Cultural Heritage Science

Francesca Gherardi
Pagona Noni Maravelaki *Editors*

Conserving Stone Heritage

Traditional and Innovative Materials and Techniques

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Editors

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Editors
Francesca Gherardi
Investigative Science
Historic England
Portsmouth, UK

Pagona Noni Maravelaki
School of Architecture
Technical University of Crete
Chania, Greece

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We dedicate this book to Susanna Bracci, for her remarkable contribution and inspiring dedication to heritage science.

Preface

This book intends to provide guidance to heritage stakeholders for the design and selection of materials and techniques for natural and artificial stone conservation, with a focus on cleaning, consolidation, protection, and repair mortars. It aims to bridge the gap between laboratory studies and conservation interventions, by linking together the diverse scientific areas involved in the preservation of stone heritage.

The design and implementation of conservation treatments for historical buildings is a complex and challenging task, as a deep knowledge of the working properties and performance of the available conservation materials and methods is required. The variety of decay patterns often encountered in historical buildings is the result of the use of several types of materials in their construction, which, in turn, are subjected to different micro-environments.

In the past decades, climate change has impacted the decay processes and their kinetics, with the rise in the concentration of air pollutants and the increase in surface recession, erosion, and biofilm formation as a result of more frequent and aggressive precipitations. The changing climate has been affecting the properties and durability of stone substrates, highlighting the crucial role of conservation treatments needed to tackle these problems. In this context, many research studies have been focused on the developments of materials specifically designed for stone heritage conservation, often utilising nanotechnology. Thanks to the possibility to adapt their properties, these innovative treatments are very versatile, and they often display high compatibility with the historical substrates, as well as new functional properties. This book showcases recent developments in the application of new materials, methods, and testing techniques for stone conservation, with a focus on future outlooks.

A great deal of research succeeded in the full characterisation of different classes of products available on the market, as well as newly developed materials for stone conservation. Despite the promising results, only a few studies have included in their design experiments relative to the investigation and monitoring of the changes occurring in the treatments after long-term natural weathering. Indeed, few applications and assessments of the performance of conservation treatments on naturally aged substrates in trial areas in historical buildings are available. The effectiveness of some products can be very different once applied onsite, as environmental and operational factors can affect the application methodology and the curing of the products. The long-term monitoring of conservation treatments is crucial for the evaluation of their suitability for built heritage conservation, in order to provide guidelines for their selection and application.

In the last decades, several groups and national standardisation bodies have been working in the set-up of guidelines and recommendations for the testing and evaluation of materials and methods for stone conservation. However, by comparing the number of European (EN) and American Society for Testing and Materials (ASTM) standards for materials used in the building sector (e.g. concrete, cement, polymeric materials), it is clear that there is still some work to do in the standardisation of protocols and procedures in conservation, especially regarding onsite testing, and the definition of common threshold values for the assessment of their efficacy. In this sense it is particularly interesting to confine the standard guidelines within the framework of reversibility, retreatability, and compatibility, which are the pillars in each conservation treatment.

In some of the case studies illustrated in this book, the selection of a specific treatment able to meet every performance requirement was not possible, due to the substrate characteristics (mineralogical composition, porosity, etc.) and their decay patterns. This is particularly true for the selection of consolidants and protective treatments, whose working properties are sometimes not compatible with historical surfaces. As mentioned above, the concepts of compatibility and reversibility/retreatability of conservation treatments are important requirements for treatments in heritage conservation, and they have been defined and discussed in this book.

To avoid the selection of unsuitable products, a condition survey in each of the areas under investigation should be carried out, aiming to identify the type of stones, their state of preservation, their exposure to the environment, and any past conservation treatments. These studies combined with the setup of treatment trial areas are essential to achieve successful results. The possibility to test several formulations is critical for the selection of the technical parameters (materials, methods, and equipment) and working protocols to be followed. Decision support tools and "incompatibility risks" assessment have been proposed by different scholars to make comparisons among several options and help in the selection of the treatments for the specific case study. In addition to the implementation of these tools, we believe that the collaboration of different professionals (conservators, architects, scientists, etc.) in the decision-making process is important to solve complex problems, and it is instrumental in the success of the conservation interventions. The chapters in this book provide the state of the art on traditional and innovative materials and methods for stone conservation, highlighting current trends and future perspectives. Each of them critically examines one phase of the conservation intervention: preliminary investigations, condition assessment, and mapping of the deterioration patterns; surface cleaning, with a specific focus on laser technology; consolidation; protection; repair mortars and grouts; and onsite assessment and monitoring of conservation treatments.

In Chap. 1, Gulotta and Toniolo present different strategies to carry out the condition assessment of stone surfaces to identify and map the deterioration patterns, by discussing international standards and providing guidelines. As showcased by the reported case studies, this preliminary phase is crucial for the design of the most accurate conservation interventions for built heritage.

In Chap. 2, Maravelaki provides an overview of the main cleaning techniques used in the past and the future trends in cleaning interventions. The importance of the nature of the substrate, deterioration patterns, micro- and macro-environmental factors, specific guidelines, interdisciplinary, and people awareness are discussed. Particular focus has been given on the best methodologies and materials for mechanical and chemical cleaning applied in case studies, while innovative nanogels, nanofluids, poultice, micelle solutions, and microemulsions for stone cleaning and desalination are also described.

In Chap. 3, Pouli introduces the reader to the basic concepts of laser cleaning, while highlighting the critical and decisive parameters that enable the laser light to selectively remove unwanted layers and encrustations from the surface of cultural heritage. The case studies presented are good practices of laser cleaning referring to different substrates, encrustations, and environmental conditions. Emphasis has also been given to the necessity of monitoring the cleaned surface with reliable nondestructive techniques.

Chapter 4 by Delgado Rodrigues highlights the main challenges in stone consolidation. It provides guidelines to the professionals in their decision-making process, by helping to understand complex deterioration patterns in their specific case studies, propose potential solutions, and select and implement the best procedure in terms of materials and methodologies. Some practical examples are discussed, describing issues and factors to consider in order to identify the best solutions.

Chapter 5 by Gherardi gives an overview on properties, effectiveness, and durability of several classes of protective treatments. Indications on performance requirements, working properties, and the criteria for the selection of the materials for specific case studies are discussed. The recent developments in terms of sustainability and environmental impact in the use of innovative technologies and nanomaterials in stone protection are also explored, with recommendations for further studies.

In Chap. 6, Apostolopoulou and Moropoulou present the design parameters of conservation mortars related to compatibility and durability issues. The design takes into account the physico-chemical and mechanical characteristics of the historical materials, as well as the environmental stresses of the monument, the raw materials used, and any architectural or geometric characteristics that influence the performance of the restoration mortars. Principal component analysis (PCA) is a decisive tool to discriminate the most high-performance and compatible restoration mortars.

Chapter 7 by Papayianni deals with repair mortars/grouts for reinstatement of stone units found in archaeological sites, ancient theatres, castles, monasteries, arched bridges, and industrial buildings. The repair mortars/grouts are designed while taking into account the original stone characteristics and the environmental conditions. Improved compositions of the repair materials were designed using additives, ensuring they are compatible to the historic ones in terms of colour, texture, and good adhesion to substrate. The case studies presented confront practical issues of applications and how these can be overcome.

Finally, in Chap. 8, Bracci and Sacchi provide a review on the main invasive/non-invasive techniques used onsite for the evaluation of conservation treatments (cleaning, consolidation, and protection of stone). Testing protocols for the assessment of the effectiveness of the treatments and for the long-term monitoring of their properties are discussed, together with threshold values for the selection of the most appropriate materials and methods to be implemented in the conservation interventions.

While writing this book, we have been discussing several topics and concepts with colleagues and practitioners working in the conservation of built heritage. We are grateful for their time and support, which was fundamental in bridging scientific studies with conservation practice. We would specifically like to acknowledge Thorsten Schneider and Annelies Kersbergen, editors for Springer Nature, for inviting us to publish this book and for their great support during these months; the editorial board of the "Cultural Heritage Science" series; the reviewers for their feedback and comments; and Michael Schredl, for proofreading the chapters.

We would like to give our profound thanks to the authors of each of the following chapters for their excellent work, their perseverance, and their dedication to this book, especially in the challenging past year.

Portsmouth, UK — Francesca Gherardi
Chania, Greece — Pagona Noni Maravelaki
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About the Editors

Francesca Gherardi is a materials scientist in the Investigative Science team at Historic England, Portsmouth, UK. She received a BSc and an MSc in Science and Technology for Cultural Heritage and a PhD in Materials Engineering from Politecnico di Milano, Italy, with a research focused on the setup of nanostructured protective treatments for stone and paint surfaces of Cultural Heritage. She was a research fellow at the Politecnico di Milano and University of Lincoln, UK, where she was involved in several international projects on the development of innovative conservation methodologies for stones, paintings, and textiles. She has contributed to different editorial and scientific boards as a reviewer and has published research papers in peer-reviewed journals, books, and conference proceedings. Her research interests are the analysis of artworks, archaeological objects and buildings, and conservation treatment strategy development.

Pagona Noni Maravelaki has obtained her PhD in Stone Decay and Conservation from the Ca' Foscari University of Venice, Italy, and her diploma in Chemistry from the National and Kapodistrian University of Athens, Department of Chemistry, Greece. She serves as a reviewer in several journals, and she has published numerous research papers (more than 120) in peer-reviewed journals, books, and conference proceedings. Dr Maravelaki is a full professor and the head of the Materials for Cultural Heritage and Modern Building Lab, School of Architecture, Technical University of Crete, Chania, Crete, Greece. Prof Maravelaki specialises in the synthesis of green materials, physico-chemical characterisation, and the application of nanostructured and composite materials for the cleaning, protection, and consolidation of historic monuments, as well as the analysis of cultural heritage materials found in archaeological areas.

Contributors

Maria Apostolopoulou Laboratory of Materials Science & Engineering, School of Chemical Engineering, National Technical University of Athens, Athens, Greece

Susanna Bracci Institute for Heritage Science of National Council of Research, ISPC-CNR, Sesto Fiorentino (FI), Italy

Francesca Gherardi Investigative Science, Historic England, Fort Cumberland, Portsmouth, UK

Davide Gulotta Getty Conservation Institute, Los Angeles, CA, USA

Pagona Noni Maravelaki Materials for Cultural Heritage & Modern Building, School of Architecture, Technical University of Crete, Chania, Greece

Antonia Moropoulou Laboratory of Materials Science & Engineering, School of Chemical Engineering, National Technical University of Athens, Athens, Greece

Ioanna Papayianni Laboratory of Building Materials, Department of Civil Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

Paraskevi Pouli Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Crete, Greece

José Delgado Rodrigues National Laboratory of Civil Engineering, Lisbon, Portugal

Barbara Sacchi Institute for Heritage Science of National Council of Research, ISPC-CNR, Sesto Fiorentino (FI), Italy

Lucia Toniolo Politecnico di Milano, Milan, Italy

Chapter 1
Preliminary Investigations, Condition Assessment, and Mapping of the Deterioration Patterns

Davide Gulotta and Lucia Toniolo

Abstract Although generally assumed as long-lasting and extremely stable materials, natural stones are subjected to complex and interconnected damaging actions over the prolonged exposure time usually associated with heritage sites. Therefore, evaluating and monitoring the state of conservation of the stone surfaces of the built heritage is integral to the design and management of appropriate and effective preservation strategies. This chapter provides a critical overview of different approaches for the condition assessments of the stone surfaces, by examining international standards, guidelines, and methodologies for the identification and mapping of the deterioration patterns. The application of theoretical frameworks to precisely describe and evaluate the actual complex field conditions requires multidisciplinary contributions and an appropriate and sustainable diagnostic support. Selected case studies are also presented to discuss objectives and challenges in applying condition assessment strategies to the long-term evaluation of past conservation treatments, to inform and design suitable conservation strategy for historic façades, and for the preservation of modern architecture.

Keywords Stone conservation · Conditions assessment · Materials mapping · Decay mapping · Damage atlases

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D. Gulotta (✉)
Getty Conservation Institute, Los Angeles, CA, USA
e-mail: dgulotta@getty.edu

L. Toniolo
Politecnico di Milano, Milan, Italy
e-mail: lucia.toniolo@polimi.it

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1.1 Introduction

Although stones can be considered one of the most stable materials used in structures and buildings since prehistoric times, it is well known that they are subjected to natural weathering and deterioration phenomena, potentially leading to dangerous, severe, and sometimes rapid consequences.

The deterioration of stones in buildings and heritage sites is a complex phenomenon that can be due to the interconnected action of physical, mechanical, chemical, and biological causes acting simultaneously and over prolonged periods of time. The deterioration effect is, therefore, the result of different synergic phenomena that concur to change the properties of the material, causing a worsening of its "state of conservation" [1]. Deterioration is largely due to natural causes, but after the mid-twentieth century it has been accelerated due to anthropogenic activity.

The level of deterioration is influenced by both the type of material and its intrinsic properties, especially physical, like porosity and pore size distribution, and chemical, like molecular and elemental composition, in addition to the characteristics of the environment, like microclimatic conditions and air quality. The interaction between material and environment determines the type and the kinetics of the deterioration. It is essential to underline how the anthropogenic contribution can change, and sometimes accelerate, the progress of the decay.

Concerning the general durability of stone materials, low-porosity magmatic and metamorphic rocks containing quartz and siliceous minerals are typically more resistant to weathering. In contrast, sedimentary and metamorphic rocks based on carbonate minerals (calcareous rocks, marbles, marls, and sandstones) of medium-high porosity are generally more susceptible to the natural and anthropic deterioration phenomena due to chemical reactions (such as hydrolysis, acid corrosion, and oxidation).

The stone deterioration mechanisms, according to the different reactivity of specific classes of lithotypes, have been elucidated in the literature from the last couple of decades with details and experimental studies [2].

The recession of the stone surfaces due to rain and wind erosion is a combined mechanical and chemical phenomenon activated by the exposure to rainfall. Water can display its ability as a chemical solvent or hydrolysis agent, according to the specific pH, and at the same time is a mechanical force in the runoff, producing the detachment of surface crystallites. This can be typically observed in many historic buildings in urban areas, where the stone's decorative and architectural elements (columns and capitals, windows and frames, pinnacles and spires, and statues) most exposed to rainfall are subjected to intense erosion. The preservation of the historic fabric in such conditions is particularly challenging. Depending on the specific conservation approach within different cultural environments, the conservation intervention can be targeted towards demanding technical operations, as well as the replacement of the damaged elements with new ones, sometimes with different lithotypes, and relying on not adequate artistic/artisanal level.

Salt crystallization is a particularly dangerous deterioration mechanism that can lead to the disintegration of the microstructure of the stone material, producing patterns like crumbling, flaking, and powdering depending on the mineralogical and micro-structural characteristics of the stone. Even intrusive magmatic rocks, like granites (considered among the most stable stone materials), can indeed suffer from salt crystallization, and the formation of efflorescence and crypto-efflorescence. The crystallization pressure inside the network of small-sized pores can reach hundreds of atmospheres, and disrupt the crystal lattice. The source of salt compounds can be internal or external: they can be dissolved in the rising damp and diffuse into the masonries, derived from the different materials used in the construction, or from runoff and condensation in a polluted atmosphere.

Actually, the most important deteriorating agent is water (liquid, vapor, or ice) [2]. It can penetrate the microstructure of the stone, trigger surface mechanical erosion after rainfall, facilitate the diffusion and crystallization of salts inside the material, and crystallize as ice with increasing volume, resulting in disintegration in cold environments and in the presence of freeze-susceptible substrates. Water is a determinant for the chemical acid attack of pollutants, like CO_2, SO_2, and NO_x, and finally, it is the limiting factor for microorganism colonization and biofilm formation. Water is, therefore, the driving force of the most critical deteriorating phenomena of stones in built heritage. Very slow deterioration phenomena generally occur in dry microclimatic environments, where the main weathering processes are due to thermal excursions in different seasons, with consequent thermal dilation in anisotropic materials, and long-term aeolian erosion.

The kinetics of deterioration depends mainly on the micro-climatic conditions and level of pollution to which the stone material is exposed. The impact of pollution is particularly important in urban areas, where built heritage is most present, and depends on the type and concentration of pollutants [3]. The traditional pollutants, such as carbon and sulfur dioxide, have decreased since the mid-twentieth century, while other rising pollutants, including nitrogen oxides and particulate matter, are nowadays acting as catalysts for the formation of different sulfates that tend to accumulate on the sheltered surfaces [4]. Indeed, the concentrations of sulfates have increased two-fold in built heritage across London over the last 50 years, despite the continuous decrease of gaseous SO_2 in the atmosphere [3]. The same authors report a careful study of the impact of climate and pollution change in the urban environment of London [3], with the progressive build-up of atmospheric nitrogen oxides, describing the possible synergic effects according to different classes of lithotypes. The role of the formation and action of nitric acid (HNO_3) in heavy traffic urban areas was also thoroughly studied in Munich and Mainz, and the recession rate of Portland stone (limestone) has been calculated through the use of dose-response functions, referred to traffic hot-spots and urban background in those cities. The differences in limestone recession rate (micron/year) between hot-spots and the urban background are due to higher concentrations of NO_x and PM_{10} (i.e., suspended particulate matter with diameter equal to or smaller than 10 microns) at traffic-rich sites [4].

Concerning the possible impact of climate change on built heritage and particularly on the conservation of stones, in the last decade, many studies have described the possible consequences of changes in the environmental parameters and air pollution [5], especially in Europe, North America, and Australia. The European Union has promoted the publication of reports that focus on this issue. In particular, Bonazza et al. [6] prepared a reference document that collected the main research efforts to identify the possible impact, and to mitigate or manage the consequences on cultural heritage. The range of natural phenomena that are being altered because of the climate change is wide, but there is consensus on the most relevant factors concerning stone decay: changes in the rainfall regime; increased risk of flooding and enhanced soil moisture content; extreme weather events (winds, rainfall, and storms); temperature and relative humidity increase; and enhanced development of microorganisms and pests [5, 7].

In the northern European countries, for instance, the generally accepted scenario predicts shorter and milder winter seasons with increased precipitations spread across the year. Therefore, cultural heritage management will have to face new challenges in conservation [8]. The temperature increase is expected to be determinant and particularly intense in some areas (3–4 °C in arctic areas); the yearly rainfall is expected to increase by about 5–10%, and extreme rainfall events will be more diffused. The impact of increased rainwater and meltwater, together with shorter drying periods, will allow moisture and liquid water to persist longer inside the building materials [8]. This phenomenon will most likely create favorable conditions for biological growth, such as fungi, algae, and mosses.

Within the community of heritage scientists engaged in the conservation of non-renewable resources, it is rather clear that, in the near future, it will be necessary to implement a sustainable maintenance strategy for the adaptation and mitigation of damages, developing innovative methodologies, and best practices.

Firstly, the need for a multidisciplinary approach in the survey of heritage structures and surfaces, along with the assessment of their state of conservation is still not fulfilled. It requires the collaborative interaction of experts and professionals involved in maintenance projects to create truly multidisciplinary teams composed of site managers, architects, engineers, and heritage scientists, such as geologists, chemists, and conservators. Even if this could seem obvious, the actual presence of such teams in the current practice of built heritage study and conservation, unfortunately, is still very rare, despite the continuous progress in the knowledge and standardization of the process [9]. The management and fruition of non-renewable built heritage sites require a systematic effort based on continuous data collection through monitoring activities and diagnostic studies (Fig. 1.1).

Moreover, any reliable conservation and maintenance project should be based on a condition survey carried out by skilled professionals, supported by an appropriate diagnostic phase. In recent years the implementation of the Historic Building Information Modeling (HBIM) approach for the preservation and management of historic buildings showed a continuous, although slow, progression [10]. The efficacy of BIM tools applied to built resources is well acknowledged among the architects' community: it is a powerful method for sharing, storing, and re-using

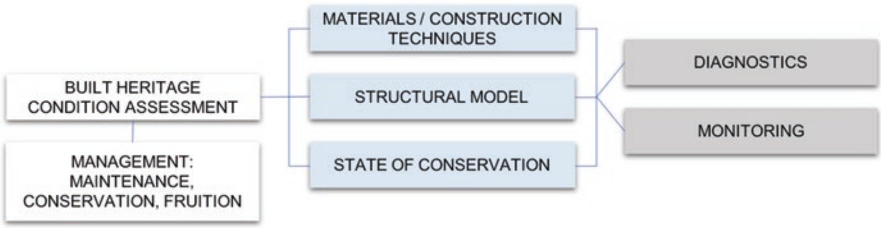

Fig. 1.1 Multidisciplinary approach for built heritage management

information acquired through archival analysis, damage survey, and diagnostic investigation. At the same time, the geometric survey of buildings or archaeological sites (the base for BIM implementation) is becoming more and more sustainable. It can now be achieved with great precision and detail, even in critical conditions, through a wide range of methodologies, including simple and inexpensive technologies [11, 12].

Finally, the conservation practice can rely on more than 30 years of experience and studies on heritage stone materials, including identification and characterization of the material properties, and the assessment of the conservation conditions. At European level, the specific Technical Committee CEN/TC 346/WG 3 – "Porous inorganic materials constituting cultural heritage"[1] is working to draft documents on criteria to select methods and/or products and operating/working conditions concerning the conservation/restoration, repair, maintenance, and preventive conservation work.

Many diagnostic and monitoring methodologies are available to characterize and investigate porous materials of the built heritage. Traditional and more sophisticated or innovative methods have been employed to characterize the materials, according to the relevance and value of the case study. The research on this topic is particularly fertile, although a gap still exists between the number of laboratory techniques available and the still rather limited portable and Non-Destructive Testing (NDT) methods for field application. Recently, a thorough literature review [13] reported a systematic analysis of the instrumental methods applied in the field of architectural heritage conservation, elucidating destructiveness, portability, and typical applications.

[1] CEN/TC 346/WG 3 – Porous inorganic materials constituting cultural heritage https://standards.cen.eu/dyn/www/f?p=CENWEB:7:0::::FSP_ORG_ID:411505&cs=11466D45DFEFF63DD425BA5D9657E4415

1.2 Condition Assessment and Mapping of Deterioration

1.2.1 Objectives of the Condition Assessment and Implications for Conservation

Dealing with stone weathering at historic sites means dealing with complexity. The built heritage surfaces are characterized by the presence of heterogeneous materials, as for the typical compositions and the inherent composite-like nature of the historic masonries' fabric, exposed outdoor for considerably long periods of time. The environmental conditions they are subjected to, and interact with can significantly change over time. The equilibrium between materials and the environment will be modified accordingly, in a continuous process of adaptation. In many cases, change in the activities and human functions hosted in heritage structures, and the deleterious effects linked to periods of disuse and abandonment can also be important drivers of change for materials. Lastly, the actions conducted as part of the regular maintenance of historic sites and the sequence of conservation operations carried out on heritage materials play a crucial role. In particular, cleaning, consolidation, materials integration, and surface protection profoundly affect the overall conditions of a site and, most of the time, further alter the pre-existing equilibrium (or lack thereof, if active damaging mechanisms are at play).

These preliminary considerations have a twofold implication on the condition assessment survey. On the one hand, the materials of historical sites must be considered as complex and layered "palimpsests," for which the existing conditions at a given moment testify the cumulative stratification of changes occurred over time. The recording and interpretation of deterioration patterns, therefore, can improve the understanding of long-term deterioration mechanisms and effects of previous treatments, and ultimately allow for better conservation [14]. On the other hand, any condition assessment is bound to be representative of a specific period in time and, therefore, is necessary that it is updated and revised. This does not diminish the fundamental role of condition assessment in the framework of the conservation practice but, on the contrary, highlights its additional potential as a monitoring tool for tracking and recording changes over time.

As part of the preliminary phases of the conservation activity, the condition assessment of heritage surfaces is integral to the overall documentation process, aiming to increase the level of knowledge and understanding of historic structures (Fig. 1.2), according to the international recommendations and standards [9, 15]. Its primary objective is to accurately record the weathering effects through the alteration and deterioration patterns developed by exposed substrates. Although such effects result from the synergic action of multifactor deterioration mechanisms, the condition assessment focuses only on the observation and documentation of their physical evidence. The information gathered in this phase will, on the one hand, inform on the visible extent and nature of the damage and, therefore, guide the field- and lab-based diagnostic; on the other hand, it will contribute to the preliminary identification of potentially critical areas requiring treatment. It is worth noting that

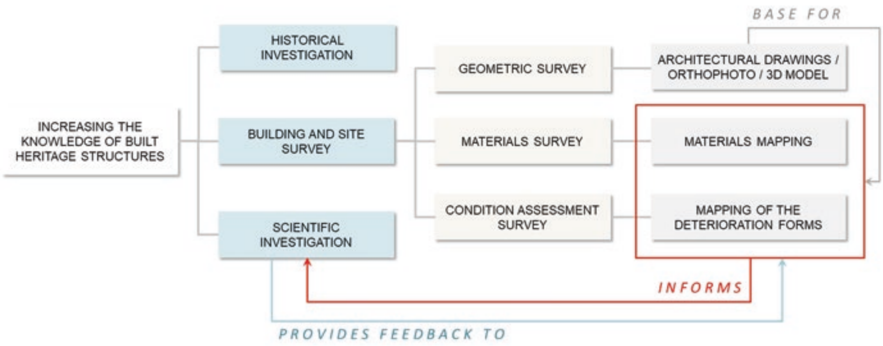

Fig. 1.2 Relationships and outputs (right column) of the condition assessment within the overall process aiming to increase the level of knowledge of the built heritage structures. (Elaborated from Ref. [18])

the precise characterization of the physicochemical deterioration processes belongs to the diagnostic investigation. The qualitative and quantitative data resulting from this further phase will eventually provide feedback to refine the initial interpretation of the damage, following an iterative process. Therefore, according to the medical analogy often employed in conservation studies [16, 17], the condition assessment can be associated with the *anamnesis* phase, as it exploits symptomatic descriptive recording to support the definition of an updated case history, and provides a contribution to reaching an accurate diagnosis [14].

The operative implementation of the condition assessment typically includes a preliminary phase of observation and documentation of the surface conditions onsite, followed by the interpretation and classification of the alteration and deterioration patterns, and a final phase of elaboration and visualization of the weathering effects. One of the most common final outputs of the assessment consists of thematic mappings designed to display all the relevant data on the location and spatial distribution of the different surface conditions documented. Such maps are particularly powerful tools for the broader interpretation of the weathering phenomena when integrated with the information on geometry, exposure, and orientation of the substrates – from the architectural survey – and on materials – from the materials mapping. The overall process, starting from the onsite identification of complex and often intertwined weathering effects, leading to their breaking down into a discreet number of deterioration forms that can be represented effectively on a map, requires a robust and consistent conceptual framework for deterioration classification based on detailed and unambiguous definitions of the physical patterns observed [19].

1.2.2 Methodological Frameworks and Glossaries for the Classification of Deterioration

The Italian Recommendation NorMaL 1/88 represents one of the earliest attempts at defining a shared glossary for the identification of alteration and deterioration patterns of stone materials [20]. The collaborative work between the Italian National Research Council and the former ICR – Institute for Conservation and Restoration (now ISCR) gave rise to a lexicon of 24 terms describing the most typical deterioration forms observed on natural stones, ceramics, and plasters. Each term is associated with a brief description of the main features to support the identification onsite and some representative pictures from real case studies. The list is ordered alphabetically, with neither systematic correlations between the different terms nor grouping according to possible common features. The effort towards a more standardized and operative methodological approach is also testified by the presence of graphic reference patterns associated with each term, to be used for consistent mapping operations. The suggested graphic coding for the thematic mapping theoretically allowed for a better comparison of conservation conditions recorded at different times or sites. On the other hand, such a system suffered from intrinsically limited flexibility that prevented the broad adaptation to the built heritage's highly heterogeneous stone substrates.

The systematic work conducted in the framework of the NorMaL commission, as well as the field experiences in the application of the lexicon, eventually converged into a national standard in 2006 (UNI EN 11182:2006) [21]. The new standard document inherits the overall structure and methodological approach of the former recommendation, as well as most of the terms describing the deterioration patterns. The updated list introduces an additional definition for biologically-induced damage, namely *biological colonization*, and a new term for *graffiti*. The photographic documentation is expanded and illustrates the occurrence of the deterioration patterns on stone, ceramic, plasters, and multi-material masonry surfaces. Still, relevant limitations remain and are related to the absence of logical correlation between weathering patterns according to similarities in the type of damage they cause (e.g., soiling and accumulation of exogeneous materials on the surfaces vs. features induced by loss of materials and/or elements). Consequently, navigating the list of terms is not always straightforward, as they are still ordered only alphabetically. Moreover, the practical usage of the lexicon as a working tool in the field requires a certain familiarity with the specific terminology and field experience. The terms are generally very concisely defined and not always unambiguous. For example, the distinction between *biological colonization*, which involves the visible presence of micro- and macro-organisms, and *biological patina*, which can be interpreted as a thin biofilm, is quite subtle and not entirely immune from a certain degree of subjectivity. Similar considerations apply to *erosion*, one of the main deterioration patterns that can be extensively observed in very different environmental conditions, which is defined as a general loss of material from a relatively sound substrate, irrespectively to the size and features of the detaching particles.

The pioneering work conducted by the “Natural stones and weathering” research group of the University of Aachen starting from the early 1990s provided a more systematic framework for the classification and mapping of weathering forms. The role of onsite observation, identification of the weathering patterns, and mapping is recognized once again as fundamental for the definition of appropriate conservation intervention, as well as for the correct interpretation of the damage mechanisms at play. The methodology is designed to record the weathering conditions according to an objective and consistent approach [22]. The identification of the weathering forms relies on a 4-level hierarchical scheme, corresponding to increasing levels of detail in the damage description: 4 groups of weathering forms (level I), defined with respect to the type of damage displayed by the stone substrate; 29 main weathering forms belonging to the different group (level II); 60 individual weathering forms to define precisely the specific deterioration pattern (level III); a final level (level IV) corresponding to damage categories, allowing to differentiate the type of damage, based on a qualitative scale of intensity ranging from very slight to very severe damage conditions. As weathering is recognized as the final result of a complex and multifactor interaction between the environmental and geo-lithological aspects, any genetically-oriented classification of stone decay is deemed inappropriate. Thus, weathering forms are categorized only according to geometric factors and phenomenological criteria [22]. The role of the documentation of the surface conditions in the overall identification and mapping process is emphasized. Also, the methodology suggests that an integrated assessment of the information on the weathering forms with the lithological mapping can provide insights into possible correlations between stone substrates and specific decay susceptibility.

This approach is developed further by introducing *damage indexes,* integrating the concept of damage quantification into the previously defined weathering categories [23]. Indexes are based on the quantitative evaluation of the damage extent, in terms of the amount of material loss, depth of the surface recession, thickness of detaching scales, etc., balanced against the scale of the building blocks or elements on which it occurs. Their actual applicability is therefore linked to the possibility of executing simple measurements on the exposed surfaces and on the detaching fragments onsite and, ultimately, to the site accessibility. The application of the indexes can potentially extend the capability of prioritizing needs for intervention through risk assessment, from the scale of building façades up to architectural complexes. The methodology has been applied and tested in several case studies to investigate the role of exposure and orientation on the weathering distribution, deterioration “zonation” effects, the differential susceptibility of heritage materials to weathering, and the durability and efficacy of conservation materials and treatments. Large-scale experimentations of the methodology have been conducted at significant monuments and archaeological sites, including ancient monuments in Petra in Jordan, and the Luxor and Karnak temples in Egypt [24, 25]. The translation of the weathering forms into damage indexes is highly site-specific and requires an expert approach, as well as collaborative multidisciplinary contributions. The overall procedure can be considered quite time-demanding, and this may have prevented a more diffused percolation within the conservation professionals working on built heritage complexes and vernacular heritage.

The theoretical approach for investigating, identifying, and mapping the deterioration patterns of the research group of the University of Aachen resonates in the following research and international efforts towards the definition of standardized nomenclatures. In particular, the rationale for the classification criteria of the main weathering groups is reflected in the International Council on Monuments and Sites (ICOMOS) glossary.

In the early 2000s, the International Committee for Stone of ICOMOS (ISCS) stated that the absence of a clear and shared language in stone deterioration and conservation was a limiting factor for effective communication between practitioners and scientific experts, especially considering the inherently multidisciplinary nature of the research in the field. The group focused its activity on the deterioration patterns identification, with the underlying assumption being that a less ambiguous identification and description of the types of damage would also facilitate a broader comparison of conditions between the sites and support the investigation. Based on the examination and revision of existing glossaries and documents, the ISCS working group first published the Illustrated Glossary on Stone Deterioration Patterns in 2008 as a bilingual English/French document 26. Although the preface clearly states that the glossary "does not aim at replacing [pre-existing glossaries], often set up originally in a language other than English, and for most of them done to a high standard", the impact of the document grew significantly over time making it a popular tool for the assessment of deterioration and supporting mapping operation. Besides the advantages resulting from a clearly structured conceptual framework and practice-oriented approach, the diffusion of the glossary has also been promoted by the number of international translations made available over time. Since its first publication, the document is currently published in ten bilingual translations (from English), including Arabic, Czech, Georgian, German, Japanese, Korean, Persian, Portuguese, and Spanish.

The glossary first clarifies a series of general terms associated with stone deterioration, which are often employed in the conservation field as interchangeable. Following the guidelines already reported in the UNI 11182 standard, a distinction is drawn between alteration, i.e., a modification that is not associated with an actual worsening of the material's characteristics, and decay, which describes a chemical or physical change of the material's characteristics to the detriment of its value or leading to an impairment of use. The concept of loss of value is also associated with weathering, which, differently from decay, is defined according to the processes – of different nature – responsible for the modification of the material's properties upon environmental exposure. The perceived evidence of decay, i.e., the physical effects of weathering on the exposed materials, is identified as damage.

The list of deterioration patterns follows a 4-level hierarchical structure, corresponding to an increasing detail in the description of the specific phenomenon (Fig. 1.3). The broader and more general level is organized in families (level 1), which in turn contains the deterioration terms (level 2) with sub-types (level 3), and sometimes additional specific terms (level 4). Such a structure supports the operator

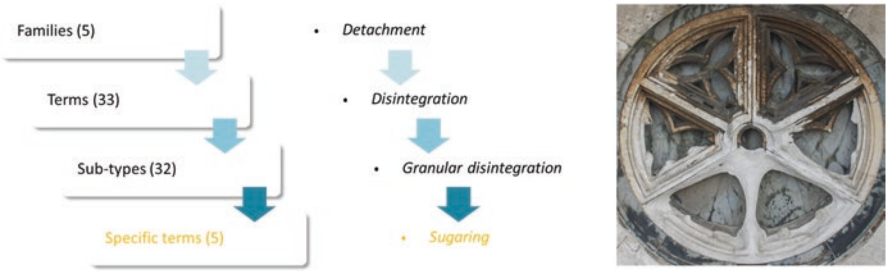

Fig. 1.3 The general structure of the glossary (left, in boxes) and example of one of the hierarchically-defined deterioration pattern identification for sugaring (middle) of a decorative marble element (right, Monza Cathedral, Italy). Specific term definitions (in yellow) are only present in a limited number of sub-types

in navigating the glossary following a logical workflow and allows for progressively in-depth classification of the type of deterioration.

The deterioration patterns are grouped into families according to the main characteristics that can be observed by the naked eye or experienced by limited and simple interactions with the surface (e.g., assessing the superficial cohesion by touching or tapping to detect loss of adhesion or areas of blistering). Therefore, the rationale for classification is entirely phenomenological, as the actual identification of the deterioration processes, as well as the quantitative assessment of the change in the material's properties, is left to the diagnostic. The five families include *crack and deformation*, *detachment*, *features induced by material loss*, *discoloration and deposit*, and *biological colonization*. Each family contains a brief definition of the related terms, describing the main features of the specific pattern to support its correct identification. For the same reason, the glossary points out possible relationships between some of the deterioration patterns and specific substrate's characteristics, such as the centimetric depth that *granular disintegration* can reach in marbles, or to the generally poor adhesion of *efflorescences* to the substrate. To limit the potential uncertainty associated with this task, a list of alternative terms from other glossaries referring to the same pattern follows the definition. Besides contributing to reducing any potential terminological uncertainty, this is a valuable set of information for establishing correlations between surveys executed with damage atlases and stone deterioration lexicons other than ICOMOS. The supporting photographic documentation for each term provides a visual description of the occurrence of the patterns on different substrates and in various exposure environments, using the scale of observation and level of detail to highlight the specific surface changes induced by the decay.

The *crack and deformation* family collects the corresponding deterioration patterns ranging in size and extension from major fractures – crossing entire stone elements – to hair-cracks of sub-millimetric thickness. The term *craquele* is specifically introduced to describe the characteristic presence of diffused networks of micro-cracks. This family also includes a general definition for *deformation*, which applies to a broad range of changes in the overall shape of a stone element (e.g., the typical bowing of slender marble slabs subjected to prolonged thermal stress) in which the structural integrity is still not lost.

Detachment groups all the deterioration patterns associated with an ongoing process of loss of material, which generally involves a reduced mechanical resistance of the substrate. The definitions included in this family are particularly comprehensive and cover a wide range of deterioration patterns in terms of extent, size, and shape of the detaching materials. References are made to some lithological features of the substrate, which are linked to characteristic weathering forms. Such references, for example, clarify the distinction between *delamination* and *scaling*, the former being associated with the presence of oriented layers in some laminated stone, while the latter describes a type of detachment that is not stone-structure related. The glossary also emphasizes the existing connections between some damage mechanisms and the visible formation of specific patterns. Thus, the occurrence of air-filled, hemispherical, and sub-surface loss of adhesion, defined as *blistering*, points to the action of soluble salts. Similarly, the typical shape and location of the loss of material resulting from *bursting* are linked to the development of internal mechanical stresses. These notes included in the definition also inform on the continually evolving nature of weathering. Typically, the onsite progression of salt-induced *blistering* results in the development of cracks once the surface deformation gets close to – and ultimately overcomes – the substrate's flexural strength. A surface loss will then occur, either as *scaling, flaking,* or *delamination*, followed by the exposure of the internal material and, possibly, of the previously concealed salt crystallization. Regarding *bursting*, the glossary highlights that star-shaped face-fracturing formation could sometimes signal the early stage of the formation of this deterioration pattern.

The *features induced by material loss* family differs from the *detachment* one primarily because it describes changes in the substrate's morphological features that are not necessarily related to an ongoing process of loss of material. In such a way, it allows for the identification of a wide range of surface deteriorations even when the primary damage mechanisms are no longer active. This is particularly useful when dealing with substrates characterized by extensive voids, discontinuities (as in the case of *alveolization*), or increased roughness. All these changes are known to increase the potential for further development of additional patterns, including, but not limited to, *soiling* and *biological colonization*. Therefore, the precise identification of deterioration through this family can contribute to the early detection of critical areas where secondary damage development can be expected.

Discoloration and deposit contains terms describing the deterioration patterns due to the accumulation of deposit from exogenous sources (including soot, dust, and materials of anthropogenic origin), the aesthetic alterations, and the secondary formation of by-products triggered by the substrate reactivity in specific environmental conditions. The latter case is characteristic of *black crust* formation, included as a sub-type of the general term *crust*. The impact of this deterioration pattern on the fabric of carbonate substrates and its potential for damage has been extensively investigated by the scientific literature. Its worldwide occurrence in urban and highly-polluted sites still makes it a significant cause of loss of value for the built heritage. The proper identification of *black crust* is therefore crucial, and the glossary provides additional details on the factors required for its activation and progression. Unfortunately, the definition is not entirely exempt from ambiguity, as it does not take into account neither the inherent layered structure of typical black crusts in polluted environments [19] nor the peculiar nature of the damage mechanism that involves a chemical alteration of the outermost substrate. This family also includes terms to describe the different types of *patina*, such as *oxalate patina*, which are defined as the result of natural and artificial alteration processes. The surface formation of soluble salts in the form of *efflorescences* is also listed among deposits. The glossary contains remarks about the crystallization process, as well as the different nature – and related solubility – of the most common salts found on architectural surfaces influencing their adhesion and permanence on the substrate.

All the effects resulting from the activity of living organisms are collected in the *biological colonization* family. This family expands the range of deterioration patterns from previous glossaries offering specific terms to describe precisely the different morphologies of subaerial biological formations. Areas of spot-like colonization or more extensive biological growths are covered with terms ranging from *alga* or *lichen*, up to the identification of actual vegetation, defined as *plant.* This accounts for the variable extent and impact of colonization, including the particularly highly damaging mechanical actions of growing roots within porous matrixes.

To highlight further the potential of the ICOMOS glossary, it is worth exploring in detail the term *erosion*, corresponding to one of the most common patterns affecting stone surfaces exposed outdoors and belonging to the *features induced by material loss* family. This pattern is defined quite broadly as the *"loss of original surface, leading to smoothed shapes."* Such a definition clearly focuses on the ultimate effect on the stone substrate rather than on the mechanisms responsible for it. It can describe a range of macroscopically altered surface conditions as a result of natural or anthropogenic actions, as well as by the synergic effect of both of them. Depending on the nature of the substrate, geometric features, and surface finishing, this pattern can be observed either as a loss of material from border areas, edges, and sculpted details, as in the case of *rounding*, or as an increase of the surface irregularity resulting in *roughening*. The presence of these two sub-types allows for a detailed identification that takes into account some peculiar substrate characteristics. *Rounding* is typically associated with stone suffering from granular disintegration, whereas *roughening* is due to the removal of superficial grains or clusters of particles, and it is therefore emphasized in medium- to coarse-grained substrates. Examples of both subtypes are reported in Fig. 1.4.

The third sub-type within the *erosion* term is *differential erosion.* It describes deterioration patterns observed as a non-homogenous loss of material from the surface due to marked compositional or microstructural variability of the substrate. Therefore, *differential erosion* is typically encountered on sedimentary stones characterized by a layered or composite-like structure (e.g., conglomerates), and mineralogically heterogeneous volcanic stones. The additional sub-division into the

Fig. 1.4 Left, rounding along the edges of blocks of fine-grained Crevoladossola marble (dolomitic marble, Monza Cathedral, Italy) due to the erosive effect of water runoff. Right, roughening of the sculpted decorative element of Candoglia marble (medium- to coarse-grained calcitic marble, Milan Cathedral, Italy) due to the combined action of rain and thermal dilation

specific terms *loss of component* and *loss of matrix* is available for specifying which part of the stone is mostly affected by the weathering effect.

The ICOMOS glossary methodological framework has found vast application on real case studies of built heritage and conservation projects. The classification of the deterioration patterns according to this glossary has been integrated with the historical data, lithological mapping, and the geometric reconstruction of the building phases, as part of the investigation activity and prior to the conservation intervention [27–29]. The additional contribution of portable NDTs and field-based diagnostic has also been explored for characterizing the actual damage extent and monitoring its evolution over time, mostly in cases of deterioration patterns associated with depleted mechanical strength, crusts development, and biocolonization [29–31].

The potential limitations in the use of the glossary include the need for well-trained and experienced operators, as the reliable interpretation of the complexity of the weathering conditions onsite and their classification still represents a difficult task, and its time-demanding nature. Also, although the process of detailed identification of the deterioration patterns according to the ICOMOS framework can effectively inform the scientific investigation activity and, ultimately, support the understanding of the deterioration processes, its integration into the actual conservation practice can be challenging. Delgado Rodrigues [19] pointed out that the breaking-down of the surface conditions into individual mapping units, following the deterioration pattern definitions, may not be an efficient approach in practice, as it cannot be translated directly into specific sets of conservation actions. He proposed the introduction of a new methodology to support the conservation professionals and contractors, possibly complementary to the traditional deterioration mapping, based on the identification of surface units sharing common conservation needs, and therefore requiring a similar set of conservation operations. Sanmartin et al. [32] discuss some potential ambiguities in the use of the ICOMOS definitions when applied to less diffused and low-porous substrates, such as granites. The authors focus on the mismatches between some of the glossary definitions, namely those belonging to the *discoloration and deposit* family, and the investigations conducted on real substrates with stratified covering layers. In conclusion, they suggest opening a discussion to revise and assess the opportunity of redefining some of the terms, to expand the applicability of the glossary to a broader range of materials and conditions.

Other researchers explored alternative approaches for concise and lower time-demanding identification and classification of decay. Thornbush and Viles [33] tested the use of close-range photography and digital image analysis to monitor temporal changes in the deterioration patterns of replaced stone blocks over a 5-year interval. Thornbush [34] later proposed a site-specific stone weathering classification system for limestone surfaces exploiting a high-resolution digital photographic survey. Such a system is meant to be more easily accessible to non-experts with respect to traditional glossaries. It applies to selected weathering forms ranging from the micro- to visible-scale that are classified according to a size-extent index. Inkpen and colleagues [35] proposed the integration of the data on the weathering forms acquired at a range of scales into a spatially referenced information system, as a complementary method to field surveys. They investigated the feasibility of the methodology by using high-resolution photography and historic series of photographic documentation for mapping the surface conditions and the relative change in the deterioration extent, according to a simplified classification scheme.

Recent contributions in the field have been targeting aspects related to the acquisition, visualization, and recognition phases of the weathering forms, exploiting the remarkable advancements of digital technologies. In particular, the potential for remote and rapid field-based recording and mapping of the surface conditions has been explored by close-range Unmanned Aerial Vehicle (UAV) photogrammetry [12] and the use of 360° cameras acquiring spherical images [36]. As the overall process for patterns recognition and classification still represents the most time-consuming phase of the condition assessment survey, innovative approaches have been proposed exploiting digitally-assisted damage detection of surface data from 3D models [37], and machine learning for supervised and fully automated recognition of specific weathering forms [38, 39].

Most of the glossaries and classification methods currently available are oriented towards the comprehensive coverage of the most diffused deterioration patterns, thus aiming for broad applicability in terms of types of substrates and surface conditions. It is worth noting that additional resources have been created to tackle specific conservation issues and damaging phenomena. The thematic glossary for the classification of salt-related damage developed in the framework of the Saltwiki online information structure [40] belongs to this group of resources. The bilingual English/German glossary comprises a list of terms and photographic descriptors of the different deterioration patterns associated with salt efflorescences, defined according to the crystallization features (size, shape, preferential location). Some additional terms are also provided to describe salt-related damage effects on building materials and wall paintings. The "European Illustrated Glossary of Conservation Terms for Wall Paintings and Architectural Surfaces" has been developed in the framework of the EwaGlos project [41]. This multilingual document – originally elaborated in

English with translations to ten European languages – addresses topics related to conditions assessment and provides a brief list of definitions of deterioration patterns focused on decorated surfaces.

1.3 Diagnostic Approaches to Assess the Deterioration of Stone Surfaces

The visual inspection and mapping of the state of conservation of stone surfaces should be complemented with the diagnostic investigation aimed to understand the major causes of decay and support the development of a sustainable conservation strategy.

The diagnostic investigation of the stone surfaces will have, therefore, the following aims:

- knowledge of details of constructive and decorative techniques;
- knowledge of the causes and mechanisms of deterioration;
- assessment of the level of damage;
- prioritization of the conservation actions; and
- identification and development of adequate methodologies for the intervention.

As reported in Fig. 1.5, the diagnostic approach [1] can be composed of three different levels of investigation: *in situ*, when the equipment can be used directly on the built surfaces in a non-invasive or micro-invasive way; in the laboratory, with equipment that requires samples from the stone surfaces; and "monitoring", using non-invasive or micro-invasive equipment, generally *in situ*, for repeated sets of measurements at established time intervals.

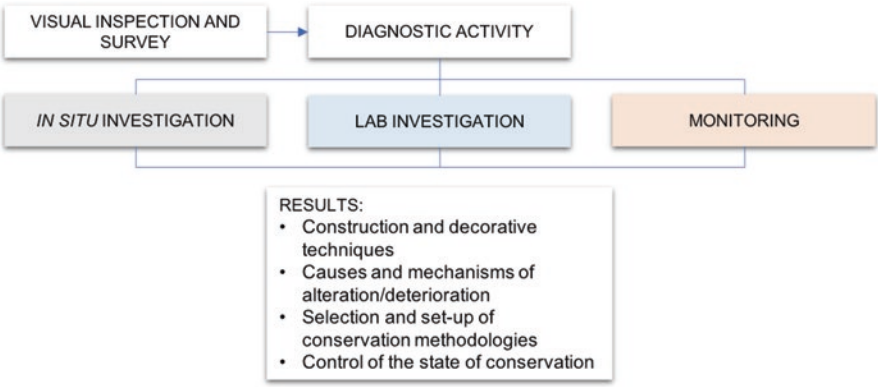

Fig. 1.5 Diagnostic approach for built heritage: three different levels of investigation can be exploited to study stone surfaces

For what concerns the study of the materials, of the details of surface decoration, of the surface stratigraphy due to specific anthropic interventions, etc., the best practice and the current literature indicate that a mix of *in situ* and *laboratory* investigation techniques should be applied to get a comprehensive and satisfactory understanding. In principle, acquiring information with non-destructive methods and avoiding sampling is highly desirable, but it is clear that onsite measurements are often affected by several constraints, including non-standard environmental conditions and surface anomalies, and deposits of extraneous materials. In actuality, physical, chemical, and mechanical characterization of the stone materials should be carried out in standard conditions, according to standard protocols and methods, in order to assess the properties of the material onsite, and sometimes it is necessary to perform a comparative evaluation with similar fresh materials.

A large variety of portable and laboratory investigation techniques are available for the characterization of materials and the study of their state of conservation. All the instrumental techniques have been transferred from materials science and analytical chemistry to the field of cultural heritage diagnostics. They can be differentiated by the technology, sensitivity, precision, and repeatability they offer. Therefore, to get an accurate and affordable diagnostic plan, it is necessary to utilise a variety of techniques, tailoring them to an analytical objective of achieving a sustainable and reliable result. The diagnostic plan is an important part of the survey of built heritage that should be carried out by expert researchers (heritage scientists) in collaboration with architects and heritage managers.

In Table 1.1, the most common instrumental techniques (non-invasive and invasive) are listed according to the materials' properties that they can explore and elucidate. Chemical and mineralogical characterization allows for assessing the composition of stones and materials of neo-formation due to the deterioration processes: the compositional features of the materials are particularly interesting when they are correlated with morphological changes at the visual or microscopic level [13]. Some of the traditional spectroscopic measurements that were previously only done on powdered samples can now be performed directly on the surface of interest (XRD, XRF, FTIR, Raman). Some of the spectroscopic techniques have been coupled with microscopy, and it is possible to localize compositional changes also at the micro and nano-scale (micro-FTIR and Raman, SEM-EDS). The study of neo-formation layers, like deposits, black crusts, and intentionally applied materials, and the knowledge of their origin and causes, is very important to set-up appropriate conservation measures or to design the cleaning strategy of the surfaces [42]. In the last decade, the progress in the application of these techniques allowed for new perspectives and enabled outstanding conservation work.

The development of imaging spectroscopic techniques (Laser-induced spectroscopies; UV-VIS Multispectral Imaging) has delivered a powerful tool to examine stones and decorative elements [43], particularly in the case of polychrome surfaces or remains of polychromies. Infrared thermography applications became a fundamental tool to examine masonries, assess discontinuity in the building structure, and evaluate the water sources and capillary rise inside the stone materials [44]. Numerous recent examples of applications deserve attention [45].

Table 1.1 Most common laboratory and portable instrumental techniques to characterize stone materials

	Field based (portable instruments)	Laboratory based
Chemical characterization		
Elemental composition	X-ray fluorescence (XRF); laser induced breakdown spectroscopy (LIBS)	Energy dispersive spectrometer (EDS); micro-XRF; atomic absorption spectroscopy (AAS); inductively coupled plasma atomic emission spectroscopy (ICP-AES); inductively coupled plasma mass spectrometry (ICP-MS); neutron activation analysis (NAA), LIBS
Molecular composition; functional groups	Fourier-transform infrared (FTIR) spectroscopy; Raman spectroscopy	UV-VIS spectroscopy; micro-FTIR; micro-Raman; FT-Raman; thermogravimetric analysis (TGA, DTA, DSC); chromatography (GC-MS, PyrGC-MS, HPLC, IC)
Physical characterization		
Interaction with electromagnetic radiation – photography and imaging	IR, UV, VIS photography; UV-VIS reflectance spectroscopy; UV-VIS-NIR multi-spectral imaging; IR Thermography	
Microstructural characterization		
Crystalline matrix and surface properties	Water absorption coefficient: “pipette” method at atm. pressure; contact sponge method; contact angle test	Mercury porosimetry; Brunauer-Emmett-Teller (BET) surface area determination; thermal dilatometry; surface roughness, profilometry; water absorption coefficient: capillary, total immersion, evaporation; contact angle
Mineralogical and petrographic characterization		
Minerals composition and characteristics	X-ray Diffraction (portable XRD)	XRD; optical microscopy in VIS polarized light
Morphological characterization		
Surface morphology and microstructure study	Digital microscopy; video-endoscopy	Stereomicroscopy; VIS-UV optical microscopy; confocal microscopy; scanning electron microscopy (SEM); transmission electron microscopy (TEM); atomic force microscopy (AFM); micro computed tomography (μ-CT)
Mechanical characterization		
Mechanical properties, cohesion	Ultrasonic testing (portable); drilling resistance measurement (DRMS)	Laboratory mechanical testing: compressive, tensile, flexural strength

Although methods for the characterization of the crystalline structure, pore size distribution, and mechanical properties provide critical information on the state of conservation of stones of the built heritage, they are used and applied less often. In general, these testing methods require several samples of a given mass and geometry that rarely can be collected from a real case study and are, therefore, carried out on reference sound samples from the quarry.

These tests are used to assess the conservation methods (surface consolidants and protectives) in the framework of standardized testing procedures, but so far, only the application of DRMS is rather diffused and performed *in situ*, and it has found increasing application in the diagnostic of stone surfaces [29, 46, 47]. The test can be used in a comparative way, both to assess the state of conservation of a given surface, and to test the performance of treatments.

Finally, the field investigation of the morphology of stone surfaces at the microscopic level is gaining increasing popularity thanks to the diffusion of video-assisted microscopy and endoscopy that allows studying surface defects, discontinuity, layers, surface treatments and finishing directly onsite. At the same time, laboratory microscopy techniques underwent major development, particularly on digital acquisition and elaboration of images (SEM, TEM and μ-CT), and currently offer a large variety of tools for analyzing, measuring and mapping [48]. Environmental scanning electron microscopy (ESEM) technology for studying construction materials and stones has been extensively developed in the last decades, with particular attention to the interpretation of morphological features [49].

In any case, the diagnostic approach requires extensive experience in the specific field of application, in material science and in the instrumental tools. The diagnostic results, both to address the problem of deterioration and to select and assess the methods for conservation, should be carefully elaborated, and interpreted in the light of the data published in the literature.

1.4 Case Studies

1.4.1 Conditions Assessment Survey as Part of Monitoring and Long-Term Assessment Strategies

The foundation of The Ca' Granda complex in 1456 represents a significant event for the historical, urban, and social development of Milan (Italy), being the first example of a hospital specifically intended for the general population. The construction works spread across three centuries, and the original function of the complex changed over time. Starting from the late 1950s, it has hosted the *Universita' degli Studi di Milano* (University of Milan). The central courtyard's current design is due to Francesco Maria Richini and dates back to the seventeenth century. A continuous columned *portico* frames the four sides of the courtyard. Half-columns are alternated to decorated windows on the two lateral sides on the upper level, while the entrance and opposite ones are designed as an open *loggia* with columns that replicate the alignment and spacing at the ground level (Fig. 1.6a–b). A remarkable sculpted decoration enriches all the architectural elements, in striking contrast with

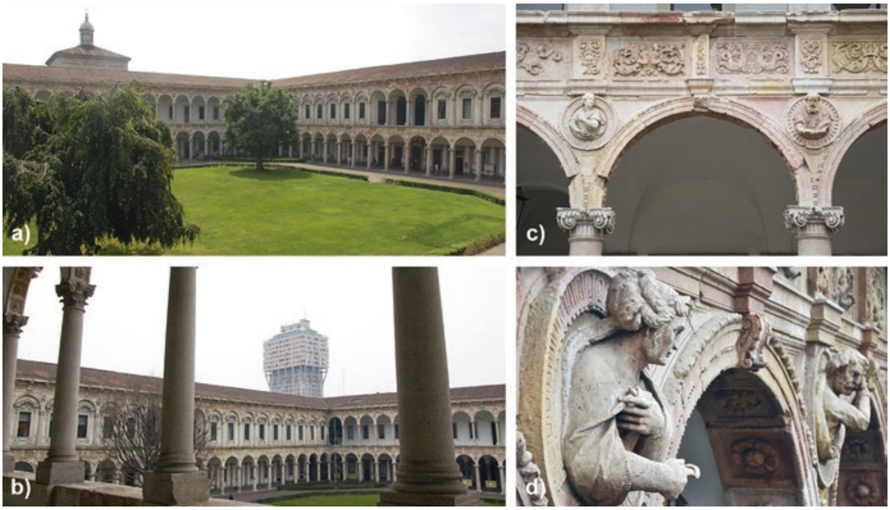

Fig. 1.6 General views of the courtyard showing the NW and NE-facing façades (**a**), and the NE and SE-facing ones (**b**) from the upper loggias; (**c**) the sculpted apparatus made of Angera stone decorating the lower level; (**d**) detail of the high-relief sculpted figures emerging from the spandrels

the sober volumes of the granitic columns. Floreal tiles cover the intrados of the arches, highly detailed bas-reliefs decorate the continuos parapet between the two levels, and high-reliefs with human figures emerge from the spandrels (Fig. 1.6c–d). Except for the columns and capitals, all the sculpted elements are made of *Angera stone*, a local dolostone with a typical color that varies, even within the same block or element, between white, yellow, and pink-orange hues [50]. The *Angera stone* is also a rather soft and porous lithotype, which makes it particularly suitable for sculpted and carved decoration. On the other hand, its characteristic microstructure and mineralogical composition are responsible for its generally low durability. The exposure to urban and highly polluted conditions, in particular, increases the stone reactivity, thus promoting erosive, corrosive, and sulfation processes [51].

The cumulative effects of the problematic conservation history of the site also added up to the intrinsic fragility of the decorative stone apparatus. The World War II bombing of Milan in 1943 caused extensive structural damage, with partial destruction and displacement of the stone elements. A challenging restoration intervention was performed in the aftermath, involving the partial rebuilding of the courtyard's structure and the reconstruction of the decoration by anastylosis. In the 90s, the critical state of conservation of the stone surfaces after decades of worsening of the air quality and increasing pollutant concentration called for a new conservation intervention. A comprehensive supporting diagnostic focused on materials characterization, identification of the deterioration mechanisms, and set-up and control of the conservation methodologies. The full integration of the scientific investigation within the overall conservation activity led to a model conservation project [52].

In 2010, after almost 20 years since the last intervention, a new project was designed with the aim of assessing the long-term performance of conservation methodologies and materials, providing an updated condition assessment of the stone surface, and investigating the new environmental threats. The working team included conservation scientists, chemists, physicists, geologists, biologists, architects, IT engineers, and art historians. The ultimate goal of such a multidisciplinary team was to define guidelines for the monitoring and preventive conservation of the courtyard, and to integrate them into an operative maintenance plan.

The entire courtyard was initially laser-scanned to create a 3D model, and the main architectural views (floor plans, cross-sections, and front views) were extracted. The project required an extremely high level of detail to track the changes in the surface conditions and investigate the weathering evolution. A comprehensive close-range photographic documentation was acquired for every single decorative element (bas-reliefs, arches voussoirs, keystones, and high-reliefs) on a pilot area on each side of the courtyard. The photo-rectified data were then assembled into a high-resolution and metrically correct orthophoto, which constituted the basic cartography for the subsequent operations.

The classification of the deterioration patterns followed the Italian national standard [21]. The type, location, and extent of the weathering forms were studied onsite during several surveys, and mapped on the orthophoto. The condition assessment survey pointed out that the weathering effects were strongly influenced by the overall orientation and local exposure conditions. The North-facing pilot areas generally showed the worst conservation conditions, being affected by diffused efflorescences and salt-related damage, scaling, and crust formation. The deterioration mapping confirmed the correlation between the local geometric features and the occurrence of weathering forms associated with the rain runoff and the accumulation of solid pollutants [51].

Consistent combinations of deterioration patterns were identified and mapped on surfaces directly exposed to the rain – mainly erosion, pitting, bleaching, and encrustation – which differed significantly from those observed on sheltered areas – mainly crust, deposit, disintegration, exfoliation and scaling (Fig. 1.7).

The condition survey was meant to provide the baseline data for future monitoring by non-expert personnel. Therefore, the mapping was integrated by a site-specific atlas of the deterioration forms, structured as a series of single-paged, two-sided working sheets for easy onsite consultation during the periodic surveys. For each deterioration pattern, the atlas provided the general standard definition, a description of the specific features characterizing their occurrence on the four sides of the courtyard, and explanatory notes for the identification, such as possible relationships with correlated damages.

An additional step to further streamline the monitoring process was implementing all the project data on a web-GIS platform specifically developed for built heritage applications [53]. The available historical data from the 1990–1993 intervention were also uploaded, including the deterioration mapping and the precise location of the different conservation treatments. The platform employed the orthophoto of the pilot areas as a spatially referenced base (a local positioning system was defined to

Fig. 1.7 Photographic documentation of characteristic deterioration patterns in sheltered conditions (**a**, crust; **b**, deposit; **c**, exfoliation) and in areas subjected to the rain runoff (**d**, erosion and encrustation; **e**, pitting; **f**, bleaching)

manage the x, z coordinates deriving from the use of a frontal view). The different sets of information were structured as single informative layers that could be selectively visualized (Fig. 1.8). A database section was also present to collect all the alphanumeric data, such as the historical and archival information, the diagnostic results, and the detailed photographic documentation.

There are several advantages in using such an approach. Tracking the evolution of the surface conditions before the previous intervention and after the prolonged exposure could be easily done by visually overlaying the related maps. This highlighted, for example, the presence of thick deposits and crusts on areas that suffered from massive black crust formation in the past, thus suggesting the permanence – and potentially still active role – of the related damage mechanisms. The same applies to the recurrent development of efflorescences and exfoliation issues in previously affected locations. Cross-referencing the data about the past intervention and the updated condition survey is an additional way to support the investigation of the treatments' durability and long term-effects. This sort of information is of great importance not only for the ex-post evaluation, but also when planning for future conservation actions.

As part of the overall preventive conservation and monitoring strategy, the combined application of the atlas and the web-GIS mapping was meant to offer a valuable option to manage and collect the results of the surveys in a time-effective manner. The results of the monitoring activity, as well as the maintenance operation, can be theoretically recorded in real-time using different electronic interfaces and uploaded to a remote server.

The main drawbacks of the platform – and similar systems later proposed – are linked to the use of proprietary software and the reliability of the storage servers. The potential risk of low flexibility and rapid obsolescence deriving from closed source codes cannot be ignored, especially if the actual percolation of the adopted

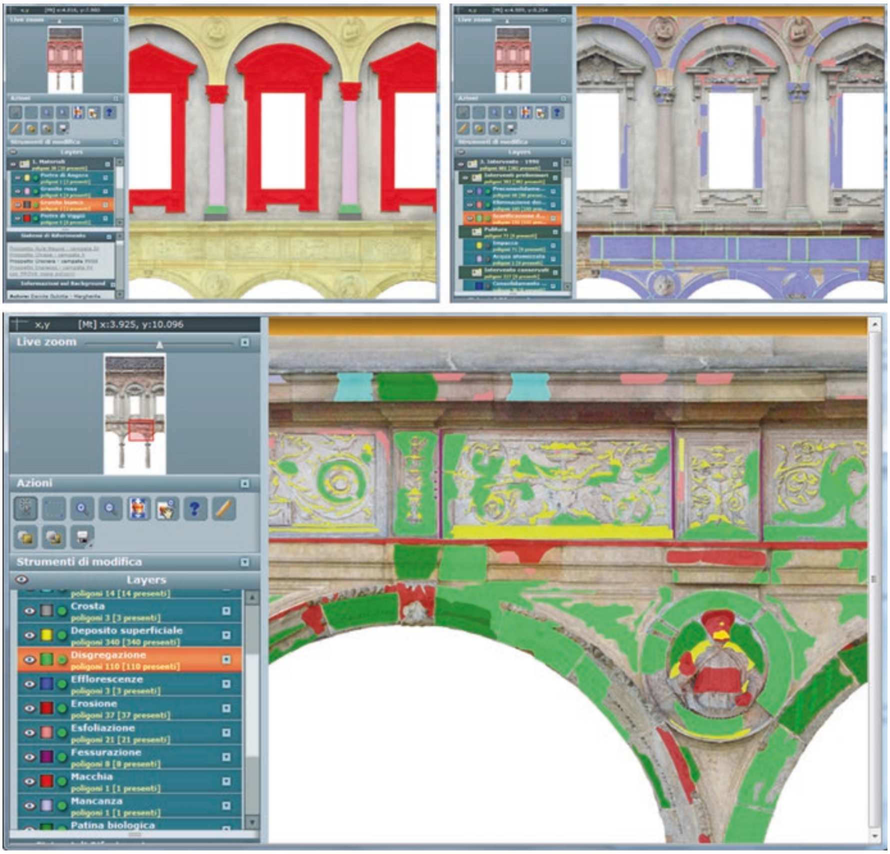

Fig. 1.8 Screenshot of the web-GIS platform for the management of the project's information. Lithological mapping (top left), mapping of the 1990–1993 conservation intervention (top right), and 2010 mapping of the deterioration patterns (bottom). In each panel, the navigation tool and the content manager (controlling the visibility option of the informative layers) are displayed on the left side

systems in the community of conservation professionals is limited. The data management is an additional issue, considering the vast amount of information usually generated during the conservation, monitoring, and maintenance operations. While the uploading process is becoming of lesser concern, as the technological advancements are continually expanding the bandwidth and pushing the data transfer speed, robust and long-lasting data centers or cloud infrastructures are key to the safe storage of the data.

1.4.2 Condition Survey Informing the Overall Conservation Strategy of Historic Façades

The Monza cathedral is a renowned heritage site in Northern Italy, which dates back to the fourteenth century. The main façade was built during several construction phases, following the floor plan configuration changes until its completion in the early twentieth century [54]. The wide range of local stones employed for the architectural and decorative elements, as well as for the sculpted figures of the upper spires, is a unique feature of the site. The lithotypes include different types of marbles, calcitic sandstones, a dolostone, and serpentinites. The local microclimate and the severe pollution conditions characterizing the Padan plain – in particular the highly-developed area centered around Milan and encompassing the city of Monza – provided an extremely challenging environment for the stone materials of the façade. The remarkable materials heterogeneity has been a critical factor influencing the overall site management and the conservation operations, because of the differential response of the various substrates to the prolonged exposure and, consequently, their rather diverse decay evolution. As a result, the historical records report a series of restoration activities conducted starting from the seventeenth century in response to the rapidly evolving weathering of the most reactive substrates. Such activities have profoundly impacted the overall aesthetic configuration. For example, they included a substantial intervention of removal and substitution of the dark slabs of the cladding, made initially of a low-durable black limestone, with a dark-green serpentinite. The last documented intervention dates back to the 1980s, during which cleaning and consolidation targeted the central sector of the façade and the large rose-window.

