Contents

Abstract 1
Introduction 2
- Background 2
- Goals of the masonry-cleaning process 2
- Preliminary testing program 3
  - Water-based cleaning techniques 3
  - Dry cleaning techniques 3
  - Conclusions 3
- Expansion of the masonry-cleaning program 3

Condition of the building stone 3
- Petrology of unweathered building stone 3
- Condition of weathered building stone 4
  - Lightly soiled, smooth 4
  - Lightly soiled, rough 4
  - Gypsum crusted, smooth 4
  - Gypsum crusted, rough 4

Methods and procedures 4
- Framework for study 4
- Measurement tools 5
- Experimental design 5

Cleaning efficacy 6
- Particulate material 6
- Salts 6
- Soiling 7
  - LSS and LSR surfaces 7
  - GCS and GCR surfaces 7

Surface structure before and after cleaning 8
- Friability of the stone before cleaning 8
- Surface fracturing and roughness after cleaning 9

Accelerated weathering of cleaned surfaces 9
- Surface recession and friability of the stone 10
- Surface reactivity to water 11
  - Theoretical summary 11
  - Results 12
  - Effect of surface reactivity to water on global variables 13
- Surface sensitivity to SO_2 and particulate matter 13

Synthesis and interpretation of results 13
- Stone stability 13
- Data-synthesis model 14
  - Soiling load 14
  - Surface microstructure 14
  - Surface recession 15
  - Surface reactivity 15
- Cleaning criteria and selection of cleaning techniques 15
  - Capacity, accuracy, and finesse 15
  - Criteria for removal of soiling load 16
  - Removal of salts 16
  - Removal of soiling 16
  - Criteria for alteration of microstructure 17
  - Surface roughness 18
  - Friability index 18
  - Statistical link between fracture density and surface roughness 18

Contents

Conclusions and preservation strategy 20
Selection of cleaning techniques 20
Summary of testing and analysis 20
Scientific cleaning criteria 20
Cleaning techniques not differentiated by surface recession 20
The role of soluble salts in marble deterioration 20
Surface reactivity 20
Selection criteria: Cleanliness and friability 20
Cleaning techniques that satisfy the selection criteria 20
Alteration of microstructure: Hard versus soft cleaning techniques 21
Cleaning criteria established by preservation architects and conservators 21
Gommage technique 21
Combination technique 21
Armax technique 21
JOS technique 22
Recommendations 22
Specification and monitoring of cleaning techniques 22
Impact of cleaning techniques on the long-term condition of the stone 22
Significance of this study as a model 22
Significance of this study to preservation strategies 22
Acknowledgments 23
References cited 23
Appendix 1. Cleaning techniques and core inventory 23
Surface-soiling conditions 23
Lightly soiled, smooth 24
Lightly soiled, rough 24
Gypsum crusted, smooth 24
Gypsum crusted, rough 24
Choice and description of cleaning techniques 24
Cleaning techniques selected for the first phase of this study 24
Power wash 24
Misting 24
Gommage 24
Cleaning techniques selected for the second phase of this study 25
Combination 25
Armax 25
JOS 25
Laser 25
Dry ice 25
Coring methods 26
Site selection and equipment 26
Use of epoxy to preserve surface soiling 26
Core inventory 26
Appendix 2. Sample preparation, image indexing, and SEM-image analysis 26
Sample preparation 26
Image generation 27
Image indexing 27
SEM-image analysis 27
Hardware requirements 27
Program SEM2BIN 27
Program SHOWPIX 28
Program PROFILE 28

Contents

Calcite and epoxy 28
Program EDGE 29
Appendix 3. Optical microscopy and gray-scale measurements 29
Visual assessment of surface soiling 29
Electronic gray-scale measurements 31
Appendix 4. Salt-penetration measurements 31
Sulfate analysis 31
Methods 31
Applications 31
Sulfate content of the applied resins 31
Sulfate content of soiling on sample surfaces 31
Sulfate content of cracks, fissures, and matrix 32
Appendix 5. Surface-recession test 32
Surface recession based on change in surface level 32
Surface recession based on surface smoothing 32
Appendix 6. Fracture-density measurements and SEM-image-analysis data 32
Appendix 7. Surface-roughness test 33
Appendix 8. Surface-reactivity test 33
Theoretical overview 33
Laboratory implementation 34
Apparatus 34
Test procedure 34
Results 34
Footnotes 35

Figures

1. Typical examples of surface-soiling conditions on Philadelphia City Hall 36
2. State diagram of stone surface, in which each surface-soiling condition is viewed as a unique thermodynamic state 37
3. Generalized cleaning process 37
4. Basic components of stone-weathering model 37
5. Primary deposition and secondary mobilization processes in stone-weathering model 38
6. Experimental design for controlling extraneous variables 38
7. Photomicrographs of typical soiled surfaces in cores series 3 through 6 before and after application of cleaning techniques 39
8. Typical cross-sectional scanning-electron-microscope images of uncleaned cores 41
9. Scanning-electron-microscope images of core samples with gypsum-crusted, rough surface-soiling condition 43
10. Surface reflectivity of soiled stone after cleaning 45
11. Friability of stone, showing near-surface fracture density versus shape factor for all cores before and after cleaning 47
12. Model of soiling-pattern development 48
13. Fracture density versus shape factor before and after cleaning for various surface-soiling conditions 49
14. R^2 value versus surface-soiling condition of stone for data plotted in figure 13 53
15. Model of surface alteration by soiling load 53
16. Output of program EDGE for cleaned side of sample GCRC–1, showing ~278 μm of surface recession 54
17. Surface recession versus friability index for two groups of smooth and rough uncleaned cores 54

