

# Contents

Foreword, V

Preface, XI

Acknowledgements, XIII

Part A: Stone weathering, 1

Chapter 1. Effects of water and soluble salts on stone decay, 2

1.1. The weathering environment, 2

1.2. Quarrying and trimming, 7

1.3. Porosity of a body, 10

1.4. Physical action of water, 12

1.4.1. Diffusion of water vapour into a porous body, 14

1.4.2. Transport of liquid water in a porous body, 16

1.4.3. Evaporation, 20

1.4.4. Frost action, 23

1.4.5. Crystallization of soluble salts: their effect on stone building materials, 28

1.4.5.1 Crystallization pressure of salts in stone, 43

1.4.5.2 Hydration pressure, 45

1.4.5.3 Most common soluble salts present in efflorescences, 46

References, 48

Part B: Environmental pollution in relation to the deterioration of stone, 53

Chapter 2. The abundance, sources and sinks of the most important air pollutants responsible for the deterioration processes in stone, 54

2.1. Introduction, 54

2.2. The structure of the atmosphere, 55

2.3. Elementary concepts of air pollution, 57

2.4. The composition of the atmosphere, 59

2.5. Oxides of carbon, 65

2.5.1. Carbon dioxide: atmospheric cycle, 65

2.5.2. The effects of carbon dioxide on limestone and sandstone, 69

2.5.3. Carbon monoxide, 74

2.6. Gaseous compounds of nitrogen, 74

2.6.1. Oxides of nitrogen, 74

2.6.2. Ammonia, 80

2.7. Gaseous compounds of halogens, 83

2.7.1. Fluorine and hydrogen fluoride, 83

2.7.1.1 Atmospheric cycle, 83

2.7.1.2 The effects of fluorides on siliceous and calcareous stone, 84

2.7.2. Chlorine and hydrogen chloride, 89

2.7.2.1 Atmospheric cycle, 89

2.7.2.2 The effects of hydrochloric acid on stone building materials, 90

2.8. Gaseous compounds of sulphur, 92

- 2.8.1. Sulphur oxides, 92
  - 2.8.1.1 Atmospheric cycle, 92
  - 2.8.1.2 Measurement of sulphur dioxide inside the Scrovegni Chapel, 95
- 2.8.2 Hydrogen sulphide, 98
  - 2.8.2.1 Atmospheric cycle, 98
  - 2.8.2.2 The effects of hydrogen sulphide on stone building materials, 100
- 2.9. Ozone and oxidants, 102
- 2.10. Aerosol particles, 104
- References, 106
  
- Chapter 3. Physical and chemical properties of aerosols, 111
  - 3.1. Classification of aerosols, 111
  - 3.2. Physical constitution of aerosol particles, 113
  - 3.3. Atmospheric aerosol particles and relative humidity, 114
    - 3.3.1. Physical adsorption. Solid particles at low relative humidity, 115
    - 3.3.2. Transition from solid particles to droplets. Hygroscopy, deliquescence, 116
    - 3.3.3. Droplets and increasing relative humidity. Growth of liquid aerosols, 117
  - 3.4. Hygroscopic properties of sulphate aerosol particles, 122
    - 3.4.1. Laboratory data, 122
    - 3.4.2. Field studies, 125
  - 3.5. Chemical composition of tropospheric sulphur aerosol particles, 127
  - References, 132
  
- Chapter 4. Wet and dry surface deposition of air pollutants on stone and the formation of black scabs, 135
  - 4.1. Dry deposition mechanism, 135
  - 4.2. Phoretic effects, 137
  - 4.3. Importance of stone surface characteristics, 138
  - 4.4. Wet deposition, 138
  - 4.5. Mechanism of stone deterioration and the formation of black scabs 141
  - References, 154
  
- Chapter 5. The influence of meteorological parameters on the dispersion of air pollutants, 156
  - 5.1. Introduction, 156
  - 5.2. Wind structure, 156
    - 5.2.1. Wind profiles, 156
    - 5.2.2. Turbulent diffusion, 158
    - 5.2.3. Wind roses, 159
  - 5.3. Stability and vertical structure of temperature, 159
  - 5.4. Plume behaviour as a function of vertical temperature gradient, 164
  - 5.5. Effects of surface discontinuities on plume dispersion, 167
  - 5.6. Topographical effects, 168
  - 5.7. Correlation between wind direction and SO<sub>2</sub> concentration, 169
  - 5.8. Correlation between the stability of the lower atmosphere and the SO<sub>2</sub> concentration, 172
  - References, 175
  