In 2016, the highly critical state of conservation of the exposed stone substrates pointed out the urgent need for a new conservation intervention. One of the primary and most evident concerns was the extensive soiling of the cladding elements, which significantly impaired the original aesthetic contrast between dark and white-colored rows of blocks. A general loss of mechanical cohesion of several decorative and sculpted elements was also reported, which posed safety issues due to the risk of detachment and falling of stone fragments on the cathedral parvise.

The preliminary assessment was conducted using an aerial work platform, which allowed for the rapid exploration of the stone surfaces of the whole façade up to the spire level, located roughly 36 meters above ground level. The information acquired during this phase, supported by the photographic documentation, provided the baseline data for the first identification of the weathering effects, their location and relationship with the architectural surfaces, and the areas displaying particularly critical conditions (Fig. 1.9b–d).

The site constraints were also identified. These included the overall accessibility for the metric survey and the condition assessment, and the request to minimize the cost and impact of the scaffolding on the Cathedral visitation, at least during the preliminary investigation. The resulting conservation plan was designed and managed in phases: (i) historical investigation of the whole complex, identification of

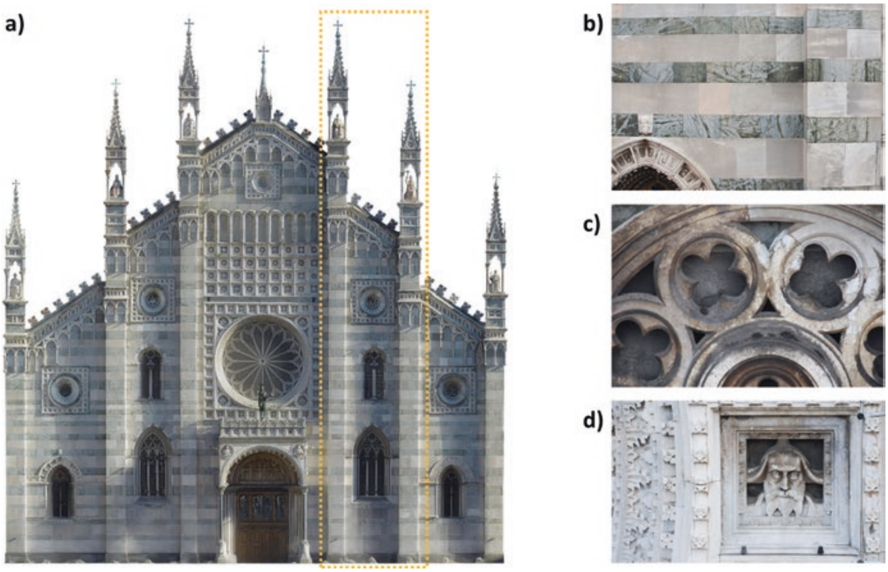

Fig. 1.9 (**a**) Orthophotographic documentation of the façade with the location of the pilot site area (yellow frame) and preliminary documentation of the weathering effects with aerial work platform: (**b**) diffused darkening of the stone cladding, (**c**) areas of crust formation, disintegration and loss of material, (**d**) detail of the intense soiling of the sculpted decorative elements framing the rose-window

the construction phases and past conservation interventions, and geometric survey of the façade; (ii) selection of a highly representative area (as for the various types of materials, geometrical features, exposure conditions, and weathering forms) for the implementation of a pilot site for materials' identification, deterioration patterns mapping, and set-up of the trial conservation methodologies; (iii) scale-up of the lithological mapping and condition assessment to the entire façade; (iv) revision and scale-up of the conservation methodologies to the entire façade (according to the corpus of information from phase iii), identification of the areas requiring specific sets of treatments, and cost estimation; (v) elaboration of the final conservation project [18].

Given the specific site requirements, the geometric survey followed a photogrammetric approach by UAV. The main architectural views were then derived from the orthophoto (Fig. 1.9a) and used as a highly-detailed cartographic base (up to 1:20 scale) for all the subsequent mapping operations. The pilot site area was established in the left sector of the façade, roughly 3.5 meters wide and encompassing the total height. In this area, a metal scaffolding was set-up for the documentation and onsite investigation. The close-range observation of the surfaces, supported by digital microscopy, allowed for the identification of the different lithotypes. Some recurrent correlations were found between materials' usage and architectural features. The dolomitic marble from *Crevoladossola* is consistently employed as slabs for the light-colored rows of the cladding, with some *Candoglia* marble elements (a local calcitic, medium- to coarse-grained marble) occasionally used for replacements (Fig. 1.10). Similarly, the dark-colored rows are made of a single type of dark-green serpentinite (*Oira stone*). Additional correlations were also identified with the building evolution, such as the prevailing use of *Candoglia* marble for the spires and top decorative elements, which all belong to the latest construction phase. Such correlations proved extremely important during the scale-up of the lithological mapping from the pilot area to the whole site, providing an additional set of information to support, and confirm the photographic- and photogrammetric-based identification of the materials used at the scale of the façade.

The onsite condition assessment was firstly conducted in the pilot area and then extended to the whole surface exploiting the highly-detailed photogrammetric

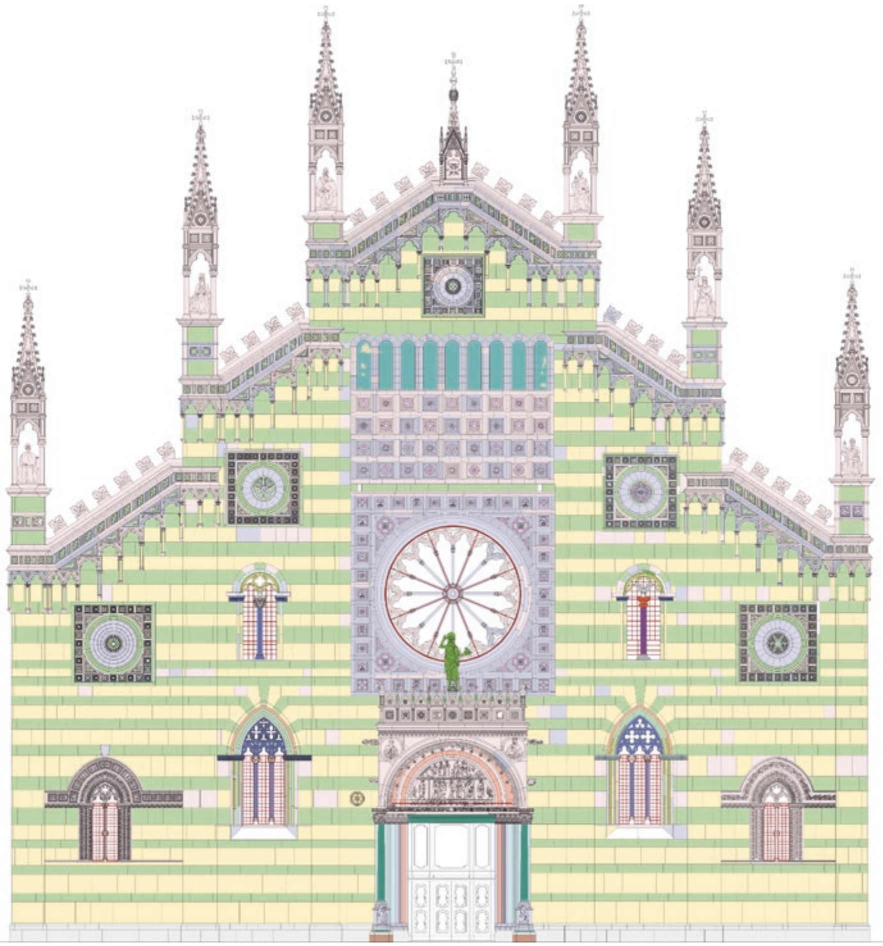

Fig. 1.10 Lithological mapping, showing the consistent usage of dolomitic marble and serpentinite for the cladding (yellow and green areas, respectively), and Candoglia marble for the spires and top elements (pink areas). Original scale 1:50

documentation. The standard Italian terminology was employed for the classification of the deterioration forms [21],[2] after naked-eye and microscopy observations. As expected, the type of exposure played a crucial role in the damage development. Crust formation and surface accumulation of deposits of different nature and variable degrees of adhesion to the substrate were diffused on the stone element in sheltered conditions. By contrast, erosion and all the patterns involving loss of material were generally observed in areas affected by rain runoff. The subsequent phase of mapping the deterioration patterns confirmed the strong location-dependency in the distribution and extent of the damage effects and provided preliminary input on the most likely weathering mechanisms at play. Extensive biocolonization and biofilm formation were concentrated on the top elements of the façade and the spires [55]. Such a preferential distribution is linked to the particularly favorable humidity conditions due to the direct exposure to the rain. The prolonged water runoff and the related chemical and mechanical erosive actions are also responsible for enhanced roughness of the substrate, which is a known factor further promoting biological growth.

The correct interpretation of what was initially labeled as soiling of the cladding proved challenging, as the survey clearly showed that its features did not entirely match the standard definition. According to the UNI-EN 11182:2006 standard [21], soiling consists of deposited material having exogenous origin (including dust, soot, and soil), variable thickness, and, generally, low adhesion to the substrate. On the contrary, the close observation of the surface indicated that the darkening effect was deeply embedded into the stone matrix. A reduction in the cohesion was also associated with the surface change, with loss of material as sanding, which was not consistent with a deposition phenomenon. The final classification was achieved through the integration of lithology, geometric data, and mapping of the weathering effects on the façade. The darkening was only concentrated on the white marble slabs, whereas the serpentinite ones were not affected. Its distribution was uneven, with increasing intensity towards the lower sector of the façade (Fig. 1.11). This pattern was ultimately defined as a discoloration, thus focusing on the main physical evidence of the weathering action, in association with erosion, where the loss of material and increase surface roughness was particularly noticeable. The damage mechanism involving inter- and intra-granular chemical corrosion of the stone matrix and soiling of the newly formed micro-cracks was later unveiled by the diagnostic investigation, which confirmed the role of the substrate mineralogy and rainwater percolation linked to the exposure conditions.

The thematic mappings were integral to the design of the final conservation plan and, in particular, informed the selection of the operative approaches and treatment procedures. The complexity of the overall condition assessment – laid out in the mapping of the weathering forms – required a clear graphic representation to become an effective working tool for conservators and contractors. To this end, the deterioration patterns were grouped according to their characteristic distribution on

[2] Here translated according to the most similar terms available in the ICOMOS glossary.

Fig. 1.11 Mapping of the deterioration patterns, showing the preferential distribution of the discoloration pattern on the with marble rows of the cladding (see Fig. 1.9 for reference) and its increasing extent towards the lower sector of the façade. Color key: discoloration, grey areas; erosion, orange areas; differential erosion, yellow areas; crack, purple areas; fracture, red lines. Original scale 1:50

the façade (localized vs. widespread patterns) and similarities in the set of conservation actions they required (e.g., stabilization > cleaning > consolidation; mechanical removal > biocide treatment > cleaning > surface protection). The condition survey was graphically represented at a 1:20 scale, breaking down the deterioration patterns information into four executive drawings: (i) disintegration, scaling, exfoliation, staining; (ii) discoloration, erosion, differential erosion, crack, fracture (Fig. 1.11); (iii) crust, black crust, efflorescence, patina, oxalate patina; (iv) biological colonization, deposit, soiling.

1.4.3 Condition Assessment for the Preservation of Modern Architecture

The "new" seat of the "Società Umanitaria" is located in downtown Milan and is an important complex of modern rationalist buildings by Giovanni Romano and Ignazio Gardella architects, built in the post-war years 1947–56, and published on "Casabella" in 1957 [56]. The complex is devoted to the educational aims of the homonym nonprofit organization, hosting a professional school composed of several buildings according to the different functions: classrooms, heavy and light laboratories, school of books, administration, and "convitto" (students' dorms). In the same squared area, the "Società Umanitaria" is complemented by the Renaissance complex of the Church and Monastery of the Peace.

Recently, the conservation state of the building "Convitto", which changed function in the last decade as the Milan Prosecutor's offices, was carefully examined and assessed, aiming to set up a rehabilitation and conservation project of the outstanding architectural evidence, and recover its original function as students' residence.

The visual examination methodology was transferred from traditional historical buildings to the modern concrete structure, including the use of the ICOMOS lexicon [26] for the identification of the weathering patterns of the reinforced concrete elements: the investigation of the deteriorated reinforced concrete pillars and the assessment of the extent of carbonation and corrosion phenomena were crucial to identify an effective conservation strategy [57, 58].

Concerning the construction materials, the building is based on a very simple reinforced concrete structure (Fig. 1.12), where vertical pillars and floor slabs emerge directly on the façade and have been exposed to the environment for more than 60 years.

These elements show a typical general erosion of the surface due to the rainfall, and diffused detachment and loss of material that can be defined "bursting" due to corrosion and expansion of the steel rebars inside the concrete [26]. In some areas, these lacunas have been integrated with cement mortar patching that looks different (Fig. 1.12, grey areas in the light yellow vertical pillars), and are quite diffused along the pillars, both in the east elevation and in the lower part of the west façade. These patch repairs (Fig. 1.13 shows a comparison of the original and integration concrete where the difference in the homogeneity of the two materials is clearly visible) demonstrate their failure with diffused new cracks, detachment and bursting (Fig. 1.14a); in many areas, the corroded rebar is exposed because of the spalling of the concrete covering due to the expansion of corrosion products (Fig. 1.14b).

Although the visual examination clearly points out that the concrete covering the rebar has been carbonated and the steel rebar is no longer passivated, the whole structure should be carefully examined through a comprehensive diagnostic procedure [57]. The diagnostic should at least include the measurement of the concrete coverings' thickness, determination of the carbonation level, the possible presence of chlorides in the concrete, and the assessment of the rebar's generalized corrosion.

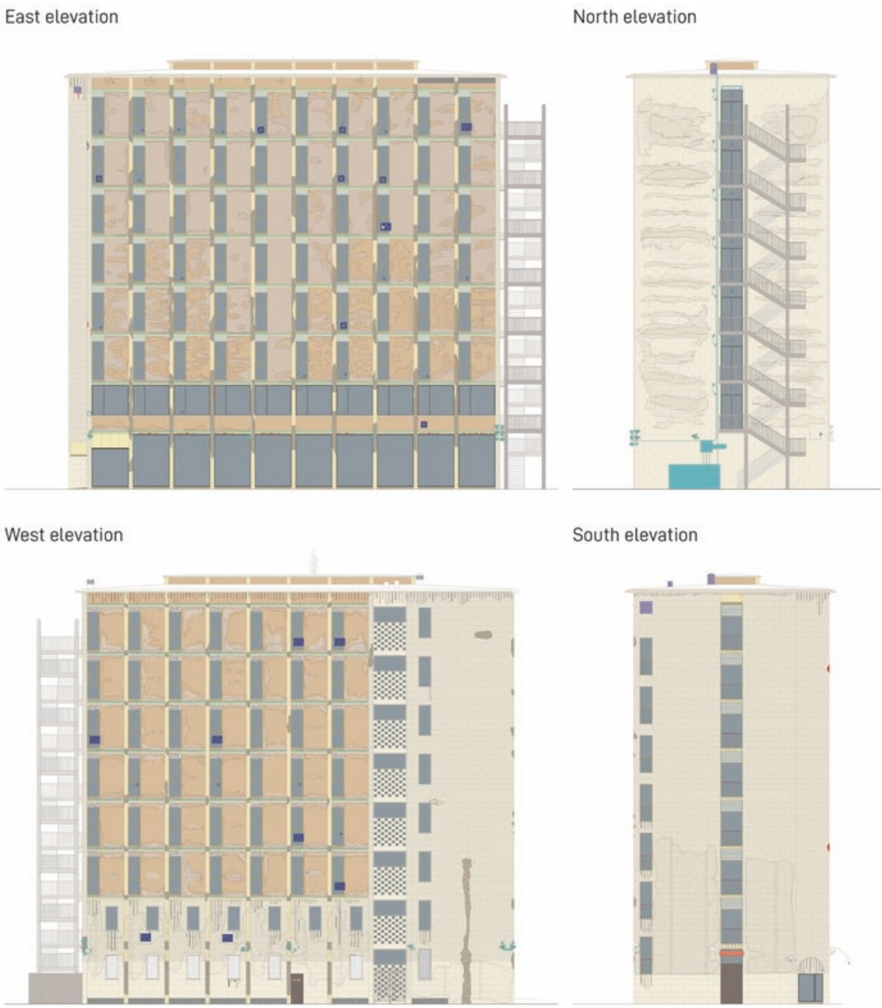

Fig. 1.12 "Convitto" by G. Romano, 1956. Mapping of materials and the deterioration patterns, original scale 1:100. Color key for materials: light yellow-reinforced concrete vertical pillars; light grey- "graniglia martellinata" hammered cement grit plaster; ochre-cement plaster with almond color silicate paint; green-copper water flashings; black and white-glass block. (Courtesy of Dr. Stefano Evangelista, MSc Thesis, Politecnico di Milano 2020)

The plastering of the façade has been carried out with two different materials and finishings that emphasize the partition of the building in the two distinctive volumes hosting the main functions, namely stairs, elevators and services, and students' rooms (Fig. 1.12, the west elevation's lower right part; left part with the windows). In the right part of the west elevation, and in the north and south elevations, the masonry is covered with a grey hammered cement grit plaster (*in italian* "graniglia martellinata", as found in the original notes of the project by Romano). It is a sort

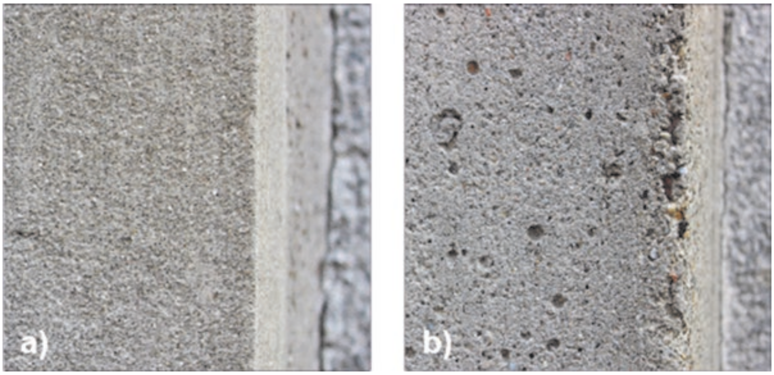

Fig. 1.13 New concrete repairs along the vertical pillars of the structure visible on the façade: comparison between the original compact concrete (**a**) and the new integration concrete (**b**)

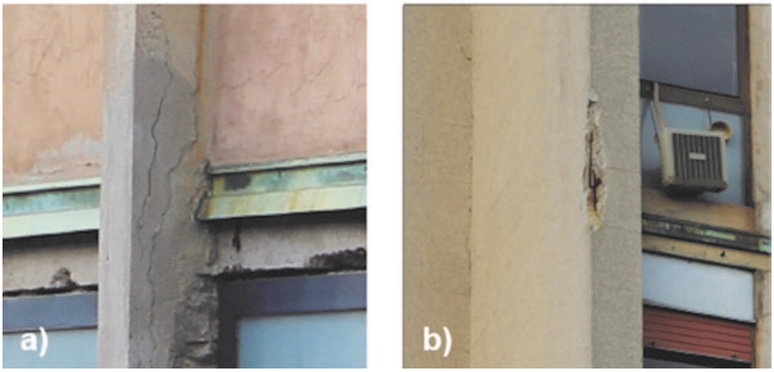

Fig. 1.14 Concrete integration patches along the vertical pillars with new formation cracks (**a**); areas along the pillars with exposed corroded steel rebar (**b**)

of artificial stone, a mortar mix using cement as the binder agent and mixed marble fragments as aggregate; the surface was hammered after hardening and smoothing, and underlined with incisions that simulate stone slabs. This surface is in a very good state of conservation and affected by minor alterations: deposit and soiling, mild surface erosion, formation of few micro-cracks, and both erosion and exfoliation of the paint layer applied, most likely, in recent times (Fig. 1.15). The application of this good quality plastering (resembling a stone cladding) proved to be very durable.

The plaster used for the rest of the façade of Convitto is a cement mortar decorated with an almond colored paint for the external render, which is most likely a silicate paint with an additional polymeric binder. Unsurprisingly, after such a long period without any maintenance work, this render is in a rather bad condition, with deep surface erosion of the paint layer, diffused detachments of the plaster and lacunas where the detached parts have fallen down. The characteristic copper flashings,

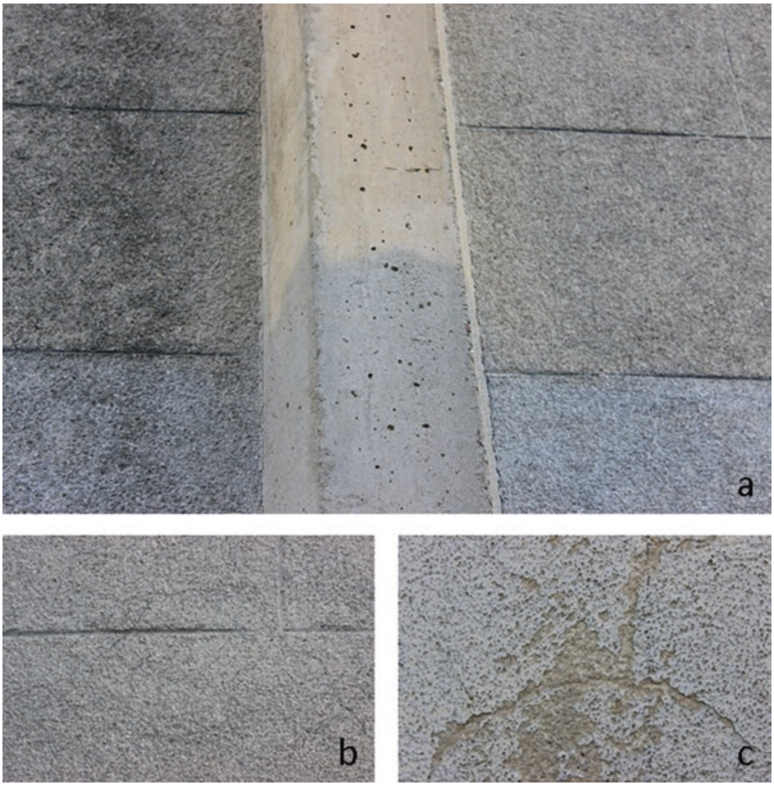

Fig. 1.15 "Graniglia martellinata": (**a**) grey hammered cement grit plaster applied around the concrete pillar; (**b**) evident white marble clasts, intentional incision and a network of hair-cracks; (**c**) light grey painting layer over the plaster

that mark off the horizontal flooring, have been passivated with a copper-green sulfate patina, although sometimes they have been deteriorated by deep localized corrosion and are covered by a dark black crust.

1.5 Conclusions

Preliminary investigation, condition assessment, and mapping of the deterioration patterns are key to the overall process of understanding and documenting stone heritage sites. Moreover, the information gathered during these phases informs the design of the overall diagnostic and monitoring activity and, in turn, provides positive feedback to strengthen the identification and interpretation of the deterioration processes. As a result, the preliminary investigation becomes dramatically important to develop coherent and effective conservation of monuments and structures.

The knowledge phase can rely on a large corpus of scientific literature built up in decades of research that have extensively elucidated most of the deterioration causes and mechanisms affecting stone substrates. Nevertheless, as the globally-changing climatic scenario is expected to alter the established and known interactions between heritage stones and the environment, the conservation community will face new threats and unprecedented challenges.

The role of the condition assessment will be, once again, fundamental for tracking the physical impact and extent of such changes and monitoring the long-term response of heritage materials. The toolkit of equipment and methodologies available to heritage scientists and conservation professionals has improved significantly in the last years, particularly in regards to the resources for the geometric survey, data visualization, and production of 3D models. New experiences shared among heritage scientists call for a more consistent interdisciplinary dialogue and broader diffusion of the outputs to the extended conservation community. For example, in the framework of the European Community program Horizon 2020, many important projects have developed instruments and advanced technological solutions in close collaboration with conservation institutions and industrial partners. However, the research outputs and the related "good practices" still percolate very slowly to field practices, and the investment for successful innovation and growth is scarce.

The examined case studies have elucidated practical methodologies for the condition assessment of stones and artificial materials like mortars, plasters, and renders. The critical review of the standards and glossaries for the classification of the deterioration patterns has clarified advantages and possible limitations in using these powerful tools.

The research perspectives in this respect may unfold in several directions, including:

- exploring methodological approaches to increase the objectivity of damage identification and weathering quantification, possibly allowing for better cross-site exchange and comparison of the condition survey data;
- expanding the field-based toolkit to increase the potential of *in situ* investigation for condition assessment, and ultimately contributing to model deterioration phenomena based on more robust field datasets; and
- refining existing approaches and investigate innovative solutions (including AI-assisted, digital "twins" and DL-based options) to improve the condition assessment and monitoring sustainability.

References

1. Siegesmund S, Snethlage R. Stone in Architecture: Properties, Durability. Springer Berlin Heidelberg; 2011.
2. Steiger M, Charola AE, Sterflinger K. Weathering and deterioration. In: Siegesmund S, Snethlage R, editors. Stone in Architecture. 2011.

3. Basu S, Orr SA, Aktas YD. A Geological Perspective on Climate Change and Building Stone Deterioration in London: Implications for Urban Stone-Built Heritage Research and Management. Atmosphere. 2020;11(8):788.
4. Auras M, Beer S, Bundschuh P, Eichhorn J, Mach M, Scheuvens D, et al. Traffic-related immissions and their impact on historic buildings: implications from a pilot study at two German cities. Environmental Earth Sciences. 2013;69(4):1135–47. https://doi.org/10.1007/s12665-013-2276-4.
5. Fatorić S, Seekamp E. Are cultural heritage and resources threatened by climate change? A systematic literature review. Climatic Change. 2017;142(1):227–54. https://doi.org/10.1007/s10584-017-1929-9.
6. Bonazza A, Maxwell I, Drdácký M, Vintzileo E, Hanus C. Safeguarding cultural heritage from natural and man-made disasters: a comparative analysis of risk management in the EU. Luxembourg: Publications Office. 2018.
7. Brimblecombe P. Refining climate change threats to heritage. Journal of the Institute of Conservation. 2014;37(2):85–93. https://doi.org/10.1080/19455224.2014.916226.
8. Carroll P, Aarrevaara E. Review of Potential Risk Factors of Cultural Heritage Sites and Initial Modelling for Adaptation to Climate Change. Geosciences. 2018;8(9):322.
9. CEN (2012). EN 16096. Conservation of cultural property – Condition survey and report of built cultural heritage. European Committee for Standardization.
10. Bruno S, Fatiguso F. Building conditions assessment of built heritage in historic building information modeling. International Journal of Sustainable Development and Planning 2018;13:36–48.
11. Ottoni F, Freddi F, Zerbi A. From "models" to "reality", and return. Some reflections on the interaction between survey and interpretative methods for built heritage conservation. ISPRS – International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences. 2017;XLII-5/W1:457–65. https://doi.org/10.5194/isprs-archives-XLII-5-W1-457-2017.
12. Russo M, Carnevali L, Russo V, Savastano D, Taddia Y. Modeling and deterioration mapping of façades in historical urban context by close-range ultra-lightweight UAVs photogrammetry. International Journal of Architectural Heritage. 2019;13(4):549–68. https://doi.org/10.1080/15583058.2018.1440030.
13. Zhao C, Zhang Y, Wang C-C, Hou M, Li A. Recent progress in instrumental techniques for architectural heritage materials. Heritage Science. 2019;7(1):36. https://doi.org/10.1186/s40494-019-0280-z.
14. Matero FG. Managing Change: The Role of Documentation and Condition Survey at Mesaverde National Park. Journal of the American Institute for Conservation. 2003;42(1):39–58. https://doi.org/10.1179/019713603806112895.
15. ICOMOS. Principle for the analysis, conservation and structural restoration of architectural heritage. 2003.
16. Warke PA, Curran JM, Turkington AV, Smith BJ. Condition assessment for building stone conservation: a staging system approach. Building and Environment. 2003;38(9):1113–23. https://doi.org/10.1016/S0360-1323(03)00085-4.
17. Smith BJ, Přikryl R. Diagnosing decay: the value of medical analogy in understanding the weathering of building stones. Geological Society, London, Special Publications. 2007;271(1):1–8. https://doi.org/10.1144/gsl.sp.2007.271.01.01.
18. Gulotta D, Toniolo L. Conservation of the Built Heritage: Pilot Site Approach to Design a Sustainable Process. Heritage. 2019;2(1):797–812.
19. Delgado Rodrigues J. Defining, mapping and assessing deterioration patterns in stone conservation projects. Journal of Cultural Heritage. 2015;16(3):267–75. https://doi.org/10.1016/j.culher.2014.06.007.
20. CNR-ICR (1988). NorMaL 1/88. Alterazioni Macroscopiche dei Materiali Lapidei: lessico (Macroscopic alterations of stone: lexicon).
21. UNI-EN (2006). 11182. Cultural heritage. Natural and artificial stone. Description of the alteration. Terminology and definition.

22. Fitzner B, Heinrichs K, Kownatzki R. Verwitterungsformen an Natursteinbauwerken – Klassifizierung, Kartierung und Auswertung/Weathering forms at natural stone monuments – classification, mapping and evaluation. Restoration of Buildings and Monuments. 1997;3(2):105. https://doi.org/10.1515/rbm-1997-0204.
23. Fitzner B, Heinrichs K. Damage diagnosis on stone monuments – weathering forms, damage categories and damage indices. 2001.
24. Fitzner B, Heinrichs K, Bouchardiere DL. Weathering damage on Pharaonic sandstone monuments in Luxor-Egypt. Building and Environment. 2003;38(9):1089–103. https://doi.org/10.1016/S0360-1323(03)00086-6.
25. Heinrichs K. Diagnosis of weathering damage on rock-cut monuments in Petra, Jordan. Environmental Geology. 2008;56(3):643–75. https://doi.org/10.1007/s00254-008-1358-1.
26. ICOMOS-ISCS: Illustrated glossary on stone deterioration patterns I ICOMOS-ISCS: Glossaire illustré sur les formes d'altération de la pierre. Paris: Monuments & Sites; 2008.
27. Stefani C, Brunetaud X, Janvier-Badosa S, Beck K, De Luca L, Al-Mukhtar M. Developing a toolkit for mapping and displaying stone alteration on a web-based documentation platform. Journal of Cultural Heritage. 2014;15(1):1–9. https://doi.org/10.1016/j.culher.2013.01.011.
28. Al-Omari A, Brunetaud X, Beck K, Al-Mukhtar M. Preliminary digital health record of limestone walls in Al-Ziggurat, Al-Nimrud city, Iraq. Journal of Cultural Heritage. 2015;16(5):737–40. https://doi.org/10.1016/j.culher.2014.11.005.
29. Theodoridou M, Török Á. In situ investigation of stone heritage sites for conservation purposes: a case study of the Székesfehérvár Ruin Garden in Hungary. Progress in Earth and Planetary Science. 2019;6(1):15. https://doi.org/10.1186/s40645-019-0268-z.
30. Akoglu KG, Kotoula E, Simon S. Combined use of ultrasonic pulse velocity (UPV) testing and digital technologies: A model for long-term condition monitoring memorials in historic Grove Street Cemetery, New Haven. Journal of Cultural Heritage. 2020;41:84–95. https://doi.org/10.1016/j.culher.2019.07.015.
31. Pozo-Antonio JS, Puente I, Pereira MFC, Rocha CSA. Quantification and mapping of deterioration patterns on granite surfaces by means of mobile LiDAR data. Measurement. 2019;140:227–36. https://doi.org/10.1016/j.measurement.2019.03.066.
32. Sanmartín P, Sanjurjo-Sánchez J, Prieto B. Covering Layers on Granite Buildings of Northwestern Iberian Peninsula: When Observable Characteristics and Lab Characterization Do Not Match. Coatings. 2020;10(2):137.
33. Thornbush MJ, Viles HA. Photo-based decay mapping of replaced stone blocks on the boundary wall of Worcester College, Oxford. Geological Society, London, Special Publications. 2007;271(1):69–75. https://doi.org/10.1144/gsl.sp.2007.271.01.08.
34. Thornbush MJ. A Site-Specific Index Based on Weathering Forms Visible in Central Oxford, UK. Geosciences. 2012;2(4):277–97.
35. Inkpen RJ, Fontana D, Collier P. Mapping decay: integrating scales of weathering within a GIS. Earth Surface Processes and Landforms. 2001;26(8):885–900. https://doi.org/10.1002/esp.234.
36. Barazzetti L, Previtali M, Scaioni M. Procedures for Condition Mapping Using 360° Images. ISPRS International Journal of Geo-Information. 2020;9(1).
37. Galantucci RA, Fatiguso F. Advanced damage detection techniques in historical buildings using digital photogrammetry and 3D surface anlysis. Journal of Cultural Heritage. 2019;36:51–62. https://doi.org/10.1016/j.culher.2018.09.014.
38. Hatir ME, Barstuğan M, İnce İ. Deep learning-based weathering type recognition in historical stone monuments. Journal of Cultural Heritage. 2020;45:193–203. https://doi.org/10.1016/j.culher.2020.04.008.
39. Valero E, Forster A, Bosché F, Hyslop E, Wilson L, Turmel A. Automated defect detection and classification in ashlar masonry walls using machine learning. Automation in Construction. 2019;106:102846. https://doi.org/10.1016/j.autcon.2019.102846.
40. Saltwiki-Contributors. "Home." Retrieved from www.saltwiki.net/index.php?title=Home&oldid=7017.: (2020). Accessed 6 August 2020.

41. EwaGlos. European Illustrated Glossary of Conservation Terms for Wall Paintings and Architectural Surfaces. Series of publications by the Hornemann Institute. Petersberg, Germany: Michael Imhof Verlag; 2015.
42. Toniolo L, Zerbi CM, Bugini R. Black layers on historical architecture. Environmental Science and Pollution Research. 2009;16(2):218–26. https://doi.org/10.1007/s11356-008-0046-8.
43. Nevin A, Spoto G, Anglos D. Laser spectroscopies for elemental and molecular analysis in art and archaeology. Applied Physics A. 2012;106(2):339–61. https://doi.org/10.1007/s00339-011-6699-z.
44. Avdelidis NP, Moropoulou A. Applications of infrared thermography for the investigation of historic structures. Journal of Cultural Heritage. 2004;5(1):119–27. https://doi.org/10.1016/j.culher.2003.07.002.
45. Ludwig N, Rosina E, Sansonetti A. Evaluation and monitoring of water diffusion into stone porous materials by means of innovative IR thermography techniques. Measurement. 2018;118:348–53. https://doi.org/10.1016/j.measurement.2017.09.002.
46. Delgado Rodrigues J, Ferreira Pinto AP. Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. Journal of Cultural Heritage. 2016;19:467–76. https://doi.org/10.1016/j.culher.2015.10.002.
47. Facio DS, Ordoñez JA, Gil MLA, Carrascosa LAM, Mosquera MJ. New Consolidant-Hydrophobic Treatment by Combining SiO_2 Composite and Fluorinated Alkoxysilane: Application on Decayed Biocalcareous Stone from an 18th Century Cathedral. Coatings. 2018;8(5):170.
48. Hughes, JJ. Ineducable us: the applications and contexts of microscopy used for the characterisation of historic building materials. RILEM Technical Letters. 2017;2:136-144. https://doi.org/10.21809/rilemtechlett.2017.52.
49. Doehne E. ESEM Applications: From Cultural Heritage Conservation to Nano-Behaviour. Microchimica Acta. 2006;155(1):45–50. https://doi.org/10.1007/s00604-006-0505-1.
50. Alessandrini G, Toniolo L, Sansonetti A, Terrani M, Cesana A. Geochemical characterization of an Italian dolostone: the “pietra d’Angera”. Journal of the “Comitato Nazionale per la Scienza e la Tecnologia dei Beni Culturali”. 1995;4(2):51–7.
51. Gulotta D, Bertoldi M, Bortolotto S, Fermo P, Piazzalunga A, Toniolo L. The Angera stone: a challenging conservation issue in the polluted environment of Milan (Italy). Environmental Earth Sciences. 2013;69(4):1085–94. https://doi.org/10.1007/s12665-012-2165-2.
52. Aa.Vv. La Ca’ Granda di Milano: l’intervento conservativo sul cortile richiniano. Snam – Amilcare Pizzi, Milano; 1993.
53. Baracchini C, Lanari P, Scopigno R, Tecchia F, Vecchi A. SICAR: geographic information system for the documentation of restoration analyses and intervention. Optical Metrology. SPIE; 2003.
54. Cassanelli R. Monza anno 1300. La Basilica di S. Giovanni Battista e la sua facciata. 1988.
55. Gulotta D, Villa F, Cappitelli F, Toniolo L. Biofilm colonization of metamorphic lithotypes of a renaissance cathedral exposed to urban atmosphere. Science of The Total Environment. 2018;639:1480–90. https://doi.org/10.1016/j.scitotenv.2018.05.277.
56. Barazzetta G. Sede e scuole della Società Umanitaria. Casabella 2007;750/751:10–5.
57. Lollini F, Redaelli E, Bertolini L. Corrosion assessment of reinforced concrete elements of Torre Velasca in Milan. Case Studies in Construction Materials. 2016;4:55–61. https://doi.org/10.1016/j.cscm.2015.12.005.
58. MacDonald S. Conserving concrete. Conservation Perspectives. The GCI Newsletter 2019;34(2):4–9.

Chapter 2
Surface Cleaning: Implications from Choices & Future Perspectives

Pagona Noni Maravelaki

Abstract In this chapter, an overview of the main cleaning techniques used in the past and trends in cleaning interventions are presented and discussed. The requirements for the selection of the best cleaning methodology according to the substrate, deterioration pattern, and micro- and macro- environmental factors are discussed. An overview of different classes of cleaning methods is presented, with a particular focus on the best methodologies and materials for mechanical and chemical cleaning. In particular, the application of innovative nanogels, nanofluids, poultice, micelle solutions, and microemulsions for stone cleaning and desalination are described. Some case studies summarising results published in the literature on the use of mechanical, chemical, and nanogel cleaning are presented and discussed. Raising awareness, providing specific guidelines, and establishing collaboration amongst experts from different disciplines in charge of carrying out diagnostic, cleaning, and evaluation methods are highlighted in this chapter.

Keywords Stone · Diagnostic · Cleaning water-based methods · Cleaning nanogels · Evaluation · Case studies

2.1 Cleaning from a Philosophical and Compatibility Point of View (Background)

This chapter is not a technical description of cleaning technique but rather a summary to the different possibilities of cleaning and evaluation. The main purpose is to provide information on the effects of the applied cleaning methodology and products to the surface of historic masonry, as well as innovative concepts of cleaning

P. N. Maravelaki (✉)
Materials for Cultural Heritage & Modern Building, School of Architecture, Technical University of Crete, Chania, Greece
e-mail: pmaravelaki@isc.tuc.gr

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with corresponding cases of application (e.g. new nanofluids and nanogels). The chapter is intended to raise awareness on the cleaning procedure applied to historic masonry and to provide specific guidelines for a safe intervention.

To begin with, the necessity of cleaning should be clearly documented with diagnostic analyses, clarifying the origin and composition of the accumulating layers on the surface. The diagnostic enables the conservators to fully overcome objections raised in regard to removing dark encrustations from monuments because of the misleading idea that they are original patinas [1].

The cleaning conservation approach intends to remove any unwanted and harmful layers formed on the monument surface, as a result of both environmental impact and anthropogenic activities. All these influences are stored on the stone surface and the accumulation of layers, with their transformation over time, show the different conditions the surface experienced. It is well-established and generally accepted that the surface of monuments represents the whole history of the monument, as the relationship and interaction with the environment and human activities is reflected on it. Therefore, any unwanted layer formed on the surface should be removed with extreme precaution, otherwise not only will the substrate will be harmed, but most importantly, the cumulative history of the monument and the long-term historical air quality, both reflected on the stratigraphy of layers that function as a proxy archive of the sequence of the historic and pollution effects, will be lost [2–4].

Applying the concept of compatibility to the cleaning performance, the definition proposed by the EU-POINTING project team was adopted considering that cleaning should be an intervention that "*shall not cause any damage (technical or aesthetical) to the historic material and the intervention or the new material must be as durable as possible*" [5]. According to the CEN Standard EN 15898:2011, compatibility is defined as "*the extent to which one material (or action) can be used with another material without putting significance or* stability *at risk*" [6]. The undisputable requirement of "compatibility", greatly required in the irreversible cleaning intervention, was further elaborated by Rodriguez and Grossi, who introduced the "compatibility indicators" in the cleaning procedure, thus enabling cleaning methods and agents to be quantified according to a universally acceptable "rating system" that can assist in the planning of a built heritage cleaning [7].

The literature on cleaning monument surfaces encompasses exemplary texts dealing with theoretical instructions and practical issues. Among these works, the two volume "Cleaning Historic Buildings" by Ashurst Nicola, 1994 [1], the volume dedicated to cleaning practical cases in the "Journal of Architectural Conservation", 2005, curated by Ashurst Nicola [8], the chapter of Snethlage Rolf (2014) entitled "Stone Conservation" in the book Stone in Architecture [9], the articles in building conservation forum (https://www.buildingconservation.com/articles/articles.htm#cleaning), the Historic England and English Heritage publications, the Preservation Briefs from Heritage Preservation Services [10] and numerous papers published in journals and Conference Proceedings were classified as tools offering primary instruction for the design of a cleaning operation.

This chapter will present the necessity of cleaning as related to the categories of deposits that should be either removed or maintained, the parameters that will be taken into account before advancing with cleaning, past cleanings and their consequences on the stone surface, as well as perspectives and future trends offered with the nanotechnology.

2.2 Performance Requirements and Steps of a Cleaning Project

2.2.1 Surface Diagnostics Before Starting a Cleaning Project

The reasons for cleaning can be separated into: aesthetic, protective, enabling repair or redecoration, removing harmful by-products originating from the environment and past treatments, augmenting the historic significance, and showcasing the transformations that have occurred, as a result of the action of extrinsic anthropogenic and weathering factors, etc. Often in the built environment, monuments and buildings with signs of dirt evoke memories of abandoned structures, which would be served as substrates to intensively receive the impact of decay and/or vandalism. Given the irreversible nature of cleaning, at first, the reasons for cleaning should be considered and documented in detail in order to proceed with the selection of the appropriate cleaning methodology. In this context, the close collaboration of disciplines including scientists and conservators is of paramount importance in each step of the cleaning process: from the diagnostics of the surface condition to the selection of cleaning, the verification both in lab and *in situ*, and finally the assessment and monitoring.

The first step before advancing to cleaning is to identify the eventual presence of past cleaning and coating/consolidation treatments that left harmful remnants on the surface and may have promoted the deterioration. The second step involves the identification of the soiling and compounds, originating from the interaction between polluted environment and surface, which are considered harmful and should be removed (Fig. 2.1a). In this context, particular emphasis should be given to the analysis of the composition of the layers to be removed and the substrate that they are adhered to. However, the discrimination of boundary among patinas, polychromies, and soiling is a difficult task and requires selective cleaning to be understood (Fig. 2.1b). The samples illustrated in Fig. 2.1 are fragments of Pentelic marble originating from Parthenon, Athens, Greece and were studied in a previous work [11]. The dendritic black encrustation on marble in Fig. 2.1a displayed three distinctive layers: (C) the internal marble, which is consisted of calcite, (B) the intermediate layer of microcrystalline gypsum with calcite and, the external one (A) consisted of macrocrystalline gypsum with aluminosilicates and soot particles. In Fig. 2.1b a thin section of a patina sample of Pentelic marble is illustrated, in which the layers observed correspond to an internal layer of calcite, iron oxide, quartz, calcium oxalate, and calcium phosphate (C), an intermediate one of gypsum, calcite, and aluminosilicates (B), and, an external one (A) of gypsum, aluminosilicates, and soot particles. The examples illustrated in Fig. 2.1 demonstrate the difficulty in recognizing the boundaries of the layers in order to apply a selective and

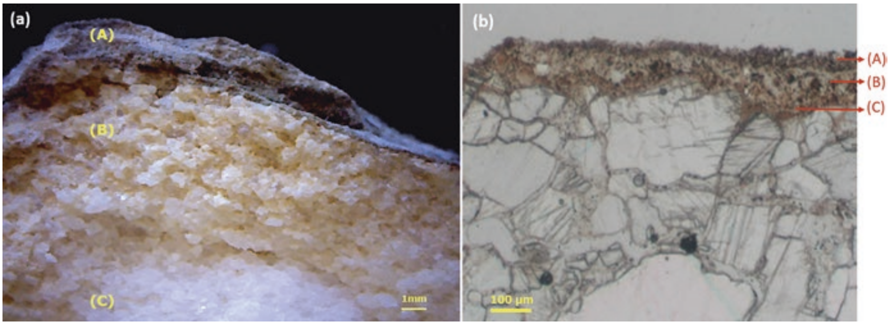

Fig. 2.1 (**a**) Dendritic black encrustation on Pentelic marble under the digital fiber microscope displaying two layers: (A) macrocrystalline gypsum with aluminosilicates and soot particles, (B) microcrystalline gypsum with calcite adhered to marble (C); (**b**) a thin section of a patina sample on Pentelic marble under the polarizing microscope showing an internal layer of calcite, iron oxide, quartz, calcium oxalate and calcium phosphate (C), an intermediate of gypsum, calcite and aluminosilicates (B), and, an external one (A) of gypsum, aluminosilicates and soot particles (pol.//, 50x)

controllable cleaning. In practice, this means that any cleaning should leave the layer close to the original surface (Fig. 2.1a, layer C) intact, since this preserves the reliefs of the surface [11]. Therefore, the acceptance threshold levels and extension of cleaning could be defined by studying the boundaries and stratigraphy of deposits and original surface through thin and cross sections by optical microscopy.

Moving forward from monuments to traditional and modern buildings, eventual paint layers that should be removed deserve further attention. Except for considering protection issues of the building, it would be most appropriate to think whether these paint layers represent exemplary phases of the history of building that have to be maintained and transmitted to future generations. On the selection of the cleaning methodology, it has to be taken into account that not all the construction materials behave similarly in the presence of different cleaning methods and agents. Furthermore, a distinction between natural and artificial materials is imperative, since most materials appearing as natural ones are cast stone or concrete.

Discoloration spots can be entirely due to remnants of previous treatments and not to dirty residues. This is a particular case of cleaning that frequently requires several cleaning methods to be combined and tested, without guaranteeing an efficient outcome of the intervention. Past treatments, up to a certain depth from the surface, are particularly demanding in their removal and cleaning may still leave evident spots on the newly cleaned surface. In other cases, intensive efflorescence could appear as a result of the migration towards the external surface of soluble salts, which already exist in the interior, and, therefore, desalination is imperative before cleaning. All the mentioned parameters evidence the complexity of the cleaning and the uniqueness of each case study, which makes any cleaning operation a specific procedure that should be thoroughly designed, tested, and applied. Most importantly, cleaning interventions on historic structures should be performed by specialized personnel, including different disciplines stemming from the materials scientists to preservation architects and skilled conservators.

The identification of the layers to be removed is an important task to be undertaken and the literature highlights that the gypsum layers formed in polluted environments act as catalysts in promoting the weathering of the surface, therefore, their removal is imperative [12]. Although this statement is well accepted and documented from different studies and practical cases, it remains uncertain when dealing with gypsum-based layers. Indeed, it is quite challenging to recognize the boundaries among the first microcrystalline gypsum layers, which maintain the surface relief, patinas and polychromies, and gypsum dendritic fabric, in which soiling, black carbon particles, etc. can be entrapped (Fig. 2.1a). In other cases, gypsum layers bound with animal glue represent the preparation layer that is destined to receive the polychromies and should be preserved in all circumstances. The diagnostics of the surface characteristics and the study of the sequence of layers originating from the action of exogenous parameters is the first step to be included in the planning of cleaning historic surfaces.

2.2.2 Criteria for the Selection of Cleaning Treatments

The selection of the effective cleaning methods is primarily based on compatibility criteria which ascertain how the significance and stability of the heritage object has been impacted and to what extent. In an attempt to collect supporting criteria for a cleaning intervention, the damage in the significance and stability of the work of art induced by the operation may result in undesirable mass loss, discoloration, and indirect damage, which are caused by several parameters generated after cleaning, such as infiltrations, clay swelling, soluble-salt mobilization, flora development, hygric dilatation, etc.

The cleaning incompatibility risk factors (IR) were classified by Delgado [7] as: (a) “hard”, corresponding to parameterized and semi-quantitatively evaluated; (b) “soft” that are difficult to grade due to their anthropogenic origin; “hard” and “soft” factors are directly interrelated with the likelihood of damage (L) and cleaning consequences (D). Therefore, according to Delgado, the “hard” factors include: (A) the vulnerability of the target surface to cleaning, which is rated according to surface type and condition; (B) the aggressiveness of the cleaning method, expressed by its potential to induce damage regardless of the substrate; (C) the synergistic effects that may occur with specific method/substrate combinations, leading to a risk increase, and (D) the impact on the significance of the object. The (A), (B) and (C) “hard” factors are interrelated to the likelihood of damage (L = A x B x C), whereas the fourth one (D) represents the damage consequences impacting both the stability and significance of the object.

Computing all these factors through the equation (Eq. 2.1):

$$\begin{aligned} \mathrm{IR} &= \mathrm{L}\times\mathrm{D}, \text{where}\, \mathrm{L} = \mathrm{A}\times\mathrm{B}\times\mathrm{C}\ (\text{likelihood of damage}), \\ &\text{and } \mathrm{D} = \text{consequences of damage}, \end{aligned} \tag{2.1}$$

The choice and planning of the cleaning method may result in diminishing the risk consequences.

As reported in the previous section, the nature of both substrate and deposits, along with the micro- and macro-environment play a determinant role for the selection of the appropriate cleaning methodology. The lithic substrates consist of a variety of minerals that could be acid- or base-resistant and could also vary in hardness and compactness. Furthermore, several minerals in stones can be oxidized, such as iron compounds, and this makes the selection of cleaning even more demanding, since a combination of cleaning techniques should be followed with the aim of achieving the removal of discoloration. Other items of buildings that are embedded in the construction and are not visible may be affected by the cleaning agents, leading to the appearance of discoloration.

Research has pointed out that deposits mainly consist of extrinsic matter, such as remnants of soot, grease, dust particles, heavy metals, reaction products from air pollutants, and calcite resulting in the formation of gypsum and other salts that promote the deterioration rate of the substrate. The presence of gypsum and salt can also affect the efficacy of future treatments. Apart from these depositions, living and dead biological matter alter aesthetically, mechanically, and chemically the surface of buildings, creating disfigurements of the original surface [13, 14].

Therefore, after evaluating the condition of stone by identifying the soiling, patinas, polychromies, etc., the criteria for the cleaning selection and a careful planning becomes viable. Surface parameters such as composition, texture, cohesion, roughness, specific surface area, and color are vulnerable to changes after cleaning and should be carefully evaluated.

Several authors reported surveys of the condition of more than 150 sandstone façades in Scotland, which were either chemically or physically cleaned, or uncleaned, showing that a higher proportion, even double in some cases, of the surface areas chemically and physically cleaned were affected by decay compared to the uncleaned facades [15]. More specifically, abrasive cleaning to sandstone abraded the stone surface and blurred some decorative details; chemical cleaning systems caused staining or bleaching, whereas chemical retention within porous stone resulted in the formation of potentially damaging salts [16]. Therefore, taking into account the associated costs, along with the aesthetics, integrity, and maintenance implications, there is a need to balance the perceived benefits with the consequences [17].

The overall study of the monument façades, considering environmental parameters like ambient conditions, location, orientation to the rain, and wind action, along with intrinsic properties like textural characteristics, compactness, specific surface area, porosity, and, especially, microporosity, is of primary importance in order to define in an accurate manner the criteria for the selection of the appropriate cleaning methodology [18].

2.3 Cleaning Methods and Materials Frequently Used

Historic building cleaning methods can be divided according to the main exerted action into water-, chemical-, and abrasive-based (or chemical, physico-chemical and mechanical). Water softens and dissolves the dirt and any soluble materials, such as gypsum and salts. The chemical agents react with the surface impurities or paints and their removal became easier after rinsing off with water. Solvents are often proposed as agents for dissolving the organic substances contained in the dark layers.

Abrasive methods, ranging from micro- and hydro-sandblasting to grinders, sanding discs, scalpels, and engraving pens, all give rise to the mechanical removal of all the unwanted layers and most often parts of the substrate. The effectiveness of the abrasive methods strongly depends on the worker's skills. A rinsing off with water, that follows this operation, especially when the quantity and pressure of the water are non-controllable, can negatively affect the surface masonry, due to the opening of pores during the cleaning, thus facilitating the water infiltration. An important point on water and abrasive cleaning is related to the starting area of the cleaning intervention in a monument and building façade. It is always recommended to start from the bottom and then proceeding to the top, since a cleaned moistened area prevents from the accumulation of dirty residues that can derive from effluents of the above areas to the parts below during the cleaning process.

Laser cleaning is a safe but expensive and skilled (sophisticated) cleaning technology, which is discussed in detail in Chap. 3. This method exploits the laser ablation induced by the irreversible irradiation effect due to the absorption and evaporation of certain material.

2.3.1 Water Based Methods

The water-based methods can be considered as a safe means for removing dirt when the application conditions are regulated to ranges that have been determined as non-dangerous to the lithic substrate. The soaking of surfaces with spraying or misting water may remove sulphated crusts with soot particles, but may also damage the substrate, patinas, polychromies, and precious ornamental features that are sensitive to prolonged moisture. Water washing with low to medium pressure, starting from 2 MPa and not higher than 4 MPa, followed by a gentle scrubbing with natural bristle brushes, may effectively remove hard dendritic crusts and dirty areas of masonry [9]. It is a common practice to facilitate the dirt and soiling removal using nonionic detergents or surfactants that act in combination with a gentle scrubbing of a natural bristle.

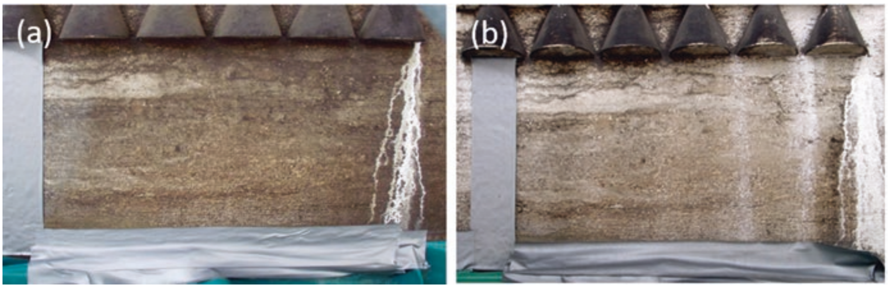

Fig. 2.2 A nebulized water cleaning applied to a compact black crust on Istria stone from Procuratie Piazza San Marco (Venice, Italy), before (**a**) and after cleaning (**b**), © Archive Arcadia Ricerche Srl (Italy)

In cases of acid-sensitive surfaces (calcareous stones, such as limestones and marbles) the steam cleaning may result as effective for carved and relief parts of stone because it provides prolonged wetting with a large specific area. However, the water-based methods are not selective and cannot be easily monitored by the operators to keep to the safe instructions of the cleaning process, as many parameters, like the water pressure and temperature, the nozzle direction and distance from the surface, the time of soaking, and the different response of the layers to be removed along with the substrate, determine the effectiveness of the operation.

The water-based methods accompanied by pressures higher than 4 MPa are more effective for the removal of black crusts, but they are aggressive for the porous substrate, as excessive water can be absorbed. On the other hand, nebula spray of deionized water shows a very good compatibility with the lithic materials, along with the steam jet techniques that show an enhanced dissolving effect to the unwanted layers compared to the other water-based cleaning systems. The cleaning with nebula spray of deionised water effectively removes gypsum deposits, thanks to the physical action exerted by the water run-off [9, 10, 17]. In Fig. 2.2, the gentle nebulized water applied to a compact black crust on Istria stone originating from Procuratie in Piazza San Marco (Venice, Italy) eliminated the soiling up to an acceptable level. However, steam water methods may prove inefficient in removing several dendritic encrustations, which should be further treated with poultice-assisted techniques using specific chemical agents.

Among the risks of the water-based cleaning techniques, even with the gentlest ones with low pressure, the moistening of the masonry, the water penetration from several parts of the surface to the interior, generating staining and efflorescence formation, the material loss in cases of surfaces with exfoliation and other severe decay patterns, such as flaking, sugaring, and sanding, are of primary importance.

2.3.2 Chemical Agents for Cleaning

The chemical agents of acid, alkaline, and organic nature used for cleaning are particularly utilised in the removal of discolorations, such as stains from metal, flora, fauna, paints, coatings, and graffiti present on the monument and building surface. The acid-based compounds are prohibited for cleaning surfaces of calcareous nature given the extreme solubility of calcite in acids. They are not also recommended for surfaces rich in silica and other acid-resistant minerals, because of the potential oxidizing effect of acids and the transformation of feldspars and clays in amorphous silica, leading to material loss and a discolored appearance. In the literature, cases of application of muriatic and hydrofluoric acid exist with severe decay and loss of details from the carved surface [19]. The strong acids that are available on the market and make the basis of these acidic cleaners are often formulated with milder acids, such as phosphoric, formic, acetic, and sulamic acid, in order to drastically reduce the adverse effects of dissolving and staining.

The alkaline cleaners recommended for limestones, marbles, brick, and terracotta contain the alkali substance with a nonionic surfactant to facilitate the adhesion to the surface and the dissolving capacity of the cleaner. All these chemical agents should be applied to surfaces pre-wetted with water; afterward, these compounds should be rinsed off firstly with neutralizing water (weakly acidic or alkaline, depending on the cleaner used), and secondly with pure water to remove any harmful residues [1, 9]. When the removal of synthetic organic paints is necessary, either alkaline cleaners consisting of strong hydroxides and phosphates or a combination of organic solvents, such as methylene chloride, methanol, acetone, xylene, toluene, N-methyl-2-pyrrolidone, etc, could be effective. The removal of stains often requires the application of different cleaning agents, solvents, or detergents and finally extensive washing with water.

The chemical cleaning can be hazardous for the lithic surface, environment, and operators; therefore, careful precautions are usually associated with this kind of intervention. Pilot application in inconspicuous parts of monuments not directly exposed to view can assist in deciding on the application or not. Numerous examples of surface decay after application of hydrofluoric acid and hydrochloric acid have been reported, showing how they compromised the conservation state of the stone, by feeding furnishing it with soluble salts and cracking [1, 9, 20, 21]. The gentlest alkaline cleaners are also potential damage factors, as they leave soluble salts and, in some cases, alter the surface.

Poultices are absorbing materials with highly specific surfaces, such as clay minerals, cellulosic nature, etc., and they are usually mixed with chelating agents, chemical compounds, solvents, and water. They have been applied to parts of the masonry with discoloration to remove stains and graffiti, at different times, which are set-up according to preliminary trial tests, and at the end, a thorough water washing is required [22]. The removal of black crusts has been accomplished with two very well-known and applied poultices containing sodium salt of the ethylenediaminetetraacetic acid, abbreviated as (Na-EDTA), and ammonium carbonate as active ingredients. The action of Na-EDTA is based on its chelating activity towards the Ca^{2+} ion, which forms a stable complex, but means that Ca^{2+} can be chelated both from the crust and the substrate, resulting in harmful consequences if the cleaning process is not carefully monitored. Moreover, gypsum, which is transformed into the soluble sodium sulphate (Na_2SO_4), requires a precise water rinse to be removed and excessive moistening of the surface becomes inevitable. The same applies for the second active ingredient, the ammonium carbonate $(NH_4)_2CO_3$, which transforms gypsum into the soluble ammonium sulphate $(NH_4)SO_4$; the latter, similar to $Na_2SO_{4,}$ in cases of insufficient removal, can cause disruptive effects on the stone due to the presence of more water molecules in its crystals.

The ion exchange resins with exchangeable ions, carbonate or hydroxide (CO_3 $^{2-}$ or OH−), have shown very promising results as active ingredients in poultices, as they produce calcium carbonate or calcium hydroxide from gypsum, and both transformations are considered beneficial to the stone [23, 24]. Boccalon et al. proposed a two-ion exchange system consisting of a layered double hydroxide (LDH) acting as an ion exchanger, exhibiting a high affinity between the LDH and sulphate anions which makes this material a good candidate to capture the sulphates from gypsum [25]. In the same formulation, a layered zirconium phosphate combined with propylamine and a sodium chloride solution was also introduced, exhibiting the cation exchange activity, thus replacing any free calcium ions from gypsum with sodium ions. According to the researchers, the developed method is much faster than commonly used procedures and it uses nontoxic and inexpensive materials. However, multiple treatments might be needed to remove thick gypsum crusts [25].

Conservators often use Japanese paper between stone and poultice, in order to facilitate the removal of poultice without leaving any traces on the surface. Another kind of poultice recently reintroduced is natural latex, which is a polymer emulsion that is sprayed on the surface containing, in some cases, Na-EDTA, which therefore simultaneously acts as a peeling and chelating agent, and is capable of removing deposits from compact surfaces [26]. Recently the use of agar gels loaded with different cleaning agents was successfully proposed and applied to clean interior stone decorations of the Milan Cathedral, Milan, Italy [27].

2.3.3 Mechanical (Abrasive) Cleaning

The action of abrasive techniques relies on the elimination of the unwanted layers by the mechanical pressure exerted through grit blasters, sanding discs, grinders, and micro-sandblasting with finely ground materials. In the latter, silica, glass, walnut and nut shells, sodium bicarbonate, alumina, plastics, sponge, ice particles, or pelletized dry ice are the most used for historic masonry and they frequently follow dry application. The size of particles ranges from 0.1 to 0.5 mm in the particle jet and from 0.05 to 0.1 mm in the micro particle jet technique [28]. The pressure exerted during the application and the nature of particles can definitively vary their impact of the cleaning on the surface. Coarse sand blasting particles increase damage risk and dust is created in the air in this process [29].

Important negative consequences of the abrasive cleaning are the etching of surfaces, the increase of specific surface and roughness, the loss of carved details with a surface rounding, and the likelihood of subsurface cracking. Moreover, it is probable that the difference in hardness of the surface material makes them respond differently to the exerted mechanical pressure. Erosion of sensitive elements such as joint mortars of bricks can result in enhancement of the decay state, as water infiltration is more facilitated after abrasive cleaning. Generally speaking, this method should be avoided for historic masonry and applied with maximum caution in cases where other cleaning techniques failed to remove unwanted surface layers. The only recommended method is the micro-particle jet cleaner that uses particles up to 0.1 mm of soft powders like cork, plastic granulate, or sometimes calcite powder, even though they can prove inappropriate in the removal of crust as they leave a polished surface rather than cleaning it [30]. Other authors stated that glass bead blasting, having previously adjusted the bead size and pressure conditions, showed more effective results than alkaline gels, pressurized hot water, and latex peeling for cleaning the limestone façades of the former Workers Hospital of Madrid, Spain [31]. However, given the uncontrollable character of this technique and the direct relationship to the particle used, the deposit, and the substrate, preliminary tests are compulsory to indicate the most effective choice [32]. In Fig. 2.3 applications of micro-sandblasting with different abrasive material to different deposits are shown. In Fig. 2.3 (a) the deposit on a fountain made of the organogenic limestone Rosso di Verona was efficiently removed (b) by using micro-sandblasting with silica microparticles of 100 μm, 1 bar pressure, and 1 mm of nozzle diameter. In the same figure (c), the biocolonization on an Istria stone archaeological find was cleaned (d) by cryosandblasting technique using dry ice pellets at 10 bar pressure.

2.3.4 Precautions to be Taken in the Cleaning Process

After thoroughly evaluating the layers to be removed, the substrate, the condition of the masonry, as well as the environmental factors that influence the conservation state of the monument, the cleaning steps can be designed. It is wise firstly to test the gentlest possible means of cleaning, such as water washing of low pressure, increasing to a controlled higher pressure with a nonionic detergent, and then to poultices with appropriate chemical agents in pretested time. The acceptance thresholds of cleanliness should be defined before advancing with the cleaning application and this depends on the deposits and the substrate [7]. Given the variety of the materials used for the construction of a monument or building and the diversity of the removable layers, it may be necessary to use variable cleaning methodologies in order to achieve the best result. Figure 2.4 illustrates examples of different cleaning tests conducted for removing encrustation on a limestone of Saltrio, Lugano,

Fig. 2.3 (**a**) Deposit on a fountain of the organogenic limestone Rosso di Verona; (**b**) after micro-sandblasting, silica microparticles 100 μm, 1 bar pressure, and 1 mm of nozzle diameter; (**c**) Biocolonization on an Istria stone archaeological find; (**d**) after cleaning with cryosandblasting (dry ice pellets) at 10 bar pressure, © Archive Arcadia Ricerche Srl (Italy)

Switzerland. In this case, a poultice with ammonium carbonate, applied to area E1a, a micro-sandblasting of low (E1b1), medium (E1b2) and high (E1b3) intensity, along with a laser of 1064 nm (E1c) were compared for their efficiency. The selection of the best treatment cannot be based on the macroscopical observation, and, as it becomes evident from this case, non-destructive techniques can assist in the selection of the best performed treatment.

Finally, each cleaning procedure should be considered and analyzed in terms of the impacts to the environment and the operators and should be carefully chosen. Some chemical cleaners endanger fauna and flora, and the effluents of the cleaning process cannot be successfully neutralized before discharging into sewers. The release of the volatile organic compounds (VOCs) is a source of concern when selecting a cleaning methodology.

In Franzoni et al.'s paper, the environmental impact of the most used cleaning techniques was described in detail and the sustainability of the cleaning intervention was evaluated by life cycle assessment (LCA) analysis, also taking into account a

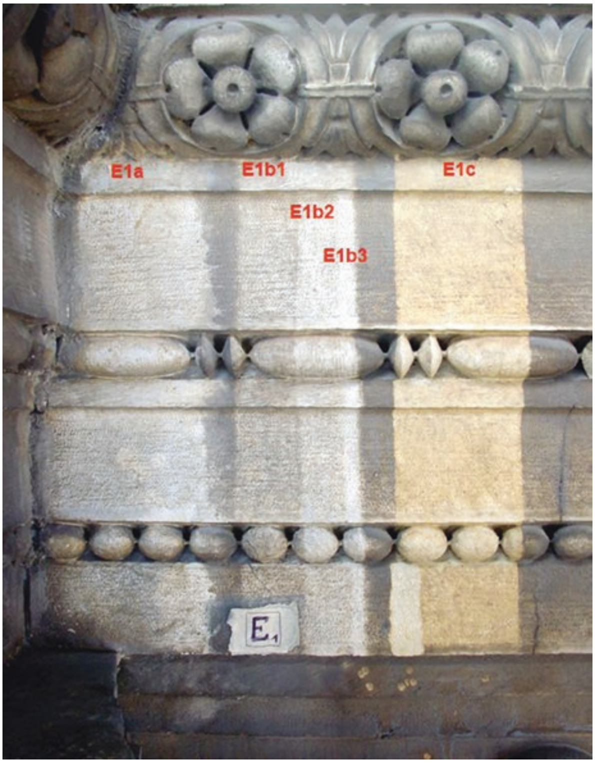

Fig. 2.4 Cleaning tests on encrustation on a limestone of Saltrio, Lugano, Switzerland: a poultice with ammonium carbonate (E1a), a micro-sandblasting of low (E1b1), medium (E1b2) and high (E1b3) intensity, along with a laser of 1064 nm (E1c). © Archive Arcadia Ricerche Srl (Italy)

quantitative evaluation of other key aspects of the different methods, such as workers' health, acoustic impact, and waste produced in the building site [33]. The results also show that the methods involving the lowest environmental impact are not necessarily the best ones in terms of safety and waste production in the building site. An example to this statement is represented by the higher environmental impact of the anionic resins more frequently used than the cationic ones for the removal of gypsum black crusts. Similarly, the very effective laser cleaning method is characterized by a high environmental impact relative to the water consumption necessary for the device operability [34].

