals 248
  4.8.3 Significance of arsenic methylation 248
  4.8.4 Molecular basis of the metabolism of inorganic arsenic 248
  4.8.5 Reconciling experimental data and the Challenger scheme 251
4.9 Arsenic excretion 252
4.10 Effects of arsenic exposure 253
  4.10.1 Acute exposure 253
  4.10.2 Chronic exposure 254
4.11 Cardiovascular 254
  4.11.1 Introduction 254
  4.11.2 Peripheral vascular disease 255
  4.11.3 Ischemic heart disease 255
  4.11.4 Cerebrovascular disease 255
  4.11.5 Atherosclerosis 255
  4.11.6 Hypertension 256
4.12 Endocrine 256
4.13 Hepatic 257
4.14 Neurological 257
4.15 Skin 257
4.16 Developmental 258
4.17 Other organ systems 258
4.18 Cancer 259
  4.18.1 Introduction 259
  4.18.2 Skin 259
  4.18.3 Lung 260
  4.18.4 Bladder 260
4.19 Animal models for arsenic-induced cancer 260
4.20 Mechanism of action 261
  4.20.1 Introduction 261
  4.20.2 Replacement of phosphate 262
  4.20.3 Enzyme inhibition 262
  4.20.4 Oxidative stress 262
  4.20.5 Genotoxicity 263
  4.20.6 Alteration of DNA repair 263
  4.20.7 Signal transduction 263
  4.20.8 Gene transcription 263
  4.20.9 DNA methylation 264
  4.20.10 Growth factors 264
4.21 Regulation of arsenic 264
References 265
5 Arsenic in Human History and Modern Societies 277

Kevin R. Henke and David A. Atwood

5.1 Introduction 277
5.2 Early recognition and uses of arsenic by humans 278
5.3 Alchemy, development of methods to recover elemental arsenic, and the synthesis of arsenic compounds 279
5.4 Applications with arsenic 279
   5.4.1 Medicinal applications: dangerous quackery and some important drugs 279
   5.4.2 Pesticides and agricultural applications 280
   5.4.3 Chemical weapons 282
   5.4.4 Embalming fluids 282
   5.4.5 Paints and dyes 283
   5.4.6 Wood treatment 284
   5.4.7 Semiconductors 286
5.5 Increasing health, safety, and environmental concerns 286
5.6 Arsenic in crime 287
5.7 Poisoning controversies: Napoleon Bonaparte 288
5.8 Arsenic in prospecting, mining, and markets 289
   5.8.1 Arsenic as a pathfinder element in prospecting 289
   5.8.2 Arsenic mining, production, and market trends 290
5.9 Arsenic in coal and oil shale utilization and their by-products 291
   5.9.1 Coal cleaning and combustion 291
   5.9.2 Arsenic behavior during combustion 291
   5.9.3 Postcombustion flue gas treatment 295
   5.9.4 Arsenic chemistry in coal combustion byproducts 295
   5.9.5 Coal gasification 296
   5.9.6 Oil shale utilization 296
References 297

6 Major Occurrences of Elevated Arsenic in Groundwater and Other Natural Waters 303

Abhijit Mukherjee, Alan E. Fryar, and Bethany M. O'Shea

6.1 Introduction 303
6.2 Arsenic speciation and mobility in natural waters 304
6.3 Immobilization of arsenic in hydrologic systems 304
   6.3.1 Precipitation, coprecipitation, and association with sulfides 304
   6.3.2 Arsenic sorption on metal (oxy)(hydr)oxides 305
   6.3.3 Arsenic sorption on clay minerals 306
   6.3.4 Carbonate interactions 306
6.4 Mobilization of arsenic in water 309
   6.4.1 Competitive anion exchange 309
   6.4.2 Effect of natural organic matter (NOM) 310
   6.4.3 Effect of pH 310
   6.4.4 Redox-dependent mobilization 311
   6.4.5 Complex and colloid formation 311
6.5 Natural occurrences of elevated arsenic around the world
6.5.1 Introduction 313
6.5.2 Bengal basin, India and Bangladesh 317
6.5.3 Middle Ganges Plain, India 324
6.5.4 Donargarh rift belt, Chattisgarh, central India 326
6.5.5 Terai alluvial plain, Nepal 326
6.5.6 Indus alluvial system, Pakistan 327
6.5.7 Irrawaddy delta, Myanmar 328
6.5.8 Mekong plain and delta, Cambodia, Vietnam, and Laos 328
6.5.9 Red River delta, Vietnam 331
6.5.10 Yellow River plains, Inner Mongolia, China 332
6.5.11 Taiwan 333
6.5.12 Coastal aquifers of Australia 334
6.5.13 Sedimentary basins and basement complexes of West Africa 334
6.5.14 Western USA 335
6.5.15 New England, USA 336
6.5.16 Northern Chile 337
6.5.17 Chaco and Pampa plains of Argentina 338
References 339

7 Waste Treatment and Remediation Technologies for Arsenic
Kevin R. Henke
7.1 Introduction 351
7.2 Treatment technologies for arsenic in water
7.2.1 Introduction 352
7.2.2 Preoxidation of As(III) in water 353
7.2.3 Sorption and ion-exchange technologies 357
7.2.4 Precipitation/coprecipitation 390
7.2.5 Permeable reactive barriers 394
7.2.6 Filtration, membranes, and other separation technologies 395
7.2.7 Biological treatment and bioremediation 398
7.2.8 Natural remediation 401
7.3 Treatment technologies for arsenic in solids 401
7.3.1 Introduction 401
7.3.2 Review of various treatment technologies for arsenic in inorganic solids 402
7.3.3 Review of various treatment technologies for chromated copper arsenate (CCA)-treated wood 410
7.4 Treatment technologies for arsenic in gases 414
References 415

APPENDICES

A Common Physical and Chemical Constants and Conversions for Units of Measure 431
## Glossary of Terms

**B.1 Introduction** 437  
**B.2 Glossary** 437  
**References** 437

## Arsenic Thermodynamic Data

**C.1 Introduction** 475  
**C.2 Modeling applications with thermodynamic data** 493  
**C.3 Thermodynamic data** 493  
**References** 493

## Locations of Significant Arsenic Contamination

**References** 524

## Regulation of Arsenic: A Brief Survey and Bibliography

**E.1 Introduction** 545  
**E.2 Regulation of arsenic in water** 545  
**E.2.1 Drinking water** 546  
**E.2.2 Arsenic standards of natural surface waters and groundwaters** 549  
**E.3 Regulation of arsenic in solid and liquid wastes** 549  
**E.3.1 Bangladesh** 549  
**E.3.2 European Union (EU)** 550  
**E.3.3 Japan** 550  
**E.3.4 Norway** 550  
**E.3.5 Taiwan** 550  
**E.3.6 United States of America** 550  
**E.4 Sediment and soil guidelines and standards for arsenic** 553  
**E.4.1 Introduction** 553  
**E.4.2 Australia** 553  
**E.4.3 Canada** 553  
**E.4.4 European Union** 554  
**E.4.5 Italy** 554  
**E.4.6 Japan** 554  
**E.4.7 Korea (South)** 554  
**E.4.8 Thailand** 554  
**E.4.9 United States of America** 554  
**E.5 Regulation of arsenic in food and drugs** 555  
**E.5.1 Australia and New Zealand** 555  
**E.5.2 Canada** 555  
**E.5.3 United States of America** 555  
**E.6 Regulation of arsenic in air** 556  
**E.6.1 European Union** 556  
**E.6.2 United States of America** 556  
**References** 556

## Index

559