- Chapter 6. The Oxidation of sulphur dioxide, 177
  - 6.1. Homogeneous gas-phase oxidation of sulphur dioxide, 177
  - 6.2. Heterogeneous oxidation of SO<sub>2</sub> in aqueous systems, 178
    - 6.2.1. Dissolution of gaseous SO<sub>2</sub> into droplets, 179
    - 6.2.2. Oxidation of SO<sub>2</sub> in the droplet phase, 186
      - 6.2.2.1 Liquid-phase oxidation of SO<sub>2</sub> by oxygen in the absence of catalysts, 187
      - 6.2.2.2 Liquid-phase oxidation of SO<sub>2</sub> by oxygen in the presence of ammonia, 189
      - 6.2.2.3 Liquid-phase oxidation of SO<sub>2</sub> by ozone in the absence of catalysts, 198

- 6.2.2.4 Liquid-phase oxidation of SO<sub>2</sub> by hydrogen peroxide in the absence of catalysts, 200
- 6.2.2.5 Liquid-phase oxidation of SO<sub>2</sub> by oxygen, ozone, hydrogen peroxide in the absence of catalysts. A comparison, 201
- 6.2.2.6 Liquid-phase oxidation of SO<sub>2</sub> by oxygen in the presence of catalysts, 205
- 6.2.3 Application of laboratory results to atmospheric aerosols, 209
  - 6.2.3.1 Absorption of sulphur dioxide by water drops containing heavy metal ions, 209
  - 6.2.3.2 SO<sub>2</sub> oxidation in rainwater samples, 210
  - 6.2.3.3 Catalytic oxidation of SO<sub>2</sub> in urban fogs, 211
  - 6.2.3.4 Comparison between catalyzed and uncatalyzed rates, 211
  - 6.2.3.5 Kinetic mechanism, 213
- 6.2.4. Summary, 215
- 6.3. Heterogeneous oxidation of SO<sub>2</sub> adsorbed to solid particles, 216
- References, 217

### Part C: Conservation of stone in monuments and building materials, 223

#### Chapter 7. Generalities of stone treatment, 224

- 7.1. Introduction, 224
- 7.2. Diagnosis and morphology of deterioration, 225
- 7.3. Treatment of stone — basic consideration, 238
- 7.4. Choice of products for treatment of stone, 243
- 7.5. Methods of application of stone-treatment products, 248
- 7.6. Reconstitution, 250
- References, 250

#### Chapter 8. Cleaning of external surfaces, architectural ornaments and stone sculptures, 254

- 8.1. The need for stone cleaning, 254
- 8.2. Relationship between soiling and stone decay, 255
- 8.3. Molecular attraction between deposits of dirt and stone materials, 267
- 8.4. General criteria for the cleaning of natural stone, 269
- 8.5. Cleaning methods, 270
  - 8.5.1. Water sprinkling, 270
  - 8.5.2. Water spray, 270
  - 8.5.3. Steam, 272
  - 8.5.4. Wet grit blasting, 273
  - 8.5.5. Dry grit blasting, 274
  - 8.5.6. Microblasting, 275
  - 8.5.7. Chemical cleaning, 278
  - 8.5.8. Absorbent powders and special clays, 282
  - 8.5.9. LASER cleaning, 287
  - 8.5.10. Stains and graffiti, 291
  - 8.5.11. Final considerations on cleaning, 294

References, 296

### Part D: Products for treatment of stone: chemical and physical properties, reaction mechanisms and use, 299

#### Chapter 9. Adhesion and Adhesives, 300

- 9.1. Introduction, 300
- 9.2. Theories of adhesion, 301
  - 9.2.1. Mechanical adhesion, 301
  - 9.2.2. Specific adhesion, 302
    - 9.2.2.1 Adhesion by chemical bonding, 302
    - 9.2.2.2 Electrostatic theory of adhesion, 302