Care should be taken not to damage other materials of masonry, such as glass, metal, wood, glazed terracotta, etc. and, therefore, covering them with plastic or polyethylene protects them from circulating airborne dust, water, and chemical effluents of cleaning to the surrounding yards and basements.

Each method selected for the cleaning process should be evaluated and all the precautions should be thoroughly followed. This is especially so in cleaning with chemical agents- the Material Safety Data Sheets (MSDS) should be unequivocally followed [35]. The skilled personnel carrying out the cleaning operation is another important issue to be taken into account in a well-planned cleaning project.

The introduction of decision-making systems, such as fuzzy logic models incorporated into a GIS platform that encompass spatial data from a monument with specific parameters related to the cleaning assessment criteria and the cleaning acceptance threshold levels, is of great assistance in the planning and execution of cleaning [36].

2.4 Special Cases of Cleaning: Removal of Discoloration from Non-porous Lithic Surfaces

2.4.1 Discoloration

The discoloration that appeared on the stone surface is the result of chemical, environmental, or biological factors originating from: (a) the oxidation of metal-bearing minerals which constitute a component of the substrate [37, 38]; and (b) the interaction with external parameters, such as protective materials, cleaning agents, dust, particulate, biological colonization, corrosion of metalwork, etc. [39, 40]. The most common type of staining is created by the decomposition and oxidation of iron minerals in the stone matrix, which are usually concentrated along the veins of the material, due to the impact of oxygen and acid rain. During the evaporation of humidity, those minerals migrate to the surface causing the staining and subsequently, a patina that is very difficult to remove [41]. However, metallic staining can be also caused by external factors, such as the corrosion of architectural metalwork, which is mainly made of iron, copper, and the copper alloys, such as brass and bronze [42]. Humidity oxidizes the metal of these objects, which are located on or close to the exposed material, producing staining on the surface of the stone.

The use of synthetic materials, such as epoxy and polyester resins, synthetic waxes, or polymers is very common in the conservation of cultural heritage [43]. The main goals are to improve resistance to abrasion, to provide surface with strength, to consolidate, to prevent the water absorption, and to protect from further deterioration. Compatibility and performance should be taken into consideration during the treatment of the substrates with synthetic materials. Performance is related to the physico-chemical stability of the applied materials over time. The lifetime of a polymer is expected to be from about 20 to 100 years, but its useful life is undefined. It can become yellowish, brittle, breakable, it may lose its strength, shrivel, or even interact with the substrate that is applied onto, after a long or shorter period of time, under the influence of chemical, physical, or biological factors. The main parameters that influence the deterioration of the polymers are light, temperature, and oxygen inducing discoloration of the substrates [44].

When the polymers, resins, or waxes deteriorate, affecting the underlying surfaces, new conservation treatment is necessary. This procedure is not easy, as polymers have limited removability. To increase reversibility, various methods have been used, each bearing both advantages and disadvantages [44]. Agrawal et al.

[37], reported on the discoloration of Taj Mahal marble showing: yellow-grey deposits originating from residues of polymethyl methacrylate resin and calcium oxalates, the latter derived from oxalic acid and ammonium oxalate, commonly used in India to clean masonry; and brown spots derived from iron minerals present in the marble structure and black patches from biofilm formation in long-term moistened areas. The staining of marble due to previous treatments was reported earlier in the nineteenth century (1858) by the conservator Oddy [45], who was in charge of the conservation of the marble sculptures of the British Museum in London, and he specified that substances like oil, lard, and wax induced discoloration.

2.4.2 Cleaning Methods for Discoloration

In recent years, several cleaning procedures of discoloured Cultural Heritage monuments have been developed based on mechanical, chemical, or physical mechanisms. As previously stated, the selection of the most appropriate method for the cleaning procedure is related to the cause of the surface alteration, the extension of staining both on surface and depth, and the composition of the substrate [27]. The cleaning agents should not only be effective in removing the staining, but should also be unharmful to the substrate of the monument.

Pure solvents and liquid solutions were proposed for cleaning discoloration due to iron staining or aged polymer coatings. The most common method to remove deteriorated polymers from treated surfaces is the use of solvents, usually organic, such as acetone, xylene, toluene, alcohols, or mixtures of them. Unfortunately, these solvents are not only toxic and harmful to workers' health, but they might induce further migration of the dissolved polymer inside the stone and spread the discoloration to even deeper layers [43]. Moreover, when solvents are used for the removal of the applied polymer, swelling of the polymer can be observed on the surfaces, thus demanding further mechanical abrasion, in order to complete the polymer removal. However, through this abrasion, especially in porous materials, parts of the material underneath could be disrupted [43]. These were considered important drawbacks of the use of pure solvents, which were replaced by nanotechnology agents, which are described in detail in the following section.

Acidic solutions in combination with chelators counteract with the metallic ions, which are the main cause of the discoloration, and diffuse them into a solvent solution, thus removing stains from the surface. An effective agent should have a rapid reaction with the metallic stain, avoiding any interaction with the components of the stone, such as calcium or magnesium carbonate. An appropriate cleaning solution should have suitable pH, chelating agent, and ionic strength. The pH of the solution should be close to that of the material substrate, in order to minimize any possible damage. Concerning the marble and limestone substrate with calcite as the main component, the pH of the liquid solution should not vary from 7 to 10 [33].

Macchia et al. [42] proposed and evaluated a cleaning procedure to remove bronze corrosion products on travertine by using environmentally friendly copper complexing or chelating agents, including three amino acids, and compared those with some ion exchange resins.

Chelating materials can solubilize the compounds found in marble, and therefore, the complexes that react only with the iron of the substrate are considered the most appropriate agents for iron removal. EDTA (ethylenediaminetetraacetic acid) is a widely used compound for the removal of salts, iron, and copper stains, but cannot be considered an appropriate agent for marble and limestones, due to its chelation activity with calcium [9]. Citrate and oxalate ions could also be used for marble cleaning. The use of ammonium citrate in conservation has been reported to clean the rust, but it damages the carbonate surface [46]. According to the literature, the efficiency of phosphates, fluorides, oxalate ions, and salicylate has been also studied for iron staining removal from surfaces [47]. Furthermore, the TPEN (N,N,N,N-tetrakis-(2-pyridylmethyl) ethylenediamine) agent can form complexes with metal elements and can disintegrate iron (II) complexes without affecting the marble [38]. Due to the fact that iron (II) can be easily removed from the surface, the reduction of iron (III) to iron (II) is considered as prerequisite stage for this treatment.

2.4.3 Cleaning Biological Colonization Using Biocides

Biological colonization from algae, lichens, bacteria, fungi, and mosses are common on building and monument façades; they are often considered undesirable as they disfigure and exacerbate stone decay. It is recommended to avoid any treatment with pressurized and superheated systems and apply the cleaning methodology on a dry surface, since then the removal of the microorganisms becomes easier, without leaving stains from the colonization [9]. In a study by Young and Urquhart, residues of some phosphate-rich stone cleaning chemicals acted as nutrients, accelerating algal growth on vulnerable building sandstones [48]. According to European regulations, the use of biocide toxic agents, such as toxic organo-tin or -mercury and other heavy-metal components cannot be used in conservation [49]. Particular attention should be paid to the addition of some organic acids in biocide formulations with the aim of enhancing the metabolic activity against the cells. In such cases, a risk exists to harm adversely the substrate, especially calcareous materials. The commercial biocides that proved to be effective in the abatement of fungi, bacteria, algae, moss, and lichen are classified in these categories: (a) products that contain formaldehyde releasers; (b) products consisting of quaternary ammonium salts, such as benzalkonium chloride (Neo Desogen, Dimanin, Antimoos); (c) products containing dithiocarbamates (Ziram, Thiram) [9]. In the literature, good biocidal effects were reported for the quaternary ammonium salts used on façades, like the product with a 1% benzalkoniumchloride and 0.045% isothiazolon (Remmers BFA), and another one based on 2,3,5,6-tetrachloro-4 (methyl sulphonyl) pyridine (Algophase®) [50].

Toreno et al. proposed a solvent gel containing dimethyl sulphoxide (DMSO) to clean colonized marble artefacts at the monumental cemetery of Bonaria (Cagliari, Italy), and compared this treatment with traditional biocides [51]. The biocide efficiency was evaluated by scanning electronic microscopy, roughness and colorimetric measurements, and growth tests. The results demonstrate superiority of DMSO solvent gel compared to traditional biocide treatments in terms of low impact, ease of use, and low-cost; therefore, it can be considered an alternative to biocide treatments. Pinna et al. evaluated an 8-year-long study involving mixtures of consolidants, water-repellent products (tetraethylorthosilicate, methylethoxy polysiloxane, Paraloid B72), and biocides (tributyltin oxide, dibutyltin dilaurate, copper nanoparticles) applied to the archaeological area of Fiesole (Florence, Italy), to prevent biological growth on stones [52]. The applied mixtures resulted in effective reduction of the recolonization, but they did not prevent the growth of biofilms and lichens. This study demonstrated the complexity of the biocide treatment, especially when it should be combined with protectives and consolidants, as it usually occurs in the conservation practice. The bioremediation described in Sect. 2.5.5 could be a safe alternative in combatting the adverse effects of the biological colonization on stones.

2.4.4 Desalination of Surfaces

The process of desalination, an important step before advancing with surface cleaning, deserves a chapter itself. In Chap. 8 of this book there is also a reference to this crucial topic in the conservation field, and methods to evaluate the presence of salts in a qualitative and quantitative manner are provided. Salts are severe deteriorating factors in the masonry and many decay forms are totally interrelated to salt crystallization due to the volume change that is observed with humidity and temperature changes [53].

The desalination process should precede any other intervention on the monument surface and constitutes a preventive step in the whole conservation process. The extraction of salts becomes reliable with the aid of specific poultices that absorb water, mostly consisting of mineral, clay, and cellulose components. It was reported that in poultices, the right ratio between the components controls the drying behavior, reduces shrinkage, and increases the efficiency of salt extraction [54]. Bentonite-rich poultices are more efficient initially, while Na-zeolite and kaolinite-rich mixtures required more time to reach saturation [54].

In another desalination study concerning a 300-year-old boundary wall of the Worcester College in Oxford, UK, the behavior of salt solutions during the drying process in porous stone, and the efficiency in the extraction of salts by paper pulp poultices were investigated [55]. Comparisons made between the field work and laboratory tests revealed that even though a higher content of salts was extracted in saturated lab samples, nevertheless, the results from the field tests were comparable with the laboratory experiments. Most importantly, the spatial distribution of the identified salt ion concentrations in poultices corresponded with the 'hot spots' of weathering.

Regarding the microstructure of poultices, van Hees et al. developed a modular system that can be adapted and fine-tuned to different types of substrates, with consideration to the transport of salt ions with water flow [56]. In order to optimize salt extraction, a poultice should have smaller pores than the substrate, and therefore, the pore sizes of different desalination materials, such as sand, cellulose, kaolin, and bentonite, mixed in different proportions, have been measured and recipes for poultices, adapted to a specific substrate, have been formulated accordingly [57]. Granneman et al., in an attempt to mitigate the salt damage in building materials, introduced the crystallization modifiers (e.g. ferrocyanide for sodium chloride and borax for sodium sulphate) that reduce the salt crystallization pressure and favour the formation of less harmful efflorescence on the surface, instead of the dangerous 'subflorescence' in the substrate [58].

2.5 New Trends in Cleaning Methodology

2.5.1 Nanofluids (Microemulsions and Micellar Solutions)

Conservation research has progressed significantly in recent years, thanks to methods that rely on nanoscience. Instead of using organic solvents that induce adverse effects, nanostructured fluids (NFs), such as micelles solutions (MS) and microemulsions (ME), were proposed to efficiently remove coatings from hydrophilic porous materials [59]. The MS solutions consist of amphiphile-based formulations, such as surfactants, using a system of water, oil, and surfactant. The ME system consists of two liquids phases which are well dispersed with the formation of microspheres stabilized through an amphiphilic agent (surfactant). The phase of this ME formulation could be either hydrophilic (oil in water) or hydrophobic (water in oil), depending on the cleaning procedure. This amphiphile-based system is used to remove synthetic polymers, sulphates and chlorides, unwanted graffiti, vinyl and acrylic coatings, polysiloxane resin, waxes, polymers, or varnishes, which are difficult to remove with traditional cleaning methods. In literature, there are several papers describing the removal of polymer coatings with MS and ME in laboratory conditions and *in situ* applications, from various substrates, such as Carrara marble, wall painting mock-ups, stucco masks, frescos, canvas, etc. [60–63]. Taking into account that MS and ME have the ability to solubilize the ingredients of the protective materials, they can be considered as innovative "green" approach in cleaning of surfaces [61, 64]. NFs act as solvent containers that interact with the polymer film, swelling and detaching it from the surface, then the polymer segregates into a liquid droplet, and can be phase-separated from the aqueous bulk. After the polymer removal, the NFs are depleted from the organic solvents, and it becomes smaller in size and can easily be detached from the surface. In the following section, applications of NFs for cleaning stone materials are presented.

2.5.2 Removing Polymers

Removal of Acrylic-Silicone Based Polymers from Stone Grassi et al. proposed a nanocontainer aqueous system consisting of MS and ME in order to remove acrylic polymer (Paraloid B72), silicone-based resin (Dri-Film 104, DF), and their mixture (Bologna Cocktail, BC) from artificially deteriorated marble with the aid of a cellulose pulp [64]. MS consists of Sodium Dodecyl Sulphate (SDS) as surfactant, 1-pentanol, water, and p-xylene as solvents, whereas the ME also contains SDS, 1-pentanol, water, and propylene carbonate. The results of these cleaning applications revealed that MS and ME systems showed a similar behaviour for the removal of these specific polymers from marble substrate. The high effectiveness of MS and ME as removal agents of the polymers was confirmed through analytical techniques. Factors such as the application time of the cleaning agent and the ageing of the polymers influence the removal of the applied materials. By studying the poultice after the application, it was found that it contained deterioration chains of the polymer, thus proving that the nanocontainer pulp succeeded in removing great parts of the deteriorated polymer. It is of great importance to have in mind that an aged polymer cannot be fully removed from the surface, probably because of the stone's porosity and the material's migration inside the substrate [43]. It was observed that a surface with a freshly applied polymer, after treatment with MS and ME, has residues of the polymer, mainly concentrated on the fissures.

Removal of Styrene/Acrylate coatings – Polymers from Stucco and Stone Baglioni et al. undertook research in order to use Sokrat 2820A® (commercially also known as Axilat 2802®), to remove an anionic aqueous dispersion of a styrene/acrylate copolymer that was used in the building sector, as well as a fixative to provide protection to stucco artefacts in Guatemala [62]. Due to the special climate conditions, the copolymer, when applied, instead of creating a thick elastic protective film, turned sticky and consequently attracted grime and degraded. An aqueous ME with SDS, 1-pentanol, and p-xylene, named XYL, was proposed as a cleaning system and tested both in laboratory and *in situ*. The XYL system was able to swell the polymer film without breaking it, and its removal could be easily performed softly with a cotton swab soaked in water. Capillary rise and water vapor permeability data after treatment showed acceptable values indicating that the physico-chemical properties of the stucco were restored.

Paraloid B72 was widely used as protective material in stone conservation treatments, despite its tendency toward chemical and physical decaying, such as cracking, discoloration, brittleness etc., leading to acceleration of the deterioration conditions of the underlying surface of the monument or artefact [65]. As mentioned above, typical organic solvents are not suitable cleaning agents; therefore, a cleaning system named EAPC (ethyl acetate and propylene carbonate) was tested, to assess the interaction of this nanostructure fluid with the polymer coating [63]. A solute that contained biodegradable amphiphilic non-ionic surfactants was used, instead of the anionic ones (e.g. SDS), with cleaning ability and sensitivity to the divalent cations, such as calcium ions, creating salts that are difficult to rinse off the surface of the artefact. Those non-ionic surfactants can self-assemble easier, clean the surfaces from the oil and dirt, and the presence of salts does not affect their solubility.

The removal of Paraloid B72 was attempted using pulp poultices soaked with two nanofluids in the micellar solution, along with a sheet of Japanese paper. The first nanofluid was a traditional alcohol ethoxylate with a minimum amount of by-products, namely polyethylene glycol, which is water soluble and does not affect the performance of cleaning. The other nanofluid was ethoxylate, with BF3 as an ethoxylation catalyst, known for producing dioxane, a toxic component which must be carefully removed. The components of the poultice interacted with the polymer, causing it to swell and detach as a film. As the cleaning procedure followed, all the residues were removed [66].

2.5.3 From Traditional Gels to Nanogels

Traditional Gels for the Removal of Grime Physical gels used to clean artwork surfaces must be chemically inactive with the materials of the objects and they should be physico-chemically stable to diminish the interactions between residues of gel and cleaned surfaces. At the beginning of the 90s, the gelator was a polyacrylic acid, with low solubility in water, which upon neutralization, was converted into a carboxylate anion container. The intramolecular interactions between the anions forced the chains into random rearrangement, maximizing the solubility. The polyacrylic acid is deprotonated by adding basic non-ionic surfactant. Of course, the gelator capabilities were influenced by the chemical structure of the surfactants [67]. The use of these gels can be performed by either applying directly onto the surface and left for 1–5 min, or with the use of a swab roll, combining a soft mechanical continuous action to maximize the interaction with the surface's soil. These gels are capable of removing soiling, grime, and polymers, and can be formulated according to the specific characteristics of the layer that has to be removed.

Residues of the gelator may be left on the surface with unpleasant outcomes, e.g. the increase of the solubility of the substances and the chemical alteration of the paint layer. In literature, holes, cracks, and other unwanted side effects are due to the residuals of the gel system, but this problem is still unresolved, as it is connected with the solvent mixtures confined into the gel phase [67].

To minimize the impact of water, physical hydrogel formulations have been used, based on natural polysaccharides like gum and agar, which provide an emulsion with thickness and stability that can bind high amounts of water, thus avoiding its penetration into the porous matrix, but they can only be used in works of art which are not water sensitive [59].

Agar gels proved to be effective when applied on the marble statue "Fuga in Egitto" in the Milan Cathedral [27]. They were effective in removing soil, salts, and soot without any detriment to the marble surface, being more efficient than simple water-based cleaners, making the treatment easy, low cost, and less time-consuming. In addition, it is safe for the specialists applying it. The optimum cleaning result was after 1h of application of 3% agar gel concentration, providing cleaning with homogeneity and no whitening effect. Before cleaning, there were different grades of discoloration on the statue, depending on the inclination and therefore the different soiling. After treatment, the variable texture and coloration of the marble was revealed [27].

Nanogels Nanogels are composed of hydrogels, which are synthetic hydrophilic polymeric networks or biopolymers chemically or physically crosslinked. Nanogels show a diameter ranging from tens to hundreds of nanometers and have many advantages. Firstly, at the liquid phase (where the upper layers of the polymer begin to reorganize), they can slowly release the cleaning agents at the interface, thus reducing the risk of the underlying layer swelling and lowers the grade of ingression into the pores of the material. The high viscosity decreases the solubilisation rate but provides perfect control of the interaction and limits it to the interface between the cleaning agent and the artwork. Additionally, it decreases the evaporation rate of the solution, thus enhancing the cleaning action and reducing the solvent toxicity. The nanogels can embed a variety of liquid media, such as organic solvents, MS solutions, oil-in water ME, aqueous solutions with enzymes or chelates, etc., and can have successful applications in a great range of materials apart from works of art [68].

As mentioned above, MS and ME are the most effective systems for the removal of polymer coating from works of art. The organic solvents can be rapidly infused into the stone, due to capillary forces, and cause severe damage to the surface, swelling, softening, and leaching it. To avoid those drawbacks, the use of flocculent systems, such as gels and nano-structured fluids is an effective alternative intervention. However, it should be mentioned that the particularly demanding design and application of those gels make them a non-cost-effective procedure for the cleaning of large areas.

Nanostructured Gels for Grime and Other Substances Removal The chemical structure of the formulation of nanostructured gels allows a quick, complete, and not invasive removal. Once the gel has carried out its cleaning action, with the addition of a small amount of weak acidic solution, it can be completely removed from the treated surface, as it changes to liquid state and can be wiped away with dry cotton swabs. Their cleaning ability is excellent but controlling the application is difficult [69].

It is possible to combine the gel cleaning method with microemulsions. The main idea is to use magnetic nanoparticles and oil-in-water microemulsions to produce a magnetically responsive gel-system that will attract the unwanted substance from a surface of a material. The nanomagnetic sponges were mostly used to remove dirt, varnishes, or polymers from the surface of artworks, especially paintings [70]. A polyacrylamide based chemical gel doped with ferrite magnetic nanoparticles chemically linked to the polymer can provide a completely removable cleaning agent. The gel can combine the magnetic capability of ferrite and the typical properties of an acrylamide gel, improving the elasticity, and it offers complete spatial control as can be shaped as desired. The way of how MS or ME apply on polymers remains the same, even if they are loaded on the nanomagnetic gel, and most importantly both structures retain their characteristics. The advantage is that when they move to the interface of the artwork, they solubilize the polymer, capture its components, and incorporate them into the gel's structure. After the removal, the microemulsions can be retracted from the gel by washing with water and the nanomagnetic sponges can be dried as a powder and stored to be reused. The magnetic nanoparticles do not reduce the water retention ability of the gel structure, while the system stability over evaporation is elongated; these properties support their suitability for cultural heritage conservation applications.

Applying this method on the surface of a marble sample consolidated with Paraloid B72, the aged polymer has proven to be completely removed. The technique used was the direct application of the microemulsion-loaded magnetic gel onto the treated surface and it removed with a magnet about 2 hours later. Since there is no need for contact between the magnet and the treated surface, this method is most appropriate for the conservation of valuable artworks [70].

Peelable Gels These gel systems have high intrinsic elasticity that allows them to be easily removed by peeling, without leaving residues on the treated surface. Peelability is provided by the addition of a polyvinyl alcohol (PVA) or a network of polyvinyl-1-pyrrolidone and poly(2-hydroxyethylmethacrylate) as gellants. It is possible to optimize their gel formulation to provide better visco-elastic behaviour, amphiphilic character to their network, etc., but above all, their main advantage is that they can be loaded with both aqueous cleaners and organic solutions, making them effective in a wide range of materials with different physicochemical properties [71]. Riedo et al. effectively removed acrylic coating from of porous limestone with the aid of a PNA-borax and poly(ethylenoxide) (PEO), which maintained the shape of the hydrogel and increased the relaxation time [72].

Semi-interpenetrating peelable gels have high water retention ability and mechanical properties that allow them to be used efficiently on water-sensitive artefacts. Using the appropriate microemulsion, a hydrogel formulation can provide sufficient cleaning from aged polymers. These kinds of hydrogels are usually pellucid and smooth but differ in hydrophilic ability. Additionally, they can be loaded with pure solvents, but to ensure a controlled cleaning process there must be a limitation of oil-in-water microemulsion into the hydrogel, to avoid fibre swelling [71].

Artificially aged Paraloid B72, PVAC (polyvinyl acetate) and silicone acrylic were tested for the removal of different types of hydrogels from murals. The tests showed that the cleaning gels could remove the polymers efficiently, especially Paraloid B72 in concentration of 80%, which can be improved if the treating also involves a smooth wiping with swaps to wipe off the swollen polymer. The experiment compared the aging time with the reversibility, the superiority in efficiency of the cleaning gel with ME against pure organic solvents, and finally the environmental friendliness, control of the treatment, and protection of the treated surface [73]. Boccalon et al. designed PVA-borax hydrogels containing active ingredients with antimicrobial effects, such as silver nanoparticles and tested over two biodeteriorated stones of different nature and composition with very promising results, opening new pathways in bioremediation, defined as a natural solution to contamination mitigation [74].

2.5.4 Plasma as a Cleaning Tool

Plasma is an ionised gas containing highly reactive compounds according to the gas used (air, oxygen, hydrogen, etc.), with applications often conducted at room temperature and related to the chemical and physical etching, coatings deposition, or ion implantation, etc. [75]. This method can be applied on the upper layers of the surface; it is accurate and contactless, and does not possess the unwanted side effects of a chemical cleaning, such us the spreading of the solvent and the insertion of by-products in the pores of the material. Despite being firstly applied on metallic objects under vacuum conditions, the use of atmospheric plasma can be used on a wide range of materials. The EU-founded project PANNA (Plasma and Nano for New Age soft conservation) studied the applications of atmospheric plasma on a variety of materials. The results report the capabilities and drawbacks of the commercial plasma apparatus as cleaning tools [76]. Studies were carried out on Serena sandstone, Istria limestone, thermally-aged Carrara marble, and wall paintings, covered with epoxy resin, siloxane, acrylic coating, graffiti paint, and black crust. After cleaning each surface with different plasma torches, techniques, such as macro- and micro-microscopy, were used to evaluate the effectiveness of the method.

Depending on the plasma plum (PVA Tepla, Tigras, DBD, etc.) used, the temperature, and the exposure time, plasma is able to reduce the acrylic coating, epoxy resins, and siloxane coating, regardless of whether they are freshly applied or aged, so the surface of the material begins to regain physical properties from before treatment. Unfortunately, this method has drawbacks that need to be resolved before being safe for application on cultural heritage objects, such as metal deposition due to the electrode deterioration. The studies suggest that a balance between viable cleaning times and preservation of surfaces should be the main goal [75].

2.5.5 Cleaning with Microbial Compounds

One potential approach for cleaning and restoring historic monuments is using microbial compounds. These methods not only have scientific merit, but also provide socio-economic benefits. Biotechnology can provide a method that is easily applied, controlled, and is low cost [77]. There are several microorganisms that can cause biological degradation of the synthetic polymers, and they can be used in their removal. For example, it is known that bacterial strains and fungi can deteriorate even freshly applied synthetic acrylics [78]. Cappitelli et al., in order to remove black gypsum crusts on marble of the Milan Cathedral (Italy), compared two cleaning methods, one involving an ammonium carbonate-EDTA mixture and the other involving the sulphate-reducing bacterium *Desulfovibrio vulgaris* subsp. *vulgaris* ATCC 29579 [79]. The biological procedure showed superiority to chemical cleaning and homogeneously removed the surface deposits, preserving the patina noble under the black crust. On the other hand, the bio-procedure released no by-products, while the chemical treatment led to the release of undesirable sodium sulphate [80].

Unfortunately, some of these heterotrophic microorganisms can be harmful to the stone, so there must be a very careful selection. Research projects were dedicated to the effectiveness of the bacterial treatments, in terms of optimizing time and number of applications, and on finding the best delivery systems [81]. As reviewed by Bosch et al. [81], several delivery systems of bio-cleaning formulations, such as sepiolite, hydrobiogel-97, cotton wool, carbogel, mortar and alginate beads, agar, and arbocel, were compared and evaluated on the basis of workability, ease application, non-harmful ingredients, in order to help conservation scientists, conservator-restorers, and researchers to choose the most appropriate delivery system for any specific application. They concluded that: *D. vulgaris* in arbocel and carbogel are suggested for black crust, nitrate, and sulphate removal; *P. stutzeri* and agar or cotton wool can remove salt efflorescence and organic matter.

Romano et al., proposed the use of *Halomonas campaniensis* to remove nitrate salt efflorescence from the surfaces of stone samples [82]. Molecular spectroscopy proved that the nitrate content in artificially enriched samples was reduced as a function of incubation/treatment time, both in a controlled laboratory environment for temperature and relative humidity and in real outdoor environmental conditions. Another bio-cleaning procedure used a model enzyme system based on glucose oxidase, which is capable of producing *in situ* hydrogen peroxide, a cleaning agent with oxidizing properties. It has been applied on travertine and peperino samples originating from the Villa Torlonia in Rome (Italy), showing extensive biofilm [83]. The effectiveness of the glucose oxidase compared with traditional approaches using ammonium carbonate and EDTA in a buffer solution and the enzyme lipase showed better effectiveness in biofilm removal.

Further studies are needed in order to fully elucidate the long-term safety of bio-cleaning. Monitoring and onsite assessment techniques will definitely support decision making of using those innovative systems.

2.6 Evaluation of Stone Cleaning

In the scientific community the cleaning assessment methodology and criteria were established through strict procedures and guidelines that should be followed in the evaluation process both in lab and *in situ*. However, objective difficulties arose when a common framework in the cleaning evaluation process should be followed, as many factors relevant to the stone type and decay, environmental conditions, cleaning methods, and agents have a different impact in the whole process. These considerations on the irreversible cleaning intervention are framed within the "compatibility" concept as above mentioned, under the definition of the "*extent to which one material can be used with another material without putting significance or* stability *at risk*" [7]. Improved considerations of "compatibility" encompasses parameters such as type of stone, micro- and macro-climate, past treatments, skilled personnel, and budget [7].

The major analytical techniques used so far for the evaluation of cleaning are presented in detail in Chap. 8, since most of them coincide with the *in situ* applied assessment techniques. In this section the main properties that need to be evaluated after cleaning are summarized along with the relevant assessment methodology. Optical microscopy (OM) in polarized and non-polarized light with digital images, scanning electron microscopy with energy dispersion X-ray analysis (SEM-EDS), X-ray diffraction (XRD), and various spectroscopies are analytical techniques systematically used by the scientific community for the identification of the morphology, mineralogical, and chemical composition of the stone surface before and after cleaning [84]. The study of cross-sections of samples under optical microscope provides invaluable insights into the nature, stratification and thickness of the deposits and should be accomplished before cleaning [28]. SEM could further assist in identifying the sequence and origin of surface layers, their complete removal or maintenance in case of patinas ad polychromies, and eventual by-products left by the cleaning. The surface cohesion and roughness are parameters to be taken into account in the evaluation process and should remain in high and low level, respectively, indicating that no micro-fissures or increased roughness, that could accelerate the decay state, were acquired [36]. The evaluation of surface texture, cohesion, and microstructure before and after cleaning is progressed in recent years through the advances of digital image processing of microscopy images, which allowed the comparison of the results of different analytical techniques [85, 86].

The aesthetics and the color of a cleaned stone surface constitute unambiguously the most significant parameters that determine the decision making of a cleaning intervention [22, 87]. The color parameters and their modification are commonly evaluated by colorimetry, by means of laboratory spectrophotometers/colorimeters using the CIE L*a*b* color space 1976, as described in the European standard EN 15886:2010 [88]. Hauff et al. proposed, in additional to visual and optical observations, water uptake and water transport properties, along with the evaluation of salt content for eventual residues to be determined in the holistic assessment of cleaning [89]. Delegou et al. developed a "cleaning performance index" based on a

GIS-based graphical interface and a fuzzy logic model, encompassing parameters such as surface colour and roughness and their acceptance threshold levels, as well as data concerning the micro- and macro-environment. They applied this methodology in the cleaning of the façade of the National Archaeological Museum in Athens, Greece [90].

To provide guidelines for a more objective evaluation, the Working Group 3 of the European Committee for Standardisation (CEN-TC346) proposed a relevant standard on the evaluation of harmfulness and effectiveness, both in laboratory and *in situ,* for the various cleaning methods applied to porous inorganic materials (EN 17488) [91]. In this EN 17488:2020, the harmfulness evaluation has a priority over the effectiveness, and the fundamental analyses which must be carried out before and after cleaning were classified as: optical observations, chemical and physical analyses involving elemental and composition characterization, colour and surface measurements, and water absorption.

2.7 Case Studies of Stone Cleaning

In the last decades, papers focusing on the assessment of cleaning methods have been published in journal or conference proceedings [92]. All the cleaning methods should take into account the compatibility concept, as introduced and developed by Delgado, based on the assessment of the risks of cleaning, associated with parameters relevant to the method and substrate, as well as the skills of operators and budget [93].

Gaspar et al. recommended abrasive cleaning, steam cleaning, and chemical cleaning (using hydrofluoric acid, ammonium carbonate, and EDTA) for marble, oolitic limestone, and architectural terracotta surfaces; these were assessed by means of light interferometry, optical microscopy, colour measurement, chemical (EDS), and petrographic analyses of the cleaned surface [94]. The use of abrasive cleaning removed the pollutant crusts but etched the oolitic limestone surface and left abrasive particles (aluminium oxide). Chemical agents, such as ammonium carbonate and hydrofluoric acid, effectively removed the pollutants, but the latter discoloured the surface. The steam cleaning resulted as the most innocuous method for the substrate, but with a low success in removing the black crusts; the topographical modifications that were found were attributed to differentiation in the nozzle distance and contact time.

Inglesias et al. assessed the most appropriate cleaning technique for the very dolomitized calcisiltite from the middle Miocene (Serravallian) from Tarragona, used in the Church of Les Saleses Convent (Barcelona, Spain) [95]. This stone was covered with highly reactive black crusts, contained a high percentage of soluble salts, and showed advanced disaggregation. The use of cleaning methods based on water and chemicals agents, such as ammonium carbonate or AB-57 poultices, had to be rejected, since they resulted as harmful for patinas and stone surface. Cleaning with 100–250 μm granulated glass abrasive at low pressure 0.5 bar, 10 cm of distance between sample and nozzle was effective in removing the black crusts, without altering the substrate.

Sanmartin et al. reported on graffiti removal methods that were proposed and used on different substrates [96]. It was emphasized that there are minimal available cleaning methods that are capable of removing the graffiti from substrates, without also affecting the underlying material. Typical chemical solvents of methyl ethyl ketone, methylene, chloride, and phenol may cause irreversible damage to the substrate due to their penetration, and they are highly aggressive for the environment and health. The mechanical cleaning is also placed into the same direction as the chemical one, as it may release in the surrounding environment harmful by-products such as fine dusting particulate, originating both from the substrate and the method itself. The urgent need of an environment-friendly and safe method of graffiti removal from porous substrates places the novel approach of bioremediation as a green solution for the graffiti decomposition by using specific culturable microorganisms. According to the authors, this cleaning method is environmentally friendly and is safe for human health, and, once implemented, it will not be harmful to the substrates [96].

Sun et al. designed and tested hydrogels based on 2-hydroxyethyl methacrylate, poly-vinylpyrrolidone, Azoisobutyronitrile, and N,N-methylene-bis (acrylamide), which effectively removed past conservation treatments, such as Paraloid B72, acrylic, and silicone-acrylic from the water-sensitive Dunhuang mural, which is a splendid cultural relic from the Silk Road in northwest China [97]. The assessment through 3D microscopic observations revealed that gel cleaning is more selective, environmental-friendly, without producing mechanical damage on the sensitive surface as with pure organic solvent cleaning.

Pozo-Antonio et al. applied to sulphated black crusts on granite various mechanical and chemical cleaning methods consisting of a micro-blasting technique, poultices containing chemical agents such as the standard AB57, consisted of EDTA, sodium bicarbonate, ammonium bicarbonate, and the biocide Neodesogen, as well as acidic mixtures with hydrochloric acid and ammonium bifluoride in aqueous solution [98]. Various thickeners like a synthetic clay composed of sodium, lithium, and magnesium silicates, carboxymethylcellulose and a neutralized polyacrylic acid, were also used. Finally, the application of Amberlite 4400 OH, a strong exchange resin, was also tested. The results indicated that none of the above methods removed completely the black crust, whereas residues of cleaning, thickener agents, absorbent paper and by-products were also identified. The authors suggested extensive water rinsing or use of water vapor after the treatment and to carefully remove any residues of the absorbent cellulose paper.

Baglioni et al. proposed nanostructured fluids as an efficient means for the removal of graffiti originating from 17 commercial spray-can paints [99]. The authors designed and tested two different amphiphile-based nanostructured fluids (NSFs), on the same paint samples. The NSFs consist of surfactants, such as the Sodium dodecylsulphate (SDS), co-surfactants: 1-pentanol (PeOH) or 2-butanol (2-BuOH), organic solvents: ethyl acetate (EA), propylene carbonate (PC), 2-butanone (MEK), $C_{9-11}E_6$ ethoxylated alcohol, as well as purified water in a 60–70%

(w/w) content in the whole composition of the systems. Those two nanostructured cleaning systems successfully removed vandalistic graffiti from stones decorated with red pre-Hispanic paintings in the archaeological site of Ba’ Cuana, Asunciòn Ixtalpetec, Oaxaca, Mexico.

In 2019, Musolino et al. proposed a two-component system with low environmental impact to remove graffiti, which is based on silica sol-gel chemistry, using hybrid silica gels, ethylene, and propylene glycols as co-solvents and dimethyl carbonate as green solvent [100]. The efficiency of those new systems of absorbing commercial spray components was assessed by nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopies, giving promising results for the implementation of those systems as green agent in graffiti removal.

Zykubek et al. tested 16 biocides available on the British and European markets *in situ* at 11 properties of the National Trust (NT) located in England and Wales. The testing areas include limestone, sandstone, marble, slate, and granite, as well as cast concrete, terracotta, and brick. This survey also included evaluation of the local microclimate, the condition assessment of the objects, past treatments, and identification of the micro-organisms present, such as algae, lichens, and mosses. After 24 months from the application of biocides, monitoring of the effectiveness was conducted with an adenosine triphosphate luminometer to measure eventual biological growth. Three of the most effective biocides, namely StoPrim Fungal, Moss Remover Pro50, and Preventol RI50, were further assessed. However, an occasional brown discolouration of Carrara marble was observed, due to the release of pigments by colonies of black cyanobacteria when treated by benzalkonium chloride-based biocides, as those used in this study. Further work is required to elucidate the dependency of the side effects that may accompany any biocide used on individual substrates [101].

Ricci et al. performed cleaning of two graffiti paints with different compositions (an alkyd- and an acrylic–based paints) from two stones (gneiss and travertine), by combining a low-toxic solvent ternary mixture consisting of ethyl alcohol/ acetone/ isooctane, followed by an Nd:YAG laser [102]. This study brings up the necessity in identifying the composition of the paints, in order to select the most appropriate solvent system, avoiding further interaction with the substrate.

Baglioni M. et al. removed paints based on vinyl, acrylic, and alkyd polymers, which are commonly found in contemporary street art, with a low-toxicity hydrogel system consisting of alkyl carbonates, a biodegradable non-ionic surfactant, 2-butanol, and an alkyl glycoside hydrotrope [103].

Pozzo et al. applied the anionic detergent Teepol® to granite tiles widely used as flooring material in private and public buildings [104]. It is recommended to clean polished granite cladding tiles with anionic detergents, without chelating agents in order to prevent damaging the material. The use of anionic detergent Teepol® facilitated extraction of iron forms, reducing the red discoloration, as opposed to mechanical cleaning with water, that caused an increase of red discoloration and darkening of the surface of the tiles, due to the spreading of the iron-based compounds from the cracks in the minerals.

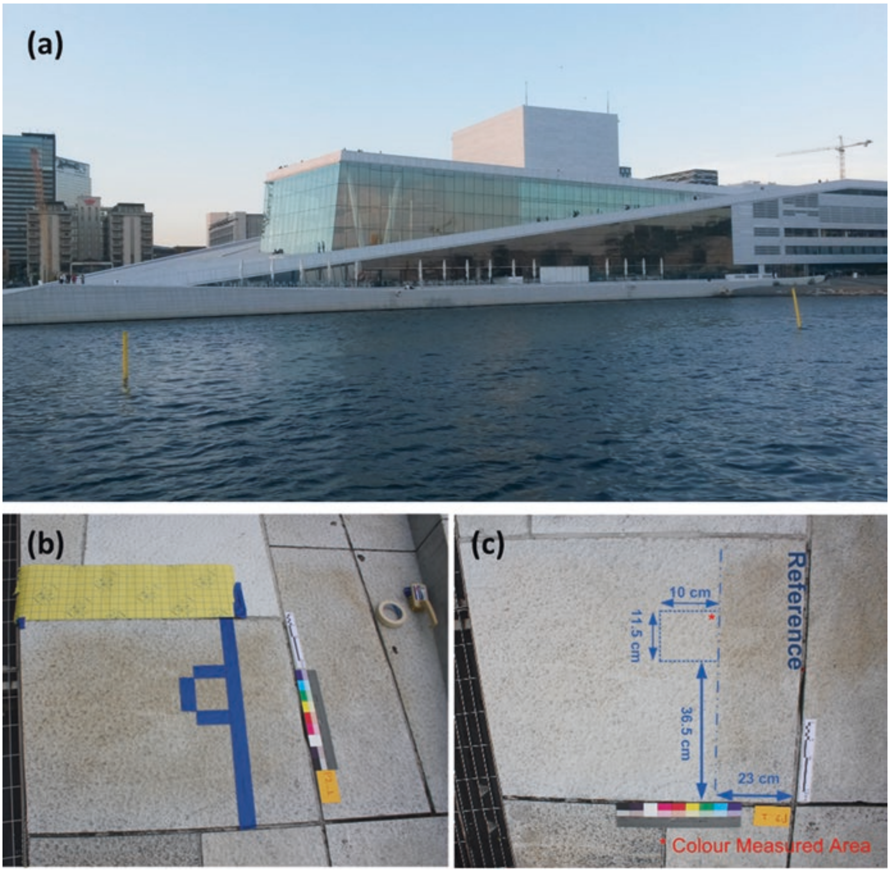

Fig. 2.5 View of the Opera Oslo House (Norway) (**a**), the area with discolouration (**b**) and the corresponding are after cleaning (**c**)

A very challenging example of cleaning discoloration is found in the Norwegian National Opera and Ballet House (OOH), which is a contemporary architecture listing monument, designed by Snøhetta Architects and built in Oslo from 2000 to 2008 [105]. The OOH was constructed by cladding, mainly Carrara marble tiles, both in the roof and the main plaza, all accessible to the public. It represents a connection of the city with the fjord landscape, and it is therefore of outstanding importance for the culture of the country and its population [106] (Fig. 2.5a).

In 2007–2008 the external marble slabs of OOH were impregnated, upon their placement, with a fluorinated acryl copolymer, followed by a polysaccharide-based product for anti-graffiti protection on the vertical surfaces [106]. The poor performance of the fluorinated acryl copolymer led to subsequent applications of other siloxane-based protectives in 2012. Despite cleaning operations that were regularly performed on the surfaces using hot water and alkalines, an intense yellow discoloration has appeared since 2008, altering the aesthetical characteristics and aspect of the building (Fig. 2.5b). The hard and sticky coating formed on the treated surface further attracted grime and pollutants, making the discoloration removal more difficult. Research carried out on the spot areas detected siloxanes and oxidized by-products, such as esters and carboxylates originating from previous treatments [107].

To remove the discolouration, specific formulations involving pure solvents, nanofluids, and nanogels using different cleaning supports like pulp poultices, cotton fabrics, and agar gels were designed and tested on samples from OOH in laboratory experiments. Figure 2.6 illustrates a macroscopical image of a discoloured Carrara sample from OOH (a) treated in laboratory with nanogels (b and in detail in e), the efficient cleaning macroscopical result (c), as well as images under the stereomicroscope before (d) and after cleaning (f). The best formulations were also applied and tested *in situ* [108].

This study proved the difficulty in removing aged polymers, especially when they have deeply penetrated inside the stone matrix, such as in this case, where the discoloration exceeded the depth of 2 cm from the surface. Furthermore, the hard coating did not allow any solvent penetration. Therefore, it was deemed necessary to first apply a chelating agent which, through capturing calcium ions, performed a microcracking to the coating (Fig. 2.7, 1first step). Subsequently, the nanofluids containing industrial solvents were able to further dissolve the coating and to detach it from the surface (Fig. 2.7, second step). The third step involved the application of

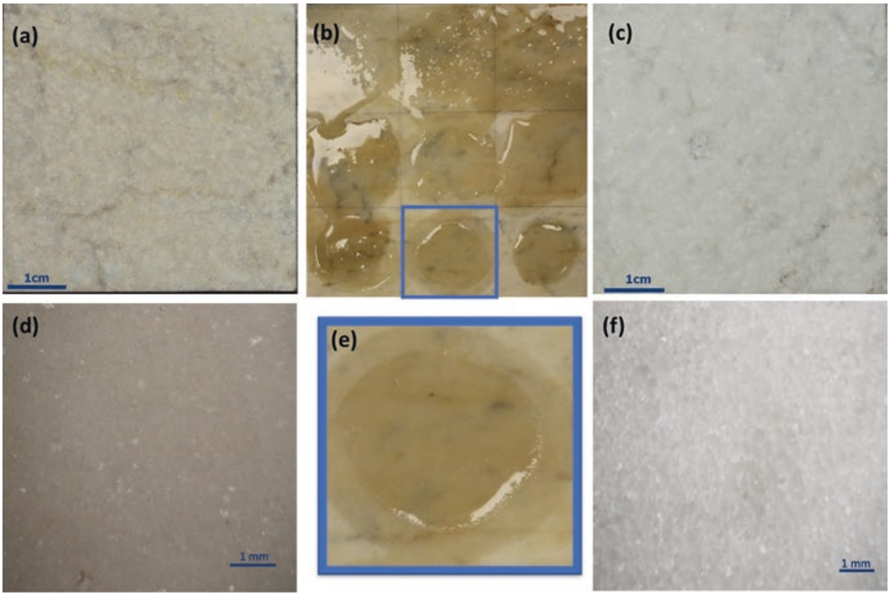

Fig. 2.6 Macroscopical image of a Carrara sample with discolouration from Opera Oslo House (**a**); a sample treated in laboratory with nanogels (**b**), the sample after cleaning (**c**), detail of cleaning gel (**e**), and sample with discolouration under the stereomicroscope before (**d**) and after cleaning (**f**)

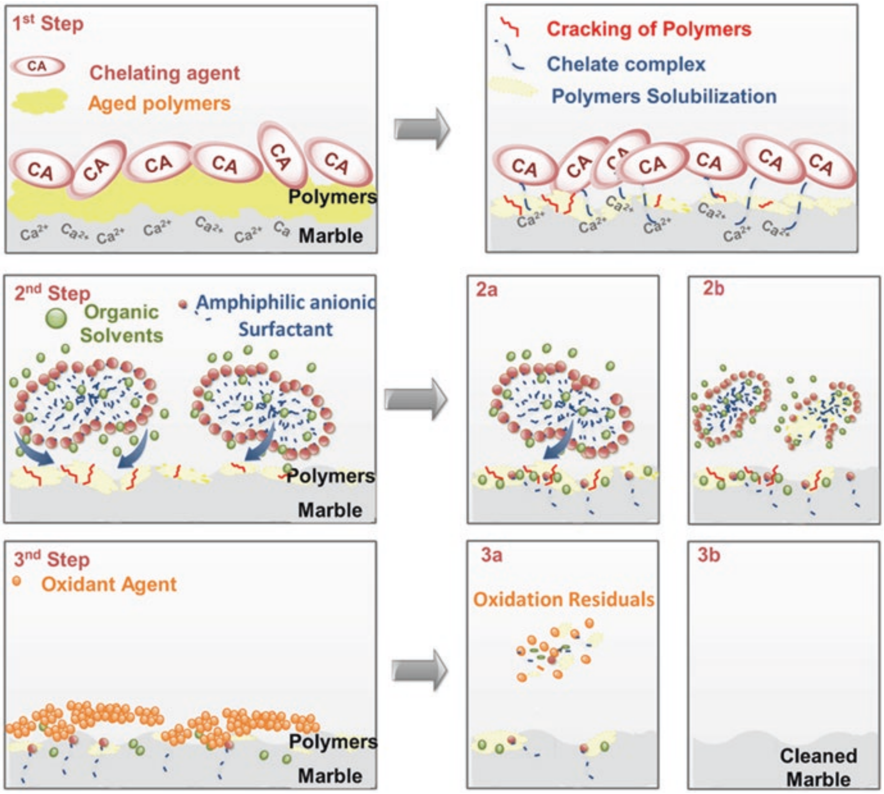

Fig. 2.7 A three-step cleaning methodology to remove the discolouration: first step: application of a chelating agent and cracking of polymer; second step: the nanogel application and detachment of polymer; third step: the oxidant removes the polymer residues

an oxidizing agent to facilitate the removal of polymeric residues decomposed from the previous treatments (Fig. 2.7, third step).

The changes induced after the three-step cleaning process in the b* colour parameter and the total colour difference ΔE referred to discoloured marble indicated that the three – step cleaning methodology induced more than a 50% change in the b* parameter related to yellowness, while luminosity also increased (Figs. 2.5c and 2.6c, f). Optical, 3D, and scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), colorimetric measurements, and FTIR spectroscopy proved that the three-step cleaning tests applied to stained samples can successfully remove the yellowing, as illustrated in Fig. 2.6c, f, without affecting the marble substrate.

2.8 Conclusions

Cleaning is the first conservation intervention in stone monuments. Since it is an irreversible procedure, it should be approached with maximum caution and scientific evidence. The effectiveness and the accuracy of the cleaning approach depends on the specialized personnel stemming from: (a) material scientists who are in charge of the diagnostic of the involved substrate characteristics, and micro- and macro-environmental parameters; (b) historians, curators, and architects that can document and integrate all the necessary steps to be followed in an inventory tool; (c) conservators that supervise any step of intervention, apply the recommended methods and products, and monitor the results of treatment; and last but not least (d) the citizens that can support and assist in the decision making, reasoning, and maintenance of the cleaning procedures.

Nowadays the advancement of the non-destructive techniques offers an enriched palette of tools that can unequivocally assist during the diagnostic phase of the substrate that should be cleaned. In addition, advanced systems regarding green chemicals, mechanical tools, specific devices with improved characteristics, ecological, controllable, and selective methods, as well as a mentality of starting with pilot *in situ* applications and then proceeding to the large area intervention are among the factors that could mitigate the risk of a treatment. All these parameters were approached and described in detail in exemplar papers dealing with stone cleaning. These data can be computed in mathematical models and digital systems that allow their elaboration and reliable-reasonable acceptance when a cost-effective decision has to be made. In addition, the dissemination of the results can raise public awareness and unanimity in order for successful treatments to be designed and applied. Furthermore, sustainable cleaning is directly related to a compatible protective treatment that should be applied to the cleaned surface.

Cleaning depends on the substrate, in terms of mineralogy, chemical composition, deposits, the stratigraphy of the layers formed, the deterioration pattern that should be healed, the surrounding environment in which the object is placed, etc. After the diagnostic survey of these factors, the causes of deterioration are identified, and the cleaning intervention can be planned.

Among the best performing techniques, specific attention should be paid to the cleaning with nebula water, micro-sandblasting, specific poultices with cleaning agents, ion-exchange resins, nanostructured fluids and nanogels, ion plasma, and bio-cleaning. It should be emphasized that the cleaning of the historic stone façades always requires a combination of methods and agents, selectivity, and controllability of the process, in order to remove damaging layers, without compromising the condition of the surface.

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References

1. Ashurst N. Cleaning Historic Buildings. Volume One: Substrates, Soiling & Investigation. Volume Two: Cleaning Materials & Processes. London: Donhead Publishing Ltd.; 1994.
2. Wilhelm K, Longman J, Orr SA, Viles H. Stone-built heritage as a proxy archive for long-term historical air quality: A study of weathering crusts on three generations of stone sculptures on Broad Street. Oxford, Science of The Total Environment. 2021; 759. https://doi.org/10.1016/j.scitotenv.2020.143.
3. Maravelaki-Kalaitzaki P and Biscontin G. Origin, characteristics and morphology of weathering crusts on Istria stone in Venice. Atmospheric Environment. 1999;33(11):1699–1709.
4. García-Florentino C, Maguregui M, Ciantelli C, Sardella A, Bonazza A, Queralt I, Carrero JA, Natali C, Morillas H, Madariaga JM, Arana G. Deciphering past and present atmospheric metal pollution of urban environments: The role of black crusts formed on historical constructions. Journal of Cleaner Production. 2020;243. https://doi.org/10.1016/j.jclepro.2019.118594.
5. Maintenance of pointing in historic buildings: decay and replacement. Final Report, EU-project POINTING, contract ENV4-CT98-706.
6. EN 15898:2011. Conservation of cultural property – Main general terms and definition.
7. Delgado Rodrigues J, Grossi A. Indicators and rating for the compatibility assessment of conservation actions. Journal of Cultural heritage. 2007;8:320–43.
8. Ashurst N. Introduction, Journal of Architectural Conservation. 2005; 3:2–6. DOI: https://doi.org/10.1080/13556207.2005.10784949
9. Snethlage R. Stone Conservation. In: Siegesmund S., Snethlage R. editor. Stone in Architecture. Springer, Berlin, Heidelberg. 2014. https://doi.org/10.1007/978-3-642-45155-3_7
10. Robert CM, Grimmer EA. Assessing Cleaning and Water-Repellent Treatments for Historic Masonry Buildings. National Park Service. 2000
11. Maravelaki-Kalaitzaki P. Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): characterization and origin. Analytica Chimica Acta. 2005;532:187–198.
12. Gomez-Heras M, Smith BJ, Viles, H. A Laboratory modelling of gypsum crust growth on lime-stone related to soot pollution and gaseous sulphur: implications of 'cleaner' environments for stone decay. In:Lukaszewicz J.W.&Niemcewicz P, editors. Proceedings of the 11th International Congresson Deterioration and Conservation of Stone, Nicolaus Copernicus UniversityPress Torun, 2008. 105–112
13. Ashurst J, Dimes FG. Conservation of buildings and decorative stone. London: Butterworth Heineman vol 2; 1990. p 174–184, 229.
14. Martin B Cleaning British limestone –what are the methods to arrive at optimal solutions. In: Domstiftung Regensburg Turm Fassade Portal. Regensbur: Sept. Schnell & Steiner; 2000a. p 99–103.
15. Ball J, Laing R, Young M. Stone Cleaning: Comparing Perceptions with Physical and Financial Implications, Journal of Architectural Conservation. 2000; 6:2: 47–62. DOI: https://doi.org/10.1080/13556207.2000.10785269
16. Young ME, Urquhart DCM, Laing R, Maintenance and repair issues for stone cleaned sandstone and granite building façades. Building and Environment. 2003;38:9:1125–1131. DOI: https://doi.org/10.1016/S0360-1323(03)00084-2
17. Maxwell, I. Stone cleaning: for better or worse? An overview. In Robin G.M. Webster, editor. Stone cleaning and the nature, soiling and decay mechanisms of stone. Proceedings of the international conference held in, Edinburgh UK, 14–16 April 1992. London: Routledge; 1992. p. 3–49. ISBN 1-873394-098.
18. Winkler EM. Properties, Durability. In Stone in Architecture. 3rd ed, Berlin: Springer-Verlag, 1997.

19. De Frascá MHBO, Navarro FC, Quitete EB. Staining tests for granitic stone conservation. In Preservation of Cultural Heritage. Engineering Geology for Society and Territory; 2015;8:511–514.
20. Torraca G. Porous Building Materials, Rome: ICCROM (International Centre for the Study of the preservation and the restoration of Cultural Property). 1982.
21. Conahan, Heather. An Assessment of the Effects of Hydrofluoric Acid Based Cleaner on Unglazed Architectural Terracotta. (Masters Thesis). Philadelphia, PA: University of Pennsylvania. http://repository.upenn.edu/hp_theses. 1999.
22. Vergèc-Belmin V, Heritage A, Bourgèc A. Powdered Celluloce Poulticec in Stone and Wall Painting Concervation - Mythc and Realitiec. Studiec in Concervation. 2001;56:4:281–297. DOI: https://doi.org/10.1179/204705811X13159282692923
23. Guidetti V, Uminski M. Ion Exchange Resins for Historic Marble Desulfatation and Restoration. In Vasco Fassina, editor. Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19–24, 2000, vol. 2. Amsterdam: Elsevier Science B.V.; 2000. p. 327–333.
24. Giovagnoli A, Meucci, Tabasso Laurenzi M. Ion Exchange Resins Employed in the Cleaning of Stones and Plasters: Research of Optimal Employment Conditions and Control of their Effects. In Deterioramento e Conservazione della Pietra: Atti del 3 Congresso Intemazionale, Venice, October 24-27 1979. Padova: Instituto di Chimica Industriale, Università degli Studi di Padova; 1982. p. 499–510.
25. Boccalon E, Nocchetti M, Pica M, Romani A, Casciola M. Layered double hydroxide and zirconium phosphate as ion exchangers for the removal of 'black crusts' from the surface of ancient monuments. Dalton Trans. 2018. DOI: https://doi.org/10.1039/c7dt0395
26. Willett C. The Conservation, Repair and Management of War Memorials, Published by Historic England. 2017 HistoricEngland.org.uk/advice/caring-for-heritage/war-memorials/. Published 14 June 2017
27. Gulotta D, Saviello D, Gherardi F, Toniolo L, Anzani M, Rabbolini A, Goidanich S, Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan. Heritage Science. 2014;2:1.
28. Appolonia L, Bertone A, Brunetto A, Vaudan D, The St. Orso Priory: the comparison and testing of cleaning methods. Journal of Cultural Heritage. 2000;1:S105–S110.
29. Werner M. Research on cleaning methods applied to historical stone monuments. In Baer NS, Sabbioni S, Sors AI, editors. Science, technology, and European cultural heritage: proceedings of the European symposium. Boston: Published for the Commission of the European Communities by Butterworth-Heinemann Publishers. 1991. p. 688–691.
30. Iglesias-Campos MÁ, Prada Pérez JL, Fortes SG. Microblasting cleaning for façade repair and maintenance: Selecting technical parameters for treatment efficiency. Construction and Building Materials. 2015;94: 605–612.
31. Perez-Monserrat E, Varas M, Fort R, De Buergo M. Assessment of Different Methods for Cleaning the Limestone Façades of the Former Workers Hospital of Madrid, Spain. Studies in Conservation. 2011; 56(4):298–313.
32. Normandin KC, Weiss NR, Slatonm D. Cleaning techniques in conservation practice. Donhead. 2005; 146. ISBN 978-187-3394-748.
33. Franzoni E, Volpi L, Bonoli A, Spinelli R, Gabrielli R. The environmental impact of cleaning materials and technologies in heritage buildings conservation. Energy and Buildings. 2018;165:92–105. https://doi.org/10.1016/j.enbuild.2018.01.051.
34. Franzoni E, Volpi L, Bonoli A. Applicability of life cycle assessment methodology to conservation works in historical building: the case of cleaning. Energy and Buildings. 2020; 214. ISSN 0378-7788.
35. Odgers D, Henry A. Practical Building Conservation: Stone. Ashgate Publishing, Ltd. 2012; 338.
36. Moropoulou A, Delegou ET, Avdelidis NP, Koui M. Assessment of cleaning conservation interventions on architectural surfaces using an integrated methodology. In: Vandiver P,

Goodway M, Druzik JR, Mass JL, editors. Materials issues in art and archaeology VI, vol. 712. Pittsburgh: Publ. Materials Research Society. 2002;69–76.
37. Agrawal OP, Singh T, Kharbade BV, Jain KK, Joshi GP: Discolouration of Taj Mahal marble – a case study. In: Grimstad K, editor. ICOM committee for conservation: 8th triennial meeting. Volume II. The Getty Conservation Institute; 1987: 447–52.
38. Cushmann M, Wolbers R. A new approach to cleaning Iron stained marble surfaces. WAAC Newsletter. 2007;29: 23–28.
39. Bams V, Dewaele S. Staining of white marble. Materials Characterization. 2007; 58:11: 1052–1062.
40. Pinna D, Galeotti M, Rizzo A. Brownish alterations on the marble statues in the church of Orsanmichele in Florence: what is their origin?. Heritage Science. 2015;3:7 https://doi.org/10.1186/s40494-015-0038-1.
41. Matero FG, Tagle AA. Cleaning, iron stain removal, and surface repair of architectural marble and crystalline limestone: The metropolitan club. Journal of the American Institute for Conservation. 1995;34:1:49–68.
42. Macchia A, Sammartino MP, Laurenzi Tabasso M. A new method to remove copper corrosion stains from stone surfaces. J Archaeol Sci. 2011; 38:1300–7.
43. Werner A, Synthetic Materials in Art Conservation. Journal of Chemical Education. 1981; 58:4: 321–324.
44. Horie CV. Materials for conservation: organic consolidants, adhesives and coatings. Routledge; 2010.
45. Oddy A. The conservation of marble sculptures in the British Museum before 1975. Stud Conserv. 2002;47:145–54.
46. Gervais C, Grissom CA, Little N, Wachowiak MJ. Cleaning Marble with Ammonium Citrate. Studies in Conservation. 2010;55(3):164–176. https://doi.org/10.1179/sic.2010.55.3.164
47. Taxiarchou M, Panias D, Douni I, Paspaliaris I, Kontopoulos A. Removal of iron from silica sand by leaching with oxalic acid. Hydrometallurgy. 1997;46:1:215–227.
48. Young ME, D. Urquhart CM. Algal growth on building sandstones: effects of chemical stone cleaning methods. Quarterly Journal of Engineering Geology and Hydrogeology. 1998;31:315–324. https://doi.org/10.1144/GSL.QJEG.1998.031.P4.04
49. Overview report Biocides DG Health and Food Safety Luxembourg: Publications Office of the European Union, 2019, doi:10.2772/55801 ND-BC-14-001-EN-N.
50. Urzí C, de Leo F. Evaluation of the efficiency of water repellent and biocide compounds against microbial colonization of mortars. Int Biodet Biodeg. 2007;60:25–34.
51. Toreno G, Isola D, Meloni P, Carcangiu G, Selbmann L, Onofri S, Caneva G, Zucconi L. Biological colonization on stone monuments: A new low impact cleaning method. Journal of Cultural Heritage. 2018;30:100–109. https://doi.org/10.1016/j.culher.2017.09.004.
52. Pinna D, Galeotti M, Perito B, Daly G, Salvadori B. In situ long-term monitoring of recolonization by fungi and lichens after innovative and traditional conservative treatments of archaeological stones in Fiesole (Italy). International Biodeterioration & Biodegradation. 2018;132:49–58. https://doi.org/10.1016/j.ibiod.2018.05.003.
53. Charola AE, Bläuer C. Salts in masonry: an overview of the problem. Restor. Build. Monuments. 2015;21:119–135.
54. Lombardo T, Simon S. Desalination by poulticing. Laboratory study on controlling parameters. In: Kwiatkowski D, Löfvendahl R, editors. Proceedings of the 10th international congress on deterioration and conservation of stone, Stockholm, 27 June–2 July. Stockholm: ICOMOS; 2004. p 323–330.
55. Egartner I, Sass O. Using paper pulp poultices in the field and laboratory to analyse salt distribution in building limestones. Herit Sci. 2016;4:41. https://doi.org/10.1186/s40494-016-0110-5
56. van Hees RPJ, Naldini S, Lubelli B. The development of MDDS-COMPASS. Compatibility of plasters with salt loaded substrates. Compass – Construction and Building Materials. 2009; 23(5):1719–173.

57. Lubelli B, Van Hees RPJ. Desalination of masonry structures: Fine tuning of pore size distribution of poultices to substrate properties. Journal of Cultural Heritage. 2010;11(1):10–18.
58. Granneman SJC, Lubelli B, van Hees RPJ. Mitigating salt damage in building materials by the use of crystallization modifiers – a review and outlook. Journal of Cultural Heritage. 2019;40:183–194. https://doi.org/10.1016/j.culher.2019.05.004.
59. Baglioni P, Berti D, Bonini M, Carretti E, Dei L, Fratini E, Giorgi R. Micelle, microemulsions, and gels for the conservation of cultural heritage. Advances in colloid and interface science. 2014;205:361–371.
60. Domingues J, Bonelli N, Giorgi R, Baglioni P. Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings. Applied Physics. 2014;A 114:705–710.
61. Carretti E, Dei L, Baglioni P. Solubilization of acrylic and vinyl polymers in nanocontainer solutions. Application of microemulsions and micelles to cultural heritage conservation. Langmuir. 2003;19:19:7867–7872.
62. Baglioni M, Benavides YJ, Desprat-Drapela A, Giorgi R. Amphiphile-based nanofluids for the removal of styrene/acrylate coatings: Cleaning of stucco decoration in the Uaxactun archeological site (Guatemala). Journal of Cultural Heritage. 2015;16:862–868.
63. Baglioni M, Raudino M, Berti D, Keiderling U, Bordes R, Holmberg K, Baglioni P. Nanostructured fluids from degradable nonionic surfactants for the cleaning of works of art from contaminants. Soft Matter. 2014;10:6798–6809.
64. Grassi S, Favaro M, Tomasin P, Dei L. Nanocontainer aqueous systems for removing polymeric materials from marble surfaces: A new and promising tool in cultural heritage conservation. Journal of cultural heritage. 2009;10:3:347–355.
65. Tabasso ML, Simon S. Testing methods and criteria for the selection/evaluation of products for the conservation of porous building materials. Reviews in conservation. 2006;7:67–82.
66. Baglioni M, Alterini M, Chelazzi D, Giorgi R, Baglioni P. Removing polymeric coatings with nanostructured fluids: Influence of substrate, nature of the film, and application methodology. Front Mater. 2019;6:311. doi: https://doi.org/10.3389/fmats.2019.00311
67. Stulik D, Miller D, Khanjian H, Khandekar N, Wolbers R, Carlson J, Petersen WC. Solvent gels for the cleaning of works of art: the residue question. Getty Publications. Research in Conservation by Stulik; 2004.
68. Mastrangelo R, Montis C, Bonelli N, Tempesti P, Baglioni P. Surface cleaning of artworks: Structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks. Physical Chemistry Chemical Physics. 2017;19:35:23762–23772
69. Carretti E, Dei L. Gels as Cleaning Agents in Cultural Heritage Conservation. In: Weiss RG, Terech P, editors. Molecular Gels. Dordrecht: Springer;2006. https://doi.org/10.1007/1-4020-3689-2_28
70. Bonini M, Lenz S, Giorgi R, Baglioni P. Nanomagnetic sponges for the cleaning of works of art. Langmuir. 2007;23:17: 8681–8685.
71. Domingues JA, Bonelli N, Giorgi R, Fratini E, Gorel F, Baglioni P. Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts. Langmuir. 2013;29:8:2746–2755.
72. Riedo C, Caldera F, Poli T, et al. Poly(vinylalcohol)-borate hydrogels with improved features for the cleaning of cultural heritage surfaces. Herit Sci. 2015;3:23. https://doi.org/10.1186/s40494-015-0053-2
73. Sun M, Zou J, Zhang H, Zhang B. Measurement of reversible rate of conservation materials based on gel cleaning approach. Journal of Cultural Heritage. 2015;16:5:719–727. https://doi.org/10.1016/j.culher.2014.11.006
74. Boccalon E, Nocchetti M, Pica M, Romani A. Sterflinger K. Hydrogels: A 'stepping stone' towards new cleaning strategies for biodeteriorated surfaces. Journal of Cultural Heritage. 2021;47:1–11. https://doi.org/10.1016/j.culher.2020.07.008.
75. Voltolina S, Aibéo C, Cavallin T, Egel E, Favaro M, Kamenova V, Patelli A, Nodari I, Pavlov I, Pavlova I, Schalm O, Scopece P, Simon S, Storme P, Falzacappa Assessment of plasma torches as innovative tool for cleaning of historical stone materials, Journal of Cultural Heritage. 2016;2: 940–950, https://doi.org/10.1016/j.culher.2016.05.001.