Contents

18. Average friability index after application of each cleaning technique for all cores tested..... 55
19. Model of laboratory configuration used for implementation of surface-reactivity tests..... 57
20. Absolute rate of release of Ca^{2+} ions for all cores tested..... 58
21. Absolute rate of release of Ca^{2+} ions versus shape factor for all cleaned cores..... 58
22. Average absolute rate of release of Ca^{2+} ions for each cleaning technique for various surface-soiling conditions..... 59
23. Change in absolute rate of release of Ca^{2+} ions versus surface color for all cores and for various surface-soiling conditions..... 61
24. Model of physical alteration of stone surface by water..... 63
25. Model of factors controlling deposition of salts and particulate matter on stone surface..... 64
26. Integrated model of dominant soiling-agent-delivery and stone-alteration processes..... 65
27. Utility versus surface cleanliness, showing general shape of esthetic-utility curve for the building..... 66
28. Finesse-classification diagrams for various surface-soiling conditions..... 66
29. Finesse-classification diagrams for gypsum-crusted, rough stone, based on a range of target-cleanliness values..... 69
30. Finesse-classification diagrams for various surface-soiling conditions..... 71
31. Approximate shape of projections of general utility curve onto utility/roughness plane for gypsum crusted, rough stone..... 73
32. Utility versus surface roughness for various target-cleanliness values for gypsum crusted, rough stone after cleaning..... 74
33. Fracture density versus surface roughness for uncleaned and cleaned sides of core samples cleaned by different techniques..... 75
34. Summary of statistical data for various cleaning techniques plotted in figure 33..... 82
35. Summary diagram showing criteria used to filter cleaning techniques applied to lightly soiled, smooth and rough stone and gypsum-crusted, smooth and rough stone..... 83
36. East façade of building, south of east portal, showing locations of masonry-testing sites..... 85
37. Ledge outside Room 428, upper and lower scaffold levels, showing lightly soiled marble on ledge and gypsum-crusted areas on projecting cornice and frieze below ledge..... 85
38. South wall, upper scaffold level, showing area of lightly soiled, rough stone..... 85
39. West wall, upper scaffold level, showing area of lightly soiled, smooth stone..... 85
40. North wall, upper scaffold level..... 86
41. Lower scaffold level..... 86
42. South side of building..... 87
43. Ashlar on ledge outside Room 622, showing area of lightly soiled, rough stone cleaned by laser cleaning technique..... 88
44. Ledge outside Room 622, showing back of capital on column..... 89
45. Marble fragment from unknown location on building, showing gypsum-crusted, smooth stone..... 90
46. Marble fragment from unknown location on building, showing lightly soiled, smooth stone after dry-ice cleaning..... 91
47. North wall, upper scaffold level..... 92
48. South wall, upper scaffold level..... 93
49. West wall, upper scaffold level..... 94
50. West wall, upper scaffold level..... 95
51. North wall, upper scaffold level..... 96
52. Entablature, lower scaffold level..... 97
53. Entablature, lower scaffold level..... 98
54. Entablature, lower scaffold level..... 99
55. Entablature, lower scaffold level..... 100
56. Entablature, lower scaffold level..... 101
57. Entablature, lower scaffold level..... 102

Contents

58. Entablature on south side, lower scaffold level 103
59. Entablature, lower scaffold level 104
60. Column base at 6th-floor level 105
61. Detail of column base at 6th-floor level 105
62. Marble fragment from unknown location on building 106
63. Marble fragments from unknown locations on building 106
64. Sample-preparation protocol for core samples selected for SEM analysis 107
65. Summary of SEM image-analysis programs 107
66. Syntax for program SEM2BIN as run from DOS command line 108
67. Syntax for program SHOWPIX as run from DOS command line 108
68. Syntax for program PROFILE as run from DOS command line 108
69. Typical output image from program PROFILE 108
70. Syntax for program EDGE as run from DOS command line 109
71. Brown stain on sample LSRP–6 109
72. Brown stain on sample GCRM–3 109
73. Zoning on sample GCRG–3 110
74. Typical stained area on sample GCRC–5 110
75. Measured color values of core samples 111
76. Electronic exposure time versus F-M color value for grayness measurements on core series 112
77. X-ray-fluorescence spectra of Devcon 5 epoxy resin and L.R. white acrylic resin 112
78. Typical X-ray-fluorescence spectra of uncleaned samples in core series GCR 113
79. Typical X-ray-fluorescence spectra of silicate and iron minerals in uncleaned samples in core series GCS and GCR 114
80. Schematic diagram of system used for surface-reactivity test 115
81. Configuration of alternative apparatus used for surface-reactivity test 115
82. Relative surface activity of samples in core series 3 115

Tables

1. Summary of technical details on four cleaning techniques selected during first phase of this study 116
2. Summary of important operational features of four of the eight cleaning techniques evaluated in this study 118
3. Inventory of core samples from the building 120
4. Inventory of SEM images for computer analysis 124
5. Summary of visual grayness measurements 125
6. Chemical analyses of rainwater in the Philadelphia area 126
7. Semiquantitative analyses of silicate inclusions on soiled stone surfaces 127
8. Estimated surface recession caused by the various cleaning techniques, as measured by two methods 128
9. Results of fracture-density measurements based on SEM-image analysis of core samples obtained in this study 129