- 9.2.2.3 Theories of diffusion and thermodynamic adsorption, 302
- 9.3. Different modes of adhesive setting, 303
  - 9.3.1. Adhesion by solvent evaporation, 303
  - 9.3.2. Adhesion by fusion, 303
  - 9.3.3. Adhesion by setting of a liquid adhesive, 304
- 9.4. Composition of adhesives, 304
  - 9.4.1. Stabilizers, 305
  - 9.4.2. Plasticizers, 305
  - 9.4.3. Fillers, 305
  - 9.4.4. Solvents, 306
- References, 307
- Chapter 10. Inorganic materials, 308
  - 10.1. Alkali silicates, 308
    - 10.1.1. Examples of use for the consolidation of stone, 308
  - 10.2. Fluorosilicon compounds, 309
  - 10.3. Barium and strontium salts, 311
- References, 312
- Chapter 11. Natural and synthetic waxes, 314
  - 11.1. Introduction, 314
  - 11.2. Surface treatment of stone, 318
- References, 319
- Chapter 12. Vinyl polymers and copolymers, 321
  - 12.1. Introduction, 321
  - 12.2. Polyvinyl acetate, 321
  - 12.3. Polyvinyl alcohol, 322
- References, 322
- Chapter 13. Acrylic resins, 324
  - 13.1. Introduction, 324
  - 13.2. Chemical nature and preparation, 324
    - 13.2.1. Polymerization, 325
  - 13.3. Analysis and identification, 327
    - 13.3.1. Qualitative analysis of methyl methacrylate monomer
  - 13.4. Characteristics and properties, 327
    - 13.4.1. Chemical properties, 327
    - 13.4.2. Physical and mechanical properties, 333
  - 13.5. Use of acrylics for treating stone, 335
- References, 347
- Chapter 14. Silicones, 350
  - 14.1. Introduction, 350
  - 14.2. Chemical composition and synthesis, 350
    - 14.2.1. Chlorosilane synthesis, 351
    - 14.2.2. Formation of siloxane polymers: hydrolysis and polycondensation, 352
  - 14.3. Chemical and mechanical properties, 353
  - 14.4. Use of silicones for treatment of stone, 354
  - 14.5. Room temperature vulcanizing silicones, 361
    - 14.5.1. Stanch joints and expansion joints, 361
    - 14.5.2. Silicone rubber supple moulds, 366
  - 14.6. Sodium methyl siliconate and silicic acid alkoxy ester, 368
- References, 372

## Chapter 15. Epoxy resins

- 15.1. Introduction, 375
- 15.2. Chemical nature and preparation, 375
- 15.3. Curing mechanism, 376
- 15.4. Heat of polymerization, viscosity, pot life, reaction temperature, 379
- 15.5. Analysis of uncured and cured epoxy resins, 381
  - 15.5.1. Qualitative tests, 382
  - 15.5.2. Determination of the epoxide equivalent, 382
  - 15.5.3. Determination of the hydroxyl equivalent, 385
  - 15.5.4. Analysis of cured epoxy resins, 385
- 15.6. Characteristics and properties, 387
- 15.7. Additives and fillers for epoxy systems, 389
  - 15.7.1. Diluents, 389
  - 15.7.2. Fillers, 389
- 15.8. Use of epoxy resins for impregnation and surface protection of stone, 391
- 15.9. Mortars and adhesives, 398
- References, 409

## Chapter 16. Unsaturated polyesters, 413

- 16.1. Introduction, 413
- 16.2. Preparation and curing mechanism, 413
- 16.3. Analysis and identification, 415
- 16.4. Properties, 416
- 16.5. Mortars and concretes, 417
- 16.6. Impregnation of stone, 420
- References, 423

## Chapter 17. New possibilities: block copolymers, 426

- 17.1. Introduction, 426
- 17.2. Chemical blends of polymers, 426
  - 17.2.1. Random copolymers, 426
  - 17.2.2. Graft copolymers, 426
  - 17.2.3. Block copolymers, 426
- 17.3. Anionic synthesis of block polymers, 427
- 17.4. Block copolymer characterization, 429
- 17.5. Physical properties of block copolymers, 430
- References, 431

## Part E: Degradation of synthetic resins used in stone conservation, 433

## Chapter 18. Degradation, stabilization and weathering tests on polymers, 434

- 18.1. Introduction, 434
- 18.2. Oxidative degradation, thermal decomposition and protection of polymers, 435
- 18.3. Ultraviolet radiation and photooxidation, 438
- 18.4. Stabilization and protection against effects of UV radiation, 440
  - 18.4.1. Ultra-violet light screens, 440
  - 18.4.2. Ultra-violet absorbers, 441
  - 18.4.3. Quenchers, 441
- 18.5. Natural and accelerated weathering of polymers, 442
  - 18.5.1. Carbon arcs, 443
  - 18.5.2. Fluorescent lamps, 444
  - 18.5.3. Mercury-vapour discharge sun lamps, 444
  - 18.5.4. Xenon arcs, 445

References, 445

Subject Index, 449