76. Aibéo C, et al. EU-PANNA project: development of a portable plasma torch for cleaning multi surfaces and coating deposition. In Dahlin E, editor. 2nd European Workshop on Cultural Heritage Preservation, NILU – Norwegian Institute for Air Research. 2012; p.55–64.
77. Soffritti I, D'Accolti M, Lanzoni L, Volta A, Bisi M, Mazzacane S, Caselli E. The Potential Use of Microorganisms as Restorative Agents: An Update. Sustainability. 2019; 11(14):3853. https://doi.org/10.3390/su11143853
78. Webster A, May E. Bioremediation of Weathered-Building Stone Surfaces. Trends Biotechnol. 2006;24:255
79. Cappitelli F, Toniolo L, Sansonetti S, Gulotta D, Ranalli G, Zanardini E, Sorlini C. Advantages of Using Microbial Technology over Traditional Chemical Technology in Removal of Black Crusts from Stone Surfaces. Historical Monuments Applied and Environmental Microbiology. 2007; 73 (17):5671–5675. DOI: https://doi.org/10.1128/AEM.00394-07.
80. Troiano F, Gulotta D, Balloi A, Polo A, Toniolo L, Lombardi E, Daffonchio D, Claudia Sorlini, Cappitelli F. Successful combination of chemical and biological treatments for the cleaning of stone artworks. International Biodeterioration & Biodegradation. 2013;85:294–304. https://doi.org/10.1016/j.ibiod.2013.08.011.
81. Bosch-Roig P, Lustrato G, Zanardini E, Ranalli G. Biocleaning of Cultural Heritage stone surfaces and frescoes: Which delivery system can be the most appropriate? Ann. Microbiol. 2015;65:1227–1241.
82. Romano I, Abbate M, Poli A, et al. Bio-cleaning of nitrate salt efflorescence on stone samples using extremophilic bacteria. Sci Rep. 2019;9:1668. https://doi.org/10.1038/s41598-018-38187-x
83. Valentini F, Diamanti A, Palleschi G. New bio-cleaning strategies on porous building materials affected by biodeterioration event. Applied Surface Science. 2010;256:22: 6550-6563. https://doi.org/10.1016/j.apsusc.2010.04.046.
84. Ďoubal J. Cleaning Stone – The Possibilities for an Objective Evaluation. In Hughes JJ and Howind T, editors. Proceeding of the 13th International Congress on the Deterioration and Conservation of Stone: Conservation. 2016;729–736.
85. Kapsalas P, Maravelaki-Kalaitzaki P, Zervakis M, Delegou ET, Moropoulou A. Optical inspection for quantification of decay on stone surfaces. NDT & E Inter. 2007;40:2–11.
86. Manganelli Del Fà R, Riminesi C, Tiano P. Monitoring of surface pattern of artistic and architectural artefacts by means of ultra-close range photogrammetry. In Nardini, editor. Proceeding of Kermes Quaderni ESRARC2014, 6th European Symposium on Religious Art, Restoration and Conservation. 2014;164–167. ISBN: 978-88-404-4365-2.
87. Fort R, Mingarro F, Lopez de Azcona MC, Rodriguez Blanco J. Chromatic parameters as performance indicators for stone cleaning techniques. Color Res Applic. 1999;25:442–6.
88. EN 15886: Conservation of cultural property – Test methods – Color measurement of surfaces. 2010.
89. Hauff G, Kozub P, D'ham G. Which cleaning method is the most appropriate one? A systematic approach to the assessment of cleaning test panels. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Torun, Poland:Nicolaus Copernicus University Press 2008;381–388.
90. Delegou ET, Ntoutsi I, Kiranoudis CT, Sayas J, Moropoulou A. Advanced and novel methodology for scientific support on decision-making for stone cleaning. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing AG. 2018;299–234. https://doi.org/10.1007/978-3-319-72260-3_14
91. EN 17488:2020. Conservation of cultural heritage – Procedure for the analytical evaluation and selection of cleaning methods for porous inorganic materials used in cultural heritage.
92. Vergés-Belmin V. Towards a definition of common evaluation criteria for the cleaning of porous building materials: a review. Science and Technology for Cultural Heritage. 1996;5(1):69–83.
93. Revez MJ, Delgado Rodrigues J. Incompatibility risk assessment procedure for the cleaning of built heritage. J Cult Herit. 2016;18:219–228.

94. Gaspar P, Hubbard C, McPhail D, Cummings A. A topographical assessment and comparison of conservation cleaning treatments. Journal of Cultural Heritage. 2003; 4, Suppl 1:294–302. https://doi.org/10.1016/S1296-2074(02)01211-6.
95. Iglesias M, Prada JL, Guasch N. Technique for cleaning Tarragona Miocene age dolomitized silty limestone, altered by urban pollution. Materiales de Construccion. 2008; 58(289–290):247–262.
96. Sanmartín P, Cappitelli F, Mitchell R. Current methods of graffiti removal: A review. Construction and Building Materials. 2014;71:363–374. DOI: https://doi.org/10.1016/j.conbuildmat.2014.08.093
97. Sun M, Zou J, Zhang H, Zhang B. Measurement of reversible rate of conservation materials based on gel cleaning approach. J. Cult. Heritage. 2015;16 (5): 719–727. DOI:https://doi.org/10.1016/j.culher.2014.11.006
98. Pozo-Antonio JS, A. Ramil, T. Rivas, A.J. López, M.P. Fiorucci Effectiveness of chemical, mechanical and laser cleaning methods of sulphated black crusts developed on granite Constr. Build. Mater. 2016;112:682–690
99. Baglioni M, Poggi G, Benavides YJ, Martínez Camacho F, Giorgi R, Baglioni P. Nanostructured fluids for the removal of graffiti – A survey on 17 commercial spray-can paints. Journal of Cultural Heritage. 2018;34:218–226.
100. Musolino M, Aricò F, Tundo P. An innovative and sustainable approach to spray paint graffiti removal from Istrian stone through the silica sol-gel chemistry: A preliminary assessment. Journal of Cultural Heritage. 2019:36:268–274.
101. Zykubek K, Proudfoot T, Lithgow K, Carpenter D. Research on the selection of biocides for the ‘disinfection’ of statues and masonry at the National Trust (UK). Journal of the Institute of Conservation. 2020;43:3:225–241.
102. Ricci C, Gambino F, Nervo M, Piccirillo A, Scarcella A, Zenucchini F, Pozo-Antonio JS. Developing New Cleaning Strategies of Cultural Heritage Stones: Are Synergistic Combinations of a Low-Toxic Solvent Ternary Mixtures Followed by Laser the Solution? Coatings. 2020;10(5):466. https://doi.org/10.3390/coatings10050466
103. Baglioni M, Poggi G, Giorgi R, Rivella P, Ogura T, Baglioni P. Selective removal of over-paintings from “Street Art” using an environmentally friendly nanostructured fluid loaded in highly retentive hydrogels. Journal of Colloid and Interface Science. 2021. https://doi.org/10.1016/j.jcis.2021.03.054.
104. Pozo-Antonio JS, Rocha CSA, Pereira MFC, et al. Evaluation of side effects of mechanical cleaning with an anionic detergent on granite cladding tiles. Environ Sci Pollut Res. 2021; 28:15173–15184. https://doi.org/10.1007/s11356-020-11733-9
105. http://snohetta.com/projects
106. Nilsen, B. Maintenance Operations Management (MOM) Information for the project: The Oslo Opera House – Condition analysis and proposal for cleaning, protection and maintenance of exterior marble. s.l. : Betong Consult as, 04.11.15. doc 201501489 Operaen i Oslo – Utendørs marmor, rev. 02.
107. Gherardi F, Kapridaki C, Roveri M, Gulotta D, Maravelaki PN, Toniolo L. The deterioration of Apuan white marble in contemporary architectural context. J Cult Herit. 2019;35:297–306.
108. Maravelaki PN, Toniolo L, Gherardi F, Kapridaki C, Arabatzis I. The Oslo Opera House – Condition Analysis and Proposal for Cleaning, Protection and Maintenance of Exterior Marble. In: Transdisciplinary Multispectral Modeling and Cooperation for the Preservation of Cultural Heritage. TMM_CH 2018. Communications in Computer and Information Science. Springer, Cham.2019: Springer International Publishing.

Chapter 3
Laser Cleaning on Stonework: Principles, Case Studies, and Future Prospects

Paraskevi Pouli

Abstract The use of laser light to selectively remove and/or precisely reduce unwanted layers and encrustations from the surface of cultural heritage (CH) objects and monuments was systematically investigated during the past 30 years bringing about a significant breakthrough in the field. This chapter aims at briefly introducing the reader to the basic concepts of laser cleaning, while highlighting the critical and decisive parameters that determine an efficient and successful laser ablation on stonework. Limitations ensuring a safe process are discussed, and good practice guidelines for laser cleaning interventions are presented, with emphasis to their practical implementation in three laser cleaning projects with different conservation challenges. Finally, ongoing issues related to careful assessment and reliable monitoring of the process are discussed.

Keywords Laser cleaning · Stonework · Good-practice guide

3.1 What Is Laser Cleaning: Principles of Operation

LASER (Light Amplification by Stimulated Emission of Radiation) is a unique illumination source that nowadays holds a vital role in many every-day applications (i.e., material science, communications, medicine, entertainment, etc.). Laser light was born in the laboratories in the early 60s based on Einstein's studies on the absorption and emission of light. It was progressively established as a valuable diagnostic and material processing tool due to its distinctive features such as monochromaticity (it is emitted in light beams of single or narrow bands of wavelengths), high directionality, and coherence, in addition to its high energy. These unique properties enable laser-material interactions that are characterised by selectivity, spatial confinement, remote action, immediate control, and feedback, and made possible

P. Pouli (✉)
Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Heraklion, Crete, Greece
e-mail: ppouli@iesl.forth.gr

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the broad use of lasers for analytical and cleaning purposes in a number of material processing applications, as well as in the cultural heritage (CH) field [1, 2].

Laser-assisted removal is realized with the deposition of light energy in a controlled volume of material (in the range of a few cubic micrometres)[1] within a short time frame (usually a few nanoseconds).[2] This rapid energy deposition results, through a series of processes, in material breakdown, generation of a micro-plasma plume, and eventually in material removal. In fact, the interaction of intense laser light with matter is a complex process, also known as laser ablation, to which many parameters play important role.

Physical and chemical properties of the material, such as the absorption coefficient[3] (a), the thermal conductivity[4] (k), the heat capacity[5] (C), etc., are decisive for the quality of the cleaning intervention. For materials that strongly absorb the laser light, laser-ablation is effectively taking place within a well-defined and restricted volume (Fig. 3.1), and thus any thermal or photo-chemical effects to the underlying or surrounding material are minimal. Given that the properties of the material are inherent and cannot be changed, a safe and precise laser cleaning process can be influenced and controlled by the careful selection of the characteristics of the laser light. The wavelength[6] (λ), the applied energy density or fluence[7] and the pulse duration[8] (τ_p) have a major role in ensuring efficient and satisfactory cleaning processes. Other important factors are the laser beam quality and profile, the repetition rate and the use of enhancing liquids, e.g. water. Fine-tuning of all these parameters enables the development of an appropriate cleaning methodology and is crucial for successful conservation interventions that will respect and safeguard the original surfaces.

In this respect, another very important condition refers to the "self-limiting" mechanism, i.e., the significant difference that characterizes the onset for ablation (*ablation threshold*) between the (unwanted) over-layer and the original surface [1, 2]. As a rule of thumb this condition is effective for most of the cases involving dark encrustations (e.g., soiling and pollutants accumulations) on light-coloured

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[1] 1 cubic micrometer (μm^3) is a SI measurement unit of volume with sides equal to one micrometer (1 μm = 1 10^{-6} meter = 1 millionth of a meter).

[2] 1 nanosecond (ns) = 1 10^{-9} second = 1 billionth of a second.

[3] The absorption coefficient (a) defines how much light of a given wavelength/color (λ) is absorbed by a material of a given thickness.

[4] The thermal conductivity (k) of a material is a measure of its ability to conduct/transfer heat.

[5] The heat capacity (C) denotes the the amount of thermal energy required to raise the temperature of a substance by one degree.

[6] λ = The length of one complete light wave. Wavelength is a key characteristic of the laser light, usually fixed for any given laser system, and characterizes the "colour" of its monochromatic dimension (measured in *nm*).

[7] F = the energy (E) delivered per unit area. In practice this is measured as $F = E/S$ (*measured in J/cm*^{2}), where E is the output energy of the system for a single laser pulse and S the surface of the irradiated area.

[8] τ_p = The duration of a single laser pulse (τ_p ranging from several microseconds (*μs,* 10^{-6} s) to picoseconds (*ps,* 10^{-12} s) are commonly used in laser cleaning applications).

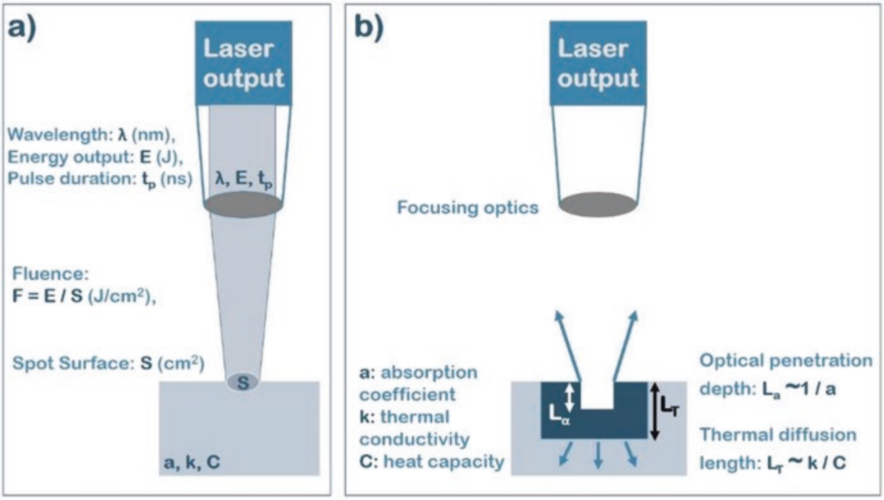

Fig. 3.1 Schematic representation of (**a**) the laser system parameters and (**b**) the material properties that rule the laser-matter interaction

stonework (e.g., white marble or limestone), but it may not apply in all cleaning challenges. Therefore, extensive studies have been carried out with the aim to prove and establish laser cleaning, while, at the same time, significant research is nowadays focused on developing reliable monitoring diagnostics.

3.2 Advantages and Limitations

Lasers offer a number of important advantages in respect to other commonly used cleaning techniques, i.e., chemical (solvent/paste) and mechanical (abrasive/scalpel) cleaning, as their unique properties allow the effective handling of a number of open and vital issues in CH conservation. Laser light is selectively interacting only with the materials that significantly absorb the specific laser wavelength, resulting in cleaning interventions confined in space and materials. Indeed, for self-limiting conditions, the removal process is restricted only to the highly-absorbing, usually dark-coloured encrustation, and thus, any risks for damages or accidents to the original surface due to over-cleaning, or operator's fatigue and inattention, are practically minimized. This is particularly important for objects with high surface relief and curved details, or for delicate and damaged original surfaces, as lasers can effectively remove the encrustation, and reveal the substrate intact. Furthermore, they enable contactless and distant operations, as no excessive pressure is exercised onto fragile surfaces, minimizing any harmful results.

In parallel, laser cleaning can offer strictly localized action, while it is spatially confined only to the size of the beam diameter,[9] without affecting the underlying or adjacent areas. As a result, issues related to precision of intervention, especially in cases of non-homogeneous surface crusts, can be easily overcome, while issues associated with uncontrolled penetration and/or spread of chemicals into the bulk of the treated surfaces and their surrounding areas, as well as difficulties in residues removal, are clearly avoided.

Finally, problems associated with the insufficient visibility of the surface under treatment and the monitoring of the process, as well as repetitive and time-consuming applications, have been significantly restrained due to the immediate control and feedback offered by laser cleaning. Issues related to the health and safety of the operators/conservators and the environment are effectively tackled, by following strict rules upon laser operation, as well as by carefully collecting and disposing the extracted dust waste.

3.2.1 Discoloration Side Effects: Darkening of Pigments and Yellowing of Stone

The wide use of lasers in CH conservation has been often restricted and criticized due to side effects associated with undesirable discoloration observed on the treated surfaces. Darkening of paints, as well as yellowing of the cleaned stonework have been reported as unfavourable fallouts of laser cleaning [3, 4] urging for further studies.

Discoloration of pigments was among the first drawbacks reported during one of the earliest laser cleaning interventions at the Portal of Amiens Cathedral in France, 25 years ago [5]. Systematic studies both on pigment powder, as well as on paint mock-ups, have been performed, aiming to investigate the sensitivity of pigments to laser irradiation, taking into account both the material properties (chemical composition of the pigment and the binding media) and the laser parameters (λ, F, τ_p, etc.) [6–17]. These studies indicated that darkening of the pigment particles and the paint (pigment-binder mixtures) appears in most of the studied cases upon direct exposure to laser light and depends closely to the chemistry of the pigment and the binder, as well as the applied irradiation parameters. Light-sensitive pigments, such as red vermilion (HgS, cinnabar), are particularly sensitive also to lasers, either due to phase transition to black meta-cinnabar [9], or chemical reduction of HgS to the darker Hg_2S [10, 13]. Lead pigments discolor only temporarily [10, 12], as their darkening appears temporal while its reversal time depends on the composition of the pigments and the applied irradiation parameters. Apparently, the chemical

[9] Transportable pulsed laser cleaning systems emit beams with circular diameter, usually in the range of 5–9 mm. Using appropriate focusing optics the size of the beam diameter can be regulated and eventually focused to as small as 1 mm.

composition of the binding medium and its absorbance to the applied laser beam are important for the appearance of darkening phenomena. It was reported that for highly absorbing binders (i.e., drying seed oils, protein-based compounds, such as eggs and glues), the interaction of the ultraviolet (UV) laser beam with the paint was restricted to a superficial layer, preventing damage to the paint bulk [4, 16, 17]. Nevertheless, as proven by the Acropolis case [31], paint layers or traces hidden behind the encrustation on polychromed stonework can be safeguarded on the condition that the operating parameters are fine-tuned, and the operator has the total control of the intervention (i.e., low pulse repetition rates are employed).

On the other hand, discoloration of irradiated stone surfaces towards yellower hues is mainly associated with infrared (IR) laser ablation of environmental encrustation from marble surfaces and has been under investigation through the past 25 years [18–34]. These studies discuss a number of hypotheses that have been put forward in order to explain its origin and, accordingly, to offer solutions for its prevention and/or remediation. Initially, it was investigated whether discoloration was due to the uncovering and revealing of pre-existing layers or patinas (i.e., scialbaturas [4, 18, 30]). These colored surfaces may have been developed naturally through the years due to the stone's exposure to the environmental conditions, or they may have been applied intentionally as protective coatings or as a preparation surface for the polychromy. The hypothesis that the color of the cleaned surface is different to what was expected because its original surface has been altered due to its proximity with the encrustation has been also considered. Indeed, it has been reported that migration of water-soluble organic compounds from the encrustation to the underlying stone can be favoured in humid environments, causing significant changes to the original stone color [20, 21]. In any case, no matter whether the colored layers have been developed naturally or they have been applied on purpose, they may keep valuable historical evidence (sculpted details and tooling traces, pigment remnants, etc.), and therefore their protection and safeguarding is considered imperative [22].

Other hypotheses refer to the chemical transformation of iron and other metallic components of the crust and stone, induced by the photo-thermal mechanisms that govern the IR laser ablation. Although the presence of iron in the crust is very low (~0.6%) [23], its chemical transformation from hematite (Fe_2O_3) into magnetite (Fe_3O_4), goethite (α-FeO(OH)) or even maghemite (γ-Fe_2O_3), may result in notably visible discoloration [19, 24–27].

Finally, attention was focused on insufficient cleaning due to the selective vaporization of the darker components of the crust. Actually, the dark-colored particles, embedded in the gypsum bulk of the pollution crusts, absorb highly the IR radiation and, thus, irradiation at relatively low F values may support their preferential removal, leaving behind remnants of the non-ablated gypsum matrix, which appear yellow [3, 34].

Apparently, given that each distinct cleaning challenge fulfils more than one of the above hypotheses, there is no unique and unambiguous answer to the origin of the yellow discoloration. Therefore, it is imperative that a thorough investigation of the stratigraphy and the components of the encrustation takes place prior to defining the optimum cleaning level, which will eventually influence the degree of the discoloration.

In parallel a series of experiments were undertaken using different laser parameters (λ, t_p, F values etc.) [4, 28–34] with the aim to avoid or rectify the unpleasant yellowing. These experiments employed real fragments, as well as technical mock-ups simulating black crusts, starting from its simplistic approach, i.e., charcoal particulates embedded in gypsum [4], to more sophisticated crust simulations [28]. Comparative tests, using the 1064 nm and 355 nm beams from a QS – Nd:YAG laser, confirmed the IR-induced discoloration on the gypsum-charcoal mock-ups. The presence of the charcoal was found to have a vital contribution to the recorded discoloration, as the intensity of the yellowing was found to be dependant to its quantity. Furthermore, voids, resulting due to preferential removal of charcoal, were reported upon irradiation with lower F values, at least for those ones that lay below the ablation threshold of gypsum and above the one of charcoal. On the contrary, no discoloration was observed to the reference gypsum mock-ups (without charcoal) or upon UV irradiation of the gypsum-charcoal ones. In this latter case, a "layer-by-layer" model of removal was confirmed for higher F values, which put into risk the gypsum crystal, as its damage threshold at 355 nm was found to be rather low. Similarly, IR irradiation on real samples verified the preferential removal of dark particulates at lower F values and the beige-yellow discoloration of the residual gypsum-rich matrix material.

These studies inspired the combined use of the two laser ablation regimes in order to exploit their advantages, and early experiments were focused on the sequential employment of the UV laser beam to rectify the IR-induced discoloration [30]. However, their result was inhomogeneous, almost at the borderline of damage, while colour rectification was not satisfactory. Further experimentation was focused to their synchronous use in partial and temporal overlapping, while the contribution of each individual ablation mechanism was regulated by adjusting the energy density ratio of the two beams (F_{IR}/F_{UV}) [4, 30–34]. Systematic studies on mock-ups and fragments with different crusts and careful assessment of the cleaned surfaces resulted in the optimization and fine-tuning of this 2-λ methodology, which was then adapted for the cleaning challenges of the Athens Acropolis sculptures described in paragraph 3.5.1.

3.3 Historical Review & Main Research Highlights

The first laser assisted removal of unwanted material on CH surface took place 50 years ago in Venice [35–38]. In the course of a project related to the holographic recording of the famous Venetian monuments, John Asmus and his collaborators experimented on the use of a ruby laser to clean black pollution crust from stonework. Several cleaning tests were performed, but it took another two decades before the scientific community considered laser ablation for conservation interventions, mainly due to restrictions posed from the laser technology itself.

In the early 90s, systematic investigation for establishing laser cleaning on stonework was reported mainly in Europe. In the UK, Loughborough University and the National Galleries on Merseyside in Liverpool collaborated towards a methodical description of the mechanisms ruling Nd:YAG laser ablation of encrusted stonework, and the definition of the first systematic methodology for cleaning interventions, with emphasis on black pollution crusts on limestones [1, 39–42]. In parallel, in France, the Laboratoire de Recherche de Monuments Historiques in Paris [18, 22, 24–27] undertook a detailed comparison of laser assisted crust removal to mechanical and chemical means and applied the technique *in situ* at Portail de la Mère Dieu in Amiens Cathedral [5]. The issue of laser-induced discoloration was reported for the first time. In parallel, St. Stephen's Cathedral in Vienna [43, 44] and Maddalena church in Venice [45] were laser cleaned *in situ*, while a very active research team was formed in Florence at Consiglio Nazionale delle Ricerche (CNR) investigating different laser ablation regimes and challenges [45–54]. Meanwhile, in Greece, the Foundation of Research and Technology-Hellas (FORTH) performed the first experiments for removing aged varnish layers from wooden icons and paintings, as well as biological stains from paper substrates using UV laser radiation (at 248 nm and 193 nm) emitted from excimer laser sources [2, 55]. Concurrently, the Greek research team, in close collaboration with the Acropolis Restoration Service, initiated a thorough research for investigating the appropriate cleaning methodology and, most importantly, the laser-diagnostic techniques for the removal of pollution crusts from the sculptures of the Acropolis in Athens [56–62]. Thereafter, significant research effort has been dedicated worldwide for the broad application of lasers in the conservation, as well as the analysis and diagnosis, of CH objects and monuments.

In 1995, validating the pioneer role of this research, the first LACONA (LAsers in the COnservation of Artworks) conference was organised by FORTH in Crete, Greece. Twelve LACONA conferences[10] were subsequently organised and the multidisciplinary research community was vigorously dedicated to the wide establishment of laser technology in the field, while showing the way to new tools and applications. Within the past three decades, several national and EU funded projects allowed the flourishing of this pioneer research, and several supporting measures, for example, the G7 COST action on "Lasers and Optical Methods in Artwork Restoration", set the basis for facilitating the communication and collaboration between the various disciplines. Finally, a number of training activities were established in order to enable the conservation professionals to become acquainted with the laser technology.

In the meantime, there was also a significant development in laser technology, resulting in a considerable number of laser cleaning systems available for use in various applications. The early experiments employed the 1064 nm beam of a QS Nd:YAG system with t_p in the range of 10–25 ns. The harmonic wavelengths of this

[10] Heraklion, GR (1995), Liverpool, UK (1997), Florence, IT (1999), Paris, FR (2001), Osnabrück, DE (2003), Vienna, AU (2005), Madrid, ES (2007), Sibiu, RO (2009), London, UK (2011), Sharjah, UAE (2014), Kraków, PO (2016), Paris, FR (2018) and forthcoming Florence, IT (2022).

laser (mainly the 2nd (532 nm) and 3rd (355 nm) and to a lesser extent the 4th (266 nm) and the 5th (213 nm)) have also been employed for a number of applications with promising results, while the combination of 1064 nm and 355 nm was proposed as a solution to prevent unwanted side effects related to discoloration of stonework. Longer laser pulses emitted from SFR[11] and LQS[11] Nd:YAG systems are also broadly used especially for applications related to removal of pollution crusts from stonework. In these cleaning regimes, photo-thermal mechanisms are important, and the presence of a moistening agent is imperative. Material is removed through vaporisation as a result of water steam formation, while the ablation depth can be controlled, allowing discrimination of the various layers. Plenty of world-known monuments and objects with complex and demanding stratigraphy and cleaning challenges have been treated successfully with these types of lasers (e.g. the Santi Quattro Coronati [50] and the Porta della Mandorla [51] in Florence). On the other hand, shorter laser pulses (of pico[12]- and femto[12]-second duration) have been also considered as they can practically minimise thermal phenomena. Irradiation using ultra-short laser pulses is associated with shorter thermal diffusion lengths, resulting into more effective material removal, which is particularly important in case of hard encrustations. The disadvantage, in this case, is the fact that the operative fluence window may be smaller than in other laser cleaning regimes, necessitating the presence of monitoring approaches, especially for multi-layered encrustations [28].

Er:YAG laser systems have also been used for cleaning applications in the CH field (initially in paintings conservation and later in other materials), in parallel to their broad implementation in medical and dental applications. IR pulses at 2940 nm emitted from Er:YAG laser systems rely on the selective excitation of molecules containing OH-groups (i.e., water and other solutions) which are the main absorbers at this wavelength. Their presence favours the thermal dissipation of the laser energy into the outer surface of the unwanted material, increasing its temperature and pressure, stimulating its removal through steam formation and gas expansion. Thus, ablation in this regime is photo-thermally dominated. A significant number of studies have been dedicated to the investigation of the potential heating effects, also aimed at defining the most suitable moistening agents and the appropriate laser parameters in order to confine the absorption of the 2940 nm radiation to the outer surface layers, and effectively control the cleaning interventions in this regime [63–68].

[11] SFR: Short free running 50–120 μs and LQS: Long Q-switched 120–950 ns.

[12] 1 ps = 10^{-12} s = 1 /1000 ns and 1 fs = 10^{-15} s = 1/1000 ps.

3.4 A Methodological approach for Laser Cleaning of Stonework

Laser cleaning, similar to any other irreversible intervention, must be approached with high level of responsibility and attention. Although it is established as a safe, controllable, and effective cleaning tool, care should be taken to determine the optimum parameters for each individual cleaning case, in order to avoid any damaging and/or irreparable situations. Along these lines, a protocol that can ensure careful and effective conservation processes is briefly presented (Fig. 3.2), aiming to indicate the main steps that must be followed, keeping in mind that every single conservation challenge, although appearing similar to previously studied ones, may vary significantly, and, thus, necessitates its own consideration.

3.4.1 Phase A: Definition of the Conservation Challenge

With the aim to define the cleaning level and ensure safeguarding of the original surface, a systematic study is essential prior to any cleaning intervention. This is well-practised in CH conservation and refers to careful analytical investigation of the involved materials and layers with emphasis to the determination of their chemical composition, their morphology, thickness, and stratigraphy, taking into account historical data and past conservation treatments. In laser cleaning, specifically, it is crucial to additionally determine the physico-chemical characteristics of the unwanted materials and the original substrate, including their absorptivity profile, as they are critical for the selection of the operational characteristics of the laser system. Other important details that characterise each unique conservation challenge refer to the presence of organic materials (due to past conservation

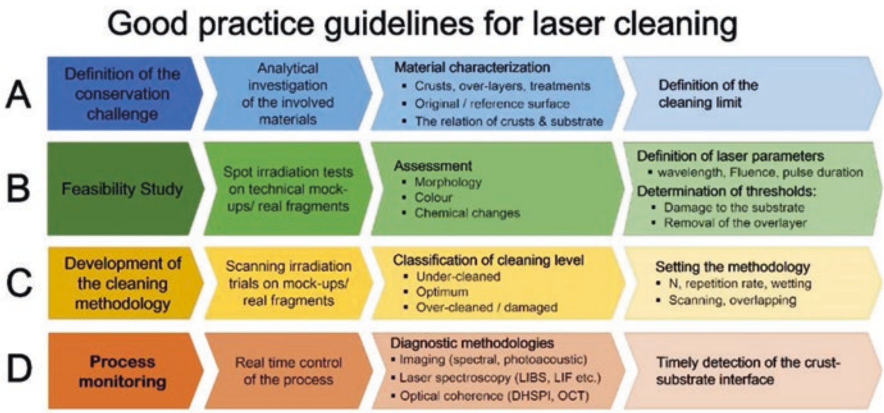

Fig. 3.2 Good practice guidelines for approaching the different laser cleaning challenges

treatments) and paint traces, the state of cohesion and adhesion of the involved materials and surfaces, their ageing condition (fresh or aged polymeric coatings), and any variations in thickness and/or stratigraphy across the surface.

3.4.2 Phase B: Feasibility Study

The ablation threshold values for the involved materials (i.e., the onset for removal of encrustation material, F_{crust}, and the onset for damage to the substrate, $F_{substrate}$) are particularly important when it comes to the decision of the appropriate laser cleaning approach. Their relative difference may ensure a self-limiting process ($F_{crust} << F_{substrate}$) or may call for extra monitoring processes. To this end, it is advisable to perform "etch-rate" studies for the encrustation and substrate in order to determine how much material is removed for different F values. Practically, this can be achieved on the basis of series of irradiation trials involving spot tests of single (1), as well as multiple (2, 5, 10 etc.) pulses at increasing F values. The resulting craters are significant for the determination of the cleaning methodology. This phase may necessitate the use of model mock-ups of the same or very similar physico-chemical properties, thickness, surface morphology, and ageing condition to the actual cleaning challenge. Alternatively, real fragments (unidentified or of lower historical importance) of the same monument or site may be also utilised.

In this stage, it is also important to investigate whether the presence of a wetting agent may enhance the cleaning efficiency [1, 4, 52] and, thus, irradiation tests on pre-wetted surfaces should be also implemented. Moistening must take place in a standard way (i.e., by means of a spray or by a clean and slightly wet cotton-swab, sponge, or brush), while care must be taken in order to avoid excessive wetting of the surface which may cause staining or other undesired surface alterations to the surrounding areas, including uncontrolled ablation.

A first indication of the ablation thresholds of the involved materials is usually based on visual and spectral imaging of the irradiated spots supported by microscopic (optical, stereo-, and scanning electron microscopy) evaluation. When applicable, determination of the depth of the laser induced craters using mechanical profilometers or optical diagnostics can be also employed in order to fully study the etching rate of the unwanted crusts.

Once the ablation thresholds of the involved materials are determined, further tests on larger areas (e.g., 1 cm^2) are advisable in order to further evaluate the result [69, 70]. Their assessment must be multi-analytical and responsibly address the cleaning result in regard to:

(a) Surface morphology: undesirable effects due to excessive or insufficient irradiation conditions may be observable as surface alteration (i.e., disrupted marble crystals, darkened ceramics, or damaged biotite grains within the granite [69]), micro-cracking, selective vaporisation of individual (darker) components of the crust leaving behind usually bleached or discoloured crust remains, melting, and other thermally induced phenomena.

(b) Colour: the cleaned surface must show similar coloration to the surface selected as reference. Discoloration can usually be detected easily, due to the high sensitivity of human eye, nevertheless, its quantitative measurement, e.g., by using a colorimeter, can be a demanding process and must be evaluated with caution.

(c) Physicochemical changes to the inorganic and/or organic components or layers of the original surface: their effects may be directly visible (i.e., darkening of pigments) or they may affect the surface in the long-term (i.e., dehydration of inorganic or polymerisation of organic molecules). Different analytical and diagnostic tools may be employed for the detection of such potential alterations, including X-ray diffraction [23, 24, 70], Raman spectroscopy [13, 34], IR spectroscopy [11, 23, 64, 94], X-ray photoelectron spectroscopy [10], fluorescence spectroscopy [11, 23], and mass spectrometric techniques [11, 30, 71], while issues of sensitivity of the analytical technique, sampling restrictions, and reliability of results, due to point or superficial analysis, are currently under discussion by researchers.

3.4.3 Phase C: Development of the Cleaning Methodology

This phase is rather technical and refers to the fine-tuning of the laser cleaning parameters to ensure a homogeneous and satisfying result. The number of applied pulses according to the thickness and the morphology of the encrustation, their repetition rate (in Hz), the spot size of the light beam, the scanning protocol (either manually or computer-driven) and the optimization of its conditions (i.e., overlapping, repetitions etc.), the most suitable moistening scheme, the archiving protocol, etc. are among the parameters that must be decided for an optimum laser-assisted encrustation removal. It is also important to clearly differentiate this optimal cleaning level compared to under-cleaned and/or damaged surfaces [80].

3.4.4 Phase D: Monitoring of the Process

Finally, to ensure a responsible and safe laser cleaning intervention, reliable and careful control of the removal process, *in situ* and, if possible, in real time with the actual process, is imperative. A key issue in this respect is to find out the appropriate controlling tool and, accordingly, to determine the critical point that denotes when the cleaning limit is about to be reached and, thus, the process must be timely terminated or continued to an adjacent point or area, ensuring that the original surface is safeguarded from any mistakes or irreversible damage. This is not an easy and straightforward procedure, as in most of the cleaning cases, the treated objects involve multifaceted layers and materials of possibly different weathering or ageing states, with heterogeneous structures and thicknesses that may significantly vary across the object. Therefore, total automation of laser-cleaning processes, as well as cleaning at high repetition rates, are not advisable, as they risk preventing the end-user to react timely to any unpredicted situation. On the contrary, it is recommended to continuously and carefully observe the treated area and employ the suitable monitoring device.

Early studies were focused on imaging approaches [72, 73], and were based on digital processing of the acquired images to quantitatively identify the differences between an optimum, under-cleaned, and damaged surface. In parallel, laser spectroscopies (LIBS, laser induced breakdown spectroscopy and LIF, laser induced fluorescence) were also considered, as they were easily adopted using the same laser beam [56–58, 74, 75]. In this case, the monitoring relies on the observation of the optical emission of the ablation plume and the recording of the intensity of specific spectral lines for successive laser pulses upon the cleaning process. Any significant changes to these spectral lines are expected to delineate the encrustation-substrate interface, on the condition that the emission spectra of the removed material and the underlying substrate are different. Another critical point is that the laser ablation plasma is associated with high F values that most of the times are close to the $F_{substrate}$ and thus, call for particular attention. Optical coherence techniques have also been investigated for their potential to control cleaning, either by determining the thickness of remaining organic coatings (optical coherence tomography [76, 77]), or by detecting structural changes (holographic interferometry [78, 79]). Recently, photoacoustic signals generated upon laser ablation have been also considered for on-line control with encouraging results [80–82].

3.5 Case Studies and Ongoing Issues

Within the past 30 years the laser ablation mechanisms have been carefully studied and different cleaning challenges and side issues have been satisfactorily tackled. The interested reader may find in various scientific journals and conference proceedings (e.g., the LACONA conference proceedings) plenty of relevant information on multifaceted laser cleaning queries, reflecting careful investigations to determine and fine-tune the appropriate ablation parameters and methodologies. In this section, selected examples of laser cleaning on stonework are briefly presented with emphasis on the dedicated cleaning approaches that have been developed for different encrustation materials on three unique Greek heritage objects and monuments.

3.5.1 Gypsum–rich Dark Pollution Encrustation on Marble – The Athens Acropolis Sculptures

A unique example of laser-assisted removal of pollution encrustation using the 2-λ methodology is the cleaning intervention at the sculptures of the Athens Acropolis [33]. This unique complex of monuments, located on a hill in the centre of Athens in Greece, has been exposed to the environmental conditions and weathering for more than two and a half millennia. Nevertheless, the main cause for its weathering is considered the rapid industrialisation of the Greek capital within the past 70 years, favouring the intense deposition of pollution particulates on these fine-sculpted objects made of exquisite white Pentelic marble. The cleaning challenge involved the controlled removal of various overlayers in order to reveal the original substrate.

Studies of the stratigraphy of the encrusted sculptures indicated a complex situation calling for careful treatment. Three main types of encrustations on the sculptures were encountered: (a) loose gypsum-rich deposits of soot and dirt forming a uniform thin veil that obscures surface details; (b) homogeneous compact crusts of well-adhered deposits that hide any surface traces and details; and (c) thicker dendritic crusts of re-crystallised and re-precipitated calcium carbonate bonded together with gypsum and dark atmospheric particles that significantly alter the surface condition. The substrate is comprised mainly of weathered marble, while two monochromatic layers of ancient origin are recorded on well preserved marble surfaces, indicating important historical details. These two layers are identified as the "epidermis", an orange-brown thin (30–100 μm) lower layer rich in calcium oxalates, calcium phosphates, and iron oxides [23, 33, 83], and the "coating", a thicker (80–120 μm) outer beige layer of calcium carbonate. They are a distinctive indication of the original surface, as they retain tool-marks and pigment traces, and they must be preserved.

To deal with this particularly challenging cleaning problem, the conservators and researchers of the Acropolis Restoration Service (ΥΣΜΑ) investigated several conservation methodologies. Laser radiation was found superior over the conventional cleaning methods due to its selectivity, effectiveness, and controllability, but scepticism regarding yellowing triggered the research related to the combination of two ablative mechanisms to reach an optimum cleaning result. Figure 3.3 shows a series of laser irradiation tests using different laser parameters (details in [33]) on a newer marble corner-complement of the Parthenon West Frieze with a thick pollution crust. The critical evaluation of these tests on the basis of the potential chemical alterations or colour changes induced to the substrate allowed fine-tuning of the method, and the development of a prototype hybrid portable laser cleaning instrument dedicated to the specific cleaning challenge. Ranges for F values that would ensure effective and safe cleaning result were determined [33, 84].

The first assemblage from the Acropolis to benefit from the laser cleaning methodology was the West Frieze of the Parthenon (2002–2005). Figure 3.4 shows an area on block N. 6 during the laser cleaning. Dendritic crusts (on the horse-rider's

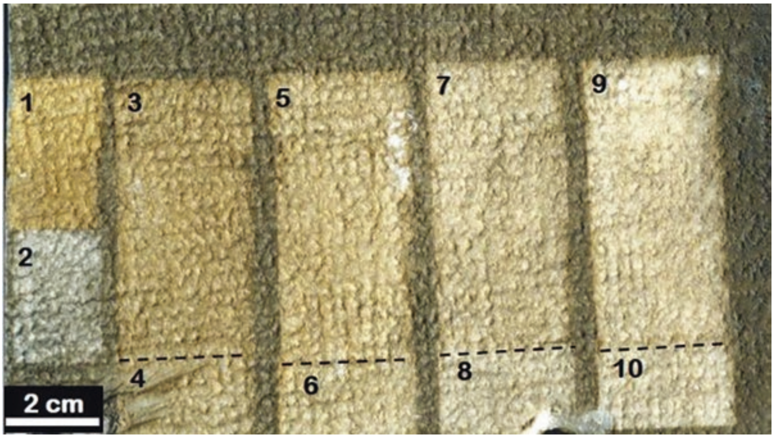

Fig. 3.3 Laser cleaning tests using different laser parameters (λ and F values, as well as F ratios upon simultaneous irradiation) on a newer marble corner-complement of the Parthenon West Frieze with pollution encrustation. Snapshot during the laser cleaning on marble substrate. Area (1) was irradiated at 1064 nm, area (2) at 355 nm and areas (3)–(10) at various combinations of the two beams. Detailed info can be found in [33]. © Hellenic Ministry of Culture and Sports, Hellenic Organization of Cultural Resources Development, Acropolis Restoration Service (YSMA) and Ephorate of Antiquities of Athens

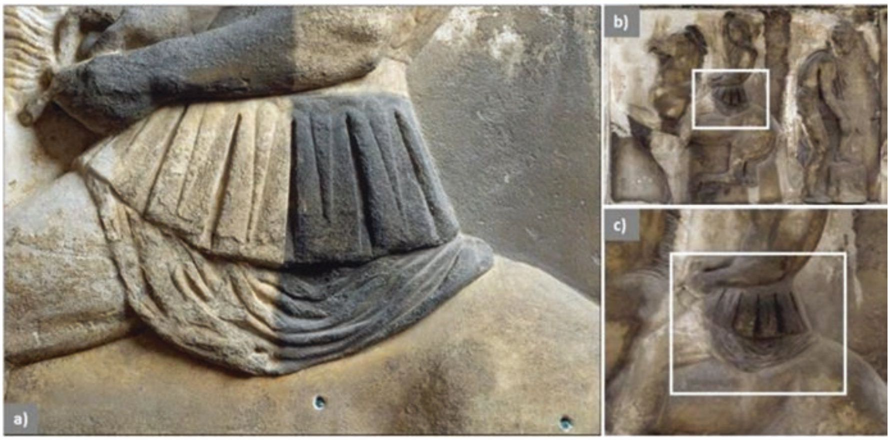

Fig. 3.4 Parthenon West Frieze, Block N. 6 (VI). (**a**) Snapshot during the laser cleaning on marble substrate, (**b**) general view, and (**c**) detail of Block N. 6 (VI) before cleaning. © Hellenic Ministry of Culture and Sports, Hellenic Organization of Cultural Resources Development, Acropolis Restoration Service (YSMA) and Ephorate of Antiquities of Athens, photos by S. Mavrommatis

cloth), compact crust (on the background), as well as loose deposits (on the horse body) were removed in an effective and controlled way, ensuring the safeguarding of the ancient surface layers and the weathered marble surface. Employment of the 2-λ laser cleaning approach has been, since then, followed for the surface treatment of these unique sculptures, either on site (i.e., for the cleaning of the coffered ceiling

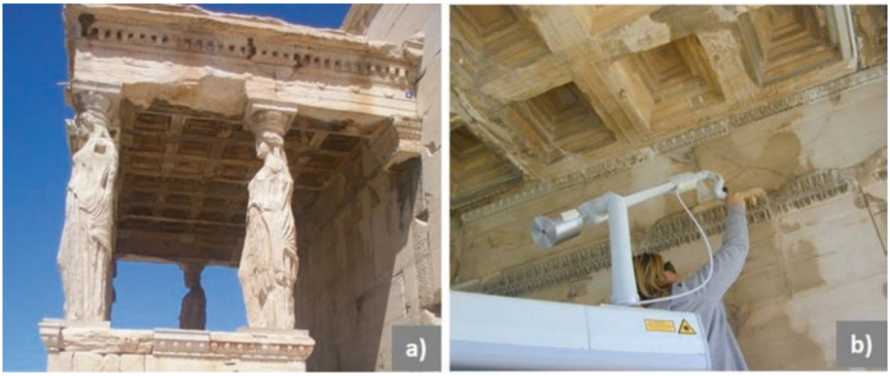

Fig. 3.5 (**a**) The porch at the Erechtheion prostasis with the Caryatids casts, and (**b**) laser cleaning of its coffered ceiling. © Hellenic Ministry of Culture and Sports, Hellenic Organization of Cultural Resources Development, Acropolis Restoration Service (YSMA) and Ephorate of Antiquities of Athens, photo 3.5a by P. Pouli and photo 3.5b by D. Garbis

of the Erechtheion prostasis at the Caryatids porch, Fig. 3.5), or inside the Acropolis conservation laboratories (for a number of sculptures such as the Northern and Eastern Parthenon metopes and the Frieze of the Temple of Athena Nike).

The inauguration of the new Acropolis Museum in 2009 also signalled a new era in the laser cleaning practice, as a temporal, but at the same time, advanced laser laboratory has been set-up inside the exhibition area to enable preservation activities *in situ* and open to the public. The specially designed platform, developed by the Acropolis Museum, is surrounded by protective curtains, in agreement with laser safety measures, and "embraces" and isolates one sculpture at a time, while it is moving in different heights to offer optimum access along the working area (Fig. 3.6). The original Caryatids, the female figures holding the Erectheion porch, were initially treated, while the visitors were able to follow the interventions in real time in a symbolic connection between ancient and modern Greece [31].

3.5.2 Insoluble Aluminosilicate Encrustations on Excavated Marble – The Hermes of Ancient Messene

The removal of inorganic encrustations from excavated objects is a controversial yet essential intervention. Such crusts are carbonatic, rich in aluminosilicates and metallic components, that may be abundant in the surrounding soil during the burial period. In most of the cases, no gypsum compounds can be detected, while the presence of surface patination layers (protective treatments or polychromy preparation layers) is uncommon. Thick layers of crust well-adhered to the substrate can be found on sound surfaces (usually on the parts of the sculptures and fragments which were buried face-down), while thinner layers occupying inter-crystalline space, due to the stone's disaggregation, are present on the parts that were buried face-up.

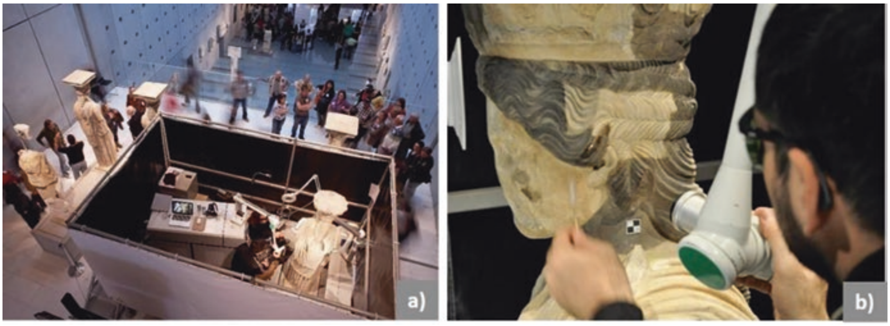

Fig. 3.6 (**a**) The open-to-the-public laboratory set-up at the Acropolis Museum dedicated to the laser cleaning of the original Caryatids, and (**b**) snapshot during the intervention. © The Acropolis Museum, photo 3.6a by G. Vitsaropoulos and photo 3.6b by C. Arvanitakis

Although burial crusts cannot be considered harmful to the object, they may undermine aesthetic, artistic, and archaeological value, as they can obscure significant details, expressions, and textures, and therefore, their removal is recommended.

Hermes is a life-size Roman (first century AD) marble statue, excavated in 37 fragments in Ancient Messene in the Peloponnese, Greece. Its appearance after conservation undermined legibility and appearance, so cleaning of the inorganic encrustations was proposed. Prior to being the first statue to be laser-cleaned *in situ* in Greece, cleaning trials were undertaken in order to compare the result of most common conventional techniques (ultrasound pick and micro-air abrasive) on a marble fragment from the same excavation, characterised by a thick dark brown crust, similar in texture and composition to the one on the Hermes statue. The cleaning results were evaluated by means of optical microscopy and spectral imaging, for different types of crust and substrate condition, as well as their performance efficiency, the degree of control, and their complexity in handling [85]. The sculpture, which is currently exhibited in the Archaeological Museum of ancient Messene, was laser cleaned on February 2001 *in situ* by "Lithou Sintirissis Conservation Associates", using a QS Nd:YAG system (Lynton Lasers) on damp surfaces. F range was 0.8–1.6 J/cm^2 (Fig. 3.7).

3.5.3 Cement on Selenite – The Peripheral Monuments of the Minoan Palace of Knossos (Crete, Greece)

Another cleaning challenge refers to the removal of hard and often insoluble encrustation (i.e., cement) from stonework. The task gets more demanding in case of sensitive surfaces (i.e., weathered marble) or other softer substrates (i.e., mineral gypsum), as the removal threshold of the overlayer can be significantly higher compared to the damage threshold of the authentic surface. Therefore, the determination of the operative laser parameters requires extra caution.

Fig. 3.7 Hermes sculpture before cleaning (left) and details of the surfaces cleaned with 1064 nm QS- Nd:YAG laser at F = 0.8–1.6 J/cm^2. © Lithou Sintirissis Conservation Associates, photos by S. Mavrommatis

Selenite (mineral gypsum, $CaSO_4 \bullet 2H_2O$) is extensively used in the Minoan Palatial architecture both as an ornamental and building element due to its exceptional iridescence properties, but it is particularly soft (2/10 on the Mohs scale of mineral hardness) and fragile (due to its susceptibility to weathering and humidity). During the reconstruction of the archaeological site of Knossos, in Heraklion, Crete, at the beginning of the twentieth century AD, dark-coloured cement was used extensively, mainly to attach the gypsum elements on their original position, but also as a "coating" covering the Minoan selenite walls. Such types of cement coatings disturb the appearance of the Knossean monuments, and endanger the longevity of the selenite surfaces, mainly due to the different mechanical properties (hardness, elasticity, etc.) of the materials, resulting in structural and surface failure. Therefore, their removal was deemed necessary. Although a significant part of the cement crust can be removed by mechanical means, attempts to remove thinner remains resulted in partial detachment of the original gypsum, due to the loss of cohesion between the surface layers of selenite crystal aggregates. Laser cleaning was considered, and feasibility tests were focused on investigating the cleaning parameters that will ensure: (a) cement removal without any change (physical or chemical) to the selenite crystalline phase (due to the de-hydration of gypsum to hemihydrate and/or anhydrous calcium sulphate), and (b) preservation of the "colored surface patination layers" (rich in calcium oxalates, calcium phosphates, calcite, and clay minerals).

Following systematic studies [70] on technical mock-ups (1 mm thin cement layer on 1–1.5 mm of tabular translucent selenite crystal layer parallelepipeds) and real fragments (collected from a stone-pile located nearby the Royal Villa, at the east of the Minoan Palace), it was shown that a short-pulse IR laser beam at 1064 nm effectively removes such thick and hard insoluble cement crusts without affecting

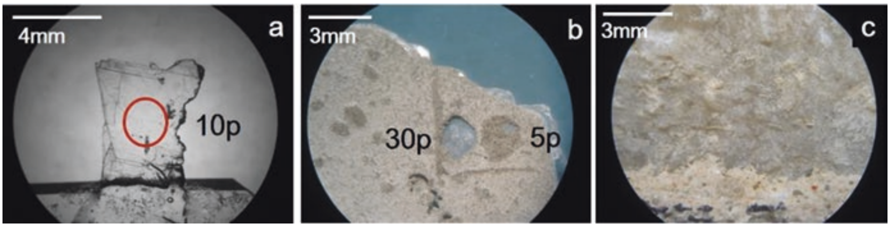

Fig. 3.8 Close magnifications of IR laser irradiation tests at 1064 nm to remove cement from selenite: (**a**) 10 pulses at F = 6.5 J/cm^2 on selenite reference "monolayers"; (**b**) 5 and 30 pulses at 3 J/cm^2 on cement covered selenite "monolayers"; and (**c**) removal of light-coloured thick cement layer from a real fragment using 30–50 pulses at 1064 nm. All irradiations were performed on wet surfaces

the gypsum surface morphology, the colour, and the chemistry of the authentic selenite surface, as it was confirmed through a number of imaging (optical microscopy, spectral imaging) and analytical (Raman spectroscopy, X-ray diffraction) techniques. Through these studies, the removal threshold of cement (F_{cement} = 1.5 J/cm^2) and the damage threshold of selenite ($F_{selenite}$ = 6.5 J/cm^2) were determined, and, accordingly, the range of cleaning F (2–5 ± 0.3 J/cm^2) was chosen (Fig. 3.8). Tests with the UV beam of the same QS Nd:YAG laser at 355 nm indicated that the damage threshold of selenite in this regime was significantly lower, and the removal efficiency of the cement was appreciably effected compared to the IR. Therefore, this cleaning regime was rejected for the purposes of this study.

3.5.4 Other Materials

Further to the above-mentioned cases, other challenging encrustations disturb CH stonework and urge for careful solutions. Biological formations, quite common in archaeological sites with high humidity, call for particular attention, as they may penetrate within the stone bulk, causing further irreversible damage. Therefore, their removal is considered a particularly demanding intervention [54, 65, 86–89]. Usually these types of crusts can be removed using the 532 nm beam of a Q-Switched Nd:YAG laser [54, 87–89], although successful approaches have been reported with the 2940 nm of an Er:YAG laser [65].

Another difficult cleaning case is the removal of graffiti from stonework, due to their diversity in pigments and binding media, and the inevitable penetration of the paints into the stone bulk. Their complete removal, especially for the paint that occupies inter-crystalline space, is challenging and was approached using mainly Nd:YAG lasers [69, 90–94]. Nevertheless, an important issue in this respect is their practical implementation, as their diversity and wide-scale use necessitates automated cleaning processes.

Other demanding cases involve removal of various crusts from plaster [31, 95], brickwork [96], and granite, to mention a few. Plaster substrates appear to get intensely discoloured upon IR irradiation, and the yellowing is being avoided using a 532 nm beam [95] of the Nd:YAG laser or an appropriate combination of the 1064 and 355 nm beams [31]. Instead, brickwork gets darkened [96] upon 1064 nm irradiation. Likewise, an ongoing issue in laser cleaning of stonework refers to the removal of overlayers (black crusts and graffiti) from granite. Granite is a rather complex substrate which, due to its polymineralic grained texture [69, 94, 97, 98], appears highly sensitive to laser cleaning. Indeed, biotite, potassium feldspar, and plagioclase grains, main constituents of the granitic stone, can be easily damaged (melted, extracted) upon non-optimised laser irradiation conditions, and, thus, careful cleaning approaches must be employed. Another important issue, posing further difficulties as regards the determination of the optimum laser cleaning parameters for granitic substrates, is the fact that gypsum rich crusts must be totally eliminated, as their calcium component does not originate from the stone itself but from external sources (i.e., from the dissolution of joint mortars). For this reason, surface layers of gypsum show different physical and mechanical behaviour with respect to granite, which may lead to detachments and surface losses. Regarding this issue, dual wavelength cleaning approaches have been considered with promising results [69, 98].

3.6 Conclusions and Future Trends

The role of lasers as reliable, safe, and controlled cleaning tools is well established in the CH conservation practice. However, given the irreversibility of the intervention, careful optimisation of the cleaning methodologies (following cautious feasibility studies and best practice protocols) and thorough assessment of the result, combined with *in situ* and real-time monitoring of the laser-ablation process, must be followed. In this respect**,** non-invasive and non-destructive analytical and diagnostic sensors must be adopted and carefully chosen on the basis of the requirements posed from each individual cleaning challenge. Their integration into agile suites of surface, optical, and chemical sensors is expected to establish the reliability, controllability, and applicability of laser cleaning, and to highly advance the conservation process. Along these lines the development of portable cleaning and analytical instrumentation, augmented with user-friendly control interfaces, is imperative. Also, the recording, handling, using, and re-using of the acquired data related to laser operational parameters, evaluation, and monitoring information [99] in a FAIR (findability, accessibility, interoperability, and reusability) perspective is expected to play an important role in the field, as this knowledge will become more reachable and comprehensive to heritage scientists and conservators.

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References

1. Cooper M. Laser Cleaning in Conservation: An Introduction. ed. Oxford: Butterworth-Heinemann; 1998.
2. Fotakis C, Anglos D, Zafiropulos V, Georgiou S, Tornari V. Lasers in the Preservation of Cultural Heritage; Principles and applications. In: Brown RGW, Pike ER, editors. New York: Taylor and Francis; 2006.
3. Zafiropoulos V, Balas C, Manousaki A, Marakis Y, Maravelaki-Kalaitzaki P, Melesanaki K, Pouli P, Stratoudaki Th, Klein S, Hildenhagen J, Dickmann K, Luk'Yanchuk BS, Mujat C, Dogariu A. Yellowing effect and discoloration of pigments: Experimental and Theoretical studies. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01205-0.
4. Pouli P, Oujja M, Castillejo M. Practical issues in laser cleaning of stone and painted artefacts: optimisation procedures and side effects. Appl. Phys. A-Materials Sci. Process. 2012. https://doi.org/10.1007/s00339-011-6696-2.
5. Weeks C. The 'Portail de la Mere Dieu' of Amiens cathedral: its polychromy and conservation. Stud. Conserv. 1998. https://doi.org/10.1179/sic.1998.43.2.101.
6. Shekede L, Post-Prints of the Analysis of Pigments and Plasters. London: United Kingdom Institute for Conservation of Historic and Artistic Works; 1998.
7. Pouli P, Emmony DC, The effect of Nd:YAG laser radiation on medieval pigments, J. Cult. Heritage, 2000. https://doi.org/10.1016/S1296-2074(00)00143-6.
8. Athanassiou A, Hill AE, Fourrier T, Burgio L, Clark RJH. The effects of UV laser light radiation on artists' pigments. J. Cult. Heritage. 2000. https://doi.org/10.1016/S1296-2074(00)00180-1.
9. Zafiropulos V, Stratoudaki T, Manousaki A, Melesanaki K, Orial G. Discoloration of Pigments Induced by Laser Irradiation, Surface Engineering, 2001. https://doi.org/10.1179/026708401101517773.
10. Pouli P, Emmony DC, Madden CE, Sutherland I. Analysis of the laser-induced reduction mechanisms of medieval pigments. Appl. Surf. Sci. 2001. https://doi.org/10.1016/S0169-4332(00)00909-0.
11. Castillejo M, Martín M, Oujja M, Silva D, Torres R, Manousaki A, Zafiropulos V, van den Brink OF, Heeren RMA, Teule R, Silva A, Gouveia H. Analytical Study of the Chemical and Physical Changes Induced by KrF Laser Cleaning of Tempera Paints. Anal. Chem. 2002. https://doi.org/10.1021/ac025778c.
12. Cooper MI, Fowles PS, Tang CC, Analysis of the laser-induced discoloration of lead white pigment. Appl. Surf. Sci. 2002. https://doi.org/10.1016/S0169-4332(02)00499-3.
13. Chappé M, Hildenhagen J, Dickmann K, Bredol K, Laser irradiation of medieval pigments at IR, VIS and UV wavelengths. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01206-2.

14. Keune K, Boon JJ. Analytical imaging studies clarifying the process of the darkening of vermilion in paintings. Anal. Chem. 2005. https://doi.org/10.1021/ac048158f.
15. Acquaviva S, Baraldi P, D'Anna E, De Giorgi ML, Della Patria A, Giotta L, Omarini S, Piccolo R, Yellow pigments in painting: characterisation and UV laser-induced modifications. J. Raman Spectrosc. 2009. https://doi.org/10.1002/jrs.2316.
16. Oujja M, Pouli P, Fotakis C, Domingo C, Castillejo M. Analytical Spectroscopic Investigation of Wavelength and Pulse Duration Effects on Laser-Induced Changes of Egg-Yolk-Based Tempera Paints. Applied Spectroscopy. 2010; 64:528–536.
17. Oujja M, Sanz M, Rebollar E, Marco JF, Castillejo M, Pouli P, Kogou S, Fotakis C. Wavelength and pulse duration effects on laser induced changes on raw pigments used in paintings. Spectrochim. Acta A Mol. Biomol. 2013. https://doi.org/10.1016/j.saa.2012.10.001.
18. Vergès-Belmin V, Dignard C. Laser yellowing: myth or reality? J. Cult. Herit. 2003. https://doi.org/10.1016/S1296-2074(02)01203-7.
19. Klein S, Ferksanati F, Hildenhagen J, Dickmann K, Uphoff H, Marakis Y, Zafiropulos V. Discoloration of marble during laser cleaning by Nd:YAG laser wavelengths. Appl Surf Sci, 2001. https://doi.org/10.1016/S0169-4332(00)00706-6.
20. Potgieter-Vermaak SS, Godoi RHM, Grieken R, Potgieter JH, Oujja M, Castillejo M. Microstructural characterization of black crust and laser cleaning of building stones by micro-Raman and SEM techniques. Spectrochim. Acta A Mol. Biomol. 2005. https://doi.org/10.1016/j.saa.2004.09.010.
21. Gaviño M, Hermosin B, Castillejo M, Oujja M, Rebollar E, Vergès-Belmin V, Nowik W, Saiz-Jimenez C. Black crusts removal: the effect of stone yellowing and cleaning strategies. Air Pollution and Cultural Heritage, CRC Press, 2004, pp. 239–245. https://doi.org/10.1201/b17004-37.
22. Vergès-Belmin V, Pichot C, Orial G. Elimination de croûtes noires sur marbre et craie : à quel niveau arrêter le nettoyage? In: Thiel M.-J. (Ed.), Conservation of Stone and Other Materials, London: E & FN Spon; 1993, pp. 534–541.
23. Maravelaki-Kalaitzaki P. Black crusts and patinas on Pentelic marble from the Parthenon and Erechtheum (Acropolis, Athens): Characterization and origin. Anal. Chim. Acta. 2005. https://doi.org/10.1016/j.aca.2004.10.065.
24. Gracia M, Gavino M, Vergès-Belmin V, Hermosin B, Nowik W, Saiz-Jimenez C. Mössbauer and XRD Study of the Effect of Nd:YAG-1064 nm Laser Irradiation on Hematite Present in Model Samples. In: Dickmann K, Fotakis C, Asmus JF, editors.Lasers in the Conservation of Artworks: LACONA V Proceedings. Berlin, Heidelberg: Springer Berlin Heidelberg; 2005. pp. 341–346. https://doi.org/10.1007/3-540-27176-7_42.
25. de Oliveira C, Vergès-Belmin V, Demaille D, Bromblet P. Lamp black and hematite contribution to laser yellowing: A study on technical gypsum samples. Stud. Conserv. 2016. https://doi.org/10.1179/2047058415Y.0000000003.
26. de Oliveira C, Vergès-Belmin V, Lafait J, Swider M, Andraud C, Tournié A, Galoisy L. Contribution of goethite to laser-induced stone yellowing. Appl. Phys. A. 2016. https://doi.org/10.1007/s00339-016-9818-z.
27. Godet M, Vergès-Belmin V, Bromblet P, Colombini A, Saheb M, Andraud C. Fly-ash contribution to Nd:YAG laser yellowing and its mitigation using UV-B light. J. Cult. Heritage. 2018. https://doi.org/10.1016/j.culher.2017.07.005.
28. Bartoli L, Pouli P, Fotakis C, Siano S, Salimbeni R. Characterization of Stone Cleaning by Nd:YAG Lasers with Different Pulse Duration. Laser Chemistry. 2006. https://doi.org/10.1155/2006/81750.
29. Marakis G, Pouli P, Zafiropulos V, Maravelaki-Kalaitzaki P. Comparative study on the application of the first and the third harmonic of a Nd:YAG laser system to clean black encrustation on marble. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01208-6.
30. Pouli P, Fotakis C, Hermosin B, Saiz-Jimenez C, Domingo C, Oujja M, Castillejo M.The laser-induced discoloration of stonework; a comparative study on its origins and remedies. Spectrochim. Acta A Mol. Biomol. 2008. https://doi.org/10.1016/j.saa.2008.02.031.

31. Pouli P, Papakonstantinou E, Frantzikinaki K, Panou A, Frantzi G, Vasiliadis C, Fotakis C. The two-wavelength laser cleaning methodology; Theoretical background and examples from its application on CH objects and monuments with emphasis to the Athens Acropolis Sculptures. Herit.Sci. 2016. https://doi.org/10.1186/s40494-016-0077-2.
32. Pouli P, Zafiropulos V, Fotakis C. The Combination of Ultraviolet and Infrared Laser Radiation for the Removal of Unwanted Encrustation from Stonework; a Novel Laser Cleaning Methodology. In: Kwiatkowski D, Lofvendahl R, editors. Proceedings of the 10th International Congress on Deterioration and Conservation of Stone: Stockholm, June 27-July 2, 2004. Stockholm: ICOMOS Sweeden; 2004. pp. 315–322. ISBN: 9163114585.
33. Pouli P, Frantzikinaki K, Papakonstantinou E, Zafiropulos V, Fotakis C. Pollution encrustation removal by means of combined ultraviolet and infrared laser radiation: The application of this innovative methodology on the surface of the Parthenon West Frieze. In: Dickmann K, Fotakis C, Asmus JF, editors. Springer Proceedings in Physics 100; 2005, pp. 333–340. https://doi.org/10.1007/3-540-27176-7_41.
34. Papanikolaou A, Siozos P, Philippidis A, Melessanaki K, Pouli P. Towards the understanding of the two wavelength laser cleaning in avoiding yellowing on stonework: a micro-Raman and LIBS study. In Targowski P, Walczak M, Pouli P editors. Lasers in the Conservation of Artworks XI, Proceedings of LACONA XI. Torun: NCU Press; 2017, pp. 95–104. https://doi.org/10.12775/3875-4.0.
35. Asmus JF, Guattari J, Lazzarini L. Holography in the conservation of statuary, Stud. Conserv. 1973. https://doi.org/10.1179/sic.1973.005.
36. Asmus JF, Murphy CG, Munk WH. Studies on the interaction of lasers with art artifacts, In Developments in laser Technology II. International Society for Optics and Photonics. 1974. pp. 19–30. https://doi.org/10.1117/12.953831.
37. Asmus JF, Seracini M, Zetler MJ. Surface morphology of laser-cleaned stone. Lithoclastia. 1976;1;23–46.
38. Asmus JF. Light cleaning: laser technology for surface preparation in the arts. Technology and Conservation. 1978;3;14–18.
39. Cooper MI, Emmony DC, Larson J. Characterization of laser cleaning of limestone. Opt. Laser Technol. 1995. https://doi.org/10.1016/0030-3992(95)93962-Q.
40. Cooper MI, Larson JH. The use of laser cleaning to preserve patina on marble sculpture, Conservator. 1996. https://doi.org/10.1080/01410096.1996.9995100.
41. Watkins KG. A review of materials interaction during laser cleaning in art restoration. In Kautek W, Konig E editors. LACONA I Proceedings –Restauratorenblätter. Vienna: Mayer & Corp; 1997. pp. 7.
42. Beadman K, Scarrow J. Laser cleaning Lincoln Cathedral's Romanesque frieze, J. Architectural Conserv. 1998. https://doi.org/10.1080/13556207.1998.10785215.
43. Calcano G, Koller M, Nimmrichter H. Laser based cleaning on stonework at St. Stephen's Cathedral Vienna. In Kautek W, Konig E editors. LACONA I Proceedings - Restauratorenblätter. Vienna: Mayer & Corp; 1997. pp. 39
44. Calcagno G, Pummer E, Koller M. St. Stephen's Church in Vienna: criteria for Nd:YAG laser cleaning on an architectural scale. J. Cult. Heritage. 2000. https://doi.org/10.1016/S1296-2074(00)00138-2.
45. Armani E, Calcagno G, Menichelli C, Rossetti M. The church of the Maddalena in Venice: the use of laser in the cleaning of the façade. J. Cult. Heritage. 2000. https://doi.org/10.1016/S1296-2074(00)00134-5.
46. Siano S, Margheri F, Pini R, Mazzinghi P, Salimbeni R. Cleaning processes of encrusted marbles by Nd:YAG lasers operating in free-running and *Q*-switching regimes. Appl. Opt.1997. https://doi.org/10.1364/AO.36.007073.
47. Salimbeni R, Pini R, Siano S. A variable pulse width Nd:YAG laser for conservation, J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01149-4.

48. Innocenti C, Pieri G, Yanagishita M, Pini R, Siano S, Zanini A. Application of laser welding to the restoration of the ostensory of the martyr St. Ignatius from Palermo. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01146-9.
49. Siano S, Salimbeni R. The Gate of Paradise: physical optimization of the laser cleaning approach. Studies in Conservation. 2001. https://doi.org/10.2307/1506776.
50. Siano S, Casciani A, Giusti A, Matteini M, Pini R, Porcinai S, Salmbeni R. The *Santi Quattro Coronati* by Nanni di Banco: cleaning of the gilded decorations. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01139-1.
51. Siano S, Giusti A, Pinna D, Porcinai S, Giamello M, Sabatini G, Salimbeni R. The Conservation Intervention on the *Porta della Mandorla*. In Dickmann K, Fotakis C, Asmus JF editors. Lasers in the Conservation of Artworks- LACONA V. Springer Proceedings in Physics 100. Berlin, Heidelberg: Springer; 2005. pp. 171–178. https://doi.org/10.1007/3-540-27176-7_22.
52. Siano S, Giamello M, Bartoli L, Mencaglia A, Parfenov V, Salimbeni R. Laser cleaning of stone by different laser pulse duration and wavelength. Laser Phys. 2008. https://doi.org/10.1134/S1054660X08010064.
53. Siano S, Agresti J, Cacciari I, Ciofini D, Mascalchi M, Osticioli I, Mencaglia AA. Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers. Appl. Phys. A. 2012. https://doi.org/10.1007/s00339-011-6690-8.
54. Osticioli I, Mascalchi M, Pinna D, Siano S. Removal of Verrucaria nigrescens from Carrara marble artefacts using Nd:YAG lasers: comparison among different pulse durations and wavelengths. Appl. Phys. A. 2015. https://doi.org/10.1007/s00339-014-8933-y.
55. Hontzopoulos E, Fotakis C, Doulgeridis M. Excimer Laser in Art Restoration. Proc. SPIE 1810, 9th International Symposium on Gas Flow and Chemical Lasers, (4 May 1993); pp. 748–751. https://doi.org/10.1117/12.144595.
56. Maravelaki PV, Zafiropulos V, Kylikoglou V, Kalaitzaki MP, Fotakis C. Laser Induced Breakdown Spectroscopy as a Diagnostic Technique for the Laser Cleaning of Marble. Spectrochim Acta Part B At Spectrosc. 1997. https://doi.org/10.1016/S0584-8547(96)01573-X.
57. Maravelaki PV, Zafiropulos V, Kylikoglou V, Kalaitzaki MP, Fotakis C. Diagnostic Techniques for Laser Cleaning of Marble. In Kautek W, Konig E editors. LACONA I Proceedings - Restauratorenblätter. Vienna: Mayer & Corp; 1997. pp. 31–35.
58. Gobernado-Mitre I, Prieto AC, Zafiropulos V, Spetsidou Y, Fotakis C. On-line monitoring of laser cleaning of limestone by laser induced breakdown spectroscopy. Applied Spectroscopy. 1997. https://doi.org/10.1366/0003702971941944.
59. Georgiou S, Zafiropulos V, Anglos D, Balas C, Tornari V, Fotakis C. Excimer laser restoration of painted artworks: procedures, mechanisms and effects, Appl. Surf. Sci. 1998. https://doi.org/10.1016/S0169-4332(97)00734-4.
60. Maravelaki-Kalaitzaki P, Zafiropulos V, Pouli P, Anglos D, Balas C, Salimbeni R, Siano S, Pini R. Short Free Running Nd:YAG laser to clean different encrustation on Pentelic marble: procedure and evaluation of the effects. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01151-2.
61. Pouli P, Selimis A, Georgiou S, Fotakis C. Recent studies of laser science in paintings conservation and research. Accounts of Chemical Research, 2010. https://doi.org/10.1021/ar900224n.
62. Anglos D, Detalle V. Cultural heritage applications of LIBS. In Mussazi A, Perini U. Laser-Induced Breakdown Spectroscopy – Theory and Applications, Springer Series in Optical Sciences 182. Berlin Heidelberg: Springer-Verlag; 2014. pp. 531–553. https://doi.org/10.1007/978-3-642-45085-3_20.
63. deCruz A, Wolbarsht ML, Hauger SA. Laser removal of contaminants from painted surfaces. J. Cult. Heritage. 2000. https://doi.org/10.1016/S1296-2074(00)00182-5.S173.
64. Bracco P, Lanterna G, Matteini M, Nakahara K, Sartiani O, deCruz A, Wolbarsht ML, Adamkiewicz E, Colombini MP. Er:YAG laser: an innovative tool for controlled cleaning of old paintings: testing and evaluation. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01232-3.

65. deCruz A, Wolbarsht M, Palmer R, Pierce S, Adamkiewicz, E. Er:YAG Laser Applications on Marble and Limestone Sculptures with Polychrome and Patina Surfaces. In Dickmann K, Fotakis C, Asmus JF editors. Lasers in the Conservation of Artworks- LACONA V. Springer Proceedings in Physics 100. Berlin, Heidelberg: Springer; 2005. pp. 113–124. https://doi.org/10.1007/3-540-27176-7_14.
66. deCruz A, Wolbarsht M, Andreotti A., Colombini M, Pinna D, Culberson C. Investigation of the Er:YAG Laser at 2.94 μm to Remove Lichens Growing on Stone. Studies in Conservation. 2009. https://doi.org/10.1179/sic.2009.54.4.268.
67. Pereira-Pardo L, Korenberg C. The use of erbium lasers for the conservation of cultural heritage. A review. J. Cult. Heritage. 2018. https://doi.org/10.1016/j.culher.2017.10.007.
68. Andreotti A, Colombini M, DeCruz A. Er:YAG laser cleaning of a marble Roman urn. Journal of the Institute of Conservation. 2020. https://doi.org/10.1080/19455224.2019.1706593.
69. Pozo-Antonio JS, Papanikolaou A, Melessanaki K, Rivas T, Pouli P. Laser assisted removal of graffiti from granite: advantages of the simultaneous combination of two wavelengths. Coatings. 2018. https://doi.org/10.3390/coatings8040124.
70. Grammatikakis G, Demadis KD, Melessanaki K, Pouli P. Laser assisted removal of dark cement crusts from the mineral gypsum (selenite) architectural elements from the peripheral monuments of the archaeological site of Knossos. Studies in Conservation. 2015. https://doi.org/10.1179/0039363015Z.000000000201.
71. Andreotti A, Colombini MP, Nevin A, Melessanaki K, Pouli P, Fotakis C. Multianalytical Study of Laser Pulse Duration Effects in the IR Laser Cleaning of Wall Paintings from the Monumental Cemetery of Pisa. Laser Chemistry. 2006. https://doi.org/10.1155/2006/39046.
72. Papadakis V, Loukaiti A, Pouli P, A spectral imaging methodology for determining on-line the optimum cleaning level of stonework. J. Cult. Heritage. 2020. https://doi.org/10.1016/j.culher.2009.10.007.
73. Kapsalas P, Maravelaki-Kalaitzaki P, Zervakis M, Delegou ET, Moropoulou A. Optical inspection for quantification of decay on stone surfaces. NDT & E International. 2007. https://doi.org/10.1016/j.ndteint.2006.07.012.
74. Fortes FJ, Cabalín LM, Laserna JJ. The potential of laser-induced breakdown spectrometry for real time monitoring the laser cleaning of archaeometallurgical objects. Spectrochim Acta Part B At Spectrosc. 2008. https://doi.org/10.1016/j.sab.2008.06.009.
75. Colao F, Fantoni R, Lazic V, Caneve L, Giardini A, Spizzichino V. LIBS as a diagnostic tool during the laser cleaning of copper based alloys: experimental results. J. of Analytical Atomic Spectrometry. 2004. https://doi.org/10.1039/B315488B.
76. Targowski P, Iwanicka M. Optical Coherence Tomography: its role in the non-invasive structural examination and conservation of cultural heritage objects—a review. Appl. Phys. A. 2012. https://doi.org/10.1007/s00339-011-6687-3.
77. Striova J, Fontana R, Barucci M, Felici A, Marconi E, Pampaloni E, Raffaelli M, Riminesi C. Optical devices provide unprecedented insights into the laser cleaning of calcium oxalate layers. Microchemical Journal. 2016. https://doi.org/10.1016/j.microc.2015.09.005.
78. Márton Zs, Kisapáti I, Török Á, Tornari V, Bernikola E, Melessanaki K, Pouli P. Holographic testing of possible mechanical effects of laser cleaning on the structure of model fresco samples NDT&E INTERNATIONAL. 2014. https://doi.org/10.1016/j.ndteint.2014.01.007.
79. Tornari V, Bernikola E, Hatzigiannakis K, Melessanaki K, Pouli P. Synchronized deformation monitoring in laser cleaning: an application for Cultural Heritage conservation. Universal Journal of Physics and Application. 2013. https://doi.org/10.13189/ujpa.2013.010215.
80. Tserevelakis GJ, Pozo-Antonio JS, Siozos P, Rivas T, Pouli P, Zacharakis G. On-line photoacoustic monitoring of laser cleaning on stone: Evaluation of cleaning effectiveness and detection of potential damage to the substrate. J Cul Her. 2018. https://doi.org/10.1016/j.culher.2018.05.014.
81. Papanikolaou A, Tserevelakis GJ, Melessanaki K, Fotakis C, Zacharakis G, Pouli P. Development of a hybrid photoacoustic and optical monitoring system for the study of

laser ablation processes upon the removal of encrustation from stonework. Opto-Electronic Advances. 2020. https://doi.org/10.29026/oea.2020.190037.

82. Tserevelakis GJ, Pouli P, Zacharakis G. Listening to laser light interactions with objects of art: a novel photoacoustic approach for diagnosis and monitoring of laser cleaning interventions. Herit Sci. 2020. https://doi.org/10.1186/s40494-020-00440-w.
83. Frantzikinaki K, Panou A, Vasiliadis C, Papakonstantinou E, Pouli P, Ditsa Th, Zafiropulos V, Fotakis C. The cleaning of the Parthenon west frieze: an innovative laser methodology. In: Kwiatkowski D, Lofvendahl R, editors. The proceedings of the 10th International Congress on Deterioration and Conservation of Stone, ICOMOS; 2004, Stockholm Sweden, pp. 801–808.
84. Frantzikinaki K, Marakis G, Panou A, Vasiliadis C, Papakonstantinou E, Pouli P, Ditsa Th, Zafiropulos V, Fotakis C. The Cleaning of the Parthenon West Frieze by Means of Combined Infrared and Ultraviolet Radiation. In: Nimmrichter J, Kautek W, Schreiner M, editors. Springer Proceedings in Physics 116, 2007. pp. 97–104. https://doi.org/10.1007/978-3-540-72130-7_12.
85. Pouli P, Zafiropulos V, Balas C, Doganis Y, Galanos A. Laser cleaning of inorganic encrustation on excavated objects: evaluation of the cleaning result by means of multi-spectral imaging. J. Cult. Heritage. 2003. https://doi.org/10.1016/S1296-2074(02)01217-7.
86. Sarantopoulou E, Kollia Z, Gomoi I. Preventing biological activity of Ulocladium sp spores in artifacts using 157 nm laser. Appl. Phys. A. 2006. https://doi.org/10.1007/s00339-006-3554-8.
87. López AJ, Lamas J, Ramil A, Yáñez A, Rivas T, Taboada J. Optimization of laser cleaning parameters for the removal of biological black crusts in granites. In: Radvan R, Asmus JF, Castillejo M, Pouli P, Nevin, editors. Lasers in the Conservation of Artworks VIII. London: Taylor & Francis Books; 2010. pp. 105. https://doi.org/10.1201/b10567-18.
88. Speranza M, Sanz M, Oujja M, de los Rios A, Wierzchos J, Pérez-Ortega S, Castillejo M, Ascaso C. Nd-YAG laser irradiation damages to Verrucaria nigrescens. International Biodeterioration & Biodegradation. 2013. https://doi.org/10.1016/j.ibiod.2012.02.010.
89. Mascalchi M, Osticioli I, Cuzman OA, Mugnaini S, Giamello M, Siano S. Laser removal of biofilm from Carrara marble using 532 nm: The first validation study. Measurement. 2018. https://doi.org/10.1016/j.measurement.2018.08.012.
90. Costela A, García-Moreno I, Gomez C, Caballero O, Sastre R. Cleaning graffitis on urban buildings by use of second and third harmonic wavelength of a Nd:YAG laser: A comparative study. Appl. Surf. Sci. 2003. https://doi.org/10.1016/S0169-4332(02)01241-2.
91. Gomez C, Costela A, García-Moreno I, Sastre R. Comparative study between IR and UV laser radiation applied to the removal of graffitis on urban buildings. Appl. Surf. Sci. 2006. https://doi.org/10.1016/j.apsusc.2005.04.051.
92. Sanjeevan P, Klemm AJ, Klemm P. Removal of graffiti from the mortar by using Q-switched Nd:YAG laser. Appl. Surf. Sci. 2007. https://doi.org/10.1016/j.apsusc.2007.04.030.
93. Samolik S, Walczak M, Plotek M, Sarzynski A, Pluska I, Marczak J. Investigation into the removal of graffiti on mineral supports: Comparison of nanosecond Nd:YAG laser cleaning with traditional mechanical and chemical methods. Stud. Conserv. 2015. https://doi.org/10.1179/0039363015Z.000000000208.
94. Pozo-Antonio JS, Rivas T, Fiorucci M.P, López AJ, Ramil A. Effectiveness and harmfulness evaluation of graffiti cleaning by mechanical, chemical and laser procedures on granite. Microchem. J. 2016. https://doi.org/10.1016/j.microc.2015.10.040.
95. Doganis Y, Galanos A, Legakis A, Pouli P, Melessanaki K. The conservation of fifteen islamic plaster stained glass windows, the Benaki Museum Islamic Art Collection. In: Kwiatkowski D, Lofvendahl R, editors. Proceedings of the 10th International Congress on Deterioration and Conservation of Stone: Stockholm, June 27-July 2, 2004. Stockholm: ICOMOS Sweeden; 2004. pp. 1025–1032. ISBN: 9163114585
96. Rozniakowski K, Klemm P, Klemm AJ. Some experimental results of laser beam interaction with surface layer of brick. Building and Environment. 2001. https://doi.org/10.1016/S0360-1323(00)00012-3.

97. Pozo-Antonio JS, Rivas T, López AJ, Fiorucci MP, Ramil A. Effectiveness of granite cleaning procedures in cultural heritage: A review. Science of the Total Environment. 2016. https://doi.org/10.1016/j.scitotenv.2016.07.090.
98. Pozo-Antonio JS, Papanikolaou A, Philippidis A, Melessanaki K, Rivas T, Pouli P. Cleaning of gypsum-rich black crusts on granite using a dual wavelength Q-Switched Nd:YAG laser. Constr. Build. Mater. 2019. https://doi.org/10.1016/j.conbuildmat.2019.07.298.
99. Platia N, Chatzidakis M, Doerr C, Charami L, Bekiari Ch, Melessanaki K, Hatzigiannakis K, Pouli P. 'POLYGNOSIS': the development of a thesaurus in an Educational Web Platform on optical and laser-based investigation methods for cultural heritage analysis and diagnosis. Herit. Sci. 2017. https://doi.org/10.1186/s40494-017-0163-0.

Chapter 4
Stone Consolidation. Between Science and Practice

José Delgado Rodrigues

Abstract This chapter deals with basic considerations about stone consolidation and aims to advance thoughts and clues to help professionals bridge the gap between science and practice. Scientific literature and personal experience serve to support and interpret the complex and intricate difficulties raised by practical consolidation needs. The reasons for these difficulties stem from the often-complex patterns of deterioration, the high potential risks of obtaining a very high or very low consolidation action, the uncertainty of medium- and long-term behaviour, and the lack of adequate guidelines for selecting a product and configuring a treatment consolidation solution for the intended objective. The purpose of this chapter is to help professionals to adapt existing knowledge on stone consolidation issues to each specific case and help them to make decisions, keeping in mind that there is no universally applicable product or treatment and that universal recipes should be clearly discarded. It is assumed here that the user works with products available on the market and, therefore, this chapter is not sufficiently detailed and is not intended to serve as a guide for testing or certifying new products or treatment techniques to be introduced to the market.

Keywords Stone consolidation · Consolidants · Consolidation treatment · Effectiveness · Compatibility

4.1 Introduction

In a recently published paper [1], a thorough discussion is made of the most relevant theoretical insights on stone consolidation and on their counterparts in field practice. The comprehensive background of stone consolidation and the discussion of the detected shortcomings of the current research and practice turn it into a must-read paper for those wishing to complement the matters addressed in the present

J. Delgado Rodrigues (✉)
National Laboratory of Civil Engineering, Lisbon, Portugal
e-mail: delgado@lnec.pt

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chapter. Other relevant comprehensive references on consolidation are also recommended [2–6].

Consolidation is certainly the most demanding intervention in the practice of stone conservation and has attracted the interest of the research community even before the conservation of cultural heritage emerged as a scientific discipline. And yet, it still remains a controversial action, where failures and mismatched cases are frequent and fully successful interventions scarce.

Multiple reasons have been advanced to explain why such a low rate of success is attained, in spite of the substantial efforts that have been put into the search for better achievements. Most difficulties stem from a basic and major intrinsic fact: the deterioration processes that lead to the loss of cohesion are inherently irreversible and there is no artificial way to reproduce or replace it in the exact quality and quantity that has been lost. As a consequence, the "solutions" introduce materials distinctly different from the original, establish connections that were not there previously, and leave a treated material that, to a lesser or greater extent, is different from the one it was supposed to "rehabilitate".

In the absence of optimum and indisputable solutions, professionals have to work bounded by two serious and troublesome constraints:

(i) a deterioration problem where the loss of cohesion configures or threatens an actual or imminent loss of value to a level that an urgent or short-term action is required; and
(ii) a shortage of applicable solutions, a lack of sufficiently-demonstrated successful case studies, and a poor conceptual framework to help transposing scientific data into their specific cases at hand.

This chapter aims to bring some thoughts and clues to help professionals to bridge the gap between science and practice. It was written aware of the inescapable trap of risking to oversimplify the existing overwhelming collection of scientific literature and of misrepresenting and misinterpreting the complex and intricate field conservation difficulties. To minimise the risk, real conservation situations will be used as support to the analyses advanced here, while following the essential relevant research data to help understand the boundaries of the discussed items.

Although looking for practice-feasible proposals, it is important to stress that universal recipes do not exist and that any potential solution needs to be adjusted and validated for any specific situation before embarking in its implementation. As summarised some four decades ago, "*Just as there can be no "universal preservative," there can be no universal evaluation procedure*" [7].

The purpose of this chapter is to help practitioners adapt existing knowledge on stone consolidation issues to each specific case; therefore, it cannot be sufficiently detailed and is probably not suitable to help certify any new product or treatment technique intended to be introduced into the conservation market.

4.2 Consolidation – Its Basic Principles and Requirements

Consolidation is a generic term used to describe any process able to induce a strength increment to the material in question. In stone conservation, consolidation is applicable when any deterioration processes have lowered the stone cohesion to a level that threatens the inherent values of the object. This action is intended to re-establish totally or partially the cohesion loss, while keeping the impact of any foreseeable negative side effect at its possible minimum.

Under this understanding, three basic principles emerge:

(i) Consolidation is supposed to be implemented in decayed materials. As a corollary, it may be concluded that sound materials are not supposed to be consolidated.
(ii) The consolidation process should be effective, meaning that the stone strength is supposedly incremented.
(iii) The negative side effects should be kept at a minimum to avoid the risk of a significant loss of value in both the short- and long-term.

The first principle sounds like a truism, but it is more than that. In fact, most research studies are made on sound materials, given the difficulty in getting naturally deteriorated materials to test and the poor reliability of the artificially aged samples. Furthermore, many tests require delicate manipulations and very precise measurements that are better achieved on sound specimens. As a consequence, most research results, even of high quality, may not be easily transposed as reliable predictions when deteriorated conditions are to be addressed.

Evaluation and demonstration of effectiveness is not a straightforward issue. It seems clear that only when a significant cohesion increment is directly measured or indirectly established can an effective action be validated. For instance, an increment of the tensile or bending strength is a direct measure of effectiveness, while a reduction in porosity or a change in the pore size distribution is only a demonstration that the consolidation product is present inside the stone, but they do not directly demonstrate that a given degree of effectiveness was achieved.

The negative side effects, usually designated as harmfulness, can be noticed immediately, for example, by a significant colour change, but the most serious problems tend to occur in the medium- and long-term. Quite frequently, the loss of performance over time in consolidated areas is simply designated as a loss of effectiveness, regardless of how good or bad the cohesive bonds are maintained. For instance, a good adhesive resin may well keep being strong and yet the treated harder crust be detaching and falling; this is not exactly a loss of effectiveness, but a delayed manifestation of its harmfulness.

This happens when the newly acquired properties of the treated zone differ from the untreated substrate to such an extent that its medium- and long-term behaviour proves incompatible with the substrate. The concept of (in)compatibility finds here its full meaning by describing a component of the stone treatment behaviour not generally included in the framework of harmfulness. Decades ago this concept was introduced into the conservation field and proposals for its application can be found elsewhere [8].

To re-establish the required cohesion level, the product, i.e., the consolidant, has to be introduced into the deteriorated stone following one of the multiple possible procedures. In short, this complex action is designated as a consolidation treatment and the term is meant to include a specific consolidant, the protocol followed to apply it, and the conditions under which it was implemented.

The published information on consolidation treatments is often overly simplified, both in research and practical fields, which may induce the reader to doubt what the working conditions and implemented actions might have been. "Treated with X by brushing until refusal…" is a common expression found in reports and research papers to describe consolidation treatments. Assuming here that product X is sufficiently described in the report, other relevant information is missing: the amount of product applied; the surface condition at the application onset; the preparatory actions; the environmental conditions; any precautionary measures taken during application; and other such information.

The most precise as possible knowledge of the actual surface conditions is an essential requisite for success. This is necessary to justify the necessary actions, select the most suitable consolidation agent, identify the best adapted treatment protocol, and anticipate possible deficiencies.

4.3 An Introduction to the Consolidation Products and Application Protocols

4.3.1 Main Families of Consolidation Products

Consolidation has been a research topic for decades, and publications about consolidation products are numerous. They are important sources of information for researchers, but extracting direct practical applicability from them is seldom a straightforward task. For professionals, reference books, manuals, and compiled documents are the recommended sources to start with. The reference books *Stone Decay and Conservation* [5], *Il Restauro della Pietra* [6], and *Stone in Architecture* [9] are recommended as a first introduction to stone treatments. Detailed information on organic consolidants, adhesives, and coatings for use in conservation at large can be found in Horie [10]. Selwitz [11] makes an extensive analysis on the use of epoxy resins, and a thorough discussion on alkoxysilanes is presented on the book *Alkoxysilanes and the Consolidation of Stone* [12].

4.3.1.1 Si-Based Products

TEOS-tetra-ethyl-orthosilicate (or ethyl silicate for short) by itself or combined with other products, with or without additives to induce specific properties, and coming from multiple suppliers, is possibly the most largely used family of stone consolidants. Its introduction as a modern research topic can be traced back to Lewin [13], and contributions to better characterise it and proposals to improve its performance have been progressively added [12, 14–17].

Si-based consolidants are well suited for application to silicate stones, such as sandstones, granites, and similar igneous rocks. Calcite, the main component in limestones and marbles, seems to negatively interfere with the curing conditions of ethyl silicates [18–22]; nevertheless, extensive documentation exists supporting the use of ethyl silicates for consolidating carbonate stones [23–26].

In spite of their wide use, the lack of chemical affinity has always been considered as a drawback of ethyl silicates, which led researchers to study and propose ways to overcome, or at least to reduce, this negative outlook. Different approaches to achieve it have been found [27–30]. Recent developments with nanosilica and other nanomaterials add new ways to overcome this limitation [31–35].

4.3.1.2 Epoxy Resins

Epoxy resins have a long tradition of use in stone conservation for gluing disjointed pieces, but specially formulated low-viscosity products have also been used for mass consolidation. Reports mention their use in the USA [36] and Poland [37] on sandstones, limestones, and marbles with reportedly satisfactory results. A successful result of mass consolidation in granite columns with a cycloaliphatic epoxy resin is reported elsewhere [38, 39]. For very porous stones, the risk of getting an over-strengthening effect needs to be carefully assessed.

4.3.1.3 Acrylic Resins

Acrylic resins are widely used in conservation [5, 10], namely as gluing agents and coatings and varnishes, but research has also been made to support their use as consolidation products [26, 40–43]. Paraloid B72 (methyl-acrylate ethyl-methacrylate) is one of the most frequently used products in conservation and is a leading representative of the family of acrylic resins [44, 45]; it has brought relevant services to conservation, but it has also been frequently misinterpreted and misused. In spite of its wide application range, it is definitely not an all-purpose product, and should not be used outside its specific applicability window or perform functions for which it is not suitable. In very porous stones, it is not easy to have acrylic resins distributed sparsely in depth and, when concentrated close to the surface, there is a great risk of creating a super-consolidated layer with a high potential of inducing negative effects.

4.3.1.4 Inorganic Products

Some inorganic products constitute an important category of stone consolidants [46]. They vary from calcium hydroxide, one of the oldest known products, to barium hydroxide, ammonium oxalate, ammonium tartrate, and ammonium phosphate. While the Si-based products are especially indicated for silicate stones due to their chemical affinity, the inorganic products typically have the carbonate stones as their main target.

Calcium hydroxide (CaHy) and barium hydroxide (BaHy) are water solutions that, once inside the stone, undergo carbonation by reacting with carbon dioxide from the air. Their major drawback is their relatively low solubility and therefore the low concentration of the consolidation agent that can be introduced into the stone.

To overcome this limiting condition, authors and practitioners have indicated that lime water (CaHy) needs to be applied in multiple steps and number up to forty times [47] and consumptions of 25 L/m^2 [48] have been reported. In recent times, the suspension of nanoparticles in alcohol (nanolimes) appeared as a possible way to increase the amount of calcium hydroxide that can be introduced into the deteriorated stone [49–53].

Barium hydroxide is best known as a component of the "Florentine method", mostly used as a sulphate blocker in combination with the application of ammonium carbonate [54, 55]. BaHy has a fast carbonation rate and therefore its direct application to the surface may be hindered by the simultaneous precipitation of barium carbonate and therefore, it is essential to avoid the free circulation of air during the treatment. When a long contact of the solution with the decayed substrate is permitted, a secondary reaction between Ba ions and the substrate takes place [56] and a significant cohesion increment may be obtained [57]. These conditions are not easy to implement in outdoor conditions and ingenious solutions must be designed to allow long contact times in the absence of carbon dioxide in air. When pieces can be moved, their immersion for a long period may produce significant strengthening effects.

On the other hand, swift applications of CaHy or BaHy can easily lead to a very shallow impregnation layer that may cause an indurated crust with risky consequences for the surface stability. Significant whitening due to a surface deposition is a common side effect and due diligence must be used to avoid or reduce it to acceptable levels.

Ammonium oxalate-, ammonium tartrate- and ammonium phosphate-based products operate as the replacement of the *in-situ* calcite for the less soluble calcium oxalate, calcium tartrate, and calcium phosphate, respectively [29, 55, 58, 59]. They aim to stabilise the stone surface by providing a less soluble cover and some intergranular cohesion, but it must be realised that this deposition is preceded by a chemical reaction with the original calcite framework. The real added value of this replacement is not of a straightforward demonstration.

4.3.1.5 Biomineralisation

This method consists of the deposition of calcite mediated by bacteria. When an appropriate pH is created, and a proper nutritional medium is available, certain bacteria produce calcium carbonate in their cell walls that are subsequently left as calcite that fill pores and cracks of the decayed stone. Two major methods have been proposed and successfully used:

- The French system [60], which is based on the inoculation of selected bacterial strains together with the appropriate nutritional medium. Positive interventions have been reported [61].
- The Granada method based on the activation of dormant autochthonous bacterial communities through the introduction of an appropriate nutritional medium [62, 63]. Demonstration of its effectiveness has been reported from laboratory [64] and field trials [65, 66].

4.3.2 Treatment Protocols

The protocol used to apply a certain product has important implications in the final consolidation action [67–70]. This influence cannot be overestimated, and the conservator-restorer must be aware that the variation or alteration of a protocol can change from a successful result to a complete failure. In case of doubt and whenever a first application is made, it is mandatory to carry out preliminary tests to model the handling and application procedures and to verify that the results correspond to expectations.

Following recommended practices, comparing different situations, and adapting from others' experiences also deserve to be critically assessed. For instance, it is usual to specify "apply until refusal", which is a possibly satisfactory specification for some cases, but it may also lead to insufficient amounts in low absorbing stones and to an excess of product in very fast absorbing ones. Furthermore, different practitioners in different places will have different perceptions of what a refusal is and results may not be comparable.

The indication that a certain amount of product should be applied is a better way to specify a practical action and a more reliable way to get comparable results. The advantages and drawbacks of the main application processes are described as follows:

- Dripping from a pipette or containers is a common application process with known advantages. It facilitates the absorption of the product without touching the object and the process is easily mastered. The duration of the application and the amount applied are controllable variables.
- Application by brushing is a very popular and versatile method that fits well for most onsite situations. It facilitates control of the treatment sequence, which allows definition and quantification of the treated area and the amount of product

applied. Unless any specific requirements or constraints exist, this is the default method to implement consolidation treatments.

- Application by spraying is a faster method, but it is less precise and practically impossible to be replicated by someone else. Part of the product may be dispersed in the air and is lost, and the solvent evaporates more easily, thus modifying the product properties. Monitoring of the applied amount is less precise, and the overall control of the operation is less reliable. Unless a very specific situation that precludes the use of direct contact with the surface exists, the only reason to choose spraying is its fast application rate and the consequent economic benefits.
- Application by poulticing is justified for delicate surfaces and when long contact times are necessary to reach the objective. The use of an interface of Japanese paper may be necessary to facilitate the removal of poultices. The contact may not be perfect and result in a discontinuous surface, and the amount applied can only be estimated. A strict and continuous control of the progress of the absorption process is necessary to have the treatment attain the defined goal.
- Long-term immersion and absorption by continuous contact ("*impregnazione per percolazione*") [71] may be applicable for moveable objects when deep impregnation is pursued. Impregnation under vacuum, an always demanding operation, has also been reported as a best or unique treatment option [39, 71–74]. In principle, a saturation of the empty space is achieved (or achievable) while it is not possible for intermediate conditions to be prescribed.

4.3.3 Onsite Circumstances and Operational Conditions

An obvious and most critical aspect embraces all the onsite circumstances (as detailed in a subsequent section) of the deteriorated area: the stone properties, the deterioration pattern, the decay profile, the significance of the exposed surface, the allowable amount of material to be lost, any existing external nuisances, any past treatment(s), and possibly others.

The end result also depends on the external conditions at the time of its implementation. The weather conditions may influence the product properties and its curing conditions, and the expertise and care of the practitioner in following the product specifications while adapting it to the actual situation may result in a non-negligible impact on the intervention. Last, but not least, the working conditions also matter, namely in terms of the worksite facilities (proper scaffolding, adequate working tools and control instruments, etc.) as well as the economic and budgetary constraints.

The quest to identify and understand the requirements of what a consolidant should be is not new and can be traced back to the early stages of the stone conservation discipline. In 1921, Heaton [75] had already established a clear perception of what a consolidation treatment has to achieve to be acceptable and proclaimed the following wise and premonitory criteria:

i) A stone preservative must penetrate easily and deeply into the stone and remain there on drying; ii) It must not concentrate on the surface so as to form a hard crust, but must, at the same time, harden the surface sufficiently to resist erosion; iii) It must prevent penetration of moisture, and, at the same time, allow moisture to escape; iv) It must not discolour or in any way alter the natural appearance of the stone; v) It must expand and contract uniformly with the stone so as not to cause flaking; vi) It must be non-corrosive and harmless in use; vii) It must be economical in material and labour of application; viii) It should retain its preservative effect indefinitely.

Even today, the search continues; the objectives do not differ significantly and only the terminology, the tools, and the instruments of study have changed, although fully mastered solutions are only available in a limited number of situations.

4.4 A Few Insights into the Selection Procedures

Extensive research has been done on consolidation products and the abundant literature provides clues to the first steps of choice. The comprehensive list of testing methods and criteria for the selection/evaluation of conservation of porous building materials products presented by Tabasso and Simon [4] can be taken as a good starting point on this subject. In their paper, the authors point out two main ways for obtaining information to support the selection of a treatment for any specific concrete situation: i) "… *to collect the required information for such careful evaluation: firstly, by surveying the condition of monuments that have been treated in the past and for which reasonably good documentation exists for the methods and materials that were used*"; ii) "… *by carrying out ad hoc tests (either in the laboratory, in situ, or in both contexts, by outdoor exposure programmes*").

Well-documented cases similar to our specific situation in terms of type of substrate, deterioration problems, and cultural restrictions are rarely encountered and therefore the first way, although entirely fair and viable, is not of general value. The second way is a good alternative, and it should be followed whenever a new product is proposed for practical use. However, most current conservation interventions cannot afford the means to carry out such a comprehensive programme and, therefore, this approach is seldom practicable.

A third way is outlined here and consists of using published information and interpreting it with the specific situation as a background. It is assumed here that the user needs to learn how to extract the relevant information from studies that did not necessarily address goals and use situations identical to the current user. In fact, most of the relevant published information comes from research that rarely has the solution of concrete conservation interventions as their main objective and, therefore, most results cannot be directly transposed as a solution to our own specific situation.

In the following paragraphs, some ideas are provided on how to analyse the available information and organize it into workable knowledge to integrate into the decision-making process. When looking for a product to use, it is advisable to start by some dichotomy eliminations: (i) identifying the families of products more suitable for silicate or for carbonate stones; (ii) understanding how products behave in high- and low-porosity stones; iii) considering how to deal with porous versus fissured stones, etc.

The chemical affinity between the major stone constituents and the consolidant is a first crossroad to determine which way to follow and, therefore, identifying whether the target substrate is a silicate- or carbonate-based stone should be the initial objective.

Silicate stones, such as sandstones and granites, show chemical affinity to alkoxysilanes, while carbonate minerals may negatively interfere with their curing conditions [20] and therefore ethyl silicates and similar products show better perspectives for the consolidation of silicate stones.

Instead, for carbonate stones, ammonium oxalate, ammonium phosphate, ammonium tartrate, and calcium and barium hydroxides are expected to be more appropriate, while being unsuitable to consolidate silicate materials. In spite of the lack of chemical affinity, ethyl silicates have been widely used in carbonate stones [12], but indications about their medium- and long-term behaviour are not convincing, leaving doubts on the appropriateness of their use [76].

Epoxy and acrylic resins adhere to all types of mineral surfaces and, therefore, chemical affinity is not an issue for them. Since they tend to induce high strength increments, their use can find a justification when load-bearing elements are envisaged, provided that due care is taken to avoid the frequent and serious incompatibility implications they exhibit.

This preliminary option based on the chemical affinity and potential adhesion capability may orient the choice for a certain family of products, but it is by no means enough to decide what product to use. Accurate support to help decide what needs to be done on a specific stone surface with its real deterioration problems is far scarcer and more difficult to find and, therefore, an informed choice needs a bit more of reasoning and fact checking, as suggested in the following paragraphs.

The selection of a consolidation treatment should follow a rational reasoning and proceed step by step:

- Understand the onsite situation,
- Consider the potential effectiveness and immediate harmfulness,
- Consider factors and parameters that may help to anticipate the occurrence of medium- and long-term incompatibility phenomena of the eligible consolidation product(s), and
- Select the consolidant and specifying the treatment protocol.

4.4.1 Understanding the Onsite Situation: My Case Is Not Your Case

A minimum of information about the composition of the stone is essential to get started, and a careful identification of the deteriorated patterns is mandatory. Understanding the causes of the observed deterioration phenomena may help to adapt procedures and to avoid possible interference from existing problems. The characterisation of any specific situation may be done in different degrees to meet the defined objectives, ranging from swift studies to validate a process already known to occur in that specific site or in similar situations, to detailed research projects of particularly difficult deterioration problems. These preparatory tasks have very specific disciplinary contents that require the involvement of conservation scientists. When these skills are not included in the conservation team, external input of technical expertise is highly recommended for each specific case.

Situations that require consolidation actions can be grouped in two major categories (Fig. 4.1):

- Large scales, chips, plaques, and plaquettes
- Thin, small scales, powdering, and granular disintegration

Both types may require consolidation, but a significant difference exists between them. The larger dimensions of the elements of the first group allow for addressing them individually, while it is unfeasible for the second group. Larger elements can be glued to the substrate, before or after consolidation, and their contours sealed, thus preventing these threatened elements from detaching completely and falling.

Fig. 4.1 Different deterioration patterns will need different treatment approaches. Thick scales, plaques and chips (top) are individually addressable, while powdering and granular disintegration (bottom) need to be addressed with a more encompassing treatment process, © José Delgado Rodrigues

On the other hand, powdering and sand disintegration cannot be addressed particle by particle and only mass consolidation treatments are practicable. The most superficial loose layers tend to be impossible to fix and in most cases are lost.

In addition to the surface appearance of the deteriorated areas, it is important to determine, or at least estimate, how thick the deteriorated zone is, as this will determine the depth of impregnation necessary to adequately address the problem.

Salts are frequently associated with these deterioration patterns. Their presence may interfere with the treatment process itself and may compromise the subsequent performance of the treated zone. Areas with a high salt content must be desalinated beforehand, to the extent permitted by the condition state.

Preparatory studies take time and consume resources and, unfortunately, are not carried out in all interventions. More often than desirable, professionals proceed by analogy with reported successes or by directly transposing their own experience. Both practices are acceptable, as long as the user is aware of the risk assumed by following this procedure and will take the necessary measures to validate the information transposed to each specific situation.

Small variations in the composition of the stone, in the exposure situations, and in the environmental factors make each situation unique (Fig. 4.2) and it should always be remembered that **my case is not your case**.

4.4.2 Determining the Potential Effectiveness

A product is potentially effective when it is possible to introduce it into the stone and a strengthening effect is produced. The products marketed as consolidants can be reasonably assumed as being able to produce a strengthening effect and, therefore, the main question the practitioner has to answer is whether it is possible to impregnate the stone to the required depth.

Fig. 4.2 Significant mass losses can occur in localised areas that require consolidation, and the approach to follow is primarily specific to each situation. Examples of granular disintegration in granite from S. Francisco church (Porto, Portugal), and powdering in a soft limestone from Avignon (France), ©José Delgado Rodrigues

In addition to considering the information provided by the product supplier, a simple test on a sample of the stone to be treated and, eventually, another test somewhere on the object are sufficient to obtain the relevant information.

The strengthening capacity is the key property for each consolidant since it largely influences the overall performance of the treated stone, and therefore must be taken as a relevant aspect in deciding which consolidant to choose. To obtain the most accurate estimate of this property, specialised equipment and trained personnel are required, conditions that are rarely available at worksites. The ideal situation is the involvement of a service provider that could take charge of this study.

When such involvement is not feasible, the remaining alternative is to search information in the published literature and interpret and adapt it to the specific case to be addressed. This adaptation may require some specialised expertise and the user must always keep in mind that taking others' results as recipes is a risky attitude and therefore should be avoided.

Reading and interpreting the published data on stone consolidation may not be easy, especially if the reader is looking for information that may directly impact their own cases. A few hints to help professionals to evolve in this domain will be presented in a subsequent section.

4.4.3 Determining the Immediate Harmfulness

The negative impacts of a consolidation treatment may be perceived and measured soon after its implementation or take some time to manifest. The medium- and long-term effects are of a different nature and will be addressed below.

The most common and best-characterised symptom is a colour change. It is often featured in the literature and most product suppliers provide adequate information about it. A simple test on a small area somewhere on the object will be enough to validate the information for each specific case.

Impregnation with a consolidation product will inevitably introduce changes in the stone's porosity and, therefore, all fluid transmission properties may undergo some change. The identification and quantification of such changes require specific equipment and trained personnel. When adequate facilities are not at hand, the user has to resort to the published literature. When doubts exist and the potential impact on the overall performance is of concern, the adaptation to each specific case may raise great difficulties and conclusions should be drawn with caution.

Large variations in water vapour permeability and drying behaviour (either when actually measured or taken from published literature) should be a warning, to the extent that they can justify the rejection of that specific treatment. Even subtle variations in the drying behaviour, for instance, those created by any eventual hydrophobic agent present in the product, may induce evaporation to occur just beneath the treated layer with serious potentially negative consequences.

4.4.4 Assessment of Medium – and Long-Term Compatibility of the Eligible Consolidation Product(s)

Quite frequently, treatments taken as successful soon after application show problems in the medium- or long-term. There are cases in which the consolidation action remained effective (in the sense that the strengthening effect is still present), but the hardened layer and the substrate behaved in a discordant manner, indicating that something had not been done correctly. The description and interpretation of this behaviour are usually made under the concept of compatibility.

The concept assumes that, for a given treatment to be totally successful, it must meet the immediate requirements of being effective and not harmful, but it is also necessary that the treated layer should not behave very differently from the substrate. Working principles and hints to implement this concept can be found elsewhere [8].

Figure 4.3 illustrates some common medium- and long-term unsatisfactory situations ascribable to incompatible behaviours.

The basic guidelines for operating with this concept are based on comparing the properties of the treated layer and the substrate directly below it. Mechanical, thermal, and fluid transport properties are key aspects to be analysed and properly taken into account.

Published research studies have been carried out mainly on fresh samples, given the difficulty in finding naturally deteriorated stones for testing and the difference between natural and artificially induced deterioration patterns. This should be a warning when looking for information and the users should always keep in mind their specific case and how the information can be adapted to it.

The most relevant aspect to be considered is the presence of a deteriorated profile that can vary gradually or abruptly from the surface inwards and that can show a slight or strong contrast of properties with the underlying unaltered substrate.

Fig. 4.3 Incompatible performance of treated limestone showing a thin hardened layer detaching from the powdery underlying stone. The strengthening of the consolidated layer was still effective, but its highly different physical properties led to a severe incompatible behaviour, ©José Delgado Rodrigues

Advice and suggestions can be put forward, but there is no way to embrace here all the peculiarities that exist onsite, which only the local expert can do properly.

The deteriorated areas are more porous than the substrate and, consequently, absorb the product in larger quantities. Therefore, any identified differences in fresh sample properties will be maximized and the risks of incompatibility increased. It must always be kept in mind that a very superficial impregnation can leave part of the deteriorated profile untreated, which will prevent the treated layer from adhering and anchoring properly to the substrate.

Performing evaluation tests directly onsite is highly recommended, but it should be noted that extracting information to predict medium- and long-term behaviour is neither a simple nor straightforward task. When an interval of months before implementation is available, careful monitoring and characterisation of the areas tested can provide valuable information. When clearly negative behaviours develop in this short-term, it constitutes a sufficient argument to discard the product, but the absence of negative signs, although desirable and promising, does not constitute a full guarantee that a long-term compatible behaviour will persist.

4.4.5 Selecting the Consolidant and Adapting the Treatment Protocol

When the necessary resources and time in the implementation schedule are available, preparatory studies are recommended to properly characterise the site condition and get the necessary information to proceed with the selection process. The priorities to be clarified and deepened were summarised above.

This background information is essential to support the decisions to be made, although, very likely, will not point to a clear and unequivocal option to adopt and the user will still need to reason and plan adaptations before a final choice is made.

As asked elsewhere [66], "*Is the decision to be made predominantly based on the product's effectiveness? Or should it be based on its incompatibility degree?*" As these authors state, "*the frequent failure or underperformance do not occur as a consequence of its insufficient effectiveness, but rather as a result of an excessive incompatibility degree*".

In theory, and taking this perspective to its limit, it can be said that the application of a treatment with low effectiveness will be a repairable problem, as long as the treatment is completely harmless; on the contrary, an incompatible treatment, regardless of its low or high effectiveness, will always constitute an irreparable situation.

Therefore, this will be the guideline suggested here to help professionals decide the way forward in choosing the treatment for their specific case.

It can be assumed, by default, that any consolidation product subject to a scrutiny has a certain strengthening capacity as a prerequisite for being called a "consolidant". What the user has to decide is whether a low or high level of strengthening is

Fig. 4.4 Different functions require distinct treatment approaches. A load bearing column (left), deeply decayed and with significant mass losses may require a strong consolidation action, while a delicate decorated surface (right) may just need a gentle consolidation action, proper maintenance, and regular monitoring, ©José Delgado Rodrigues

necessary and which product(s) is (are) capable of achieving it. A highly deteriorated column may require robust consolidation action, while a decorated surface may need a subtle and weak consolidation (Fig. 4.4). This first step will immediately discard some families of products and focus the analysis in a smaller number of alternatives.

The type of stone and its typical characteristics will allow a second level of analysis. The mineral composition and the type of voids (cracks or pores) are the main aspects to be considered at this step.

For instance, a silicate stone composition can guide the choice to a silicon-based consolidant. For this reason, sandstones, granites, and other igneous rocks can and have been widely treated with ethyl silicates.

Fissures and pores induce substantially different end-results in terms of ease of impregnation and the amount of product needed to achieve a similar treated thickness.

Marble, granites, and other similar rocks are fissured materials and, when deteriorated and in need of consolidation, their porosity is typically slightly above 2%; however, even for such low values, the absorption rate is fast, and the impregnated depth can reach significant values. With low viscosity products, the treatment of these materials can be carried out successfully and relatively large treated thicknesses are achievable [77].

Limestones and sandstones have pore-type voids that may vary widely in size and in the total amount. The pores are far more poorly connected than fissures and, therefore, absorption is significantly slower. In terms of impregnation thickness, a 3% porosity granite impregnates as fast as a 30% porosity limestone. For similar porosities, stones with larger pores will absorb faster. On the other hand, greater porosity implies that a larger amount of product is needed to obtain a similar treated thickness, and this may mean that the potential damaging effect left by the product will increase concomitantly.

These first considerations did not include any reference to the actual state of the deteriorated surface condition and, therefore, can only be taken as suggestions on how to select a family of products capable of promoting the expected level of potential consolidation. The application of the product in a representative sample of the type of stone to determine a relationship between the amount of product applied and the consolidated thickness achieved is a useful procedure to support this first selection step. This relationship is an essential tool to help users master their own treatment procedure; if a defined consolidated thickness is required, the user will estimate the amount of product to be applied to achieve it.

This approach is likely to resolve situations with a simple deterioration profile and especially in the case of low cultural value. For complex decay profiles and more valuable surfaces, such direct solutions will not be enough, and users must adapt procedures and adjust treatment to suit each specific case. Experience is essential to advance in this field, but it needs to be supported by rational reasoning to match information to any new and necessarily different situation. Experience is acquired, not taught, but helping with the reasoning is what can be contributed here.

The diversity and variability of deterioration patterns can be addressed from two opposing sides, "scaling-up" and "scaling-down" approaches, hopefully shaping a methodology in which these approaches can converge properly [66]. According to these authors, the rationale of this proposal is the following:

> *"When starting by considering effectiveness as the leading objective, the decision-making process progresses from firstly demonstrating that a certain consolidation product is effective and subsequently moves to demonstrate how compatible it is. If it is not compatible, the decision-making process tries to scale-down the effectiveness until an acceptable compatibility degree is reached. The second alternative, scaling-up, departs from searching a potential consolidation treatment of known, or assumed, low incompatibility degree, even of foreseen low consolidation action, and seeks to improve the consolidation power as far as the process can be upgraded while keeping the incompatibility degree within acceptable limits."*

For instance, the consolidation of a load-bearing element can be adequately addressed in a scaling-down perspective. A major strengthening effect is a primary requirement of the consolidation treatment and the counterpart of any risk of incompatibility must be managed by acting on the strengthening action and reducing it until an acceptable degree of incompatibility is achieved.

On the opposite side, a deteriorated decorative surface can be taken as an example of a scaling-up perspective. The risk of losing significant cultural value is high and any possibility of inducing incompatibility results should be kept to a minimum. Consolidants with a low strengthening action are the target for this objective and, among them, those with a lower degree of incompatibility are preferred. From the lowest minimum, in terms of incompatibility, an exercise of scaling-up the strengthening action can be analysed until the incompatibility risk is no longer acceptable.

This way of looking at a consolidation treatment assumes that a stronger consolidant is not necessarily better than a weaker one. It also assumes that the user at the site (the conservator-restorer) has an essential role in integrating the available scientific information to develop the appropriate treatment protocol to consolidate the specific deteriorated surface.

4.5 From Theory to Practice. May I Help You?

It is generally recognised that there is a certain distance between the academic world, where there is a prolific production of scientific information, and the practical world, where real problems are waiting to be solved, and which are often approached with little scientific support and with too much of a pragmatic and quick fix attitude. While both sides can be held responsible for not making every effort to fill this gap, it is assumed here that conservation scientists must take the lead and it is from this perspective that the next sections will be addressed.

For greater clarity, it is understood that, when making a diagnosis, characterising a specific situation or preparing supporting information for any intervention, the role is specific to a conservation scientist, whether chemist, geologist, engineer, conservator-restorer, or any other. When making an intervention, the role is exclusive to conservator-restorers.

The ideal situation is having a team of conservation scientists working closely with conservator-restorers for each specific case. Fortunately, this happens quite often, although it is still far from being a general rule. The worst-case scenario occurs when an intervention is procured as a turnkey contract, without prior preparatory studies. In such cases, competent contractors must act as a conservation scientist at first and then as a conservator-restorer.

The next sections are focused on the specific needs of the site and are mainly aimed at conservator-restorers.

4.5.1 What Problems Do You Need to Address; Is It Necessary or Not to Consolidate?

Stone problems usually occur in complex combinations that may require several different approaches throughout the project. The first great notion is to keep in mind that it is not necessary and therefore not advisable to apply the same solution/technique everywhere. In particular, in terms of consolidation, especially due to its potential harmfulness, only areas that really need to be consolidated should be considered for treatment.

Areas with advanced development of black crusts, of intense powdering, or of extensive sanding may require consolidation. The areas where these patterns of deterioration exist must be identified and duly considered as candidates for treatment.

Decorative areas are priority targets for consolidation, but they are also those showing the greatest difficulties to solve. Rapid decay rates can justify an inevitably heavy intervention, while a slow rate of evolution can accept minimal actions, allowing the postponement of a major risk-consolidation treatment. The basic information needed to make this judgment can be obtained by periodic monitoring, when possible, sought from the curators, or by comparison with old photos of the site.

Areas that change slowly may show some patinas and even incipient biocolonisation, while those with rapid evolution tend to show clean surfaces and with apparent traces of recent detachment.

Areas with active mass loss processes in load-bearing elements, such as columns, arches, and the like, generally require consolidation, as their load-bearing capacity may be at risk. The degree of urgency can be reasonably assessed by estimating the loss of the resistant section, always bearing in mind that heavily loaded elements can collapse by slightly reducing the section area.

Once it has been decided that consolidation is necessary to resolve the detected problems, the user must analyse the deterioration patterns to determine what type of consolidation is needed. The strengthening effect that is required is the key to selecting the treatment option and the selection process must follow the appropriate rationale, as suggested above.

Delicate surfaces, with deteriorated zones loosely adhering to the substrate, can accept only very light consolidation actions and, therefore, a scaling-up approach is recommended. Treatments with biomineralisation or nanolimes for carbonate substrates are good initial options to start the selection process. For load-bearing elements, deeper and stronger strengthening is required and, therefore, a scaling-down approach is more appropriate.

Often, situations are encountered in which thick scales, plaques, and chips coexist with powdery or sand disintegration zones, which may require different treatment approaches: individual treatment for larger pieces, and generalised treatment for the others.

Given the inescapable truth that every treatment has a certain potential of incompatibility, the user is forced to decide whether the risks are acceptable in the short-term and can be mitigated and accommodated in the long-term. The option zero, of non-consolidating, should be considered, always bearing in mind that "…*it is important to act only when absolutely necessary, but also not postpone the intervention until the material has degraded too much for the consolidation to be beneficial.*" [1]. Complementary actions, such as gluing loose fragments, sealing cracks and joints, filling empty spaces and other works can be sufficient to prolong the service life of surfaces and avoid a far riskier consolidation treatment.

The possibility that the treated areas may accept mitigation actions in the long run is of relevant importance here, as it can draw the line between acceptable and unacceptable treatments. This is encompassed under the concept of retreatability, meaning that a treated element must keep the possibility of accepting further treatment over the previous one once it loses effectiveness or shows any signs of incompatible performance.

4.5.2 How Can You Do It: What Product, What Protocol, What Are Your Objectives?

Consolidation is likely the most demanding operation in stone conservation and therefore only properly trained personnel, namely conservator-restorers, should be allowed to perform it. This is not a matter to be addressed here since it is assumed that these professionals are supposed to master the basics on how to perform a consolidation treatment. Instead, they may find difficulties in interpreting the condition state of the object and in properly directing their toolkit to solve the identified problems.

When preceded by a preparatory study by a conservation scientist, questions can appear well characterized and objectives well defined, and the role of the conservator-restorer is to find answers to these questions in order to meet the objectives. Otherwise, the conservator-restorer must start by taking on the role of conservation scientist and defining his own goals.

An objective is well defined when it contains information and requirements with a direct impact on the consolidation treatment. It can, for example, indicate a requirement for the strengthening effect, a depth of consolidation to be achieved, and any inconveniences to be avoided, such as the removal or destruction of surface details, aesthetic interference, etc.

The suggestions and recommendations presented above can help the user to make a preliminary selection of products that have the potential to be used and, by examining the available literature, can identify which ones were most frequently used on similar substrates. From this stage, it will be the conditions of the existing situation that will determine the procedure to be adopted, for which a careful integration of experience, observation, and judgment will be necessary.

Users should be clear about the implications that may result from choosing a certain consolidant, a certain concentration, a certain solvent, a certain amount applied, a certain application procedure, or a certain application time. These are the variables that a conservator-restorer can manage to allow themselves to achieve the desired goals and, when insufficiently mastered, some training must be taken to improve the understanding and skill of consolidation techniques.

The consideration of different products will influence the final theoretical strengthening capacity, while fine tuning it by varying the solvent, concentration, and application time, when done properly, will achieve the desired strengthening effect. Very deep and strong consolidation actions, for example, for load-bearing elements, may require the strongest consolidation products, such as epoxy resins, and more demanding application procedures. Long contact times through poultice application and vacuum impregnation are possible options to increase the amount of product absorbed.

With regard to harmful effects, the actual condition of the deteriorated area is the key to dealing with them. The effects on the colour of the object can be evaluated sometime after the application and the observation of experimental tests made on the site are good estimators of the final colour impact. The most threatening incompatibility effects, however, will appear in the medium- and/or long-term, and any eventual premonitory signs taken from the onsite tests should be taken as an indication that more serious impacts in the real condition will arise over time.

4.5.3 Reading, Interpreting, and Adapting the Published Data on Stone Consolidation

Professionals in charge of preparing and implementing a consolidation intervention need to be up to date with the scientific literature on the subject, but may encounter considerable difficulties in navigating the multiple sources, with a diverse nature and, in most cases, significantly difference from the case that they have to resolve. In the following paragraphs, some guidance will be given to help in searching for and adapting the relevant information.

This task must start with homework, namely for obtaining the essential background information about the object, the stone material, and its actual deterioration problems. These are crucial elements to keep extrapolations confined within safe and realistic limits. The type of object, its geographical location, and climatic environment can act as large-scale framing factors, while information about past interventions, treatments, and changes in use can help explain some local, distinctive features. While recognizing their relevance, these aspects will not be discussed further here.

For stone consolidation purposes, it is essential to gather basic information about the stone material, its composition, and characteristic properties as well as the significant deterioration problems in order to proceed and take advantage of the published literature. In summary, compare what is comparable and always question the validity of the extrapolations.

The simplest and most direct way is to look for information is obtained with stones with similar composition and properties: mineral composition, porosity, and voids morphology.

You should compare your limestone of 20% porosity, with another limestone with a porosity within a few percent of yours. Results from stones with 5, 20, 30, or 50% (porosity) are incomparable amongst themselves. Marbles, although they have a similar mineralogical composition (mainly calcite), cannot be compared with limestones in terms of consolidation expectations. Marbles can be compared only to other marbles.

You should compare sandstones with sandstones, where porosity restrictions apply the same as in limestones.

You should compare granites with granites. Like sandstones, they have a silicate-based composition, but their respective impregnation properties, and the thermal and mechanical impacts of consolidation are not comparable. Fresh granites have porosity below 1% and their physical and mechanical properties degrade abruptly when values exceed 2%.

Other igneous rocks, such as syenites, diorites, granodiorites, norites, gabbros, and in general all other plutonic rocks, have a silicate-based composition and a crack-like porosity similar to granites. For most aspects of consolidation treatment, information extracted from granites can also be reasonably extrapolated to them.

These basic precautions are essential to start extracting information for your case, but they are not enough. Very often, the published results were obtained in a laboratory environment while you are interested in an object exposed to external ambient conditions for a long time. One of the most difficult aspects to overcome is the fact that observations made on regular surfaces cut from fresh samples have to be adapted to more or less deteriorated surfaces, of irregular morphology, with deterioration intensity varying in depth and, possibly, partly covered by other conditions, such as the presence of salts, biocolonization, and previous treatments.

Stone consolidation tests generally report strengthening effects from "ideal" test conditions. The effect varies with the product used, the treatment protocol followed, and its impact, depending on the thickness of the consolidated layer. Therefore, the reported results should be taken as the maximum values that can be achieved at the site when a mimetic treatment is implemented. If extrapolation of the consolidated thickness is foreseen, the quantity of product applied must be taken as the transposition factor, and not any qualitative description of the application procedure.

On the other hand, information about (in)compatibility behaviour collected from "ideal" samples falls short in terms of representativeness and it is prudent to consider it as the minimum degree of incompatibility achievable. The substrate deterioration profiles are complex, varying in depth, so all information collected must be validated on the specific site before making a final decision on the treatment protocol to be adopted.

4.5.4 What Methods and Tools Can You Resort to?

The preliminary efforts must be directed to understanding the situation in question and to characterizing the problems that need to be solved. Direct observation by visual inspection is a powerful method and professionals must train themselves to become familiar in exploring the full potential of information it can provide. Start the inspection at a certain distance from the object to understand the main patterns of deterioration and progressively approach to identify local details.

Larger scale patterns can be interpreted as reflecting the impact of extensive influencing factors, such as rainwater, sunlight, air pollution, rising damp, etc. They can provide clues to interpret local problems and are of great help in predicting the conditions to which the areas will be subjected once consolidated.

A close observation will help to identify the type of stone and describe the deterioration patterns. When adequate information about the object is not provided and it is difficult to identify the type of stone and understand what is causing the problems, take some samples of the deteriorated products to the laboratory and analyse them. Care must be taken to avoid the destruction of any valuable surface.

Simple tests can be used to supplement observational information. An application of hydrochloric acid can confirm that it is a limestone or a marble, and a scratch with a knife can suggest that it is a silicate-based stone. In case of doubt, and if more detailed information is needed, observation under a petrographic microscope may be necessary, which should be requested from a professional trained in this technique.

When suspecting that the stone material may contain clay minerals, analyses with X-ray diffraction (XRD) will elucidate this.

When present, salts cause problems and will affect any planned stone treatment and, therefore, it is essential to identify them and obtain an estimate of their distribution throughout the object. The presence of visible efflorescence or of significant amounts of detached powder or sand grains are signs of a high salt contents. When salt contamination is milder, localised tests with paper poultices can help to identify and estimate the salt load.

The identification of salt species can be done by chemical methods, by XRD, Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), depending on the objectives and available means. These methods are operated only by trained personnel.

When it is necessary to confirm the effectiveness of a particular treatment, the worksite team has very few instruments to use. For limestone and marble substrates, Drilling Resistance (DRMS) profiling [78] is of great interest. It determines the strength of the stone in depth and can also identify the thickness achieved by the treatment. With 5 mm diameter holes, the method is minimally destructive.

The Scotch Tape Test [79] is a peeling test to obtain a rough indication on the hardening effect. It provides information only from the most superficial layer. A scratch made with a steel knife provides a qualitative indication of surface cohesion. Both tests must be interpreted by comparing results taken in the treated areas before and after treatment.

For fissured-type stones, such as granites and marbles, ultrasound pulse velocity (UPV) [80] is a suitable instrument, especially for silicate-based materials in which DRMS is difficult or impossible to use.

Obtaining information from a treated area to predict possible manifestations of incompatibility in the medium- and long-term is a very difficult task and little help can be obtained directly with measurements, except for the colour variations that can be quantified with a colorimeter.

Consequently, this extremely important assessment must be made by reasoning, supported by knowledge of the situation and as accurate as possible an understanding of the treatment that has just been done.

It is of critical importance to understand what contrast has been created between the treated layer and the underlying substrate. Very hard layers should always be treated with suspicion. For very weak areas and thickly deteriorated profiles, leaving any intermediate deterioration layer untreated is to be avoided absolutely.

Whenever possible, assessments carried out under on site conditions will provide relevant information to understand what can be done effectively and contribute to avoiding seriously poor performance in the future.

4.5.5 Complementary Actions to Consolidation

The application of a consolidant is just one of several actions generally necessary to treat a deteriorated area. It is understood here that initiating a stone consolidation action without considering any complementary action to solve other associated problems is irresponsible.

Powdery areas must be cleaned of loose particles since they cannot be consolidated and properly attached to the substrate. Salts must be removed to a certain depth to allow space for the consolidant to properly adhere to the solid mineral structure. Research on desalination mechanisms have progressed enormously in recent times [81–85], which have led to the development of more effective practical solutions and perspectives on how to address desalination in built heritage.

Biocolonization, when present, must be removed before applying the product [86].

The presence of past treatments can significantly hinder the absorption of product, which may imply that the impregnation is only viable through the areas where the treatment has deteriorated to the point of leaving the untreated substrate exposed.

Areas to be consolidated may also have other problems that need addressing, such as joints between stone blocks needing repair, cracks and fractures to seal, loose fragments to glue, etc. When all these operations are complete, the aesthetic appearance of the treated areas must be taken into account and some harmonization with neighbouring areas must be sought.

When the surfaces to be treated are in very bad conditions and the actions needed to apply the consolidant are deemed likely to cause mass loss, it is necessary to take all the precautionary measures to avoid these losses. Gluing of the more unstable fragments, localised consolidation of fragments to allow their stabilisation, use of interfaces to minimise direct contact with the surfaces are all examples of "comfort" measures applicable in such circumstances. These operations are sometimes designated as pre-consolidation, and the use of supposedly reversible consolidants (Paraloid B72 is frequently reported as having been used for such purpose) are often advised as a solution. However, this is not supposed to be a first stage of consolidation, since such a preliminary application, if too thorough, may seriously impair the further application of the expected consolidant.

As in any other intervention, the consolidation of the stone must be properly documented. In order to allow future actors to benefit from the knowledge acquired in the real intervention, all the results used to make decisions must be presented and the objectives defined at the beginning of the treatment should be explicit. Then, the type and quantities of product applied, the application protocol, and any specific occurrences should also be indicated.

A complete description of the condition state before and after treatment, as well as detailed, high quality photos, should be added to the contractual report. The inclusion of a condensed document containing instructions for monitoring the performance of the treated elements is highly recommended.

4.6 Learning from Past Interventions: A Few Examples

It is common to find claims that universal solutions have not been found, a particular product is not appropriate for every situation, a certain recipe cannot, unfortunately, be generalized, etc. It is time to say clearly once and for all: a recipe to solve whatever consolidation problem has not, and never will be, found. Other people's solutions, reported or even own case studies, should always be taken as learning tools and should never be used for an *ipsis verbis* transcript of any adopted process. Faced with a reported successful situation, conservator-restorers should always take it critically and start by asking some key questions: what do mine and the reported situation have in common? Will the differences found make a direct transfer unfeasible? Is the reported success well understood and demonstrated? Are the conditions for success present in my situation? If adaptations are needed, do I have the information to support them? And certainly, many other such considerations.

In this section, some examples are presented to help convey and make explicit some of the notions presented above. The case studies are not described and characterised in detail, but only the essential aspects to understand the reasoning followed.

4.6.1 Porta Especiosa, Coimbra Cathedral (Portugal)

Porta Especiosa is a Renaissance portal affixed to the Romanesque cathedral, composed of a limestone quarried in the Portunhos region in the outskirts of Coimbra. Because the portal was in poor condition, a conservation intervention was decided. The limestone used is of low quality mainly because a certain percentage of clays induces very severe deterioration patterns. The average porosity ranges between 10% and 15% [87]. A few drilling resistance measurements were carried out to help understand the stone condition at the surface and subsurface of the most deteriorated blocks (Fig. 4.5). Other measurements and analyses were made elsewhere to help understand the entire situation of the portal, but will not be discussed here.

With this example, several relevant issues can be illustrated. The presence of clays inside an exposed block, even when in the order of a few percent may significantly impair the stone behaviour, and the impact can be felt on the stone surface, but also at significant depths, as seen in the DRMS graphs (Fig. 4.5).

From the point of view of conservation, the fine powders and superficial thin scales were practically lost, since any subtle touch of the brush was enough to detach them, but there was a certain expectation that the thin cracks detected in

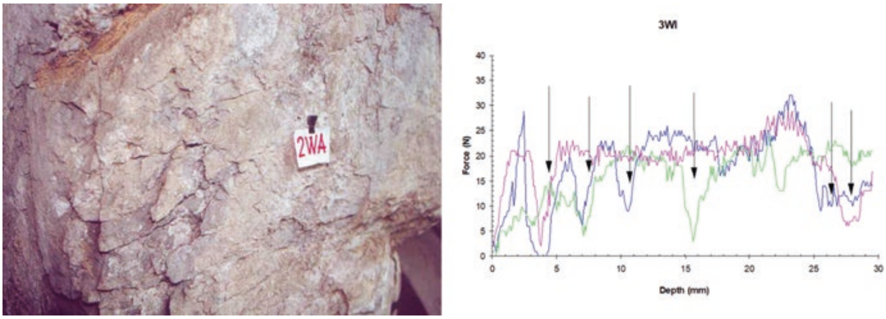

Fig. 4.5 Porta Especiosa of Coimbra Cathedral (Portugal). Clayey limestones (left) may exhibit deep fractures, detected by the large resistance drops identified with arrows in the drilling resistance graphs (right), ©José Delgado Rodrigues

depth caused by the expansion of the clay could be consolidated. As these cracks were out of reach from the surface, a test was made to fill them through holes. The result was unsatisfactory, and this possibility was discarded.

On the other hand, it was known that the consolidation of such deteriorated powdering surfaces was practically unfeasible without risks, considering the treatments available at the time. Treatments were expected to create an indurated layer as not the full decayed profile was reachable. A strong incompatibility behaviour was foreseen, and the failure risk was considered too high to take.

Therefore, the option for non-consolidation was followed. All necessary complementary conservation actions were taken, such as diverting the water that accesses the portal, introducing collecting drains on all horizontal surfaces, repairing joints and large cracks, stabilizing the most unstable parts, sealing them with light mortars specifically formulated for this purpose, etc.

Consolidation of very decayed limestone surfaces was, and still is, one of the most difficult situations to solve [88], and the presence of clays makes them practically irreparable. The option for non-consolidation assumed that the alternative of replacing some of those blocks was not yet justified and, therefore, it was considered that taking all viable relief measures and moving towards an adequate monitoring and maintenance plan would be the best decision that could be made.

4.6.2 The External Envelope of the Lantern of Évora Cathedral (Portugal)

Évora Cathedral is a Romanesque building made of granite masonry. At the intersection of the central nave and the transept, an elegant and prominent lantern provides natural light to the interior space. Several episodes of falling fragments forced the base of the lantern to be closed to protect people, and prompted the authorities to take on a conservation intervention.

The problems that triggered the intervention occurred in the dome where the intensive deterioration caused by salt crystallization phenomena was acting. Extensive water leakage events were identified, and the first step to be taken was to intervene on the outside of the lantern to prevent water from accessing the inside.

The granite used to build the lantern was extracted from nearby quarries and naturally weathered areas, which implied that its properties were, from the very beginning, far from corresponding to a fresh, low porosity and strong material. In fact, the porosity of the stone varied from 3% to 6% and the ultrasound pulse speed in many blocks was less than 3000 m/s, which are to be compared with values of less than 1% and over 6000 m/s, for a fresh, un-weathered granite.

Previous studies had shown that this granite can be easily consolidated with several products, and reasonably large impregnation depths can be achieved [77]. This information made it possible to choose a consolidation with an ethyl silicate and a depth of 2 cm was defined as a goal to be achieved. A capillarity test made with this stone and the same ethyl silicate allowed for determining that the application of 1 kg/m^2 of product was needed to reach the defined depth. As the absorption of rainwater was the main source of the infiltrations, a polysiloxane was applied to complete the hydrophobisation of the outer envelope.

As in any normal conservation intervention, several other tasks were implemented, such the elimination of biocolonisation, repair of joints, fixing of broken windows, stabilisation of unstable elements, etc. Figure 4.6 illustrates the situation during the intervention.

This case study is of particular interest to demonstrate that a satisfactory mastering of consolidation of deteriorated granites is possible with the support of simple and accessible testing means. Some 15 years after the treatment, no visible signs of performance loss are identified.

Fig. 4.6 Lantern of Evora Cathedral. Sand disintegration of granite and extensive deterioration of joints were the main problems to address, ©José Delgado Rodrigues

4.6.3 Segovia Aqueduct (Spain)

The Aqueduct of Segovia is a huge structure from Roman times, entirely constructed with granite. Despite having suffered several accidents that required localised reconstruction, most of it is still of the original material. The 2000 years of exposure to the harsh environment conditions has led to significant decay, sand disintegration, and loss of surface material, which are threatening the overall stability of the elegant and impressive arches and pillars [89].

This case study is presented here to illustrate how the lack of adequate understanding of the stone's characteristics and deterioration mechanisms can lead to an incorrect interpretation of the conservation needs. An extensive conservation intervention was carried out in the 1970s [90] and a subsequent one in the 1990s [91, 92], in which consolidation was one of the main actions implemented.

It is interesting to mention that the option for consolidating the blocks identified as needing strengthening was the use of an epoxy resin injected through regularly spaced holes, drilled deep into the blocks. Figure 4.7 shows a few examples of blocks treated with this methodology.

As can be seen in recent photos, granular disintegration continues to affect the treated blocks and mass loss continues as an active process (Fig. 4.7, right). It is well known that granular disintegration is a process that progresses from the outside to the inside, driven by external decay agents, such as rain water and pollutants, and it benefits from any inherent mineralogical weaknesses that tend to be distributed more or less regularly throughout the entire block. A logical way to approach the conservation of such blocks is to start with this basic knowledge: first to stop or slow down the deterioration process and then, add some reinforcement of their load-bearing capacity.

Deep injection was clearly not suitable for resolving the main deterioration process - granular disintegration - which is threatening the aqueduct's structural

Fig. 4.7 Segovia Aqueduct (Spain). The deep injection of epoxy resins in a fairly sound block (left) was useless, while the similar injection in the heavily decayed block (right) has left the surface unconsolidated and subject to active sand disintegration and significant mass loss, ©José Delgado Rodrigues

stability. A treatment from the surface allowing a large impregnation thickness to be achieved would be feasible and would most likely reduce the deterioration rate and increase the overall strength of the most deteriorated blocks.

4.6.4 Learning from a Poorly Understood Success: The "Bologna Cocktail"

A paradigmatic illustration of the misinterpretation and misuse of a consolidation recipe happened (is it still happening?) with the so-called "Bologna cocktail". This recipe was firstly applied in Bologna in the 1970s, in S. Petronio Cathedral [45, 93, 94], and at that time, experts had looked at it as a remarkable consolidation success. It is composed of a mixture of Paraloid B72[1] (acting as consolidant) and DRI-FILM (DF-104)[2] (acting as water repellent), in a mixture of solvents.[3] In Bologna, it was applied in surfaces of Istrian stone (pietra d'Istria) and Rosso di Verona, two very compact, low-porosity limestones.

Inspired by the success of the original application, the formula was repeated elsewhere in Italy with reportedly satisfactory results [95], while unsuccessful trials with acrylic resins have been reported, even in high-porosity limestones [88]. A poor impregnation capacity was pointed out as one of its properties [96], which is a troublesome finding given the fact that its major success was achieved in very low porosity materials (the Istrian stone and Rosso di Verona). Interestingly, this apparent contradiction contains a possible justification of its success and failures. Looking carefully at the deterioration patterns in the S. Petronio cathedral, it is possible to identify that stone surfaces evolved, forming thin scales that in normal circumstances take some time to detach and fall. Scales are reasonably cohesive, and the most obvious conservation solution is to glue them back to the substrate. This was exactly what the reputed conservator-restorer Otorino Nonfarmale had so carefully done in S. Petronio. Therefore, the action was a gluing operation and not a mass consolidation.

This interpretation was not assumed as such, where the authors considered that, despite its low impregnation capacity, it was able to "*act mainly as superficial protective*" [96]. The extrapolations made from the success of S. Petronio to other places where the "Bologna cocktail" was expected to produce mass consolidation were possibly searching for an objective that it simply could not fulfil. The specifier of the Bologna cocktail had in fact concluded that "… *B72 and DF-104 do not penetrate deeply and/or uniformly into the Finale stone* [23% porosity]. *Therefore, in*

[1] Paraloid B72 is a methyl acrylate ethyl methacrylate, from Rohm & Haas.

[2] DRI-FILM is a water repellent, methyl trimethoxysilane, from General Electric.

[3] Originally a mixture of acetone:1,1,1 trichloroethane (1:1). Another common formula is a mixture of toluene:xylene:acetone (0.7,0.1:0.2).

this case, it seems doubtful that even a mixture of these two products would be useful in conserving this stone" [97].

Under the interpretation that the "Bologna cocktail" is essentially a gluing agent, the presence of DRI-FILM in its composition has no direct function in the bonding process and was possibly totally useless since its action as a protective treatment is largely unnecessary for such compact and poorly permeable substrates. A possible justification for this treatment is its expected "reversibility", a property not entirely fulfilled, even in ideal laboratory conditions [98].

4.7 Final Remarks and Acknowledgements

It is of common knowledge that stone consolidation constitutes a complex and difficult endeavour to which no universal recipes exist or are expected to exist. The "ideal" solution is the one that properly combines the full knowledge of the situation at hand, with the appropriate knowledge of all the options eligible for the purpose, and with the optimum knowledge of how to implement the selected options. Since any situation is unique, universal recipes cannot be formulated and the role of documents like this is to help users to understand their own cases, identify the potential solutions, select the best option, and formulate the most appropriate procedure to implement it.

Aware of the huge difficulty in achieving all these established goals, the author chose to leave the safest haven of strictly scientific questions and offer some guidelines to help build a bridge between science and practice, in order to define better prepared solutions that might contribute to achieve more consistent and better performing consolidation interventions. Hopefully, readers can find some use in this regard.

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References

1. Praticò Y, Caruso F, Delgado Rodrigues J, Girardet F, Sassoni E, Scherer GW, et al. Stone consolidation: a critical discussion of theoretical insights and field practice. RILEM Tech Lett. 2020;4:145-153.
2. Clifton JR. Stone Consolidating Materials: A Status Report. Washington D.C.; 1980.
3. Doehne E, Price CA. Stone Conservation: An Overview of Current Research [Internet]. 2nd ed. Los Angeles: Getty Conservation Institute; 2010. xi, 158 p. ill. 28 cm. (Research in Conservation). Available from: http://hdl.handle.net/10020/gci_pubs/stone_conservation

4. Tabasso ML, Simon S. Testing methods and criteria for the selection/evaluation of products for the conservation of porous building materials. Stud Conserv [Internet]. 2006;51(sup1):67–82. Available from: http://www.tandfonline.com/doi/full/10.1179/sic.2006.51.Supplement-1.67
5. Amoroso GG, Fassina V. Stone Decay and Conservation: Atmospheric Pollution, Cleaning, Consolidation, and Protection [Internet]. Amsterdam: Elsevier; 1983. xix, 453 p. ill. 25 cm. (Materials Science Monographs 11; vol. 11). Available from: http://www.csa.com/partners/viewrecord.php?requester=gs&collection=ENV&recid=437337%5Cnhttp://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=1326%5Cnhttp://www.csa.com/partners/viewrecord.php?requester=gs&collection=ENV&recid=437337%5Cnhttp:
6. Lazzarini L, Laurenzi Tabasso M. Il restauro della pietra. Padova: CEDAM; 1986. xiv, 320 p., [4] p. of plates ill. (some col.) 25.
7. Price CA. The evaluation of stone preservatives. In: Conservation of Historic Buildings and Monuments. Washington, D.C.: National Academy Press; 1982. p. 329–40.
8. Delgado Rodrigues J, Grossi A. Indicators and ratings for the compatibility assessment of conservation interventions. J Cult Herit. 2007;8:32–43.
9. Siegesmund S, Snethlage R. Stone in architecture: Properties, durability. Stone in Architecture: Properties, Durability. 2011. 1–552 p.
10. Horie C V. Materials for Conservation: Organic Consolidants, Adhesives and Coatings. Amsterdam: Butterworth-Heinemann; 2010. 504 p.
11. Selwitz C. Epoxy Resins in Stone Conservation [Internet]. Marina del Rey, CA: Getty Conservation Institute; 1992. 112 p. ill. 28 cm. (Research in Conservation 7). Available from: http://hdl.handle.net/10020/gci_pubs/epoxy_resing_in_stone
12. Wheeler G. Alkoxysilanes and the Consolidation of Stone [Internet]. Los Angeles: Getty Publications; 2005. xiv, 196 pages illustrations 28 cm. (Research in Conservation). Available from: http://hdl.handle.net/10020/gci_pubs/consolidation_of_stone
13. Lewin SZ. Recent experience with chemical techniques of stone preservation. In: The Treatment of Stone - Proceedings of the Meeting of the Joint Committee for the Conservation of Stone. Bologna, Italy; 1971. p. 139–44.
14. Lewin SZ, Wheeler G. Alkoxysilane chemistry and stone conservation. In: Félix G, editor. Vth Int Cong on Deterioration and Conservation of Stone. Lausanne, Switzerland: Presses Polytechniques Romandes, Lausanne; 1985. p. 831–44.
15. Wendler E. New materials and approaches for the conservation of stone. In: Saving our architectural heritage Dahlem Workshop held in Berlin 1996. Berlin, Germany: John Wiley & Sons; 1997. p. 181–96.
16. Yang M, Scherer GW, Wheeler G, Housley RA. Compatible Consolidants. In: Compatible Materials for the Protection of European Cultural Heritage- PACT 56. 1998. p. 201–8.
17. Mosquera MJ, Desiree´ M de los S, Montes A, Valdez-Castro L. New Nanomaterials for Consolidating Stone. Langmuir. 2008;(24):2772–8.
18. Charola AE, Wheeler G, Freund GG. The influence of relative humidity in the polymerization of methyl trimethoxy silane. In: IIC Congress Adhesives and Consolidants. Paris, France; 1984. p. 177–81.
19. Wheeler G, Fleming SA, Ebersole S. Comparative strengthening effect of several consolidants on Wallace sandstone and Indiana limestone. In: Delgado Rodrigues J, Henriques F, Jeremias FT, editors. 7th Int Cong on Deterioration and Conservation of Stone. Lisbon, Portugal: National Laboratory of Civil Engineering; 1992. p. 1033–41.
20. Danehey C, Wheeler G, Su S-CH. The influence of quartz and calcite on the polymerization of methyltrimethoxysilane. In: Delgado Rodrigues J, Henriques FMA, Jeremias FT, editors. 7th International Congress on Deterioration and Conservation of Stone. Lisbon, Portugal: National Laboratory of Civil Engineering; 1992.
21. Goins ES. Alkoxysilane stone consolidants: The effect of the stone substrate on the polymerization process. University College London; 1995.
22. Goins ES, Wheeler G, Griffiths D, Price CA. The effect of sandstone, limestone, marble and sodium chloride on the polymerization of MTMOS solutions. In: 8th Int Cong on Deterioration and Conservation of Stone. Berlin, Germany; 1996.

23. Hempel K, Moncrieff A. Summary of work on marble conservation at the Victoria and Albert Museum Conservation Department up to August 1971. In: Rossi-Manaresi R, Torraca G, editors. The Treatment of Stone. Bologna, Italy: Centro per la Conservazione delle Sculture all'Aperto; 1972. p. 165–81.
24. Larson J. A museum approach to the techniques of stone conservation. In: Gauri KL, Gwinn JA, editors. Fourth international congress on the deterioration and preservation of stone objects. Louisville (Ky.): University of Louisville; 1982. p. 219–37.
25. De Witte E, Charola AE, Sherryl RP. Preliminary tests on commercial stone consolidants. In: Félix G, editor. Vth international congress on deterioration and conservation of stone. Lausanne: Presses polytechniques romandes; 1985. p. 709–18.
26. Tabasso ML, Santamaria U. Consolidant and protective effects of different products on Lecce limestone. In: Félix G, editor. Vth International Congress on Deterioration and Conservation of Stone. Lausanne,Switzerland; 1985. p. 697–707.
27. Boos M, Grobe J, Hilbert G, Muller-Rochholz J. Modified elastic silicic-acid ester applied on natural stone and tests of their efficiency. In: 8th Cong on Deterioration and Conservation of Stone. Berlin, Germany; 1988. p. 1179–85.
28. Steinhäußer U, Wendler E. Conservation of limestone by surfactants and modified ethylsilicate. In: 10th International Congress on Deterioration and Conservation of Stone. Stockholm; 2004.
29. Weiss NR, Slavid I, Wheeler G. Development and assessment of a conversion treatment for calcareous stone. In: 9th Int Cong On Deterioration and Conservation of Stone. Venice, Italy; 2000. p. 533–40.
30. Sena da Fonseca B, Ferreira Pinto AP, Piçarra S, Montemor MF. The potential action of single functionalization treatments and combined treatments for the consolidation of carbonate stones. Constr Build Mater. 2018;163.
31. Angela Calia, Maurizio Masieri, Giovanni Baldi CM. The Evaluation of Nanosilica Performance for Consolidation Treatment of an Highly Porous Calcarenite. In: 12 th International Congress on the Deterioration and Conservation of Stone. 2012.
32. Zornoza-Indart A, Lopez-Arce P. Silica nanoparticles (SiO2): Influence of relative humidity in stone consolidation. J Cult Herit. 2016;18:258–270.
33. VV.AA. Advanced materials for the conservation of stone. Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. 2018.
34. Maravelaki N, Verganelaki A, Kilikoglou V, Karatasios I. Synthesis and characterization of a calcium oxalate-silica nanocomposite for stone conservation. In: Engineering Geology for Society and Territory - Volume 8: Preservation of Cultural Heritage. 2015.
35. Maravelaki P, Verganelaki A. A hybrid consolidant of nano-hydroxyapatite and silica inspired from patinas for stone conservation. In: Advanced Materials for the Conservation of Stone. 2018.
36. Gauri KL. Efficiency of epoxy resins as stone preservatives. Stud Conserv. 1974;19:100-101.
37. Domaslowski W, Strzelczyk A. Evaluation of applicability of epoxy resins to conservation of stone historic monuments. Stud Conserv [Internet]. 1986;31(sup1):126–32. Available from: http://www.tandfonline.com/doi/full/10.1179/sic.1986.31.Supplement-1.126
38. Cavalletti R, Lazzarini L, Marchesini L, Marinelli G. A new type of epoxy resin for the structural consolidation of badly decayed stones. In: Felix G, editor. Vth International Congress on Deterioration and Conservation of Stone. Lausanne: Presses polytechniques romandes; 1985. p. 769–78.
39. Lazzarini L. The deterioration and treatment of granitic columns. In: Stone material in monuments: diagnosis and conservation CUM School, Second Course. Crete, Greece; 1993. p. 160–8.
40. Domaslowski W, Kesy-Lewandowska M. La consolidation en structure des gres a l'aide de resines thermoplastiques. In: Félix G, editor. Vth Int Cong on Deterioration and Conservation of Stone. Lausanne: Presses Polytechniques Romandes, Lausanne; 1985. p. 727–38.
41. Vassallo JC, Lewin SZ. Investigation of polymer impregnation of stone. I. In situ polymerization of methyl methacrylate. In: Rossi-Manaresi R (Eds. ., editor. The Conservation of Stone II. Bologna, Italy: Centro per la Conservazione delle Sculture all'Aperto; 1981. p. 587–603.

42. Lewin SZ, Papadimitriou AD. Investigation of polymer impregnation of stone. II. Solvent-transport of pre-polymerized methyl methacrylate. In: Rossi-Manaresi R, editor. The Conservation of Stone II. Bologna, Italy: Centro per la Conservazione delle Sculture all'Aperto; 1981. p. 605–23.
43. Accardo G, Cassano R, Rossi-Doria P, Sammuri P, Laurenzi Tabasso M. Screening od products and methods for the consolidation of marble. In: Rossi-Manaresi R, editor. The Conservation of Stone II. Bologna, Italy: Centro per la Conservazione delle Sculture all'Aperto; 1981. p. 721–35.
44. Rossi-Manaresi R. Effectiveness of conservation treatments for the sandstone of monuments in Bologna. In: Rossi-Manaresi R, editor. The Conservation of Stone II. Bologna: Centro per la Conservazione delle Sculture all'Aperto; 1981. p. 665–88.
45. Rossi Manaresi R. Scientific and technical research. In: Centro per la Conservazione delle sculture all'Aperto, editor. Jacopo della Quercia e la facciata di San Petronio, a Bologna. Bologna, Italy: Edizioni Alfa, Bologna; 1981. p. 225–78.
46. Hempel K, Hempel G. A technical report on the condition of the Porta della Carta and its restoration. In: Romano S, Clarke A, Rylands P, editors. The Restoration of the Porta della Carta, Venice in Peril Fund. Venice, Italy: Armenian Printing Press; 1980. p. 37–73.
47. Ashurst J. The cleaning and treatment of limestone by the lime method. In: Ashurst J ohn, Dimes F, editors. The Conservation of Building and Decorative Stone, Volume 2. London: Butterworth-Heinemann,; 1990. p. 169–176.
48. Brajer I, Kalsbeek N. Limewater absorption and calcite crystal formation on a limewater-impregnated secco wall painting. Stud Conserv. 1999;44:145–56.
49. Giorgi R, Dei L, Baglioni P. A new method for consolidating wall paintings based on dispersions of lime in alcohol. Stud Conserv. 2000;45:154–61.
50. Ambrosi M, Dei L, Giorgi R, Neto C, Baglioni P. Colloidal particles of Ca(OH)2: Properties and applications to restoration of frescoes. Langmuir. 2001;17:4251–5.
51. Chelazzi D, Poggi G, Jaidar Y, Toccafondi N, Giorgi R, Baglioni P. Hydroxide nanoparticles for cultural heritage: Consolidation and protection of wall paintings and carbonate materials. J Colloid Interface Sci. 2013;42–9.
52. Otero J, Charola AE, Grissom CA, Starinieri V. An Overview of Nanolime As a Consolidation Method. Ge-Conservacion. 2017;
53. Borsoi G. Nanostructured lime-based materials for the conservation of calcareous substrates. A+BE Architecture and the Built Environment. Delft University of Technology; 2017.
54. Ferroni E, Dini D. Chemical-structural conservation of sulphatized marbles. In: Rossi-Manaresi R, editor. The Conservation of Stone II. Bologna, Italy: Centro per la conservazione delle sculture all'aperto; 1981. p. 559–66.
55. Matteini M. Inorganic treatments for the consolidation and protection of stone artefacts and mural paintings. Conserv Sci Cult Herit [Internet]. 2008;8:13–27. Available from: http://conservation-science.cib.unibo.it/article/download/1393/766
56. Lewin SZ, Baer NS. Rationale of the barium hydroxide-urea treatment ofdecayed stone. Stud Conserv. 1974;19(1):24–35.
57. Delgado Rodrigues J, Ferreira Pinto AP. Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. J Cult Herit [Internet]. 2016;19:467–76. Available from: https://doi.org/10.1016/j.culher.2015.10.002
58. Matteini M, Rescic S, Fratini F, Botticelli G. Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: Preliminary research. Int J Archit Herit. 2011;5(6):717–36.
59. Sassoni E, Naidu S, Scherer GW. The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. J Cult Herit. 2011;
60. Adolphe J., Loubière JF, Paradas J, Soleilhavoup F. Procédé de traitement biologique d'une surface artificielle. European patent 90400G97.0 1990, European patent 90400G97.0 1990; 1990.

61. Le Métayer-Levrel G, Castanier S, Orial G, Loubière JF, Perthuisot JP. Applications of bacterial carbonatogenesis to the protection and regeneration of limestones in buildings and historic patrimony. Sediment Geol. 1999;
62. Rodriguez-Navarro C, Rodriguez-Gallego M, Chekroun K Ben, Gonzalez-Muñoz MT. Conservation of ornamental stone by Myxococcus xanthus-induced carbonate biomineralization. Appl Environ Microbiol. 2003;
63. Rodriguez-Navarro C, Jimenez-Lopez C, Rodriguez Navarro A, Gonzalez-Muñoz MT, Rodriguez Gallego M. Bacterially mediated mineralization of vaterite. Geochim Cosmochim Acta. 2007;71(5):1197–213.
64. Jimenez-Lopez C, Rodriguez-Navarro C, Piñar G, Carrillo Rosúa FJ, Rodriguez Gallego M, Gonzalez-Muñoz MT. Consolidation of degraded ornamental porous limestone stone by calcium carbonate precipitation induced by the microbiota inhabiting the stone. Chemosphere. 2007;68(10):1929–36.
65. Jroundi F, Bedmar EJ, Rodriguez-Navarro C, Gonzalez-Muñoz MT. Consolidation of ornamental stone by microbial carbonatogenesis. Glob Stone Congr 2010. 2010;1–5.
66. Delgado Rodrigues J, Ferreira Pinto AP. Stone consolidation by biomineralisation. Contribution for a new conceptual and practical approach to consolidate soft decayed limestones. J Cult Herit. 2019;39:82–92.
67. Ferreira Pinto AP, Delgado Rodrigues J. Stone consolidation: The role of treatment procedures. J Cult Herit. 2008;9(1):38–53.
68. Franzoni E, Sassoni E, Graziani G. Brushing, poultice or immersion? The role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone. J Cult Herit. 2015;16(2).
69. Murru A, Fort R. Diammonium hydrogen phosphate (DAP) as a consolidant in carbonate stones: Impact of application methods on effectiveness. J Cult Herit. 2020;
70. Franzoni E, Graziani G, Sassoni E, Bacilieri G, Griffa M, Lura P. Solvent-based ethyl silicate for stone consolidation: influence of the application technique on penetration depth, efficacy and pore occlusion. Mater Struct. 2014;
71. Cavaletti R, Marchesini L, Strazzabosco G. Tecnologie di consolidamento e di restauro figurativo di sculture in pietra tenera dei colli Berici. In: Badan B, editor. 3rd Int Cong on the Deterioration and Preservation of Stones. Venice, Italy: Università degli Studi di Padova; 1979. p. 453–60.
72. Wihr R. The preservation of damaged stones by the so-called acrylic-total-impregnation process. In: B. Badan, editor. 3rd Int Cong on the Deterioration and Preservation of Stones. Venice, Italy: Università degli Studi di Padova; 1979. p. 389–94.
73. Hempel K. An Improved Method for the Vacuum Impregnation of Stone. Stud Conserv. 1976;21:40–3.
74. Milchin M. Ethyl-silicate consolidation for porous limestone coated with oil paint. A comparison of application methods. In: 13th Int Cong on the Deterioration and Conservation of Stone,. Glasgow; 2016. p. Vol. 2.
75. Heaton N. Preservation of stone. J R Soc Arts. 1921;70(3606):124–39.
76. Delgado Rodrigues J, Costa D. Occurrence and behavior of interfaces in consolidated stones. In: STREMA 95. 1995. p. 71–8.
77. Delgado Rodrigues J, Costa D. Assessment of the efficacy of consolidants in granites. In: Vicente MA, Delgado Rodrigues J, Acevedo J, editors. EC Workshop Degradation and Conservation of Granitic Rocks in Monuments. Santiago de Compostela, Spain: DG XII, Science, Research and Development, Res. Rep. 5; 1996. p. 63–9.
78. Tiano P, Delgado Rodrigues J, De Witte E, Vergès-Belmin V, Massey S, Snethlage R, et al. The conservation of monuments: A new method to evaluate consolidating treatments. Int Jour Restor Build Monum. 2000;6(2):133–50.
79. Drdácký M, Slížková Z. In situ peeling tests for assessing the cohesion and consolidation characteristics of historic plaster and render surfaces. Stud Conserv. 2015;

80. Mamillan M. Méthodes d'évaluation des dégradations des monuments en pierre. In: Ciabach J, editor. VIth International Congress on Deterioration and Conservation of Stone. Torun, Poland: Nicholas Copernicus University. Press Department; 1988. p. 456–65.
81. Lombardo T, Simon S. Desalination by Poulticing: Laboratory Study on Controlling Parameters. In: Kwiatkowski D, Löfvendahl R, editors. 10th International Congress on Deterioration and Conservation of Stone. Stockholm; 2004. p. 323–30.
82. Doehne E, Schiro M, Roby T, Chiari G, Lambousy G, Knight H, et al. Evaluation of poultice desalination process at Madame Johns' Legacy, New Orleans. In: Lukaszewicz JW, Niemcewicz P, editors. 11th International Congress on Deterioration and Conservation of Stone. Torun, Poland: Nicolaus Copernicus University Press; 2008. p. 857–64.
83. Pel L, Sawdy A, Voronina V. Physical principles and efficiency of salt extraction by poulticing. J Cult Herit. 2010;11(1):59–67.
84. Lubelli B, van Hees R. Desalination of masonry structures: Fine tuning of pore size distribution of poultices to substrate properties. J Cult Herit. 2010;11(1):10–8.
85. Vergès-Belmin V, Heritage A, Bourgès A. Powdered Cellulose Poultices in Stone and Wall Painting Conservation - Myths and Realities. Stud Conserv [Internet]. 2011;56(4):281–97. Available from: http://www.tandfonline.com/doi/full/10.1179/204705811X13159282692923
86. Pinna D. Coping with Biological Growth on Stone Heritage Objects. Oakville, Canada: Apple Academic Press; 2017. xviii+359.
87. Delgado Rodrigues J, Ferreira Pinto AP, Costa D. Tracing of decay profiles and evaluation of stone treatments by means of microdrilling techniques. J Cult Herit. 2002;3(2):117–25.
88. Delgado Rodrigues J. Consolidation of decayed stones. A delicate problem with few practical solutions. In: Historical Constructions [Internet]. Guimarães, Portugal; 2001. p. 3–14. Available from: http://www.csarmento.uminho.pt/docs/ncr/historical_constructions/page03-14_DDelgado.pdf
89. Delgado Rodrigues J. Defining, mapping and assessing deterioration patterns in stone conservation projects. J Cult Herit [Internet]. 2015;16(3):267–75. Available from: https://doi.org/10.1016/j.culher.2014.06.007
90. Ramírez Gallardo A. Supervivencia de una obra hidráulica. El Acueducto de Segovia. Colección. Colegio de Ingenieros de caminos, Canales y Puertos;
91. Jurado Gimenez F. Acueducto de Segovia. Documentos para una restauración. Restauración Rehabil. 1994;1(Sept-Oct):17–31.
92. Jurado Gimenez F. El Acueducto romano de Segovia. Rev Obras Publicas. 2001;57:14–23.
93. Nonfarmale O. A method of consolidation and restoration for decayed sandstones. In: Int Symp on The Conservation of Stone, Bologna. Bologna, Italy; 1975. p. 119–25.
94. Nonfarmale O. Methods of conservation. In: Centro per la Conservazione delle Sculture all'Aperto, editor. Jacopo della Quercia e la facciata di San Petronio, a Bologna. Bologna, Italy: Edizioni Alfa Bologna; 1981. p. 279–306.
95. Rossi-Manaresi R, Charola AE, Tucci A, Koestler R, Wheeler G. Study of accelerated weathering of limestones treated with an acrylic-silicone mixture. In: ICOM Committee for Conservation 7th triennial meeting. Copenhagen; 1984. p. 84.10.1–84.10.4.
96. Rossi-Manaresi R, Alessandrini G, Fuzzi S, Peruzzi R. Assessment of the effectiveness of some preservatives for marble and limestones. In: 3rd International Congress Deterioration and Preservation of Stones. Venice, Italy; 1979. p. 357–76.
97. Rossi-Manaresi R, Tucci A. SEM examination of a biocalcarenite treated with acrylic polymers, silane or silicone resins. In: Félix G, editor. Vth international congress on deterioration and conservation of stone. Lausanne,Switzerland: Presses Polytechniques Romandes, Lausanne; 1985. p. 871–80.
98. Charola AE, Tucci A, Koestler RJ. On the reversibility of treatments with acrylic/silicone resin mixtures. J Am Inst Conserv. 1986;25(2):83–92.

Chapter 5
Current and Future Trends in Protective Treatments for Stone Heritage

Francesca Gherardi

Abstract This chapter provides a background on stone protection, taking into consideration the performance requirements, working properties, and the criteria for the selection of the most appropriate materials for specific case-studies. The main classes of protective treatments (water repellents, antigraffiti coatings, inorganic treatments, limewashes, salts inhibitors, etc.) are explored, along with information about their properties, performances, and durability once applied to naturally weathered stone surfaces. Recent trends in the development of innovative and nanostructured formulations with antibacterial, depolluting, and antifouling properties for stone protection are also examined, providing recommendations for further studies. The chapter emphasises the crucial role of multidisciplinary teams to understand and solve complex problems and challenges that arise in built heritage protection.

Keyword Protective treatments · Natural stone · Conservation · Nanomaterials · Durability

5.1 Introduction

5.1.1 Background

Decay factors can severely affect the conservation of stone materials in historical buildings, as well as promote and accelerate further deterioration. In the past decades, stone decay processes have been widely influenced by the rapidly changing climate and concentration of air pollutants due to anthropogenic activity. Climate change has been impacting the environment with increased flooding, coastal changes, and erosion, all due to the rise of the sea-level, rise of average annual

F. Gherardi (✉)
Investigative Science, Historic England, Fort Cumberland, Portsmouth, UK
e-mail: francesca.gherardi@historicengland.org.uk

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temperature, increase in the frequency of extreme weather events, and intensification of the urban heat island effect. According to several climate models, in Northern Europe (especially UK and Ireland), the precipitations will increase (especially in autumn and spring) with hotter, drier summers and wetter winters [1, 2]. The change in physical, chemical, and biological processes have been directly affecting the historical environment. Archaeological sites, maritime heritage, and cultural landscapes are particularly vulnerable. In urban areas the impact of greenhouse gas emission is more relevant, and, while the concentration of traditional pollutants such as sulphur dioxide and smoke from coal has been reduced, transport emissions have led to the increase of nitrogen oxides and particulate matter [2]. The increases in air pollution and rainfall precipitations will be the cause of surface chemical dissolution of carbonate stones [2, 3]. As a consequence of the current wetter seasons, the outer surface of stone masonry will remain wet for longer times, possibly enhancing the depth of moisture penetration, thus resulting in the growth of algae and fungi [1]. Biofilms on the stone surface can retain moisture and reduce the permeability of the masonry, which can in turn play a role in salt crystallization and efflorescence, causing exfoliation, cracking, and decohesion.

Preventive and active conservation are two strategies adopted to counteract the actions of several deterioration phenomena. The increased awareness of the risks has lead conservators and heritage managers to implement measures to monitor the state of preservation of historical surfaces as well as the environment to which they are exposed. Preventive conservation strategies, namely legislation to protect individual buildings and monuments, environmental parameters and pollution control, fruition and risk management, etc., can be applied to slow down the decay processes and prevent future damages, aiming to avoid frequent invasive interventions [4–6].

However, preventive measures alone cannot be always effective, especially for building and archaeological sites, where it is not always possible to mitigate the environmental factors, move objects in a confined environment or set-up shields and canopies.

In this context, active conservation aims to improve built heritage preservation, by using specific conservation treatments. In particular, surface cleaning, consolidation and protection are the most relevant for stone materials.

Protective treatments are materials applied on stone surfaces to prevent weathering processes that take place at the interface material-environment, such as the accumulation of soiling, biocolonisation, and the penetration of water in the stone porosity (Fig. 5.1). Most of the protective treatments for stone are water repellent, as they prevent the penetration of water inside the substrate through capillary action, which is achieved by reducing the hydrophilicity of the pores and the external surface area. Aqueous atmospheric solutions and moisture play an essential role in inducing physical, chemical, and biological deterioration to the surfaces, as they promote mechanical erosion, thermo-hygric expansion, frost damage, salt transport and crystallization, biological growth, and acid corrosion with consequent hydrolysis process of minerals. As previously mentioned, the decay processes resulting from climate change will impact stone surfaces, with the increase in surface recession and erosion by precipitation, consequently, they will severely affect the

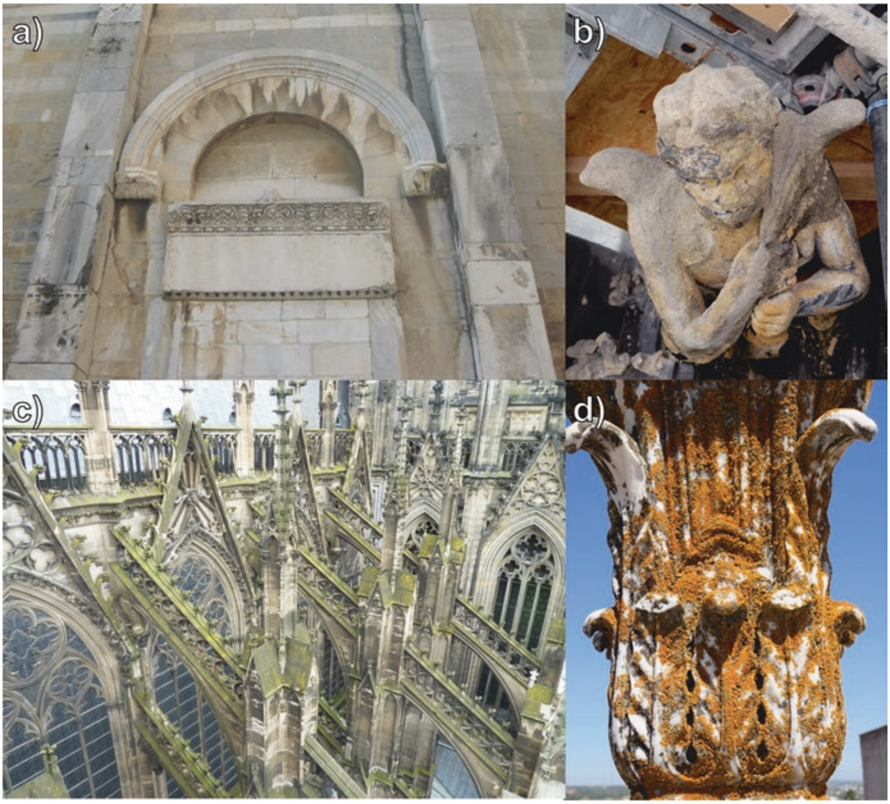


Fig. 5.1 Common decay agents for stone surfaces: (**a**) accumulation of soiling; (**b**) acid corrosion; (**c**) and (**d**) biocolonisation

strength, permeability, and durability of the masonry. In this context, nowadays and in the future, treatments for stone protection will play an essential role mitigating the effects of climate change.

In the past, waxes, vegetal oils, animal fats and natural resins were used to protect and polish stone surfaces, thanks to their ability to increase the surface tension and water-repellency [7]. Indeed, in the Craftsman's Handbook '*Il Libro dell'Arte*', Cennino Cennini gives detailed recommendations on the treatment of stone, using a wide range of materials, including skin glue, linseed oil, and egg yolk. The organic materials were either applied directly on the surface to provide smooth or matt texture, or they were used as binders of pigments and other inorganic compounds in decorations [8]. In addition, sacrificial layers, such as plaster, render, limewash, and paint, were applied for stone protection.

The rapid advances in polymer technology after the Second World War introduced synthetic coatings, replacing the natural ones, as they offer better efficacy and durability. Protective coatings developed for industrial applications were initially used for the treatment of stone in heritage contexts, but they proved to be unsuitable, as they tended to form thick waterproofing films on the stone surface, which were not permeable to water vapor. As a result of this, tailor-made products were developed for stone substrates in the past decades, with the aim of fulfilling the specific requirements for treatments to be used in heritage conservation.

Nowadays, a wide range of protective treatments are available and include water repellents, anti-graffiti coatings, salt inhibitors, inorganic coatings, limewashes, and antifouling treatments [9].

5.1.2 Performance Requirements and Working Properties of Protective Treatments

Prior to the application of any conservation treatment, a thorough condition survey in each of the areas under study should be carried out. The aim is to identify the type of stones, their decay patterns, their exposure (sheltered or unsheltered), as well as any previous repairs or conservation treatments.

Compared to other conservation treatments, such as cleaning agents and consolidants, protective treatments are not remedial, but they are preventive measures. Usually, their application is the last step of the conservation intervention and must be carried out on substrates previously cleaned to remove any soiling, biofilm, and soluble salts, then, if necessary, consolidated. According to the typology of selected consolidants and relative curing time, a protective treatment can be applied on dry and sound stone, after making sure that the area is not vulnerable to rising damp.

Protective treatments for stone conservation must fulfill specific requirements to be used in built heritage (Fig. 5.2). First of all, they must provide good protective efficacy against decay agents, such as liquid water, soiling, pollutants, and biological contamination. This can be achieved if the treatment is able to be homogenously distributed on the surface, provide good adhesion to the substrate, and penetrate into the pores of the stone. This can be particularly challenging for very compact stone such as marbles or granites, as the low open porosity affects the penetration, leading to the formation of a thin water repellent layer, and accumulation of the product on the surface [10].

Protective treatments should also coat the internal walls of the substrate, without changing the pore size distribution, by completely occluding the pores. This would result in a change of the water vapour permeability of the stone surface, and in the formation of entrapped liquid pockets in the pores. The water vapour permeability properties must not be reduced after the treatment, to avoid water condensation phenomena, especially in presence of hygroscopic salts, which may crystallize underneath the treated area, thus causing the detachment and loss of adhesion of the treated layer [11]. Indeed, hygroscopic salts can absorb or release water, depending on the relative humidity in the environment, leading to dissolution or precipitation. A masonry contaminated by hygroscopic salts can get wet beneath the treated

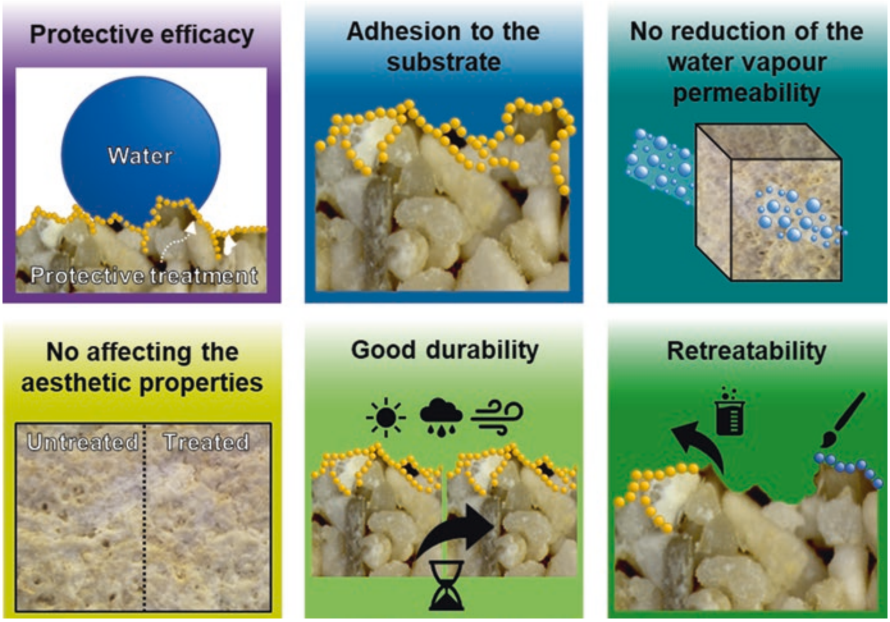


Fig. 5.2 Specific requirements of treatments for the protection of stone heritage

surface, and after several dissolution-crystallization cycles, salts tend to accumulate towards the surface, causing tensions to the stone.

To be used in heritage conservation, protective treatments must not modify the optical properties of the substrate, induce modification of the aesthetic characteristics (colour and gloss) of the stone, or obscure any surface texture or detail. Some products, especially if not carefully applied, can accumulate on the surface, especially in low porosity stones, resulting in significant variations in the morphology and the aesthetic appearance [10].

Protective treatments must exhibit good chemical and photochemical stability, without producing aggressive secondary products or damage the stone substrate. In scientific literature no solid evaluations of the durability of these treatments exist, but according to project and academic unpublished reports, after 5–7 years the properties of these materials are significantly altered [10]. The exposure of treated surface to solar radiation, thermal excursions, precipitations, and pollutants deeply impacts the properties of the treatments, especially water repellents. This results in a decrease of the water repellency of the surfaces, which undergo brittleness, loss of adhesion and elasticity, and the formation of cracks and fissures. Cracks in a treated surface can allow the absorption of water into the substrate and its accumulation beneath the water repellent area. However, in some cases while the surface reduces its water repellent properties, the interior pore space of the stone can retain hydrophobic properties after ageing [12].

Eventually every protective treatment will be altered and will need to be removed and reapplied. For many years, an important requirement for conservation treatments was the reversibility of the products, which is the ability to completely remove them, without altering the substrates. However, almost every conservation treatment involves permanent changes. For this reason, this concept has been replaced by the compatibility and retreatability requirements. The first principle requires that the conservation materials should be applied to the historic substrate, without inducing mechanical, chemical, and physical damage. The second one involves the idea that a conservation treatment used today should not preclude the possibility to apply another product over it in the future. This approach promotes the use of similar materials and sacrificial products, facilitating maintenance procedures [13].

Finally, in the last decades great attention has been given to the sustainability of the products, along with their impact on the environment and the workers' health. In this regard, protective treatments have been formulated with very low eco-toxicological impact, for example, by replacing organic solvents with water emulsions. In particular, some nanomaterials developed for conservation show lower toxicity compared to traditional materials, and they represent a more sustainable alternative to toxic products.

5.1.3 Criteria for the Selection of Protective Treatments

In the design and planning of conservation interventions, it is crucial to select the most suitable methods and materials, in particular, regarding their working properties (availability, application methods, health and safety) and performance (function, durability, and compatibility with other materials used in the building) [13]. This task can be very challenging, especially in buildings, which display several materials with different decay patterns. For this reason, it is important that different professionals (conservators, architects, scientists, etc.) take part in the decision-making process.

To face this challenge, some researchers have developed a decision support tool, which enables comparisons to be made among conservation treatments and help in the selection of the most appropriate product for the specific case-study [14]. Several selection criteria have been identified, scored, and ranked in terms of priority by a pool of heritage stakeholders. Performance characteristics and health and safety data have been considered the most relevant in the selection of a product. Reversibility, compatibility, minimum intervention, and retreatability of a treatment were also evaluated as important criteria in choosing sustainable conservation products for built heritage [14].

Potential benefits and drawbacks of the application of protective treatments should be taken into consideration while planning an intervention. The quantification of the "incompatibility risks" is another tool to be used as a guide during the assessment phase, considering technical, operational, environmental, social, and cultural criteria [15]. A rating scale of the incompatibility risks has been set-up for water repellents for stone surfaces, considering several parameters related to: (a) the substrate, such as its mineralogical composition (lithotype, presence of clays), and its physico-mechanical parameters (porosity, water vapour permeability, water absorption, colour, salt content); (b) the product, such as the chemical composition, the viscosity, and density; and (c) the treated substrate, such as water vapour permeability, drying rate, water absorption, contact angle, and colour. Indeed, the performance of a product depends on its chemical composition, viscosity, density, pH, solvent, presence of additional additives in the formulation, and the application methodology [10, 16]. Moreover, the effectiveness of a protective treatment depends on its capacity to penetrate and cover the pores of a stone substrate, and this is influenced by the open porosity and pore size distribution of the selected lithotype [17, 18]. The evaluation of the incompatibility risks can provide a tool to address whether to perform a protective treatment or not. However, to carefully collect the data and evaluate the different criteria, several laboratory and onsite tests must be carried out. A shared set of standard protocols to assess the effectiveness of a protective treatment in laboratory is available (EN 16581:2014) [19], but quite often it is unfeasible to perform every required test. In addition, it is not always possible to transfer the laboratory research results to practical situations [20]. Valuable, reproducible, and quantitative data can be obtained from laboratory tests to assess the performances of protective treatments. However, the tests are carried out in controlled environments and on fresh stone samples, which don't exhibit the decay pattern of naturally weathered surfaces [21]. Protective treatments are applied on small stone samples in simplified conditions, following methodologies which are often impracticable onsite. In this context, the application and assessment of protective treatments onsite is fundamental, as the efficiency and durability of a protective treatment is deeply influenced by the substrate, and by the fluctuations, the synergistic effects of the environment, and unique conditions in a building [13, 22]. The set-up of a monitoring program of the treated architectural stone surfaces is also relevant to study the long-term performances of the treatment. In Chap. 8 of this book a detailed overview of the major tests and analytical techniques for the onsite assessment of the effectiveness of protective treatments and their monitoring is explored.

The definition of trial areas of treatments in buildings is a sustainable strategy to identify the technical parameters (materials, methods, and equipment) and working procedures to be used, as well as carry out small-scale tests, and assess of the results (Fig. 5.3). It is a cost-effective approach to evaluate the results that can be achieved once the intervention is completed. *In situ* trial areas should be set-up considering the variability of the substrates (materials and decay patterns), and exposure (sheltered or unsheltered locations) [13], and the application of the treatments should be carried out by experienced conservators. Training for conservators and conservation scientists is also important to ensure quality in carrying out field tests and in the interpretation of the data. The results obtained from tests carried out on trial areas can be used in the scale-up of the operations (materials, operative parameters, and timing) in the conservation project design [23]. Following this process, it is possible

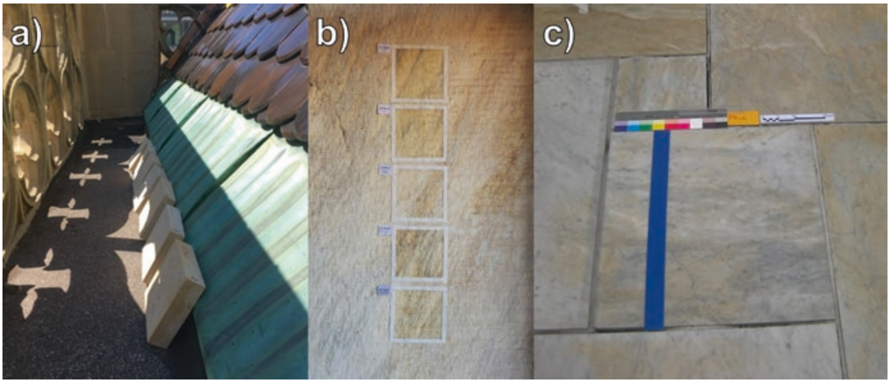


Fig. 5.3 Exposing treated stone samples to natural weathering and the set-up of trial areas of treatments in buildings are strategies to identify technical parameters, assess the effectiveness of the treatments, and monitor their performance over time. (**a**) Treated stone samples at the roof edge of St. Stephen's Cathedral, Vienna (Austria), © Archive of the workshop of St. Stephen's Cathedral, Vienna, Austria; (**b**) Treatment trial areas at the Primatial Metropolitan Cathedral of the Assumption of Mary in Pisa (Italy), © Opera della Primaziale Pisana, Pisa, Italy; (**c**) Treatment trial area at the Oslo Opera House, Oslo (Norway)

to identify the best common ground between conservation requirements and sustainability of the interventions.

As a final remark, it is important to take in consideration that protective treatments undergo deterioration and need to be renewed at regular intervals. Therefore, it is important to take measures to ensure a regular maintenance of the treated surfaces. A sustainable future plan should be designed and should include the evaluation of the cost of long-term maintenance [13, 24].

5.2 Classes of Protective Treatments

Since Greek and Roman antiquity, different strategies have been implemented to protect stone surfaces from external deterioration agents. Nowadays, a wide range of products with specific properties are available: water repellent products, anti-graffiti coatings, salts inhibitors, inorganic treatments, and limewashes. The selection of the most appropriate material should be preceded by a survey of the environmental conditions of the area under study (exposure to direct sunlight, precipitations, and wind), and of the stone surfaces (lithotype, decay patterns, and previous conservation treatments). Once the scope of the treatment and its required characteristics have been identified, specific products can be selected and applied to the area under review.

5.2.1 Application Methods

The application of protective products is a crucial aspect in the performance and durability of a treatment, as it affects both its distribution on the surface and penetration depth. Indeed, the current hesitation to use water repellent products originates from the selection of inappropriate application methodologies, which led to unsuccessful results in the past [24]. Published research and the results from experienced conservators indicate that protective products should be applied only on localized and specific areas, and not as a general treatment for large surfaces [22].

Prior to the application of protective treatments, the stone surface should be cleaned in order to remove soiling, dirt, and biofilms, and ensure that they are not embedded in the treatment. If a decayed surface requires consolidation, the protective products must be applied after the evaporation of the solvent, completed curing, and drying of the consolidant. Unfortunately, some consolidants, such as ethyl silicates, can take several weeks to complete the sol-gel process.

On architectural surfaces, protective treatments have been mainly applied by brush and by spray (Fig. 5.4). Some inorganic protective treatments are required to be applied in a cellulose-based poultice to control both their penetration in the stone pores, and the curing reaction [25]. In laboratory conditions, capillary absorption is the preferred method to apply the products on small stone samples, as it gives more reproducible results compared to brushing or spraying [7]. The selection of the most suitable method relies on the personal preference of the conservator, and on the recommendations in the technical data sheets of the products.

Standard hand-held airless sprayers can be used to apply a protective treatment, though the most appropriate nozzle and pressure must be selected according to the

Fig. 5.4 On architectural surfaces, protective treatments have been mainly applied: (**a**) by brush, © Opera della Primaziale Pisana, Pisa, Italy; (**b**) by spray. To protect the treated surfaces from environmental factors, a thin membrane can be applied, © Archive of the workshop of St. Stephen's Cathedral, Vienna, Austria

targeted area. However, the spray application does not always guarantee a homogenous distribution of the product on the surface, and sometimes lacks precision.

The use of brushes enables a more controlled and homogenous application of the treatment on the surface, especially on areas with decorative elements and carvings. In both cases, it is always recommended to use a wet sponge or a cloth under the area undergoing treatment in order to soak and remove any excess of the product and avoid accumulations on some areas. For large areas of a building, spray-coatings and roll-coatings can be used and followed by a careful soak up of the runoff.

Some commercial protective treatments are ready-to-use, while others require to be diluted before their application, and the selection of the appropriate concentration depends on the stone characteristics, especially the open porosity and state of preservation. Indeed, for high porosity stone with large pores, it is difficult to achieve a good coverage of the pores without filling them with the products, while for low porosity stone, there is the risk that the product accumulates on the surface, without penetrating into the pores.

The number and timing of applications depends on the products, and usually this information is specified in the data sheets. In some cases, a single application is sufficient, while some protective treatments need to be used until saturation of the substrate- that is, until no more product can be absorbed. Similarly, curing and drying of the protective treatments depends on their formulations (solvent, concentration), and on the environmental conditions during the application (temperature and relative humidity).

Another important factor to consider is the optimum temperature for the application of protective treatments, which is usually between 10 and 20 °C. It is highly recommended to avoid the application of protective treatments with temperatures lower than 5 °C and higher than 25 °C. In some cases, to slow down the evaporation rate of the formulation, or to protect from environmental factors (especially precipitations, direct heat, and wind), a thin membrane can be applied to cover the treated areas (Fig. 5.4c).

The recommendations provided by the suppliers in the technical data sheets of the products are often generic. Therefore, preliminary laboratory tests and the set-up of treatment trial areas are highly recommended to test several formulations, and identify the optimal materials, application methods, and operative conditions.

5.2.2 Water Repellent Treatments

Water repellents represent the broadest class of protective treatments. The main aims of these products are to prevent the ingress of liquid water into the stone pores, to reduce the accumulation of soiling and dirt, and to inhibit decay from environmental factors, pollutants and biocolonisation. Water can penetrate in the pores of the stone under the influence of some pressure and by capillarity. Ideally, the function of protective treatments is to coat and modify the surface tension of the pore walls, without completely blocking the pores or changing the pore size. In this way, the water repellent increases the surface contact angle between liquid water and the stone (Fig. 5.5). Hydrophobicity is due to the interfacial tension between the solid substrate and the liquid, and the geometrical and porosity features of the surface [26]. Stone is a polar and hydrophilic material, and the negative surface charges tend to attract the positive end of water molecules. Water repellents have a structure with a polar head and a non-polar tail, like common detergents and soaps. Thanks to this property, the polar head is attracted to the polar stone surface, which is then covered with non-polar tails, and results in a non-polar and hydrophobic surface [24].

A wide range of water repellent products have been developed, and their effectiveness deeply depends on both the stone substrate and the products' formulations, in particular on the chemical composition, the concentration of the active ingredient, the use of solvents or water emulsions, and the presence of catalysts or detergents. Usually, water-based products tend to show a lower penetration depth compared to solvent-based ones, but they can still provide homogenous surface deposition and coverage of the pore walls, especially on stone with high mean pore diameter [7, 18]. In low porosity stone, the same products can penetrate into the pores inadequately, polymerizing on the surface, and resulting in the formation of micro-cracks due to shrinkage [27].

Water repellent treatments exhibit different behaviours depending on their molecular size. In general, monomeric and oligomeric formulations should be preferred for the treatment of stone with small sized pores, while polymerized products with longer chains can successfully cover larger pores. In addition, the stone substrate is involved in the polymerization reaction and its interaction with the water

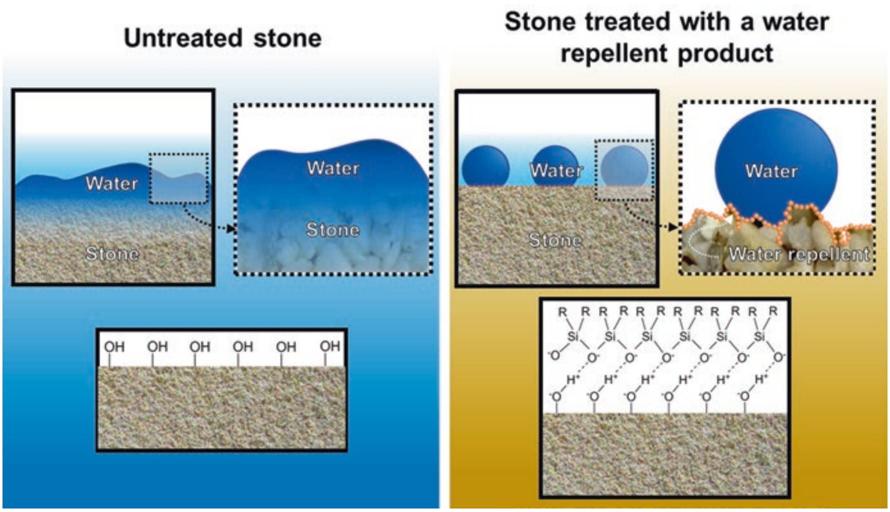
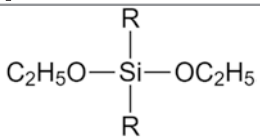
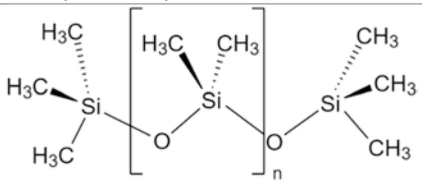
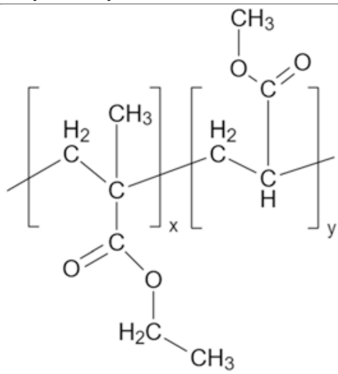
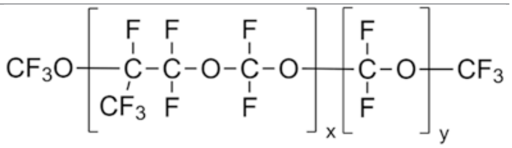


Fig. 5.5 Hydrophilic behaviour of untreated stone surface, and hydrophobic character (high static contact angle of water) of stone treated with a water repellent product based on an alkyl silicon product

repellent product depends on several factors, such as composition, texture, porosity, and moisture content [7].

The most widely used water repellent materials (Table 5.1) are from the class of alkyl silicon products. These compounds have been widely used in stone conservation, as they exhibit higher durability and stability compared to other organic materials. Acrylic resins have been also used as stone coatings in the past decades, but their performances were not satisfactory, due to poor durability and change of the water vapour permeability. Partially fluorinated polymers and perfluoropolymers are the first examples of "tailor-made" treatments for stone protection, and they

Table 5.1 Main classes of water repellent treatments and some of the most common products used in stone protection

Main classes of water repellent treatments	Common treatments from each class used in stone protection
Silanes (SiH_4)	 Di-alkyl-di-ethoxy-silane
Siloxanes ($-R_2Si-O-SiR_2-$, where R is the organic group)	 Polydimethylsiloxane
Acrylics (Acrylic acid: $CH_2 = CHCOOH$; Methacrylic acid: $H_2C=C(CH_3)COOH$)	 Paraloid B72© (ethyl methacrylate–methyl acrylate 70:30)
Fluoropolymers ($-CF_2$-CF_2-)	 Perfluoropolyether

were conceived in an attempt to improve the water repellent properties and the resistance to photodegradation of nonfluorinated polymers. However, they often display poor chemical affinity, adhesion, and inhomogeneous deposition on the stone surfaces.

5.2.2.1 Alkyl Silicon Products

Alkyl silicon compounds have been widely used in stone protection and they include a wide range of products (alkyl siliconates, alkyl silanes, siloxanes, polysiloxanes and silicone resins) (Table 5.1). One of the main advantages of these products is the possibility to tailor their properties according to the stone substrate, by modifying the chain length, the solvent, and the functional groups. These compounds were developed from the synthesis of ethyl silicate by Ebelman, starting around 1845. The first products contained solvents, while more recently (around 1990) environmentally friendly water-based formulations appeared on the market [7]. Laboratory tests aiming to assess the performance of several commercial alkyl silicon products proved that no significant differences in terms of protection efficiency were detected between solvent-based and water-soluble formulations [17].

The degree of polymerization of the products affects the performance of the treatment, particularly in terms of curing time, penetration depth, and durability. For stone protection, several studies demonstrate that silane and siloxane are the most suitable materials due to their chemical stability (resulting from the high strength of the silicon-oxygen bond), good elasticity, resistance to thermal stress, and their ability to bond to the minerals in stone substrates [22, 28].

Since silanes are mainly monomers and dimers, they are characterized by a very low viscosity, and they exhibit good penetration depth, even in low porosity stones [18, 24]. After the application and curing, they form a siloxane, which is not highly cross-polymerized, but it is highly bonded to the stone substrate [24]. Compared to siloxanes-based products, which quickly result in a highly polymerized product after the evaporation of the solvent, silanes require a longer time to complete the polymerization reactions.

Silanes form primary chemical bonds with OH groups on the surface of stones, following hydrolysis and subsequent condensation reactions, while for siloxanes the bonding mechanism to the substrate is still not fully comprehended [29].

The performance of the treatments in terms of water repellency is influenced by the type of alkyl groups attached to the silane and siloxane. Increased hydrophobicity and alkali-resistance have been achieved by products with longer and more branched alkyl groups [7].

An important factor is also the concentration of the active ingredient of the formulations. Due to the high volatility, the concentration of silanes in commercial products is usually more than 40% w/w, while the concentration of siloxanes is lower than 20% w/w. For siloxane-based products, the suppliers often recommend a dilution, and the right concentration should be selected after pre-treatments, taking into consideration the stone substrate and its state of conservation. Several studies proved that a good performance of a treatment is not proportionally correlated to the amount and concentration of the applied product, as a concentration below the manufacturer recommended minimum threshold can still confer good water repellent properties [22, 30]. On the contrary, if the concentration of the product is very high, the treatment accumulates on the stone surface, and cracks can form [30].

Similarly, the penetration depth of the treatment is important to achieve good protection, and this is influenced by the stone porous system (open porosity and pore-size distribution). For this reason, the same treatment can lead to dissimilar performances once applied on different stone varieties from the same geological formation [17]. The capacity of the treatment to homogenously deposit on the stone surface and coat the pore walls is a crucial requirement to achieve good protection [17].

The mineralogical composition of the stone can influence the performance of the alkyl silicon products, as the substrate plays an active role in the polymerization reaction [7]. In general, the application of alkyl silicon compounds on carbonate stones not containing siliceous minerals can be less effective compared to siliceous stones, as it is difficult to generate chemical bonds. Indeed, carbonates tend to slow down the curing of the products and the sol-gel reaction, as they do not have active OH groups on their surface, which can react with alkoxysilanes [31, 32]. Silanes are volatile, and the polymerization reaction occurs together with the evaporation of the solvent. If the rate of condensation is slowed down by the carbonate substrate, larger amounts of solvent evaporate, and shrinkage of the coating can occur. To overcome these problems, catalysts and surfactants have been added in the formulations, in order to accelerate the condensation process in carbonate stone [31, 32]. More recently, the introduction of nanoparticles (SiO_2, TiO_2, Al_2O_3) in alkyl silicon compounds proved to be an effective strategy to control the drying process, and avoid the formation of cracks [33]. It is still unclear whether the presence of clay in the mineralogical composition of the stone can affect the performance of alkyl silicon products. Controversial results were obtained on treated limestones and sandstone; shrinkage can occur, but it seems that it is mainly the structure of clay minerals belonging to different groups that influences the interaction with the alkyl silicon products [31].

Several laboratory studies on stone samples treated with alkyl silicon-based protective treatments have been carried out, aiming at investigating the performances of several commercial products. Siloxane and silane treatments have been applied on a wide range of carbonate substrates, with different petrographic and porosity features, such as: carbonate stones used in historical buildings in Portugal (Ança stone, Coimbra stone, Miocene stone and Lioz stone) [12, 34, 35], limestones used in the monuments and buildings in the central area of Spain [17], very porous Italian biocalcarenite (Pietra di Matera) [36] and calcarenite (Lecce stone) [30, 34], a Greek travertine [37], Italian marly limestones [38], several French limestones typical of historical buildings in the Champagne-Ardenne district (Courville, Savonnières, Langres, Jaumont and Charentenay stones, Champagne chalk) [39], and Italian tuffstones [38]. In most cases, the alkyl silicon products exhibit good coverage of the pores, resulting in excellent protection against water ingress into the pores, without affecting the appearance of the stones in terms of colour and gloss.

As expected, due to the presence of siliceous minerals with active OH groups on their surface, alkyl silicon products have shown excellent protection performance on sandstones widely used in buildings in Germany (Obernkirchener Sandstone, Red Wesersandstone, and Udelfanger sandstone) [40, 41] and on Turkish sandstone [37].

These protective treatments have resulted in good penetration and coverage of the pores of low porosity stone such as marbles or granites [21, 27, 35, 37, 42–45]. Indeed, decreasing the surface wettability and water absorption by capillarity occurred on treated Italian marble (Carrara marble) [27, 42, 43], Greek marbles (Thassos and "Ajax" of Drama marbles) [37] and on Portuguese granite [35, 44]. It is important to underline that despite the good protection performance, a severe reduction of the water vapour permeability can occur, especially on low porosity stones, if the amount of applied product and the most suitable concentration are not properly selected.

Despite the wide use of alkyl silicon products for stone protection, only few studies recently report the findings obtained from the application of these treatments *in situ*, on naturally decayed architectural surfaces. Indeed, the effectiveness of protective treatments applied onsite can be quite different compared to laboratory results, as the environmental factors and operational constraints influence the application methodology, and it is very challenging to replicate the complexity of aged substrates.

Several commercial protective treatments have been applied and tested on the marly limestone ashlars of San Fruttuoso di Capodimonte Abbey (Genoa, Italy), in order to select the most suitable product to use during the conservation intervention [38]. Trial areas were identified on the façade, considering the different state of conservation of the stone in the abbey, which has been exposed to severe marine aerosol and sea erosion. The marly limestone used in this building (Pietra di Promontorio) has been widely employed in historical buildings thanks to its good mechanical properties. However, the varieties are very inhomogeneous, as they contain different amounts of clay, which makes the stone prone to chipping and scaling when exposed to weathering. At the end of the 18-month monitoring, silane and siloxanes products showed the best performance. However, they exhibited low durability over time once exposed to the aggressive marine environment, probably due to the poor penetration in this low porosity stone. For this reason, no commercial consolidants and protective treatments were selected, but punctual interventions using mortar were carried out to fix spalling phenomena [38].

The performance of traditional (including a commercial polysiloxane product) and innovative nanostructured treatments applied on marbles on the façade of the Monza Cathedral (Italy) have been evaluated and monitored onsite for 12 months [21]. In particular, trial areas were set-up on Crevoladossola (a fine-grained dolomitic marble) and Candoglia (a medium to coarse-grain size marble) marble slabs in the framework of the conservation project of the façade. Compared to the untreated reference area, the commercial siloxane treatment induced a slight surface yellowing. However, the good effectiveness in the reduction of water absorption was maintained within the monitoring period, thanks to its good coverage of the minerals and penetration into the crystalline matrix [21].

A recent study reports the results from the selection of a suitable protective treatment for the limestone blocks of the Matera Cathedral (Italy) [36]. The very porous biocalcarenite used in the cathedral (Pietra di Matera) tends to easily decay; therefore, a protection treatment for the façade was required. Three silane and siloxane-based products (one of them in mixture with acrylic polymers) were identified, and their effectiveness and durability was assessed both in laboratory and onsite. The products provided good protection, but the results demonstrate the difficulties in finding a perfect protective treatment for this lithotype. The monitoring activity reports negligible variation of the protective effectiveness and of the esthetical properties of the treated limestone after 40 months, especially in the case of the use of a low molecular weight alkyl/alkoxysilanic resin [36].

Although silicon-based treatments exhibit the highest stability compared to other water repellents, a decrease in their protective performance occurs after artificial and natural ageing. The maximal durability of these products has been estimated to be about 15–20 years, but a significant reduction of the water repellent properties is already visible after just 5 years [7, 22, 46].

Some recent studies focus on the long-term monitoring of the durability of eleven silicon-based protective treatments applied on Obernkirchener Sandstone [40, 47]. Treated stone samples were exposed to weathering for 30 years in seven locations in Germany. Despite selecting a treatment application methodology often unsuitable for *in situ* conservation interventions (total immersion), the studies provide valuable data about the durability of the protective treatments. Some products showed a decrease in the protection effectiveness after 2 years, probably due to the poor penetration and distribution in the pores of the stone [47]. The protective treatments proved to be able to reduce the darkening due to soiling and biocolonisation of the stone surfaces only in the short term. Silicone resins and siloxanes exhibited comparable results, and, after 30 years, despite a decrease in the reduction of the water absorption, some products were still able to confer water repellency to the stone [40].

Another research study evaluates the impact of climate, atmospheric pollution and stone characteristics in the durability of four commercial water repellents (three silicon-based products and an acrylic emulsion) [39]. Stone samples from French limestones used in historical buildings in the Champagne-Ardenne district (Courville, Savonnières, Langres, Jaumont, and Charentenay stones, Champagne chalk) were treated and exposed for 6 years on upper locations of the Reims and the Langres cathedrals. Mass loss due to surface dissolution and surface darkening were more intense on samples exposed in Langres, which is characterized by lower levels of pollution, but more severe climate compared to Reims. As expected, the surface water repellency of the samples significantly decreased after ageing. However, some of the treated stone were still able to reduce the water income, proving good coverage of the pores at depth. Laboratory tests proved better performance of solvent formulations of silicon-based water products compared to water-based ones, and that the durability of the treatments was highly influenced by the porous systems of the stones. However, none of the products were effective as water repellent for limestone with fine pores [39].

Similar results were obtained on Portuguese carbonate and granite stones treated with different commercial silanes and polysiloxanes products [35]. The durability of the treatments was assessed by accelerated ageing and natural exposure to the samples in Lisbon. After 15 months of natural weathering, polysiloxanes showed a better performance compared to silanes in every lithotype. While the surface hydrophobic properties significantly decreased, the treatments still provided a good barrier against water penetration [35]. These results confirmed the data previously collected on Portuguese carbonate stones treated with similar products and left outside to be exposed to urban and marine environment. Indeed, even if siloxanes tended to lose their hydrophobic properties faster than silanes, they proved to have better long-term stability and durability [12].

Regarding the effectiveness in preventing soiling accumulation, Italian Apuan marble samples were treated with different protective treatments and naturally weathered for 12 months in Florence (Italy) [48]. Surfaces treated with silicon-based or fluorinated coatings exhibited lower accumulation of airborne particles and less significant colour change compared to marble samples, which were either untreated or treated with inorganic treatments.

Despite the good results obtained by alkyl silicon products, some factors can compromise their effectiveness and cause severe damage to the stone substrates. In particular, laboratory studies proved that stone treated with water repellents like polysiloxane undergoes intense weight loss in the presence of high amounts of salt. When desalination treatments are not successful in the complete removal of soluble salts, or in the case of salt contamination by capillary rise from the ground, polysiloxane products should be avoided, and substituted with inorganic treatment [34].

It is important to underline that water repellent products require application by expert conservators to ensure a homogenous distribution of the treatments, especially on decorated stone surfaces. If the application of the products is not accurate, the stone surfaces can undergo short and long-term damage. As an example, marble statues and vases from the gardens of the National Palace of Queluz (Portugal) showed the appearance of streaking as a result of uneven biocolonisation [49]. The sculptures were treated with a siloxane product to reduce biological decay during a previous conservation intervention. However, inhomogeneous application of the treatment on the artefacts with a complex geometry like statues may have caused the formation of preferential water paths, which, in turn, favoured biocolonisation [49].

Similar decay patterns were noticed during a survey of about 30 monuments in Rome (Italy), which were treated in the 1980's with siloxanes and acrylic products [46]. Dark, parallel, vertical lines appeared on surfaces sheltered from rain, and they were probably the result of water channelling on the treated surfaces and dusts deposition on the flow lines.

The selection of appropriate application methodology of the treatment and the definition of guidelines for maintenance of building surfaces are very important tasks to make sure that the caring procedures meet the conservation standards. A particularly challenging case-study is the Oslo Opera House (Norway), a contemporary building designed by Snøhetta architectural studio and opened to the public in 2008 [50, 51]. The building is characterized by a large ornamental pavement made of Apuan marble slabs (Bianco Carrara La Facciata, Italy) with several surface finishes, and a roof with a large plaza, where people can walk (Fig. 5.6). The building is exposed to severe marine climate (wide range thermal excursions, strong solar radiation, salt marine spray, particulate matter deposition) and mechanical wear stress. The problem of maintenance of such a huge and highly frequented surface has been pointed out since the very beginning of the construction. Once placed onsite, the surfaces were impregnated with a flouroacryl copolymer protective treatment. On the vertical surfaces, this treatment was followed by an anti-graffiti

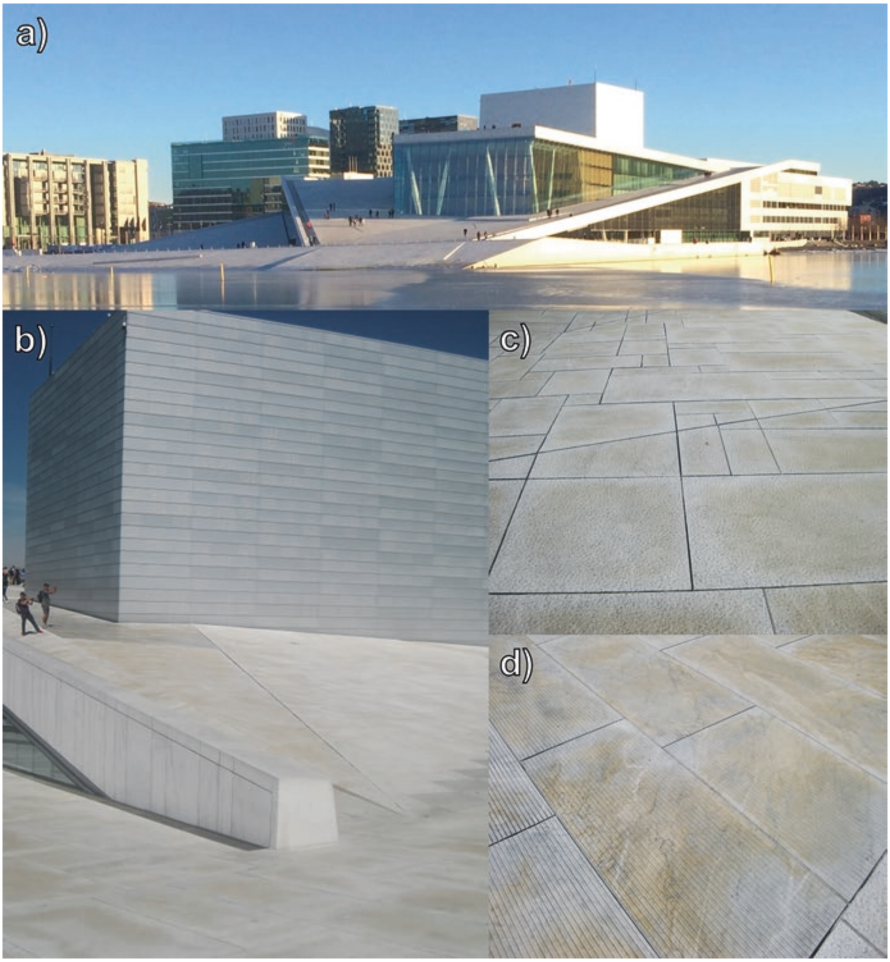


Fig. 5.6 (**a**) the Oslo Opera House, © Adriana Eidsvik, Statsbygg, Oslo, Norway; (**b**–**d**) ornamental pavement slabs made of Apuan marble and characterized by surface discoloration

application based on polysaccharides. In addition, a siloxane-based product was also applied on the marble slabs in 2012. However, after a few years, intense yellow discoloration and dirt accumulation started to appear on large areas of the marble slabs. Research was carried out to evaluate the state of conservation of the marble slabs and investigate the causes of their discoloration. Diffused presence of siloxanes and oxidized by-products (esters and carboxylates) of a mixture of treatments previously used on the marble, together with residues of the anti-graffiti product, were detected on the yellow areas. The application of several protective treatments on the same area, without a complete removal of previous coatings, led to the formation of a hard film, which then entrapped organic by-product. The degradation of the products may have originated from the exposure of the slabs to severe marine climate, and to the standard cleaning procedures using hot water and alkaline cleaning products [50, 51].

5.2.2.2 Acrylic Coatings

Acrylic resins are based on derivatives of acrylic and methacrylic acid (Table 5.1), and they have been widely used since the 1960s for the conservation of architectural heritage, as consolidants, adhesives, and varnishes. Copolymers based on different acrylics, and commercially known as Paraloids, have been used for the consolidation and protection of wall paintings, stone, and mortars. These resins can be dissolved in solvents or prepared as water emulsions, and they have previously been applied in stone protection because of their hydrophobic properties. However, several studies proved that these treatments do not fulfil several conservation requirements. Once applied on porous stone, they significantly affect the surface and the pore network by reducing the pore size distribution due to complete occlusion of the pores [52]. They deeply modify the morphological features of the surfaces of porous substrates, by creating a film on the crystals. This can greatly reduce the water vapour permeability, reducing the transfer of water vapour between the stone and the environment, with dramatic consequences due to water accumulation inside the masonry. During the ageing process, cycles of crystallisation/solubilisation of salts or ice formation into the pores can increase the mechanical stress and damage the substrate. Moreover, acrylics exhibit poor coverage of the stone pores and adhesion to the surface, resulting in a decrease of their effectiveness after just a few wet-dry cycles [53].

Another drawback of acrylics is their poor stability if exposed to photo-oxidative stress. Several studies clarified the degradation mechanism of acrylic formulations exposed to artificial weathering by photo-oxidative processes [54–56]. The results prove that severe structural changes occur, producing chain scission, the formation of oxidized compounds, and of strongly cross-linked structures. These changes increase the surface discoloration and decrease the protection performance [38]. In some cases, the production of reticulated structures prevented the complete removal of the aged acrylic treatments from the stone surfaces [56]. One of the strategies to improve the protective and physical properties, and the stability of acrylic resins is to blend or copolymerize them with other polymers.

Naturally aged acrylic resins proved to be prone to biological degradation [57]. Marble surfaces from the Milan Cathedral (Italy), previously treated with acrylic consolidants and protective treatments, displayed intense blackening. Studies investigated the possible cause of surface discoloration: air pollution, fly ash, metal oxidation, and biological pigments such as melanin. The surfaces were covered by a protein-based layer, which replaced the polymeric coating, due to the colonization by black fungi. This study proves that the oligomers produced by chain scission of the acrylic polymers are more susceptible to fungi attack. Therefore, a maintenance program of the surfaces is recommended, in order to avoid aesthetic and physical damage of the substrates due to biocolonisation [57].

Acrylic resins co-polymers (in particular the commercial product Paraloid B72) have been employed as consolidants and protective treatments of several historical buildings during the 1980's in Rome [46]. During a survey of about 30 monuments, a severe reduction of the water repellent properties was noticed on the treated surfaces within just 5 years of application. In addition, yellowing and darkening of the treated marble occurred, due to the particulate matter accumulation and retention. The poor stability of acrylic products due to weathering resulted in a decrease in the protection effectiveness of the treatments, and in difficulties with their removal from the stone substrate [46].

The poor durability of acrylic polymers was also witnessed when mixed with siloxanes [36]. The product does not affect the aesthetic properties and grants good protection of the treated biocalcarenite blocks of the Matera Cathedral after 40 months. However, laboratory tests proved that a severe reduction of the water vapour transport properties occurred, along with poor UV stability.

5.2.2.3 Fluoropolymers

Partially fluorinated polymers and perfluoropolymers were introduced in the field of stone conservation in the 1980s with the aim of improving the protection effectiveness and the durability of nonfluorinated coatings, such as acrylics. The synthesis of fluoropolymers starts from monomers in which the hydrogen atoms of the organic molecule are partially or completely substituted by fluorine atoms. Fluorinated groups in the polymeric formulations confer higher resistance to photo-degradation and improved thermal stability compared to nonfluorinated polymers, due to the higher stability of the C-F bonds compared to C-H bonds. In addition, they provide good water and oleorepellency, and they do not affect the aesthetic properties (colour and gloss) of stone surfaces.

A wide range of products (such as perfluoropolyether, fluorinated acrylic copolymers, fluoroelastomers) have been developed and applied as protective treatments for stone substrates (Table 5.1) [58–61]. However, fluoropolymers show poorer adhesion and inhomogeneous distribution on the stone surfaces compared to alkyl silicon products and acrylic coatings, which bind to the stone by covalent and dipole bonds (van der Waals forces) [9]. As a result, the water repellent properties decrease dramatically with time. To overcome this problem, manufacturers prepared formulations with blends of fluoropolymers with acrylic or silicon polymers. The introduction of functional groups, such as amide derivatives, aimed at increasing the adhesion of the coatings to the stone surfaces, therefore increasing the protective properties of the products.

Several commercial fluoropolymer products were tested in laboratory conditions for the protection of very porous stones (Lecce stone), using two different application procedures (by capillary absorption and by brush) [62]. The results indicated that the effectiveness of the treatments was deeply influenced by the application methodology and the amount of applied product. Only when higher amounts of treatments are used, the fluoropolymers are able to significantly reduce the water absorption. However, the treatments penetrate and occlude the stone pores, resulting in a severe decrease of the water vapour permeability. This research proved that these commercial products are not recommended for the protection of high porosity stones.

Once applied on a low porosity stone like Carrara marble, a commercial product based on fluoropolyethers did not show a good affinity with the stone surfaces, as it was not able to spread homogeneously, and adhere to the marble [42]. By observing the treated surfaces with scanning electron microscopy (SEM), it is possible to notice that the product did not penetrate into the pores but rather it accumulated on the surface in small clusters.

Despite the introduction of fluoropolymers in formulations with acrylic or silicon polymers, the water repellent properties significantly decrease after artificial and natural weathering. Several French limestones with different porous systems were treated with a commercial product based on acrylic emulsion with polytetrafluoroethylene (or Teflon) and exposed to natural weathering for 6 years [39]. Immediately after the application, the coating exhibited filming properties, but after ageing, several lacunas appeared in the coating on the treated surfaces, as a result of the poor durability of the product.

Similar findings were obtained on limestone samples (Trani stone) treated with a commercial product based on fluoropolyethers and left outside to be exposed to an urban environment for 1 year [63]. After ageing, the product exhibited poor durability, and an increase of the wettability and water absorption occurred, probably due to modifications to the properties of the treatment.

Despite the poor durability properties, a recent study demonstrated the effectiveness of the use of protective treatments to reduce soiling accumulation in an urban site [48]. Indeed, marble samples treated with an oil/water-based dispersion of fluorinated acrylic copolymers and exposed to weathering for 1 year exhibited lower deposition of airborne matter, as compared to samples left either untreated or treated with inorganic treatments.

5.2.3 Anti-graffiti Coatings

Anti-graffiti coatings have been designed and employed in the last few decades in order to facilitate the removal of graffiti, which are often affecting not only modern buildings but also historical monuments, especially in urban environments. Graffiti damage built heritage from the aesthetical point of view, and the cleaning methods to remove them can also affect the surfaces of the substrate, as the paints can penetrate in their pores. Anti-graffiti products produce low surface energies which reduce the adhesion of inks and paints on the surface, thus resulting in easier cleaning and protection of the stone substrates.

To be applied on architectural surfaces, the treatments have to fulfil specific conservation requirements, in particular regarding the increase of the protection efficacy, negligible change in the water vapour permeability and aesthetic properties, and stability (see §5.1.2.). Anti-graffiti coatings for historical surfaces are very valuable and sustainable, as they penetrate and coat the pore walls, forming a barrier against graffiti, and they contribute to the reduction of the risks and costs of cleaning interventions. In addition, they improve the efficiency in graffiti removal compared to the use of traditional cleaning procedures, which often exhibit several drawbacks (mechanical damage to the stone, chemical contamination, and change of the surface colour).

Three main categories of anti-graffiti coatings can be identified: sacrificial, semipermanent and permanent [64]. The first category includes coatings that are usually removed together with the graffiti, and they need to be reapplied after every cleaning process to ensure protection. The formulations are based on waxes, biopolymers (polysaccharides) and acrylates, and they usually do not significantly affect the water vapour permeability properties and the aesthetical appearance of the treated stone. They are required to be removed with medium/high-pressure hot water. Semipermanent anti-graffiti coatings are usually siloxanes-based products, they are less durable than permanent ones, and they can stand two or three cleanings before needing to be reapplied [64]. Some of these systems are layered and they consist of a sacrificial coating applied over a base layer of permanent coating. Finally, permanent anti-graffiti products can withstand more than 15 cleaning cycles. They are usually based on polyurethanes and epoxy resins, and they are used for the protection of low porosity materials such as metals or glass. They usually have filming properties and tend to affect the water vapour transport properties of stone. Graffiti can be cleaned with solvents from the treated surfaces, while the old anti-graffiti coatings can be removed with sandblasting or laser cleaning [64]. However, one of the drawbacks in graffiti removal is that mechanical and chemical methods are not always successful if the graffiti paint shows good adhesion to the surface, or if it penetrates into the pores. In addition, the use of solvents to remove permanent coatings can result in the diffusion of the paint into the coating, affecting its removal.

A valuable study for the evaluation of the suitability of anti-graffiti coatings for the protection of built heritage recommends some laboratory tests, and proposes a classification system that can be used to assess the efficiency of the products [65].

Evaluation criteria and the minimum acceptable values for properties such as colour and gloss, hydric properties, durability and cleaning efficiency are reported, and this can in turn help in the selection of the best options for a specific substrate.

To achieve good results in graffiti removal, some characteristics of the stone should be considered. This is because the performance of anti-graffiti coatings is influenced by not only the specific formulation (chemical composition, viscosity, density, etc.), but also the porous systems, and the surface finish of the stone.

Good penetration of the products grants homogenous coverage of the pores, resulting in efficient protection. The roughness of the stone influences the adhesion of graffiti paints on the stone, and the cleaning efficiency of the treated stones [66]. This is evidenced by graffiti removal being more efficient on more porous and smoother stones (limestone) compared to compact stones (granite) with a rough finish, where both were treated with two permanent anti-graffiti products [66].

The difficulty in the cleaning of graffiti from a highly porous calcarenite (Lecce stone) treated with two commercial sacrificial anti-graffiti products (the first one is based on waxes, while the second one contains waxes and acrylic-fluorinated resins applied over a primer composed of acrylic-fluorinated copolymers) was also reported [67]. The wax-based product was less successful in graffiti removal, as paints were still visible after several cleaning cycles. On the other hand, the pretreatment of the surface with a primer hindered the paint penetration in the pores, thus improving the complete graffiti cleaning.

Another study compares the effectiveness of four commercial anti-graffiti coatings (formulations based on: (1) acrylate copolymer; (2) paraffin polymers; (3) polyurethane; (4) ethyl methacrylate) applied on eight lithotypes (siliceous sandstones, calcareous sandstones, limestones, and travertine) [64]. The products based on ethyl methacrylate and on polyurethane proved to be unsuitable for use in built heritage protection, as they significantly affected the water vapour transport properties, and they induced alterations in the aesthetic appearance of the substrates. Both treatments based on aqueous emulsion of paraffinic polymers and on the acrylate copolymer did not compromise the stone hydric properties; the paraffinic based product did not affect the colour and gloss of the stones.

A recent paper demonstrates the complexity in the evaluation of the factors contributing to the cleaning effectiveness of graffiti from treated stone surfaces [68]. The chemical composition of the anti-graffiti formulations and the graffiti paints, and the cleaning procedures recommended by the suppliers played a more relevant role, than the stone properties (mineralogical composition, texture, and surface finish). By comparing a product based on an aqueous dispersion of microcrystalline wax and a water emulsion of a fluorinated polyurethane applied on four stones (a gneiss, granite, diorite, and travertine), the sacrificial coatings proved to be effective in the removal of graffiti compared to untreated stones. However, some residues of coatings still accumulated on the surface after cleaning. The composition of the graffiti inks significantly affected the results obtained in graffiti removal from the permanent coating, as the cleaning of the alkyd-based paint was unsuccessful.

Regarding the durability of anti-graffiti coatings, only few studies are available. A comparison of the stability of two anti-graffiti products (formulations based on polyurethane with a perfluoropolyether backbone and a crystalline micro wax) after accelerated ageing and natural ageing for 1 year has been reported [69]. The coatings were applied on Portland limestone and Woodkirk sandstone and the results proved that both products were affected by artificial and natural ageing, resulting in poor efficiency in graffiti cleaning. In particular, the permanent coating underwent yellowing and darkening, with poor adhesion to the stone; while the sacrificial product increased the surface wettability and affected the surface colour.

In order to improve the chemical stability of anti-graffiti coatings against weathering, the addition of silica nanoparticles in the formulations was proposed [70]. Indeed, nanoparticles are employed in coatings, as they can improve their resistance to weathering, and their mechanical and thermal properties. The use of silica nanoparticles in a permanent polyurethane-based anti-graffiti coating showed that the nanoparticles exhibited barrier properties against graffiti penetration in the polymer matrix. Moreover, silica nanoparticles exhibited UV absorption properties, and were able to protect the polymer from UV degradation [70].

5.2.4 Inorganic Protective Treatments

Instead of using polymer-based water repellent treatments, another approach for stone protection is the application of products that can penetrate into the pores and crystallise into minerals, which are more resistant to atmospheric attack. Some of these treatments can induce surface consolidation and protection with the same product [71].

In the 1980s, treatments based on dispersions of ammonium oxalate were proposed for the protection of carbonate stones, plasters and wall paintings, due to the ability to dissolve calcium carbonate followed by the precipitation of calcium oxalate and ammonium carbonate, which then decomposes into ammonia and carbon dioxide [71].

The oxalate layer displays cohesive and hydrophilic properties, and it slows down the rate of acid weathering [9]. Several synthesis routes have been proposed to produce calcium oxalate on stone, and the first applications were inspired by observations of natural oxalate patina on monuments and historical building, such as the Parthenon in Athens (Greece), the Trajan's Column in Rome (Italy), and the Moai Statues in Easter Island (Chile) [25, 71, 72]. These natural patinas act as protective layer for the underlying substrate, as calcium oxalate displays lower solubility compared to calcite. Therefore, the underlying stone substrate is usually well preserved. The solubility of calcium oxalate is significantly lower than calcium carbonate at an acidic pH; therefore it can shield the stone substrate from atmospheric pollutants, without affecting the hydric properties or occluding the pores [25]. In addition to the use of ammonium oxalate, oxalic acid solution has also been also successfully applied to marble substrates to produce calcium oxalate with good cohesive properties [73].

The selection of the most accurate concentration of ammonium oxalate in an aqueous solution depends on the stone properties and its state of conservation, and it should be selected following testing trials. Usually concentrations of about 5–7% are recommended, and the application is usually carried out in cellulose pulp poultice spread onto the surface for a period of time between several hours and a few days [71]. Application by brush proved to be effective in the crystallization of calcium oxalate on a limestone, and this method is recommended for large surfaces as it is more sustainable [74].

Successful results in the conversion of calcium carbonate into calcium oxalate have been achieved on the treatment of both limestone and marble, even in presence of sodium chloride salts [25, 75]. A saturated solution of ammonium oxalate (5%) was applied on a very porous stone such as the Maltese Globigerina limestone, and the treatment promoted an increase in the resistance to acid attack, without affecting the water transport properties of the stone [75]. On Carrara marble, solutions of ammonium oxalate of 0.4% were able to completely cover the surfaces with several crystalline layers. However, only when more concentrated dispersions (5%) were used, the treated surfaced were more resistant to weathering caused by weak acid rain exposure [25]. One of the drawbacks of the treatment is that calcium oxalate can affect the aesthetic properties of the stone, as the crystals can display a yellow-whitish colour.

In case of salts crystallisation in stone substrates, the presence of protective treatments can significantly increase the damage. The performances of a water repellent treatment based on siloxanes and a dispersion of ammonium oxalate in the treatment of salt-contaminated limestones and marbles were compared [34]. The results indicated that stones with high salts content treated with the polysiloxane product were severely damaged and caused a high weight loss, while only minor changes were noted from stones treated with ammonium oxalate. The inorganic protective treatment did not occlude the pores of the stone and proved to be more resistant to salt crystallisation and surface erosion due to natural weathering.

In onsite applications on naturally decayed stone surfaces, it is important to take into consideration the eventual presence of salts in the masonry, as they can affect the calcium oxalate crystallisation. Indeed, ammonium oxalate applied on Maltese Globigerina limestone surfaces did not completely react into ammonia, but it interacted with magnesium chloride within the stones, forming a new soluble salt (ammonium magnesium chloride) [76].

In terms of durability, a study proved that the ammonium oxalate treatment was able to prevent the decay of stone surfaces exposed to weathering in urban environment [77]. Two marble sculptures exposed in both sheltered and unsheltered conditions in Florence (Italy) were treated with ammonium oxalate and their surfaces were monitored after 4 years. The collected data proved that a patina based on calcium oxalate was still visible on the surface, and oxalate crystals were observed in marble cavities. In addition, the passivating effect of calcium oxalate layer was confirmed, as the underlying carbonate substrate was well preserved.

In addition to ammonium oxalate, other inorganic protective treatments have been developed, and some of them are available on the market. Coatings based on calcium phosphate (in particular hydroxyapatite) have been obtained from the reaction of diammonium hydrogen phosphate with calcium ions from the substrate. Hydroxyapatite displays solubility and dissolution rate much lower than those of calcite, and it has crystal lattice parameters similar to calcite, thus reducing the risk of stress within the minerals during crystallisation [78]. These treatments proved to be excellent in preventing the dissolution and corrosion of marble substrate, even after being subjected to several wet/dry cycles simulating rain-wash [79].

5.2.5 Limewashes and Shelter Coats

Limewashes and shelter coats have been traditionally used for the conservation of weak stone surfaces, to reduce their susceptibility to weathering. Both treatments do not affect the water vapour transport properties of the masonry, and they are widely used in UK and continental Europe.

Limewashes consist of aqueous dispersion of putty lime and pigments, and they are usually applied on wet surfaces in several coats, according to the substrate, the thickness of the limewash, and the preferred finish [13]. Additives and binders can be added in the formulations to increase the cohesive properties and to impart water repellent features. Limewashes have been used for the treatment of carbonate substrates such as limestones and marbles, proving to be able to be homogenously distributed on the surface and to bridge fissures in the substrates [7]. Some of the drawbacks of these treatments are the low adhesion to the substrate, and that sometimes cracks in the coatings occur, allowing the penetration of water in the stone.

Shelter coats are designed to protect the stone surfaces by filling pores and fissures with a porous medium, preventing the accumulation of soiling and pollutants. This is particularly useful after cleaning interventions, as open pores can result from the cleaning of stone surfaces [13]. Shelter coats are also used to homogenise and smooth the surfaces, in order to improve the water runoff [7]. Their composition usually consists of lime putty, finely sieved sand, stone dust, and casein to improve the binding properties of the coating, which makes the surface opaque and matt.

A recent study reports the results of the survey of several treatments, including limewashes, applied on Reigate stone walls at the Tower of London and Hampton Court Palace (UK) [80]. The coatings were prepared by using lime putty mixed with casein, linseed oil, and pigments, and applied in the late 1980s. Most of the treated areas exhibited rapid weathering, resulting in the detachment of the coatings, due to the accumulation of moisture in the stone walls, and rapidly fluctuating conditions. Diagnostic investigations proved that the rather thick limewash coatings (several mm) did not show adequate adhesion to the surface, and they were characterized by different properties compared to the underlying substrate. In other areas of the building, limewashes were still visible and they were in good condition, proving that the microclimate conditions and the mineralogical composition of the stone affected the performance of the limewash coating.

During the conservation of the New York Public Library (USA) a shelter coat was successfully used to protect the stone surfaces [81]. Highly exposed marble areas of the building's façade, such as corners, quoins, and decorative elements were characterised by sugaring. Laboratory tests and trial areas onsite were carried out to select the most appropriate conservation treatments. To consolidate, ammonium oxalate was applied; however, the layer based on calcium oxalate was not uniform on the surface. Therefore, several commercial shelter coats were also tested onsite in order to find the best formulation, that is being able to match the colour and texture of the marble substrate. Positive results were achieved, and the selected conservation treatments respected the principles of minimal intervention, compatibility with the substrate, and retreatability.

5.2.6 Salts Inhibitors

Salt decay is one of the major causes of the weathering of stone, as salts can build up deposits within the stone pores (i.e., subflorescence or cryptoflorescence), and result in mechanical stresses, consequent exfoliation, and detachment of material. In addition, salts can crystallise on the stone surface (i.e., efflorescence), affecting the aesthetic properties. Several types of chlorides, sulphates, nitrates, and carbonates are soluble salts, which are commonly found in masonry. Each of these exhibits different solubility, crystal structure, and crystallise under different parameters. Salts crystallise from a solution after the aggregation of dispersed solute ions, then nucleation starts, resulting in cluster and crystal formation. The crystallization process is influenced by several variables, including temperature, relative humidity, type of ions in solution and concentrations, impurities, type of pores in the stone, and its water transport properties.

In the last decade, crystal growth inhibitors have been proposed to control salt crystallisation in porous substrates. These compounds modify the surface properties of the crystals, and they affect the nucleation and growth, causing changes in their shape and in the way they agglomerate or disperse [82].

A couple of reviews report details about the influencing factors in salts crystallization, and explain how crystal growth inhibitors work [82, 83]. Inhibitors work according to two main strategies: they can prevent the nucleation of crystals, or they can modify the crystal structure by adsorption on specific faces of a crystal in order to slow down its growth [82].

Several additives have been studied as salts inhibitors, and the most prevalent are alkaline ferrocyanides and phosphorous-containing species [82].

Ferrocyanide has been widely studied as a modifier of sodium chloride and sodium sulphate in stone materials. It is able to change the transport of salt solutions, in order to promote the salt crystallization on the stone surface, rather than in the bulk. In addition, ferrocyanide is able to modify the crystal habit, reducing the adhesion of the salts to the surface, therefore reducing the damage to the stone [83, 84].

Citrate and the phosphorylated compounds can control the crystallization of several salts, being effective under various microclimatic conditions. Similar to ferrocyanides, they induce salts crystallization on the stone surface, where very high supersaturation conditions occur. These additives were tested on Globigerina limestone, and they successfully decreased the sodium sulphate growth, reducing crust detachment from the surface [85]. An aqueous solution of an organic phosphonate was tested onsite in the San Jeronimo Monastery (Granada, Spain), with the aim to explore its effectiveness against the severe salt damage of the biomicritic limestone and calcarenite substrates [86]. The building was affected by several salts (sulphates, gypsum, nitrates, and chlorides), with magnesium sulphates being the most diffused ones. The treatment was sprayed on the surface, and the preliminary results indicated that the efflorescence content and the stone damage were reduced within 7 months.

Other compounds have been proposed and tested as salts growth inhibitors: surfactants, borax, and biodegradable polymeric coatings.

Despite the potential benefits and promising results obtained from salts growth inhibitors in laboratory tests, there are not specific protocols and materials to be used in stone conservation, and only few onsite applications are reported.

5.3 Innovative Protective Treatments

In the last decades, a lot of effort has been invested in the synthesis of innovative treatments for stone conservation.

Since the 1980s, scientific research has been working on nanomaterials for several applications, including built heritage conservation. Nanostructured materials are very versatile, and the possibility to tailor their features at the atomic level has led to new understanding of the mechanisms at the nanoscale and new research challenges. This has allowed the design of specific nanomaterials for heritage conservation. These materials exhibit enhanced and innovative functional properties, and they show high physico-chemical compatibility with the original substrates. Compared to traditional conservation treatments, several classes of nanomaterials show less toxicity and have less impact on both the workers and the environment [87], although limited data about long-term human and environment exposures are available, and much research on the impact of nanoparticles is still ongoing. Thanks to their higher surface area, nanomaterials are more reactive, thus they show improved effectiveness in their main properties (e.g. in nanolime consolidants a reduction of carbonation reaction time occurs, compared to traditional lime). Another advantage of nanomaterials is that they improve the conservation interventions and allow a more controlled and efficient release of the material on the surface to be treated. These innovative materials also result in improved sustainability and increased social and economic benefits.

To fulfil every requirement of a treatment for stone conservation, a multidisciplinary approach involving expertise from different scientific disciplines, including materials science, chemistry, geology, microbiology, engineering, architecture, and heritage conservation, is required.

In a recent book, an overview of the current trends in the research on cutting-edge treatments and methods for stone conservation is displayed [88].

Despite the great interest and the promising results obtained from laboratory studies of stones treated with nanomaterials, little data about their effectiveness and durability after natural weathering is available. In addition, few onsite applications of nanomaterials on naturally aged substrates of built heritage are reported, especially regarding the long-term monitoring of their performance.

Improvements in the functionalisation of the nanoparticles, to enhance their interaction with the stone substrate, their stability, and therefore their effectiveness are fundamental to develop tailor-made materials for specific case-studies. In this framework, the synergy of efforts and resources from research centres, universities and industrial manufacturers is crucial to make nanostructured treatments for stone conservation available on the market. This will allow for the extensive use of the products by the conservators, their testing in trial areas, and the collection of information about the monitoring of their effectiveness and durability.

In the field of stone protection, nanoparticles with specific functional properties have been applied in aqueous or solvent dispersions or embedded in polymers or inorganic compounds (nanocomposites). Nanoparticles have been used to design hybrid coatings, with the aim of decreasing the stone wettability and reduce the water absorption, resulting in the increase of the surface roughness and the creation of superhydrophobic and superoleophobic features. In addition, photocatalytic, self-cleaning, and antifouling treatments have been developed by using titania, silver, zinc oxide, and copper oxide nanoparticles. Protective treatments based on calcium oxalate nanoparticles have also been set-up to confer enhanced acid resistance to the treated stone surfaces.

5.3.1 Superhydrophobic Coatings

Adding nanoparticles in a polymeric matrix results in the production of nanocomposites, which can to enhance the protection effectiveness and hydrophobicity of treated stone. Once these surfaces are exposed to rainfall, water forms spherical droplets which roll away, removing dust and particulate matter with them, before water evaporation, producing the so called superhydrophobic (water contact angle > 150°) surfaces. This phenomenon is known as "Lotus leaf effect", and it is used in nature by some plants and animals to prevent water adhesion. The addition of nanoparticles in polymeric coatings increases the surface roughness, without affecting the substrate morphology, resulting in enhanced water repellency.

Several formulations of nanocomposites have been developed, using different polymers (acrylates, fluorinated polymers, and siloxanes) and nanoparticles (silica, alumina, titania, etc.), which display enhanced protection performance. These superhydrophobic treatments are also able to provide additional functional properties (photocatalytic and self-cleaning) to the stone, reducing the interaction with dust particles and pollutants [89–93].

The first method was published in 2007, and since then, improved formulations were developed and successfully applied on several types of stone [26]. These products can be applied by brush or by spray, and they can be used on large areas under ambient conditions. The methodology is very flexible, and it allows for tuning of the surface roughness by modifying the concentrations of nanoparticles in the formulations, according to the properties of the substrates.

Siloxane-based coatings loaded with nanoparticles provided promising results from laboratory tests once applied on sandstones and marbles [26]. Indeed, the treated surfaces show high static contact angle and low contact angle hysteresis, and high reduction of water absorption by capillarity. In addition to superhydrophobicity, the treated surfaces can exhibit superoleophobic and oil repellent properties. The possibility to select the most appropriate concentration of nanoparticles in the polymeric matrix allows avoiding the negative impact on the aesthetic properties and water vapour transport properties of the stone substrates. Evaluation of the stability of these protective treatments under accelerated ageing and natural weathering, and the assessment of their performance in trial areas in historical buildings are crucial steps before making the formulations available to the conservators.

5.3.2 Antifouling Treatments

Biodeterioration is one of the main degradation factors of stone surfaces in historical buildings and archaeological sites. In recent years, nanostructured metal oxides have been employed as aqueous/solvent dispersion or in the design of antifouling treatments (consolidants and protective treatments) for stone conservation (Fig. 5.7).

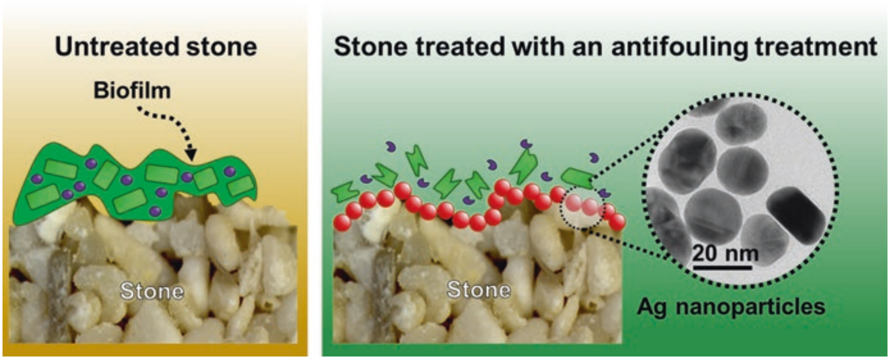


Fig. 5.7 Schematic representation of biofilm formation on untreated stone surfaces (on the left), and the antifouling properties of surfaces treated with silver (Ag) nanoparticles (on the right), together with Transmission Electron Microscopy (TEM) image of the nanoparticles

Silver nanoparticles have been used because of their effective antimicrobial properties to set-up bactericidal coatings for several materials in different fields such as medicine, cosmetics, textile industry, and environmental remediation. The antimicrobial properties of silver nanoparticles are due to their ability to inhibit protein synthesis and DNA replication, and to destroy the bacterial cell walls and membranes.

Promising results in the inhibition of microbial colonization have been obtained from the use of silver nanoparticles combined with a silane-based grafting agent on Serena sandstone stone [94]. Citrate-capped silver nanoparticles alone or in mixture with titania nanoparticles were able to prevent biofilm colonization by more than 70% when applied on several limestones [95]. The concentration of nanoparticles in the formulations should be taken into account to avoid significant alteration of the aesthetic appearance of the stone surfaces.

Moreover, a nanocomposite prepared with copper nanoparticles and a commercial product based on ethyl silicate and polysiloxane oligomers was effective in bioremediation and inhibition of biofilm formation, showing good durability as a bioactive system, thanks to the continuous and controlled release of biocide copper ions on the stone surfaces [96]. Same as for silver nanoparticles, copper nanoparticles have a dark colour, and this can limit their application in high concentration on light coloured stones.

Zinc oxide (ZnO) nanoparticles exhibit antibacterial and antifungal properties. The use of dispersions of calcium hydroxide particles, with zinc oxide and titania nanoparticles proved to be an effective antifungal treatment, under dark and illuminated exposures [97]. ZnO nanoparticles were effective in preventing biological growth if applied alongside tetraethoxysilane and polysiloxanes, keeping the biocide activity for a long timeframe [98].

5.3.3 Photocatalytic Treatments

Titania nanoparticles (nano-TiO_2) are the most popular semiconductor used for self-cleaning and depolluting applications, thanks to their availability, high chemical and thermal stability, and low toxicity and cost. Anatase, rutile and brookite are the three main crystalline phases of titania, and among them, anatase and rutile are the most commonly used ones, as they are more photoactive and stable.

When TiO_2 absorbs photons from sunlight or artificial light sources, pairs of electrons and holes are produced. Reactive radicals are formed on its surface; they promote the decomposition of organic molecules, and the oxidation or reduction of inorganic compounds. Compared to other semiconductors, nano-TiO_2 also exhibits a superhydrophilic behaviour, which results in the adsorption of OH^- groups on the surface, which, in turn, adsorb water and prevent the contact between the surface and adsorbed contaminants. This promotes an easy removal of soiling and degraded pollutants, making the surface "self-cleaning" (Fig. 5.8). In addition, since biofilm

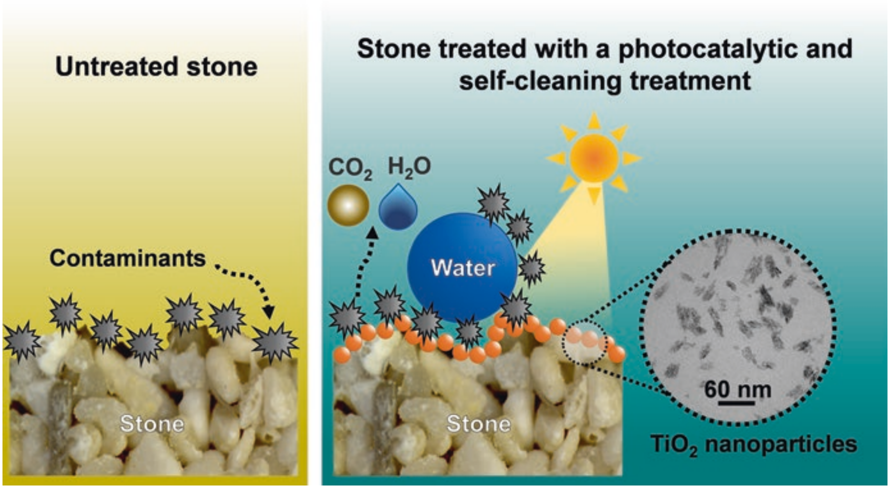


Fig. 5.8 Schematic representation of pollutants contamination of stone surfaces (on the left), and the photocatalytic and self-cleaning properties of surfaces treated with titania (TiO_2) nanoparticles (on the right), together with Transmission Electron Microscopy (TEM) image of the nanoparticles

is composed of organic compounds, surfaces treated with nano-TiO_2 also have antibacterial properties.

Two methodologies have been identified for the set-up of treatments with nano-TiO_2 for stone protection [10]. The first methodology includes hydrophilic dispersions of nano-TiO_2 in different solvents (e.g., water, alcohol, ethylene glycol), and they have been applied on compact limestones, marble, and travertine [99, 100]. The use of dispersions does not affect the natural hydrophilic behaviour of stone substrates. However, nanoparticles exhibit poor adhesion, and they can be easily washed away by rain, thus compromising their performance. To prevent the penetration of nanoparticles in the stone pores and to avoid their leaching, layered treatments based on tetraethyl orthosilicate and nano-TiO_2 were proposed and successfully tested on a porous calcarenite and marble [101].

The second approach is based on nanocomposites, in which nanoparticles are dispersed in a polymeric or inorganic matrix, in order to improve the adhesion of nanoparticles to the substrate and promote a homogenous dispersion. Polymers based on silanes and polysiloxanes, fluorinated or partially fluorinated polymers and acrylics have been employed to confer hydrophobic properties [42, 91, 102–104]. Hybrid treatments based on nano-TiO_2 dispersed in organic and inorganic matrices were designed for stone consolidation and protection [33, 105, 106]. In addition, nano-TiO_2 were incorporated in hydroxyapatite coatings in order to graft them to the stone surface [107]. One of the drawbacks of polymer-based nanocomposites is that the organic binder can be subject to photocatalytic degradation. For this reason, a balance between high photoactivity and stability of the formulations should be achieved [10].

The evaluation of the durability of these treatments once applied onsite and exposed to natural weathering is a fundamental requirement to be taken into account in built heritage conservation. Few studies evaluated their stability after accelerated weathering cycles in order to assess their photostability and resistance to rain-wash [69, 108–110]. Laboratory experiments indicate that treatments based on nano-TiO_2 retain their photocatalytic properties, only when the nanoparticles are embedded in polymeric and inorganic media. In particular, if the polymeric treatments are able to penetrate and coat the stone pores, the protective and photocatalytic properties are not compromised, although photochemical degradation of the polymeric matrix occurs on the stone surface [110]. The alkyl-silica matrix proves to be suitable to ensure the stability of the nanoparticles, which were not removed after simulated rain washout [110].

Field exposure of treated compact limestone in an urban environment for 12 months proved the good performance of photocatalytic nanocomposites in preventing soiling accumulation [63]. However, dispersion of nano-TiO_2 applied on a marble surface and naturally weathered for 1 year exhibited brittleness, low adhesion to the surfaces, and low performance in soiling reduction [48].

Finally, promising results were achieved on the application of several nano-TiO_2 based treatments on marble surfaces on the façade of Monza Cathedral (Italy), displaying good compatibility and protection efficacy [21]. The obtained results prove the importance of a long-term monitoring of the treated surfaces to evaluate their suitability for the conservation of architectural heritage.

5.4 Conclusions

The protection of stone heritage is a challenging task, as the most suitable treatment needs to be selected considering the stone properties (mineralogical composition, porosity features, and state of preservation), the product characteristics (chemical composition, viscosity, density), and the environmental factors to which the treated surfaces are exposed.

For these reasons, each conservation intervention needs to be considered on a case-by-case basis. Testing of several formulations onsite on trial areas is crucial to evaluate and select the most appropriate materials and methods, to be implemented in the conservation project and scaled-up. Only the synergy of expertise from different scientific areas, which include materials science, architecture, conservation, geology, and biology, can help to solve complex problems and bridge the gaps between laboratory studies and practical interventions.

Promising results have been achieved by innovative protective treatments, which, thanks to their unique properties (antifouling, photocatalytic, depolluting) and improved sustainability, will have an important role in future research outlooks.

A multidisciplinary approach needs to be followed not only in the design of innovative materials, which take into consideration the important requirements of novel formulations, but also in the testing and monitoring of their long-term performance once applied on naturally weathered architectural surfaces.

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References

1. Smith BJ, McCabe S, McAllister D, Adamson C, Viles HA, Curran JM. A commentary on climate change, stone decay dynamics and the 'greening' of natural stone buildings: new perspectives on 'deep wetting'. Environ Earth Sci. 2011;63(7):1691–1700. https://doi.org/10.1007/s12665-010-0766-1.
2. Basu S, Orr SA, Aktas YD. A Geological Perspective on Climate Change and Building Stone Deterioration in London: Implications for Urban Stone-Built Heritage Research and Management. Atmos. 2020;11(8):788.
3. Bonazza A, Messina P, Sabbioni C, Grossi CM, Brimblecombe P. Mapping the impact of climate change on surface recession of carbonate buildings in Europe. Sci Total Environ. 2009;407(6):2039–2050. https://doi.org/10.1016/j.scitotenv.2008.10.067.
4. Waller R. Conservation risk assessment: a strategy for managing resources for preventive conservation. Stud Conserv. 1994;39(Supplement-2):12–16. https://doi.org/10.1179/sic.1994.39.Supplement-2.12.
5. Corfield M. Preventive conservation for archaeological sites. Stud Conserv. 1996;41(Supplement-1):32–37. doi:https://doi.org/10.1179/sic.1996.41.Supplement-1.32.
6. EN 16096:2012. Conservation of cultural property – Condition survey and report of built cultural heritage. European Committee for Standardization; 2012.
7. Charola AE. Water Repellents and Other "Protective" Treatments: A Critical Review. Hydrophobe III – 3rd International Conference on Surface Technology with Water Repellent Agents. Hannover: Aedificatio Publishers; 2001.
8. Martín-Gil J, Ramos-Sánchez MC, Martín-Gil FJ. Ancient pastes for stone protection against environmental agents. Stud Conserv. 1999;44(1):58–62. https://doi.org/10.1179/sic.1999.44.1.58.
9. Doehne EF, Price CA. Stone conservation: an overview of current research. Research in conservation. Los Angeles: Getty Conservation Institute; 2010.
10. Toniolo L, Gherardi F. The protection of marble surfaces: the challenge to develop suitable nanostructured treatments. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing; 2018. p. 57–78.
11. Hansen CM. Water transport and condensation in fluoropolymer films. Prog Org Coat. 2001;42(3):167–178. https://doi.org/10.1016/S0300-9440(01)00168-0.
12. Ferreira Pinto AP, Delgado Rodrigues J. Assessment of the durability of water repellents by means of exposure tests. In: V F, editor. Proceedings of the 9th international congress on deterioration and conservation of stone, 19–24 June. Venice: Elsevier; 2000. p. 273–285.
13. Odgers D, Henry A. Practical Building Conservation: Stone. Ashgate; 2012.
14. Turk J, Mauko Pranjić A, Hursthouse A, Turner R, Hughes JJ. Decision support criteria and the development of a decision support tool for the selection of conservation materials for the built cultural heritage. J Cult Herit. 2019;37:44–53. https://doi.org/10.1016/j.culher.2018.10.001.
15. Delgado Rodrigues J, Grossi A. Indicators and ratings for the compatibility assessment of conservation actions. J Cult Herit. 2007;8(1):32–43. https://doi.org/10.1016/j.culher.2006.04.007.

16. Casadio F, Toniolo L. Polymer Treatments for Stone Conservation: Methods for Evaluating Penetration Depth. J Am Inst Conservat. 2004;43(1):3–21. https://doi.org/10.2307/3179848.
17. Alvarez de Buergo Ballester M, Fort González R. Basic methodology for the assessment and selection of water-repellent treatments applied on carbonatic materials. Prog Org Coat. 2001;43(4):258–66. https://doi.org/10.1016/S0300-9440(01)00204-1.
18. Roveri M, Gherardi F, Brambilla L, Castiglioni C, Toniolo L. Stone/Coating Interaction and Durability of Si-Based Photocatalytic Nanocomposites Applied to Porous Lithotypes. Materials (Basel). 2018;11(11). https://doi.org/10.3390/ma11112289.
19. EN 16581:2014. Conservation of Cultural Heritage — Surface protection for porous inorganic materials — Laboratory test methods for the evaluation of the performance of water repellent products. European Committee for Standardization; 2014.
20. Praticò Y, Caruso F, Delgado Rodrigues J, Girardet F, Sassoni E, Scherer G. W. et al. Stone consolidation: a critical discussion of theoretical insights and field practice. RILEM Technical Letters. 2020;4(0). https://doi.org/10.21809/rilemtechlett.2019.101.
21. Gherardi F, Gulotta D, Goidanich S, Colombo A, Toniolo L. On-site monitoring of the performance of innovative treatments for marble conservation in architectural heritage. Herit Sci. 2017;5(1):4. https://doi.org/10.1186/s40494-017-0118-5.
22. Siegesmund S, Snethlage R, editors. Stone in Architecture. Properties, Durability. Springer; 2014.
23. Gulotta D, Toniolo L. Conservation of the Built Heritage: Pilot Site Approach to Design a Sustainable Process. Heritage. 2019;2(1):797–812.
24. Charola AE. Water-Repellent Treatments for Building Stones: A Practical Overview. APT Bull. 1995;26(2/3):10–17. https://doi.org/10.2307/1504480.
25. Doherty B, Pamplona M, Selvaggi R, Miliani C, Matteini M, Sgamellotti A, et al. Efficiency and resistance of the artificial oxalate protection treatment on marble against chemical weathering. Appl Surf Sci. 2007;253(10):4477–4484. https://doi.org/10.1016/j.apsusc.2006.09.056.
26. Karapanagiotis I, Hosseini M. Superhydrophobic Coatings for the Protection of Natural Stone. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing; 2018. p. 1–25.
27. Gherardi F, Roveri M, Goidanich S, Toniolo L. Photocatalytic Nanocomposites for the Protection of European Architectural Heritage. Materials. 2018;11(1):65.
28. Tesser E, Antonelli F, Sperni L, Ganzerla R, Maravelaki N-P. Study of the stability of siloxane stone strengthening agents. Polym Degrad Stab. 2014;110:232–240. https://doi.org/10.1016/j.polymdegradstab.2014.08.022.
29. Cappelletti G, Fermo P. 15 – Hydrophobic and superhydrophobic coatings for limestone and marble conservation. In: Montemor MF, editor. Smart Composite Coatings and Membranes. Woodhead Publishing; 2016. p. 421–452.
30. Lettieri M, Masieri M. Performances and Coating Morphology of a Siloxane-Based Hydrophobic Product Applied in Different Concentrations on a Highly Porous Stone. Coatings. 2016;6(4):60.
31. Wheeler G. Alkoxysilanes and the Consolidation of Stone. Research in Conservation. Los Angeles: Getty Conservation Insitute; 2005.
32. Pinho L, Elhaddad F, Facio DS, Mosquera MJ. A novel TiO_2–SiO_2 nanocomposite converts a very friable stone into a self-cleaning building material. Appl Surf Sci. 2013;275(0):389–96. https://doi.org/10.1016/j.apsusc.2012.10.142.
33. Kapridaki C, Maravelaki-Kalaitzaki P. TiO_2–SiO_2–PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection. Prog Org Coat. 2013;76(2–3):400–410. https://doi.org/10.1016/j.porgcoat.2012.10.006.
34. Salvadori B, Pinna D, Porcinai S. Performance evaluation of two protective treatments on salt-laden limestones and marble after natural and artificial weathering. Environ Sci Pollut Res. 2014;21(3):1884–1896. https://doi.org/10.1007/s11356-013-2032-z.

35. Ferreira Pinto AP, Delgado Rodrigues J. Effectiveness and stability over time of water repellent treatments in carbonate and granitic stones. In: Charola EA, Delgado Rodrigues J, editors. Hydrophobe VII 7th International Conference on Water Repellent Treatment and Protective Surface Technology for Building Materials. Lisbon: LNEC (Laboratório Nacional de Engenharia Civil); 2014. p. 151–160.
36. Sacchi B, Vettori S, Andreotti A, Rampazzi L, Colombini MP, Tiano P. Assessment of Water Repellent Treatments for the Stone of the Matera Cathedral Facade (Italy). Int J Archit Herit. 2020:1–9. https://doi.org/10.1080/15583058.2020.1782532.
37. Tsakalof A, Manoudis P, Karapanagiotis I, Chryssoulakis I, Panayiotou C. Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. J Cult Herit. 2007;8(1):69–72. https://doi.org/10.1016/j.culher.2006.06.007.
38. Vecchiattini R, Fratini F, Rescic S, Riminesi C, Mauri M, Vicini S. The marly limestone, a difficult material to restore: The case of the San Fruttuoso di Capodimonte Abbey (Genoa, Italy). J Cult Herit. 2018;34:1–12. https://doi.org/10.1016/j.culher.2018.01.019.
39. C. Moreau, L. Leroux, V. Vergès-Belmin, G. Fronteau, Barbin V. Which factors influence most the durability of water repellent treatments: stone properties, climate or atmospheric pollution? Hydrophobe V 5th International Conference on Water Repellent Treatment of Building Materials: Aedificatio Publishers; 2008. p. 129–142
40. Orlowsky J, Braun F, Groh M. The Influence of 30 Years Outdoor Weathering on the Durability of Hydrophobic Agents Applied on Obernkirchener Sandstones. Buildings. 2020;10(1):18.
41. Behre S, Littmann K. Measurement of Humidity in Sandstones Treated with Water Repellent Agents Hydrophobe V 5th International Conference on Water Repellent Treatment of Building Materials: Aedificatio Publishers; 2008. p. 75–84.
42. Gherardi F, Goidanich S, Toniolo L. Improvements in marble protection by means of innovative photocatalytic nanocomposites. Prog Org Coat. 2018;121:13–22. https://doi.org/10.1016/j.porgcoat.2018.04.010.
43. Pargoletti E, Motta L, Comite V, Fermo P, Cappelletti G. The hydrophobicity modulation of glass and marble materials by different Si-based coatings. Prog Org Coat. 2019;136:105260. https://doi.org/10.1016/j.porgcoat.2019.105260.
44. Costa D, Delgado Rodrigues J. Testing new water repellent solutions to protect deteriorated granite. In: Charola EA, Delgado Rodrigues J, editors. Hydrophobe VII 7th International Conference on Water Repellent Treatment and Protective Surface Technology for Building Materials. Lisbon: LNEC (Laboratório Nacional de Engenharia Civil); 2014. p. 179–188.
45. Kronlund D, Lindén M, Smått J-H. A polydimethylsiloxane coating to minimize weathering effects on granite. Constr Build Mater. 2016;124:1051–1058. https://doi.org/10.1016/j.conbuildmat.2016.08.146.
46. Roby T. *In-situ* assessment of surface consolidation and protection treatments of marble monuments in Rome in the 1980s, with particular reference to two treatments with Paraloid B72. In: Riederer J, editor. Eighth International Congress on Deterioration and Conservation of Stone. Berlin: Moller Druck und Verlag; 1996. p. 1015–1028.
47. Braun F, Orlowsky J, Brüggerhoff S. Analyzing Near-Surface Regions of Hydrophobic and Long-Term Weathered Natural Stones at Microscopic Scale. Heritage. 2020;3(2):457–473.
48. Becherini F, Pastorelli G, Valotto G, Gambirasi A, Bianchin S, Favaro M. Effects of protective treatments on particle deposition and colour variation in stone surfaces exposed to an urban environment. Prog Org Coat. 2017;112:75–85. https://doi.org/10.1016/j.porgcoat.2017.06.029.
49. Charola AE, Rodrigues JD, Anjos MV. An unsatisfactory case of water repellents applied to control biocolonization. Hydrophobe V 5th International Conference on Water Repellent Treatment of Building Materials: Aedificatio Publisher; 2008. p. 117–128.
50. Gherardi F, Kapridaki C, Roveri M, Gulotta D, Maravelaki PN, Toniolo L. The deterioration of Apuan white marble in contemporary architectural context. J Cult Herit. 2019;35:297–306. https://doi.org/10.1016/j.culher.2018.06.008.

51. Maravelaki P-N, Toniolo L, Gherardi F, Kapridaki C, Arabatzis I. The Oslo Opera House – Condition Analysis and Proposal for Cleaning, Protection and Maintenance of Exterior Marble. Springer International Publishing; 2019. p. 104–116.
52. Carretti E, Dei L. Physicochemical characterization of acrylic polymeric resins coating porous materials of artistic interest. Prog Org Coat. 2004;49(3):282–289. https://doi.org/10.1016/j.porgcoat.2003.10.011.
53. Borgia GC, Camaiti M, Cerri F, Fantazzini P, Piacenti F. Hydrophobic Treatments for Stone Conservation – Influence of the Application Method on Penetration, Distribution and Efficiency. Stud Conserv. 2003;48(4):217–226. https://doi.org/10.1179/sic.2003.48.4.217.
54. Chiantore O, Trossarelli L, Lazzari M. Photooxidative degradation of acrylic and methacrylic polymers. Polymer. 2000;41(5):1657–1668. https://doi.org/10.1016/s0032-3861(99)00349-3.
55. Chiantore O, Lazzari M. Photo-oxidative stability of paraloid acrylic protective polymers. Polymer. 2001;42(1):17–27.
56. Favaro M, Mendichi R, Ossola F, Russo U, Simon S, Tomasin P, et al. Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering. Polym Degrad Stab. 2006;91(12):3083–3096. https://doi.org/10.1016/j.polymdegradstab.2006.08.012.
57. Cappitelli F, Nosanchuk JD, Casadevall A, Toniolo L, Brusetti L, Florio S, et al. Synthetic Consolidants Attacked by Melanin-Producing Fungi: Case Study of the Biodeterioration of Milan (Italy) Cathedral Marble Treated with Acrylics. Appl Environ Microbiol. 2007;73(1):271–277. https://doi.org/10.1128/aem.02220-06.
58. Ciardelli F, Aglietto M, Castelvetro V, Chiantore O, Toniolo L. Fluorinated polymeric materials for the protection of monumental buildings. Macromol Symp. 2000;152(1):211–222. https://doi.org/10.1002/1521-3900(200003)152:1<211::aid-masy211>3.0.co;2-u.
59. Toniolo L, Poli T, Castelvetro V, Manariti A, Chiantore O, Lazzari M. Tailoring new fluorinated acrylic copolymers as protective coatings for marble. J Cult Herit. 2002;3(4):309–316. https://doi.org/10.1016/S1296-2074(02)01240-2.
60. Poli T, Toniolo L, Chiantore O. The protection of different Italian marbles with two partially flourinated acrylic copolymers. Appl Phys A. 2004;79(2):347–351. https://doi.org/10.1007/s00339-004-2530-4.
61. Sacchi B, Giannini L, Frediani M, Rosi L, Frediani P. Methyl acrylate polymers as suitable materials for the conservation of stone: performance improvements through atom transfer radical polymerization. J Coat Technol Res. 2013;10(5):649–657. https://doi.org/10.1007/s11998-013-9495-1.
62. Licchelli M, Malagodi M, Weththimuni ML, Zanchi C. Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure. Prog Org Coat. 2013;76(2):495–503. https://doi.org/10.1016/j.porgcoat.2012.11.005.
63. Colangiuli D, Lettieri M, Masieri M, Calia A. Field study in an urban environment of simultaneous self-cleaning and hydrophobic nanosized TiO_2-based coatings on stone for the protection of building surface. Sci Total Environ. 2019;650:2919–2930. https://doi.org/10.1016/j.scitotenv.2018.10.044.
64. García O, Rz-Maribona I, Gardei A, Riedl M, Vanhellemont Y, Santarelli ML, et al. Comparative study of the variation of the hydric properties and aspect of natural stone and brick after the application of 4 types of anti-graffiti. Materiales de Construcción. 2010;60(297):69–82. https://doi.org/10.3989/mc.2010.45507.
65. García O, Malaga K. Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials. J Cult Herit. 2012;13. https://doi.org/10.1016/j.culher.2011.07.004.
66. Carmona-Quiroga PM, Martínez-Ramírez S, Sánchez-Cortés S, Oujja M, Castillejo M, Blanco-Varela MT. Effectiveness of antigraffiti treatments in connection with penetration depth determined by different techniques. J Cult Herit. 2010;11(3):297–303. https://doi.org/10.1016/j.culher.2009.09.006.

67. Lettieri M, Masieri M. Surface characterization and effectiveness evaluation of anti-graffiti coatings on highly porous stone materials. Appl Surf Sci. 2014;288:466–477. https://doi.org/10.1016/j.apsusc.2013.10.056.
68. Ricci C, Gambino F, Nervo M, Piccirillo A, Scarcella A, De Stefanis A, et al. Anti-Graffiti Coatings on Stones for Historical Buildings in Turin (NW Italy). Coatings. 2020;10(6):582.
69. Carmona-Quiroga PM, Martínez-Ramírez S, Viles HA. Efficiency and durability of a self-cleaning coating on concrete and stones under both natural and artificial ageing trials. Appl Surf Sci. 2018;433:312–320. https://doi.org/10.1016/j.apsusc.2017.10.052.
70. Rabea AM, Mohseni M, Mirabedini SM, Tabatabaei MH. Surface analysis and anti-graffiti behavior of a weathered polyurethane-based coating embedded with hydrophobic nano silica. Appl Surf Sci. 2012;258(10):4391–4396. https://doi.org/10.1016/j.apsusc.2011.12.123.
71. Hansen E, Doehne E, Fidler J, Larson J, Martin B, Matteini M, et al. A review of selected inorganic consolidants and protective treatments for porous calcareous materials. Reviews in Conservation. 2003;4(Supplement-1):13–25.
72. King HE, Mattner DC, Plümper O, Geisler T, Putnis A. Forming Cohesive Calcium Oxalate Layers on Marble Surfaces for Stone Conservation. Cryst Growth Des. 2014;14(8):3910–3917. https://doi.org/10.1021/cg500495a.
73. Burgos-Cara A, Ruiz-Agudo E, Rodriguez-Navarro C. Effectiveness of oxalic acid treatments for the protection of marble surfaces. Mater Des. 2017;115:82–92. https://doi.org/10.1016/j.matdes.2016.11.037.
74. Mudronja D, Vanmeert F, Hellemans K, Fazinic S, Janssens K, Tibljas D, et al. Efficiency of applying ammonium oxalate for protection of monumental limestone by poultice, immersion and brushing methods. Appl Phys A. 2013;111(1):109–119. https://doi.org/10.1007/s00339-012-7365-9.
75. Dreyfuss T, Cassar J. Ammonium Oxalate Treatment Application in the Presence of Soluble Salts: Laboratory Results on Soft Limestone. In: Toniolo L, Boriani M, Guidi G, editors. Built Heritage: Monitoring Conservation Management. Springer International Publishing; 2015. p. 403–412.
76. Dreyfuss T. Interactions on site between powdering porous limestone, natural salt mixtures and applied ammonium oxalate. Herit Sci. 2019;7(1):5. https://doi.org/10.1186/s40494-019-0247-0.
77. Doherty B, Pamplona M, Miliani C, Matteini M, Sgamellotti A, Brunetti B. Durability of the artificial calcium oxalate protective on two Florentine monuments. J Cult Herit. 2007;8(2):186–192. https://doi.org/10.1016/j.culher.2006.12.002.
78. Sassoni E. Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review. Materials. 2018;11(4):557.
79. Graziani G, Sassoni E, Scherer GW, Franzoni E. Resistance to simulated rain of hydroxyapatite- and calcium oxalate-based coatings for protection of marble against corrosion. Corros Sci. 2017;127:168–174. https://doi.org/10.1016/j.corsci.2017.08.020.
80. Michette M, Viles H, Vlachou-Mogire C, Angus I. Assessing the Long-term Success of Reigate Stone Conservation at Hampton Court Palace and the Tower of London. Stud Conserv. 2020:1–8. https://doi.org/10.1080/00393630.2020.1752427.
81. Charola AE, Centeno SA, Normandin K. The New York Public Library: Protective Treatment for Sugaring Marble. J Archit Conserv. 2010;16(2):29–44. https://doi.org/10.1080/13556207.2010.10785068.
82. Bracciale MP, Sammut S, Cassar J, Santarelli ML, Marrocchi A. Molecular Crystallization Inhibitors for Salt Damage Control in Porous Materials: An Overview. Molecules. 2020;25(8). https://doi.org/10.3390/molecules25081873.
83. Granneman SJC, Lubelli B, van Hees RPJ. Mitigating salt damage in building materials by the use of crystallization modifiers – a review and outlook. J Cult Herit. 2019;40:183–194. https://doi.org/10.1016/j.culher.2019.05.004.
84. Selwitz C, Doehne E. The evaluation of crystallization modifiers for controlling salt damage to limestone. J Cult Herit. 2002;3(3):205–216. https://doi.org/10.1016/S1296-2074(02)01182-2.

85. Cassar J, Marrocchi A, Santarelli ML, Muscat M. Controlling crystallization damage by the use of salt inhibitors on Malta's limestone. Materiales de Construcción. 2008;58(289–290):281–293. https://doi.org/10.3989/mc.2008.v58.i289-290.83.
86. Ruiz-Agudo E, Lubelli B, Sawdy A, van Hees R, Price C, Rodriguez-Navarro C. An integrated methodology for salt damage assessment and remediation: the case of San Jerónimo Monastery (Granada, Spain). Environ Earth Sci. 2011;63(7):1475–1486. https://doi.org/10.1007/s12665-010-0661-9.
87. Baglioni P, Carretti E, Chelazzi D. Nanomaterials in art conservation. Nat Nano. 2015;10(4):287–290. https://doi.org/10.1038/nnano.2015.38.
88. Hosseini M, Karapanagiotis I. Advanced Materials for the Conservation of Stone. Springer International Publishing; 2018.
89. Manoudis P, Papadopoulou S, Karapanagiotis I, Tsakalof A, Zuburtikudis I, Panayiotou C. Polymer-Silica nanoparticles composite films as protective coatings for stone-based monuments. J Phys Conf Ser. 2007;61(1):1361.
90. Manoudis PN, Karapanagiotis I, Tsakalof A, Zuburtikudis I, Kolinkeová B, Panayiotou C. Superhydrophobic films for the protection of outdoor cultural heritage assets. Appl Phys A. 2009;97(2):351–360. https://doi.org/10.1007/s00339-009-5233-z.
91. Manoudis PN, Tsakalof A, Karapanagiotis I, Zuburtikudis I, Panayiotou C. Fabrication of super-hydrophobic surfaces for enhanced stone protection. Surf Coat Technol. 2009;203(10–11):1322–1328. https://doi.org/10.1016/j.surfcoat.2008.10.041.
92. Karapanagiotis I, Manoudis PN, Savva A, Panayiotou C. Superhydrophobic polymer-particle composite films produced using various particle sizes. Surf Interface Anal. 2012;44(7):870–875. https://doi.org/10.1002/sia.4930.
93. Facio DS, Mosquera MJ. Simple Strategy for Producing Superhydrophobic Nanocomposite Coatings In Situ on a Building Substrate. ACS Appl Mater Inter. 2013;5(15):7517–7526. https://doi.org/10.1021/am401826g.
94. Bellissima F, Bonini M, Giorgi R, Baglioni P, Barresi G, Mastromei G, et al. Antibacterial activity of silver nanoparticles grafted on stone surface. Environ Sci Pollut Res. 2014;21(23):13278–13286. https://doi.org/10.1007/s11356-013-2215-7.
95. Becerra J, Mateo M, Ortiz P, Nicolás G, Zaderenko AP. Evaluation of the applicability of nano-biocide treatments on limestones used in cultural heritage. J Cult Herit. 2019;38:126–135. https://doi.org/10.1016/j.culher.2019.02.010.
96. Ditaranto N, Loperfido S, van der Werf I, Mangone A, Cioffi N, Sabbatini L. Synthesis and analytical characterisation of copper-based nanocoatings for bioactive stone artworks treatment. Anal Bioanal Chem. 2011;399(1):473–481. https://doi.org/10.1007/s00216-010-4301-8.
97. Gómez-Ortíz N, De la Rosa-García S, González-Gómez W, Soria-Castro M, Quintana P, Oskam G, et al. Antifungal Coatings Based on $Ca(OH)_2$ Mixed with ZnO/TiO_2 Nanomaterials for Protection of Limestone Monuments. ACS Appl Mater Inter. 2013;5(5):1556–1565. https://doi.org/10.1021/am302783h.
98. van der Werf I, Ditaranto N, Picca R, Sportelli M, Sabbatini L. Development of a novel conservation treatment of stone monuments with bioactive nanocomposites. Herit Sci. 2015;3(1):1–9. https://doi.org/10.1186/s40494-015-0060-3.
99. Quagliarini E, Bondioli F, Goffredo GB, Cordoni C, Munafò P. Self-cleaning and de-polluting stone surfaces: TiO2 nanoparticles for limestone. Constr Build Mater. 2012;37(0):51–57. https://doi.org/10.1016/j.conbuildmat.2012.07.006.
100. Gherardi F, Colombo A, D'Arienzo M, Credico B, Goidanich S, Morazzoni F, et al. Efficient self-cleaning treatments for built heritage based on highly photo-active and well-dispersible TiO_2 nanocrystals. Microchem J. 2016;126. https://doi.org/10.1016/j.microc.2015.11.043.
101. Gherardi F, Goidanich S, Dal Santo V, Toniolo L. Layered Nano-TiO_2 Based Treatments for the Maintenance of Natural Stones in Historical Architecture. Angew Chem Int Ed. 2018;57(25):7360–7363. https://doi.org/10.1002/anie.201712752.
102. Cappelletti G, Fermo P, Camiloni M. Smart hybrid coatings for natural stones conservation. Prog Org Coat. 2015;78:511–516. https://doi.org/10.1016/j.porgcoat.2014.05.029.

103. Colangiuli D, Calia A, Bianco N. Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage. Constr Build Mater. 2015;93:189–196. https://doi.org/10.1016/j.conbuildmat.2015.05.100.
104. La Russa MF, Rovella N, Alvarez de Buergo M, Belfiore CM, Pezzino A, Crisci GM, et al. Nano-TiO_2 coatings for cultural heritage protection: The role of the binder on hydrophobic and self-cleaning efficacy. Prog Org Coat. 2016;91:1–8. https://doi.org/10.1016/j.porgcoat.2015.11.011.
105. Pinho L, Mosquera MJ. Titania-silica nanocomposite photocatalysts with application in stone self-cleaning. J Phys Chem C. 2011;115. https://doi.org/10.1021/jp2074623.
106. Kapridaki C, Pinho L, Mosquera MJ, Maravelaki-Kalaitzaki P. Producing photoactive, transparent and hydrophobic SiO2-crystalline TiO2 nanocomposites at ambient conditions with application as self-cleaning coatings. Applied Catalysis B: Environmental. 2014;156:416–427. https://doi.org/10.1016/j.apcatb.2014.03.042.
107. Sassoni E, D'Amen E, Roveri N, Scherer GW, Franzoni E. Durable Self-Cleaning Coatings for Architectural Surfaces by Incorporation of TiO_2 Nano-Particles into Hydroxyapatite Films. Materials (Basel, Switzerland). 2018;11(2):177. https://doi.org/10.3390/ma11020177.
108. Munafò P, Quagliarini E, Goffredo GB, Bondioli F, Licciulli A. Durability of nano-engineered TiO_2 self-cleaning treatments on limestone. Constr Build Mater. 2014;65(0):218–231. https://doi.org/10.1016/j.conbuildmat.2014.04.112.
109. Calia A, Lettieri M, Masieri M. Durability assessment of nanostructured TiO_2 coatings applied on limestones to enhance building surface with self-cleaning ability. Build Environ. 2016;110:1–10. https://doi.org/10.1016/j.buildenv.2016.09.030.
110. Roveri M, Goidanich S, Toniolo L. Artificial Ageing of Photocatalytic Nanocomposites for the Protection of Natural Stones. Coatings. 2020;10(8):729.

Chapter 6
Mortars for Restoration: Set-up Parameters and Developing Mortar Design Areas

Maria Apostolopoulou and Antonia Moropoulou

Abstract Designing mortars for restoration work is a crucial step in any conservation project. Mortars are complex, composite materials and their characteristics are dependent upon the raw materials used, as well as several design parameters. Especially in the case of monument protection, it is important to design a mortar with required characteristics to ensure its compatibility in relation to the historical materials, and its effectiveness in terms of the restored monument's mechanical performance. In this chapter, first, a discussion is made on the effect of the design parameters and raw materials of a mortar on its characteristics, taking into account international literature. Following this, an interdisciplinary methodological approach is presented, focused on the design of restoration mortars, considering the characteristics of the historical materials of the monument, the environmental stresses it is subjected to, and the vulnerability of the structure to mechanical stresses. This approach considers any architectural or geometric characteristics which may set limitations to which the restoration mortar must abide by. Principal component analysis (PCA) is used to correlate and examine mortar characteristics within a combined space, where compatibility and performance are simultaneously achieved.

Keywords Mortars · PCA · Restoration · Compatibility · Performance · Mortar design

M. Apostolopoulou (✉) · A. Moropoulou
Laboratory of Materials Science & Engineering, School of Chemical Engineering, National Technical University of Athens, Athens, Greece
e-mail: amoropul@central.ntua.gr

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6.1 Introduction: The Importance of Compatibility and Performance of Restoration Mortars

In the beginning of the twentieth century, the use of lime-based mortars was substituted extensively by cement-based mortars [1, 2]. Cement mortars, although presenting positive qualities (fast setting and hardening, high mechanical performance at early ages), proved to be inappropriate for use in restoration projects, as the different physicochemical and mechanical characteristics they present, in relation to traditional building materials, led to the development of stresses, with negative effects on the historical building materials and the longevity of the historical structures and monuments where they were applied [1, 3–5].

Thus, in recent years, the requirement for compatible and performing restoration mortars has emerged, and researchers have shifted their attention to the re-discovery of traditional mortar production techniques [e.g. 1–3, 5–8], as well as methodologies to design compatible and performing restoration mortars [3, 9–12].

Two materials are compatible when the one does not have a negative effect on the other, in any way; thus, compatibility is a complicated term, as it is associated with a variety of characteristics. In order for a restoration mortar to be compatible, it must present:

(i) **chemical** compatibility with the historical materials, thus, not release dangerous compounds or trigger deterioration mechanisms [11, 13, 14];
(ii) **microstructural** compatibility with the historical materials, where a homogenous hygric behavior is required, in order to avoid increase of water intake, accumulation of moisture and/or soluble salts in the historical materials, as well as water vapor permeability issues [15, 16];
(iii) **mechanical** compatibility with the historical building elements, in order to avoid the development of stresses with consequent damage of the weaker historical materials [17];
(iv) **dimensional** compatibility, which is interlinked with the: (a) dynamic modulus of elasticity, and the ability of the mortar to accommodate stresses without the manifestation of cracking, as well as allow the structure as a whole to accommodate movement [18, 19], (b) the thermal expansion coefficient, which must be as close as possible to the historical materials, in order to avoid stresses due to differential dimensional alterations [20], and (c) shrinkage of the restoration mortar, which is associated with dimensional changes during setting and hardening, which could lead to the development of stresses between materials and microcracking within the restoration mortar-matrix [7, 21, 22]; and
(v) **aesthetical** compatibility [11, 12, 23–25], which is assessed in terms of where the applied mortar is visible.

A material is performing when it has the ability to enhance the mechanical performance of a structure, under static and dynamic stresses [17]. Compatibility and performance must always be simultaneously achieved, as a mortar which is not compatible will negatively affect the performance of the other building elements.

On the contrary, a mortar, which is not performing will fail in terms of durability, and will, in the long run, no longer be compatible in the structure as a whole.

In the following subchapters, different aspects of mortar design and selection will be presented, aiming to establish a methodological approach for the design of compatible and performing restoration mortars.

6.2 Mortar Design

6.2.1 Raw Materials and Mortar Mix Design Parameters

Several research studies are available in the international literature on the study of restoration mortars, and particularly, the relationship between the raw materials selected, the mortar mix design, and the developed mortar characteristics. Most studies are not orientated towards a specific case study, but rather towards revealing the behavior of different types of restoration mortars. These studies are increasingly important as a high amount of data is accumulated regarding the behavior of different mortar mixes, which in the future can be utilized in big data management and analysis methods. In most studies, only a general observation is made regarding the compatibility of the designed mortars with historical materials and structures.

In restoration mortar studies, research expands in different directions, examining (i) raw materials, (ii) parameters of synthesis, (iii) curing conditions, and (iv) mortar characteristics after setting and hardening. The production of restoration mortars can be achieved using different raw materials. However, in most research, traditional materials are the materials of choice, as the use of more "modern" materials has in many cases led to the production of mortars incompatible for restoration purposes.

6.2.1.1 Raw Materials

The raw materials selected for restoration purposes must abide by specific criteria [3, 26], and always be in accordance with the standards [27, 28]. The demand for low soluble salts is set for all raw materials, in order to ensure that the restoration mortar does not introduce potentially dangerous soluble salts into the structure.

The most usual binder systems examined are:

(i) aerial lime ($Ca(OH_2)$), in powder or putty form [21, 29], especially in the case where researchers aim to simulate historical lime mortars and examine pure lime mortar systems;
(ii) quicklime (CaO), mainly selected by researchers which aim to simulate the hot lime technology of historical mortars [30, 31];
(iii) aerial lime with the addition of pozzolanic additives, either natural or manufactured, aiming to produce a mortar with enhanced characteristics in relation

to aerial lime mortars, or in cases where a lime-pozzolan mortar is required [7, 22, 32, 33];

(iv) natural hydraulic lime (NHL), NHL2, NHL3.5, NHL5,[1] again, when a mortar with enhanced characteristics is necessary [5, 34–38];

(v) natural hydraulic lime, with the addition of pozzolans [6], especially when early consumption of all free lime (calcium hydroxide) is demanded;

(vi) gypsum, either as the sole binder, or in combination with other binders, such as lime [39, 40];

(vii) clay, either as the sole binder, or combined with another binder, such as lime, aiming to enhance the stability of the mortar [8]; and

(viii) cement, either as the sole binder, or combined with aerial lime, although it should be noted that research has shown that even a small addition of cement to lime mortars is not advisable for restoration purposes [41].

In the relevant research, in many cases, a comparison of either (i) the same binder, procured by a different manufacturer [21, 34], or (ii) different types [5, 35, 41–43] or different forms of binder (for example lime powder vs lime putty [29]), or (iii) combinations of binders [44], is conducted. In the cases where pozzolans are added, a comparison between the use of different pozzolans is carried out [6, 32]. The selection of the binder system plays an important role in the development of a mortar's characteristics, while the characteristics of the added aggregates also influence the final mortar product [23]. Thus, a number of research takes into account the effect of different aggregates on mortar characteristics [21, 36–38, 42, 45, 46]. Aggregates may be differentiated by: (i) their composition, (ii) gradation, (iii) the geometry of the aggregate grains, or all of the above. These parameters influence the characteristics of a fresh mortar, as well as those after setting and hardening. The effects of other additives, such as organic additives, water-repellent agents, etc., on mortar characteristics are also under investigation in mortar research, especially taking into account their use in historical mortars [13, 47–50].

6.2.1.2 Mortar Mix Design Parameters

Mortar mix design parameters examined by most researchers are: (i) the binder to aggregate ratio (B/A) [1, 21, 33, 36, 37, 43, 46], where pozzolanic additives (if present) are considered as part of the binder; and (ii) the amount of water added to the mortars in order to achieve the appropriate consistency, which is linked to workability and high quality application of the mortars, and is usually expressed as the water to binder ratio (W/B) [33, 38, 51]. In some cases, where the influence of an additive is examined, an additional mortar mix parameter is examined, which is (iii) the ratio of the additive (pozzolanic or other) in relation to either the main binder or

[1] *NHL2: low hydraulicity NHL, compressive strength tolerance 2–7 MPa; NHL3.5: moderate hydraulicity NHL, compressive strength tolerance 3.5–10 MPa; NHL5: high hydraulicity NHL, compressive strength tolerance 5–15 MPa, in accordance to EN 459-1* [27].

the total mortar [6, 7, 22, 48, 50], in order to assess its effect on mortar characteristics. It should be noted that, in addition to the W/B ratio, consistency of the fresh mortar must also be noted, as it relates to workability, and thus, good practice and high quality in terms of correct mortar application. All the above parameters influence the mortar characteristics in a different manner, according to the type of binder system and the aggregate characteristics, further complicating mortar design.

6.2.1.3 Curing Conditions

Curing conditions (temperature and relative humidity) during setting and hardening play an important role in the development of a mortar's characteristics. Thus, a number of researchers have examined restoration mortars cured in different humidity conditions [1, 6, 51, 52]. The optimum curing conditions are dependent on the hydraulicity of the binder. Mortars with hydraulic binders develop enhanced characteristics when cured in high humidity environments, especially during early stages where the hydration of hydraulic compounds takes place. On the other hand, when an aerial binder is used, a lower humidity environment is beneficial for the carbonation of calcium hydroxide. In any case, relative humidity must not be under 65%, as even carbonation is delayed [53]. Additionally, it is important to identify the effect of curing conditions on a mortar's characteristics, as each monument is in a different environment. If high relative humidity conditions are necessary, special care can be taken to provide a high humidity environment, *in situ*, for the first days of curing. It is interesting to note that even the respective standards propose different curing regimes (in relation to relative humidity conditions) for the same type of mortar [28, 54].

Thus, mortar design, in terms of raw materials, mortar mix parameters, and curing conditions are examined in the international literature by evaluating these parameters, in accordance to Fig. 6.1. Of course, each researcher examines different

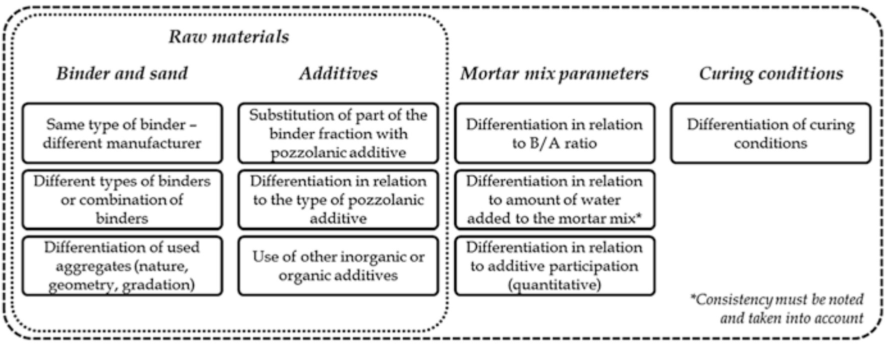

Fig. 6.1 Methodology of mortar design and investigation in international research in relation to different influencing parameters

mortar mixes altering one, or more, of the influencing parameters, according to the focus of each respective research.

A restoration mortar is evaluated in terms of their fresh state characteristics, as well as hardened characteristics, after setting and hardening. It is assessed in terms of compatibility and performance, in relation to its compliance with specific criteria, which are dictated by the specific characteristics of the monument/historical building on which it is to be applied. These issues are further investigated in the next two subchapters.

6.2.2 Mortar Assessment in Fresh and Hardened States

Mortars, independent of their specific use, are assessed in fresh state immediately after mixing, as well as after setting and hardening, in relation to their chemical, mechanical, and physical characteristics.

The most usual fresh state characteristics evaluated are:

(i) *Consistency of fresh mortar*, determined by flow table, in accordance with EN 1015-3 [55]. Consistency is interlinked with workability of the mortar, and, thus, with applicability *in situ*, as well as the high-quality application of the mortar. Each type of mortar, depending on the binder, may present optimum workability at different consistency values [56]. The consistency of a mortar mix increases in a non-linear manner as the W/B ratio increases [57].

(ii) *Air content of fresh mortar*, determined in accordance with EN 1015-7 [58], is the percentage of air entrapped within the mortar during mixing, as it becomes part of the pore structure as the mortar sets and hardens. Although it is known to negatively affect the mechanical strength of a mortar, and, thus, is usually limited by the standards (for example EN 459-1 demands natural hydraulic lime mortars to exhibit air content lower than 5% [27]), some researchers have proven that this alteration in the pore system may be beneficial in cold climates, allowing space for absorbed water to expand in the case of freeze [59].

(iii) Bulk density *of fresh mortar* is determined in accordance with EN 1015-3 [60]. It is an indication of the bulk density that the mortar will acquire after setting and hardening, but most importantly, it can allow for the dimensioning of the restoration project, and the amount of the necessary raw materials.

(iv) Retained water *of the fresh mortar* is determined in accordance with EN 1015-8 [61]. It should be as high as possible, in order to ensure that the mortar system will not be disturbed after application, during the setting and hardening, especially when in contact with porous materials.

Most researchers focus on the mechanical characteristics of a mortar, however, in order for a mortar to be appropriate for use, other characteristics must also be evaluated, as they affect not only compatibility of the restoration mortar with the historical materials, but also hygric performance and durability of the structure as a whole.

The most common mortar characteristics evaluated during and/or after setting and hardening, are:

(i) *Evolution of chemical reactions*, ideally monitored at different mortar ages, up to the time that they are completed (e.g., in lime mortars, when carbonation is complete). The evolution of chemical reactions within the mortar is ideally conducted through thermogravimetric and differential thermal analysis (TG/DTA) in order to obtain both qualitative and quantitative data, while mineralogical analysis should also be conducted, in a complimentary manner, in order to obtain as much information as possible, together with the application of microscopy techniques [5, 7]. Thus, one may study the mortar's hardening products, the hydration process of hydraulic compounds, the evolution of carbonation, and the remaining calcium hydroxide at different mortar ages and evaluate the hydraulicity of the mortar and its stability at different mortar ages. Additionally, the formation of any undesirable/dangerous byproducts can also be investigated.

(ii) *Microstructural characteristics of the restoration mortar* is important not only in terms of achieving compatibility with the historical building materials, but also in terms of ensuring the restoration mortar's durability. Mercury intrusion porosimetry is the optimum method for revealing the microstructure of a mortar, which evaluates the pore size distribution [62–66]. Simpler methods, such as total immersion in water, can also be applied to study basic microstructural characteristics, without, however, obtaining information regarding the characteristics of the pore structure [67].

(iii) Shrinkage *(in relation to volume) of the restoration mortar* is also an important mortar characteristic. This is estimated by comparing the volume of the mortar after setting and hardening in relation to the initial volume of the fresh mortar specimen (i.e., the dimensions of the mold), and it is attributed to different setting and hardening mechanisms [68]. It is expressed as a percentage, and it must be as low as possible. Low shrinkage is attributed to higher quality mortars, as shrinkage can lead to the occurrence of microcracking within the mortar with negative consequences on its mechanical and hygric performance. When applied as joint mortar, low shrinkage ensures minimum movements and occurrence of stresses regarding the structure as a whole [7, 22, 30].

(iv) *Mechanical performance of restoration mortar* is of extremely importance, as it is interlinked with the mechanical performance of the whole structure. Mechanical compatibility with the historical materials must be ensured, while at the same time performance of the structure must be enhanced [68]. The most usual mechanical properties examined are flexural and compressive strength, in accordance to EN1015-11 [54]. It is important to study mechanical properties in relation to time, in order to (i) ensure that the mortar will not develop mechanical strength values that are too high at later mortar ages, thereby deeming it incompatible with the historical materials [69], while also noting that early acquisition is important in some cases, especially in seismic areas [17].

(v) *Hygric behavior of the restoration mortar* is also an important parameter which must be evaluated in the set-up of a restoration mortar. The capillary rise coefficient, which is measured in accordance with EN 1015-18 [70], is especially important, as it is related to the hygric performance of a structure, compatibility issues, comfort of the inhabitants, and, in the long term, durability. Additionally, soluble salts may enter the structure, especially in the case of intense rising damp, thus allowing them to move and accumulate either in the building elements of the structure or at their interface. Therefore, it is important to select a mortar which can achieve a homogenous thermohygric behavior for the structure as a whole, without increasing the water uptake and, at the same time, without preferentially transferring moisture to the historical building materials [71]. Another important hygric characteristic is the water-vapor permeability; it is widely accepted that traditional materials present satisfactory behavior in this sense, allowing breathability, in contrast to more modern cement-based mortars [72].

In the following figures, methodologies for the assessment of restoration mortars in fresh state (Fig. 6.2), as well as after setting and hardening (Fig. 6.3), are presented.

6.2.3 Compatibility and Performance Criteria

Mortars must be assessed in relation to fresh and hardened characteristics, but it is the monument/historical structure which plays the key role in the selection of the appropriate restoration mortar.

In order to ensure compatibility and performance of a restoration mortar, one must first define a multidimensional area of characteristics, within a range of values for different criteria, where a mortar meets both compatibility and performance

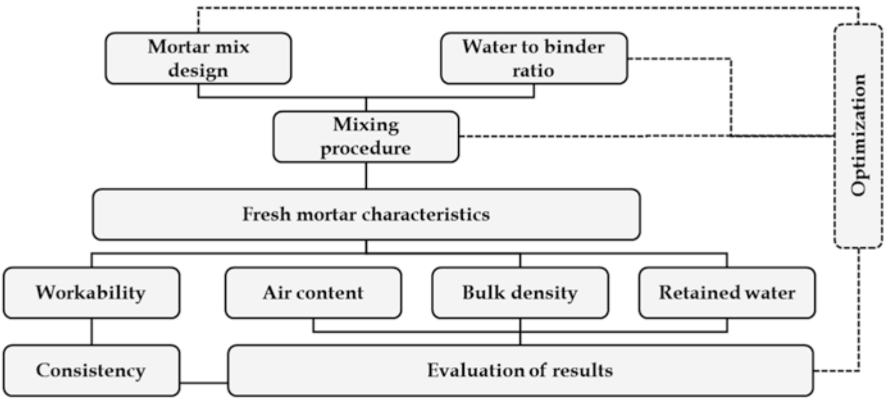

Fig. 6.2 Methodology for the assessment and optimization of fresh mortar characteristics

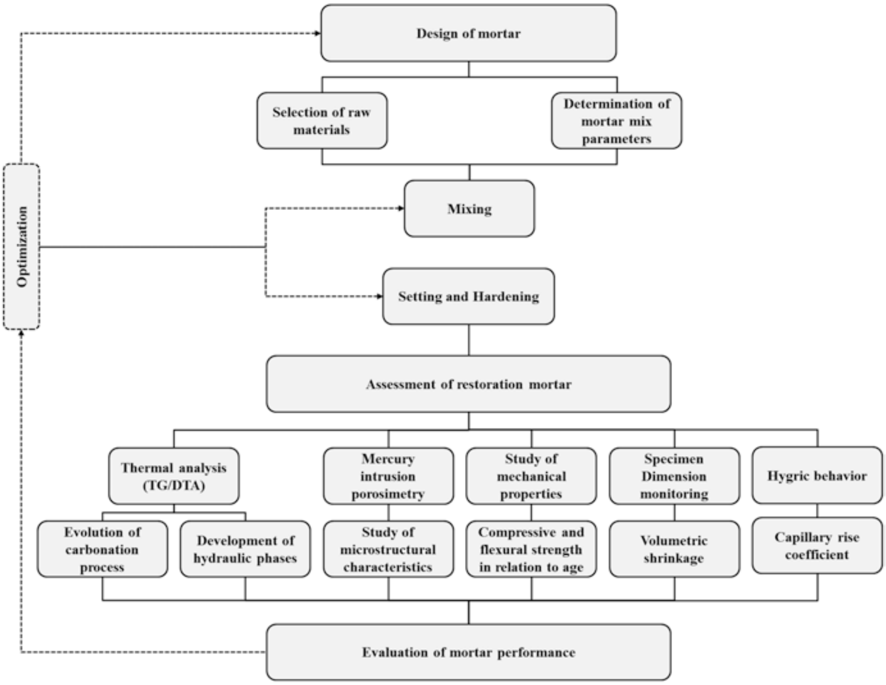

Fig. 6.3 Methodology for the assessment and optimization of hardened mortar characteristics

requirements. This area can only be fully defined within a multidisciplinary framework. Compatibility and performance criteria, regarding different mortar characteristics, are defined according to: (i) the characteristics of the historical mortars; (ii) the characteristics of the main building elements, that are stones and/or bricks; (iii) the environmental loads that the monument/historical structure is subjected to; (iv) the vulnerability of the historical structure to static/dynamic loads; and (v) architectural and geometrical characteristics. These parameters set limitations, to which the restoration mortar must abide by, thus playing a crucial role in its design (Fig. 6.4).

6.2.3.1 The Analysis of Historical Mortars: Synthesis Guidelines, Compatibility, and Performance Criteria

The analysis of the historical mortars of a monument or historical building [62, 63, 65–67, 73–89] can serve as an important basis, providing crucial information for restoration mortar design.

Microscopical investigation can assist in revealing the nature of the mortar, identify decay patterns and products, and provide information regarding raw materials used for the production of the mortar [75, 76]. If, for example, pozzolanic material is identified in a historical mortar (Fig. 6.5), the use of a pozzolanic additive in the restoration mortar is suggested [90].

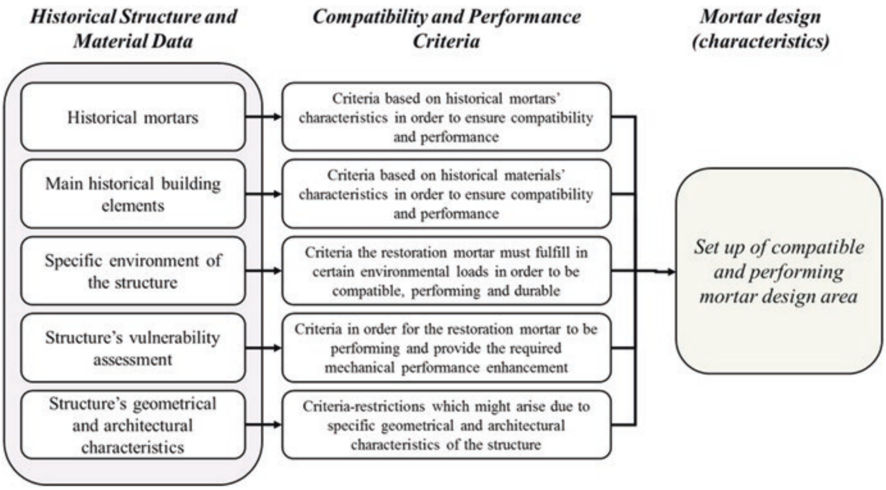

Fig. 6.4 Interdisciplinary analysis of the monument-structure to achieve set up of compatible and performing mortar design area

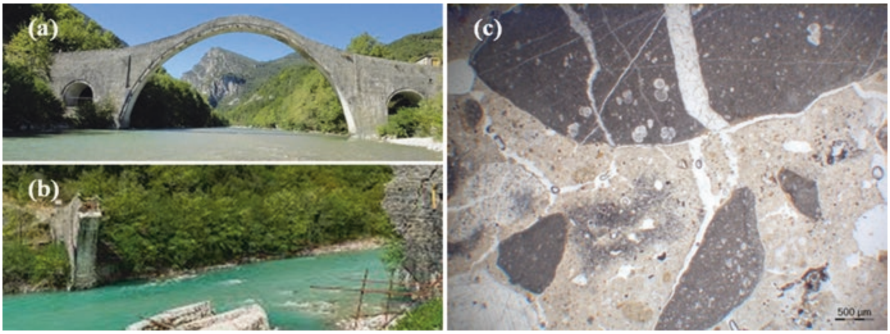

Fig. 6.5 Plaka bridge in Epirus (Greece): (**a**) before its collapse, (**b**) after its collapse in 2015; (**c**) presence of pozzolanic material throughout the mortar, as detected through polarized optical microscopy, dictated the design of a lime-pozzolan restoration mortar. (Adapted from [90])

The mineralogical analysis can serve as a guide regarding the type of restoration mortar one must design. Ideally, the restoration mortar must present a similar mineralogical composition to the historical mortars. Furthermore, the presence of certain compounds may induce certain demands regarding the restoration mortars, in order to ensure chemical compatibility. For example, if gypsum is present (however not as the sole binder, nor universally present in all mortars of said structure), early carbonation of the restoration mortar may be a prerequisite, in order to avoid the attack of free lime by SO_3^- ions, towards the formation of gypsum [91]. In addition, if calcium hydroxide is detected in the historical mortars, indicating that the conditions in the structure prohibit carbonation, again, fast consumption of calcium hydroxide is a prerequisite, and a hydraulic lime mortar or lime-pozzolan mortar is suggested [91].

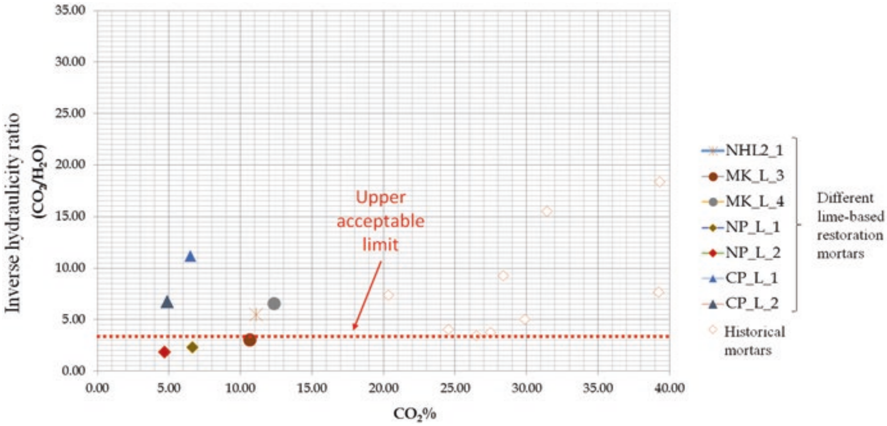

Fig. 6.6 The inverse hydraulicity ratio of the historical mortars can act as an upper limit of the hydraulicity ratio of the restoration mortars. (Case of Kaisariani Monastery in Greece, adapted from [68])

The qualitative and quantitative analysis of the mortar's constituents through thermal analysis (TG/DTA) is an important tool in identifying the technology of the historical mortar's production and can guide the design of new restoration mortars. The inverse hydraulicity ratio of the historical mortar (in the case of lime-mortars) can indicate the hydraulic or non-hydraulic nature of the mortar. The inverse hydraulicity ratio is equal to the amount of CO_2% loss attributed to the decomposition of calcareous compounds divided by the amount of H_2O% attributed to hydraulic compounds, as measured through TG/DTA. As a rule, mortars with an inverse hydraulicity ratio lower than 7.5 are considered hydraulic in nature, while values higher than this indicate aerial mortars [92]. Thus, aiming to create a compatible mortar, the inverse hydraulicity ratio of the historical mortars can act as a target value for the inverse hydraulicity ratio of the restoration mortar. Especially in cases where the mortar has been in place for centuries or has served in a corrosive environment, the inverse hydraulicity value of the historical mortar can act as an upper limit value (Fig. 6.6).

The identification of the historical mortar's production technology can be achieved by correlating thermal analysis and mercury intrusion porosimetry results [68, 92], providing guidelines regarding the type of restoration mortar which should be designed and, in particular, its raw materials.

As previously mentioned, a mortar's microstructure plays an important role, as it affects both hygric and mechanical performance [67]. In the case where the mortar seems to have served its purpose in a compatible and performing manner, and the historical mortar's microstructural characteristics (as evaluated through mercury intrusion porosimetry) are found within a relatively tight range of values, they can serve as target values for the microstructural characteristics of the new mortars. If not, the new mortars microstructural characteristics must lay within acceptability limits, which have been set forth by different types of restoration mortars [93].

Soluble salt measurements play an important role in new mortar design, as the evidence of high soluble salts (>3%) in historical mortars is an indication of a corrosive environment [94]. The new mortar must not introduce new soluble salts into the masonry, while still exhibiting a suitable microstructure, durable in the presence and crystallization of salts, without conducting them to the historical materials. Studies of historical mortars have proven that lime-pozzolan mortars present a microstructure suitable for this purpose [93], and have shown remarkable durability in high soluble salt environments [95–97]. Additionally, a highly soluble salt environment may also favor the selection of a siliceous sand for the restoration mortars, as its use seems to lead to a mortar with higher durability in corrosive environments [3, 26].

Regarding the mechanical properties of the historical mortars, usually it is not possible to extract a specimen of appropriate geometry and size in order conduct compressive strength measurements. The fragment method is usually applied, in order to estimate the tensile strength of the mortar, which does not have strict limitations in relation to specimen geometry [98]. The restoration mortar should present a tensile strength value similar to the historical mortar's, but not lower, in order to enhance mechanical performance.

Physical separation of the historical mortar can provide data for the assessment of several compatibility and performance criteria:

- Sieve analysis of the aggregate, and specifically the gradation curve, can serve as a guideline for the selection of an aggregate with an appropriate gradation for the restoration mortar.
- The binder to aggregate ratio can serve as a starting point for the selection of the new restoration mortar's B/A ratio. As historical mortars carry the effects of ageing and degradation processes, which may have altered their characteristics, and, considering the differences in historical raw materials and those produced today, optimization is necessary.

Some of the above compatibility and performance criteria, which arise from the characterization of historical mortars, are taken into account during the mortar design process, in terms of raw materials and mortar mix parameters selection, while others are related to the characteristics that a compatible and performing restoration mortar must develop.

6.2.3.2 The Analysis of Main Building Elements: Synthesis Guidelines. Compatibility, and Performance Criteria

The analysis of the main building elements of the monument (stones and/or bricks) can also lead to compatibility and performance criteria that the restoration mortar must abide by, such as:

- The capillary rise coefficient (CRC) of the main building elements can limit the acceptable value of the restoration mortar's capillary rise coefficient [15]. This value can be evaluated by performing water absorption by capillarity test, in accordance with EN15801 [99]. Two contradictory considerations are considered: the restoration mortar must not present a much lower capillary rise coefficient in relation to the main building elements, as moisture will be transferred to – and concentrated in – the main building elements. However, it must be as low as possible, within a compatible range, so as to avoid an increase of moisture content in the structure, due to higher water uptake through capillary rise [68]. Therefore, a similar CRC among the restoration mortar and the historical main building elements is desired.

- The mechanical behavior of the main building elements is also of utmost importance. The restoration mortar must be performing. However, in order to ensure mechanical compatibility, it must not exceed the compressive strength of the weakest building element [17].
- The aesthetic characteristics of the main building elements may impose some limitations on the color properties of the restoration mortars, as aesthetical compatibility [100, 101] needs to be ensured. Colorimetric measurements can be carried out to provide target values for colour data of the restoration mortars.

The above considerations are represented in the following general criteria in Fig. 6.7.

6.2.3.3 Specific Environment of the Monument/Building: Synthesis Guidelines, Compatibility, and Performance Criteria

The specific environment of the building may also require the restoration mortars to hold specific characteristics. For example:

- Intense rising damp of the structure from the underground (Fig. 6.8) intensifies the demand for an appropriate CRC of the restoration mortar, as close as possible

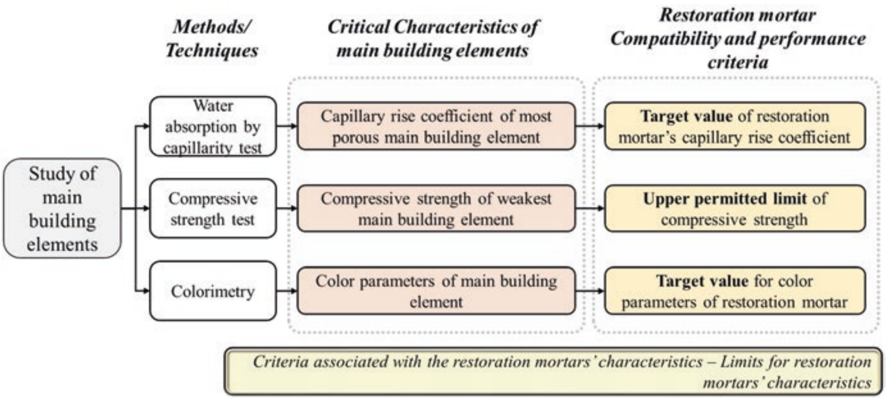

Fig. 6.7 Development of indicative compatibility and performance criteria deriving from the study of the main building elements

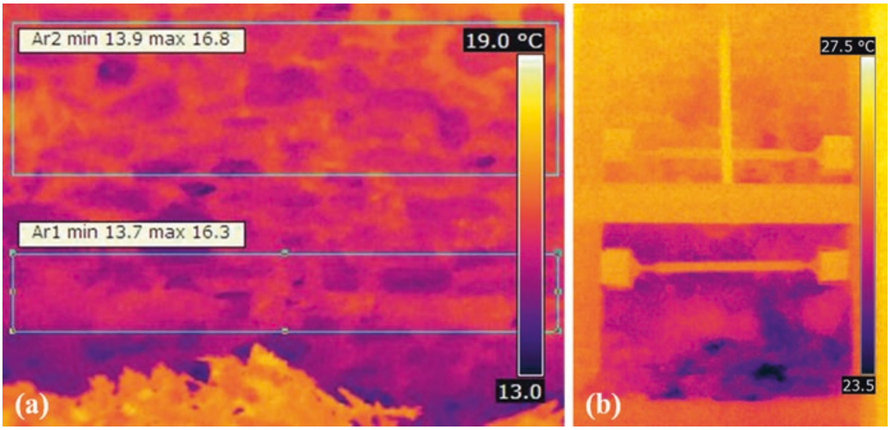

Fig. 6.8 Cases of monuments where rising damp must be taken into consideration in the design of restoration mortars: (**a**) rising damp, as detected on the northern façade of Kaisariani Monastery in Athens (Greece), through infrared thermography; (**b**) intense rising damp, as detected on the interior historical masonry of the Holy Aedicule in Jerusalem (Israel), through infrared thermography

to the value exhibited by the historical structural materials. Furthermore, intense rising damp creates an environment with high moisture within the structure, thus demanding hydraulic mortars, which have the ability to harden, set, and properly perform in this environmental conditions [96, 102]. Hydraulic mortars present an inverse hydraulicity ratio (H_2O_{cb}/CO_2, as measured though thermal analysis) of at least 7.5 [93]. Furthermore, intense rising damp creates a dynamic environment, where soluble salts may transfer from one area of the masonry to another. Therefore, it is important that early carbonation and hydration take place, because remaining free lime will be transferred to other parts of the masonry. In this environment, the ratio of pozzolanic additive to aerial lime must be enhanced, or a higher hydraulicity natural hydraulic lime binder must be selected [17]. Additionally, as previously mentioned, the selection of siliceous sand would be preferable, on account of its higher durability in corrosive environments [3, 26].

- In areas of dynamic moisture conditions, such as historical bridges, fast consumption of calcium hydroxide is important, as this compound is relatively soluble in water. Indeed, it is 100 times more soluble than calcium carbonate [102], thus allowing it to be washed away and transferred to other areas and building elements of the structure [16]. Again, this demands the use either of a natural hydraulic lime mortar or a lime-pozzolan mortar.
- In cold climates, or areas where frost is frequent in winter, the restoration mortar is required to acquire mechanical strength early (before freeze-thaw cycles begin), while the mortar must present a certain level of mechanical strength in order to better withstand the stresses due to volume increase of absorbed water [102]. This creates a demand for early acquisition of high values of compressive strength for the restoration mortar.

The above considerations are summarized in Fig. 6.9.

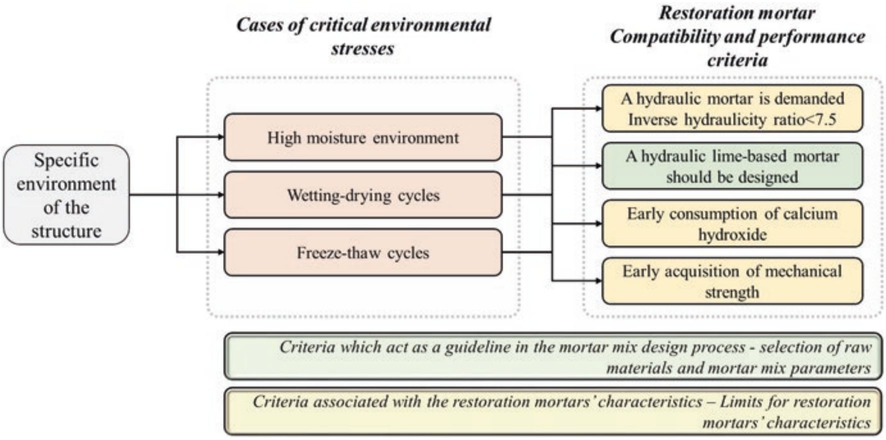

Fig. 6.9 Development of indicative compatibility and performance criteria which may derive from specific monument/historical building environments

6.2.3.4 Vulnerability Assessment of the Structure in its Current State and for Different Repair Scenarios: Synthesis Guidelines, Compatibility, and Performance Criteria

The main aim of any restoration project is to preserve the asset for future generations. The application of any restoration mortars must not only achieve compatibility, but also enhance the mechanical performance of the monument/historical building, in order to endure static and dynamic stresses. Thus, prior to the design of any restoration intervention, the monument/historical building should be evaluated regarding its vulnerability to static and dynamic stresses, in the structure's current state, and then examined for different repair mortar scenarios, usually implementing computational analysis methods (e.g. finite element model analysis, fragility curves, etc. [17, 103–106]). By examining different repair scenarios, the engineer may estimate the lower limit of the restoration mortar's compressive strength, so that the restoration mortar can perform and enhance the mechanical performance of the structure. This procedure ideally requires a multidisciplinary approach, in order to incorporate geometrical data, materials' properties data, as well as structural and earthquake data into a computational model of the structure.

The assessment of a structure's vulnerability in its current state, for restoration scenarios, along with the derived compatibility and performance criteria demanded of the restoration mortar, are presented in Fig. 6.10.

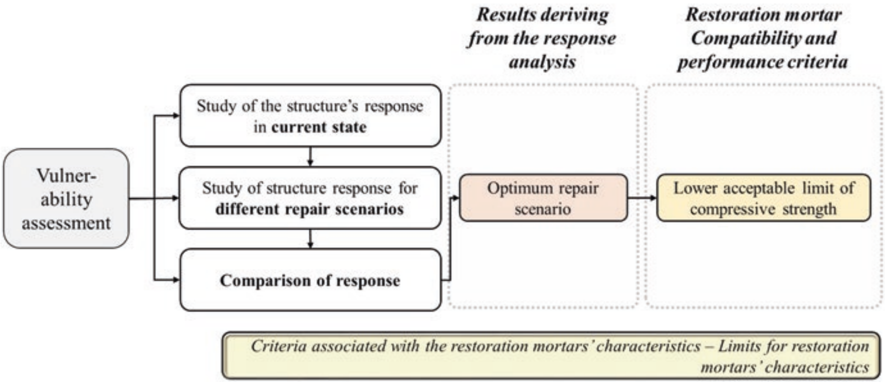

Fig. 6.10 Development of indicative compatibility and performance criteria which may derive from the vulnerability assessment of the structure

6.2.3.5 Geometrical and Architectural Characteristics of the Structure: Synthesis Guidelines, Compatibility, and Performance Criteria

Geometrical and architectural characteristics of the structure play an important role in the restoration design, and they represent the basis of any computational model for the vulnerability assessment stage. Therefore, additional compatibility and performance criteria of the restoration mortar need to be considered:

- In the case of three-leaf masonry, especially in areas of high seismicity, it is important for the restoration mortar to present adequate plasticity, in order to be able to accommodate movements without the occurrence of microcracking, which negatively affects the mechanical and hygric performance of the structure. In such cases, a low modulus of elasticity is demanded, which can also be connected to the ratio of compressive to flexural strength, in which case values between 2.5 and 5 are optimum [42, 44, 57, 107, 108].
- In the case of complicated structural geometry, as well as multiple internal layers of a structure, shrinkage of the restoration mortar is also an important criterion. Shrinkage must be as low as possible in order to avoid movements and microcracking during setting and hardening of the mortar [68].
- In some cases, carbonation of the mortars applied in the interior layers may be inhibited due to low diffusion of CO_2 from the external layers of a structure (Figure 6.11a) [91]. In this case, calcium hydroxide of the mortar must be consumed as early as possible, and the use of a pozzolanic additive is advised for this purpose, in order for the mortar to harden mostly through hydration, rather than carbonation.
- When the mortar is used as joint mortar, the width of the structure's joint must be taken into account (Figure 6.11b, c). For example, in typical Byzantine thick joint masonries, the mortar may be produced with larger aggregates [109]. In any case, the width of the joint limits the size of the used aggregate, as the diameter of the aggregate's largest grain must be less than 1/2 the width of the joint [110].

Fig. 6.11 (**a**) Thick marble facings cover the historical masonry of the Holy Aedicule in Jerusalem (Israel), prohibiting CO_2 diffusion to the internal masonry; (**b**) narrow mortar joint of the Plaka Bridge in Epirus (Greece) (2–10 mm) allow the use only of fine sand in the restoration mortar; (c) thick byzantine mortar joint (1.5–2.5 cm) at the Kaisariani Monastery in Athens (Greece) allows for the use of coarser aggregates in the restoration mortar (up to 8 mm)

Architectural characteristics may also play an important role in the application of the mortar *in situ*. Indicative criteria for the design of compatible and performing restoration mortars, which arise from the structure's geometrical and architectural characteristics, are summarized in Fig. 6.12.

6.2.3.6 The Role of the Restoration mortar and Criteria Weights

Through the proposed methodology, the monument is in the focus of the restoration mortar design process. The multidisciplinary analysis of the structure (Figs. 6.7, 6.9, 6.10, and 6.12) provides the input data for the design of the appropriate restoration mortar (Fig. 6.1), as well as limit values, which can assist in the assessment of the restoration mortar (Fig. 6.3), to ensure compatibility and performance.

Of course, the importance of each criterion that arises is highly dependent on the role of the mortar in the structure. Thus, for bedding and joint mortars, the structural integrity achieved for the monument/historic building (performance of the restoration mortar) is of high importance. On the other hand, for renders and plasters, which have a different role in the monument/historic structure, that is, protecting the structure, compatibility is the most important factor.

In the case of designing a restoration render/plaster, a similar procedure is undertaken: (i) characterization of historic render/plaster (composition, chemical and mineralogical characteristics, microstructural characteristics, hygric characteristics, adherence to the substrate, mechanical characteristics, aesthetic and chromatic characteristics, number of applied layers, gradation of aggregates, use of additives, etc.); (ii) design of new restoration mortars through a reverse engineering approach,

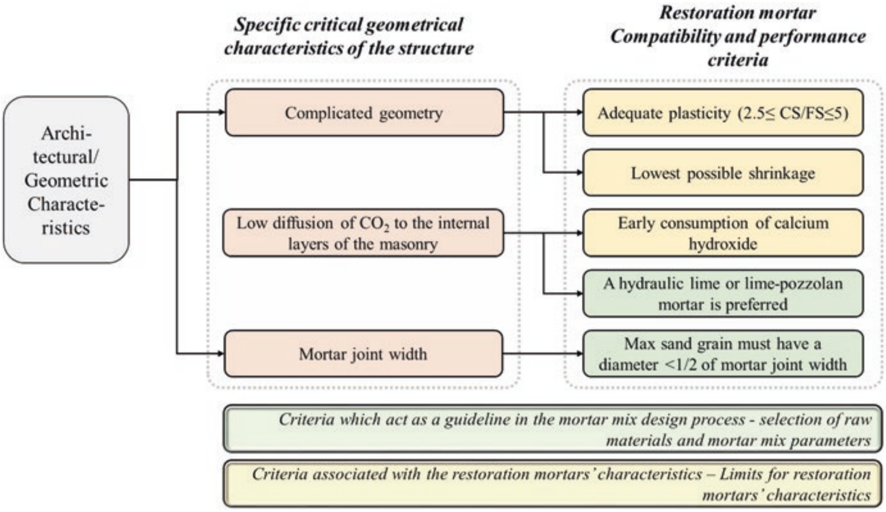

Fig. 6.12 Development of indicative compatibility and performance criteria which may derive from the structure's geometrical and architectural characteristics

and in terms of raw materials selection, aggregate gradation and restoration render/plaster mix design; and (iii) assessment of restoration render/plaster in relation to their compliance with compatibility criteria (mechanical, chemical, physical, and aesthetical) [111, 112]. As historic renders/plasters are usually multilayered, the above procedure is done for each layer, from the coarser inner layer to the finer outer layer and the final assessment must be made in relation to the combination of the render/plaster layers and the substrate.

In this way, the characteristics of the historic materials of a monument/building, the specific characteristics of the structure and its environment, and the characteristics and the role of the mortar in the monument/building: (i) guide mortar design, (ii) reveal the important parameters which must be examined and assessed, while providing information as to the importance (weight) of each parameter, and (iii) assist in the development of a "mortar design area". This is a defined multidimensional space (n-dimensions, where n = number of critical mortar characteristics, where the values of each characteristic are limited by the compatibility and performance criteria for each specific case) of compatibility and performance.

6.3 The Use of Principal Component Analysis (PCA) as a Tool for the Design and Selection of the Optimum Restoration Mortar

Mortar design is a complicated and demanding, mainly on account of the multiple parameters which influence a mortar's characteristics and the non-linear relationship between mortar mix parameters and mortar characteristics. Statistical methods and computational techniques are now in the focus of research, as they can greatly assist in the management of big data by accumulating the results from different researches. In the future, it is expected that new methods will assist in revealing the mechanisms governing the development of mortar characteristics, in order to obtain compatible and performing mortars [57].

Principal component analysis (PCA) is a statistical method, which can correlate different parameters, highlighting the important ones, and create new components as linear combinations of the original parameters, thus lowering the dimensions of a matrix. PCA has been used in the study of historical and restoration mortars, in order to group different mortar types and correlate parameters, and to study the influence of different mortar additives on mortar characteristics [47, 89, 113].

In the present chapter, PCA refers to its use on mortar design. The study of numerous restoration mortars, taking into account the variety and number of compatibility and performance criteria that they must fulfill and the subsequent demands on mortar characteristics, leads to a large amount of data, which must be assessed in order to select the optimum mortar or optimize the mortar mix. PCA can assist in correlating the mortar characteristics and creating new areas where compatibility and performance can be simultaneously examined and assessed, while also being able to serve as an optimization tool, indicating which mortar mix is closer to the set values of the characteristics for achieving compatibility and performance.

Regardless of analysis method used, when dealing with a large amount of data, it is important to select the necessary parameters, data, and criteria in order to create the appropriate database. Thus, in the case of restoration mortars, one must first select the restoration mortar characteristics which are considered important in terms of compatibility and performance and register the respective values. This is conducted by reviewing the available characteristics that have been measured and selecting the characteristics which are interlinked with the derived compatibility and performance criterion.

In the present study, a database was utilized in order to illustrate the way PCA can be used in order to assist with the design and classification of mortars. The mixed design of the different mortars is presented in Table 6.1, for the case where a lime-pozzolan mortar is demanded. In order to select the characteristics which will serve as input data in the PCA system, the compatibility and performance criteria were taken into account, and the respective parameters included (Table 6.2).

An examination of the correlations of the variables (mortar characteristics in Table 6.2) through the CORREL function of Microsoft Excel software was conducted (Table 6.3). Bulk density seems to be inversely related to total cumulative volume and total open porosity of the mortars, while total cumulative volume is correlated to total open porosity. These three microstructure characteristics are also related to specific surface area. Compressive strength is inversely related to bulk density and is correlated, however with a weaker relationship, with total open porosity, total cumulative volume, and the mortars' specific surface area. Flexural strength is correlated to total cumulative volume and inversely related to bulk density, with a weak correlation. The ratio of compressive to flexural strength, inversely associated with the plasticity of a mortar, is inversely correlated to the mass loss due to the

Table 6.1 Lime and lime-pozzolan restoration mortars mix design (wt%)

Restoration mortar code	Aerial lime	Putty lime	Ceramic powder	Natural pozzolan	Meta-kaolin	Siliceous sand 0–2 mm
ALP_1	30	–	–	–	–	70
ALPu_1	–	40	–	–	–	60
MK_L_1	15	–	–	–	15	70
MK_L_2	20	–	–	–	10	70
MK_L_3	25	–	–	–	5	70
MK_L_4	27.5	–	–	–	2.5	70
NP_L_1	15	–	–	15	–	70
NP_L_2	10	–	–	20	–	70
NP_L_3	7.5	–	–	22.5	–	70
NP_L_4	6	–	–	24	–	70
CP_L_1	15	–	15	–	–	70
CP_L_2	10	–	20	–	–	70
CP_L_3	7.5	–	–	22.5	–	70
CP_L_4	6	–	–	24	–	70

Data deriving from [32]

Table 6.2 Characteristics of different restoration mortars related to compatibility and performance criteria

Mortar code		Thermal analysis results		Microstructural characteristics					Mechanical properties			Shrinkage
		H_2O_{cb} (wt%)	CO_2 (wt%)	TCV (mm^3/g)	BD (g/cm^3)	Por (%)	MPR (μm)	SSA (m^2/g)	CS (MPa)	FS (MPa)	CS/FS	Shrink (v/v%)
1	ALP_1	0.00	11.24	186.23	1.74	32.38	0.72	2.13	3.07	1.46	2.10	4.00
2	ALPu_1	0.00	8.59	187.89	1.75	32.85	14.01	3.52	2.20	1.40	1.57	6.60
3	MK_L_1	5.27	2.14	224.69	1.63	36.61	0.05	15.66	8.95	1.59	5.63	0.30
4	MK_L_2	5.38	4.85	219.03	1.63	35.77	0.05	10.38	7.76	1.54	5.04	0.90
5	MK_L_3	3.60	10.70	191.63	1.75	33.57	0.29	5.56	5.88	1.51	3.89	1.40
6	MK_L_4	1.91	12.38	198.78	1.73	34.30	0.32	4.15	3.92	1.59	2.47	1.80
7	NP_L_1	2.87	6.65	178.36	1.82	32.37	0.57	2.91	1.78	0.70	2.54	2.10
8	NP_L_2	2.54	4.70	170.15	1.84	31.31	0.71	2.51	1.25	0.26	4.81	2.00
9	NP_L_3	1.97	3.19	164.35	1.85	30.40	0.87	2.85	1.67	0.27	6.19	1.90
10	NP_L_4	2.39	2.68	162.11	1.86	30.15	1.57	2.41	1.25	0.20	6.25	1.40
11	CP_L_1	0.58	6.49	189.94	1.79	34	0.56	3.05	2.07	0.61	3.39	2.00
12	CP_L_2	0.72	4.86	177.61	1.83	32.5	0.46	3.18	1.88	0.67	2.81	1.80
13	CP_L_3	0.92	4.23	174.67	1.84	32.14	0.65	3.02	1.63	0.35	4.66	1.60
14	CP_L_4	0.53	3.37	170.82	1.85	31.51	0.52	3.35	1.65	0.40	4.13	1.30

Data deriving from [32]

These data were used to carry out PCA analysis

H_2Ocb water chemically bound to hydraulic phases (wt%), *CO_2* mass loss due to decomposition of calcareous compounds (wt%), *TCV* total cumulative volume, *BD* bulk density, *Por* total open porosity, *MPR* average pore radius, *SSA* specific surface area, *CS* compressive strength, *FS* flexural strength, *CS_FS* ratio of compressive to flexural strength, inversely related to the ductility of the mortar, *Shrink* shrinkage (%) per volume

Table 6.3 Correlation matrix of the restoration mortar characteristics

	H_2O_{cb}	CO_2	TCV	BD	Por	MPR	SSA	CS	FS	CS_FS	Shrink
H_2O_{cb}	1.00	–0.26	0.60	–0.59	0.55	–0.37	0.78	0.77	0.34	0.54	–0.62
CO_2		1.00	0.19	–0.25	0.19	0.19	–0.26	0.06	0.61	–0.75	0.47
TCV			1.00	–0.97	0.98	–0.05	0.86	0.92	0.84	–0.09	–0.18
BD				1.00	–0.91	–0.03	–0.82	–0.92	–0.89	0.09	0.06
Por					1.00	–0.09	0.82	0.87	0.78	–0.14	–0.22
MPR						1.00	–0.15	–0.19	0.18	–0.42	0.86
SSA							1.00	0.93	0.57	0.34	–0.43
CS								1.00	0.77	0.18	–0.36
FS									1.00	–0.42	0.18
CS_FS										1.00	–0.66
Shrink											1.00

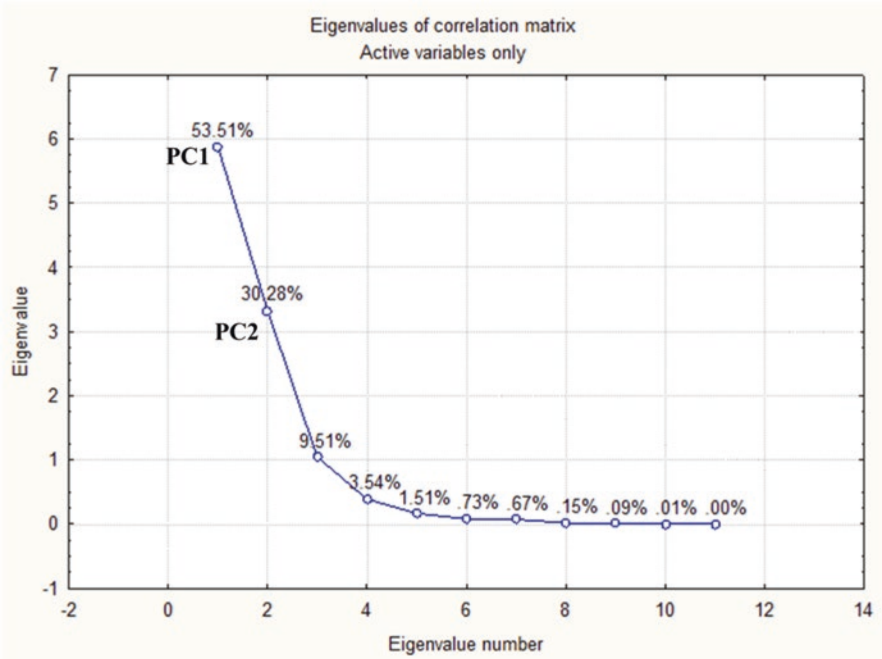

Fig. 6.13 Scree plot with eigenvalues of the correlation matrix

decomposition of calcareous compounds, with a weak correlation. Shrinkage seems to be correlated with the average pore radius.

The restoration mortars' characteristics data (Table 6.2) were incorporated in the Statistica v7 program (TIBCO/StatSoft), where principal components and classification analysis were then conducted. The eigenvalues (characteristic values) of the correlation matrix (Fig. 6.13) were assessed as acceptable, as the first two principal components, PC1 and PC2, received values higher than one, while, together, they have the ability to express 83.79% of the variance (>70% is a limit value).

The projection of the variables on the factor-plane (Fig. 6.14) reveals the relationships between the mortar characteristics. In addition, through the projection of the different mortar mixes on the factor-plane, one can assess which mortar is closer to the desired area where both compatibility and performance is achieved.

CS/FS, CO_2, MPR, and Shrink are most expressed by PC2, while the rest of the characteristics are most expressed by PC1 (Fig. 6.14, top). FS is expressed by both factors (Fig. 6.14, top). The length of the vectors expresses the intensity by which each characteristic is displayed.

By analyzing the correlation of the mortars through their principal components (Fig. 6.14, bottom), it is obvious that, in relation to all other mortars, the aerial lime mortars (assigned 1 and 2) are placed within the lower right quadrant, characterized by their higher average pore radius and shrinkage. The mortars produced with the use of natural pozzolan and the mortars produced with the use of ceramic brick dust (assigned 7–10 and 11–14, respectively) are noticed in the same area of the factor plane, that is, the upper right quadrant, where the mortars are characterized by higher bulk density, but lower mechanical strength values. As the participation of the pozzolanic additive decreases in the mortar mix (10➔7 and 14➔11, respectively) the mortars are found closer to the center of the factor plane and closer to the lower right quadrant, where the pure lime mortars are found.

The lime-metakaolin mortars are found in the left quadrants. In particular, the mortars with the higher participation of metakaolin (lime/metakaolin 1/1 – labelled 3; lime/metakaolin 1/2 – labelled 4) are in the upper left quadrant and are characterized by higher compressive strength, higher presence of hydraulic compounds, lower shrinkage, and average pore radius. The mortars with the lowest participation of metakaolin (labelled 5 and 6) are in the lower left quadrant. Thus, the use of metakaolin seems to lead to enhanced lime-pozzolan mortars, while by altering the participation of metakaolin in the mortar mix, one may achieve different levels of physicochemical and mechanical performance, tailored for each case scenario.

6.4 Conclusions

Mortar design is a difficult task, mainly due to the non-linear development of mortar characteristics in relation to mortar mix parameters and constituents. In addition, each restoration project places different demands on the mortar in terms of compatibility and performance. These demands highly affect the design process, as different levels of mechanical and physical performance are required.

The first step for any restoration mortar design is the determination of compatibility and performance criteria, which are linked with the process of diagnosing the historical structure and its materials, through an interdisciplinary approach.

The second step is to determine which restoration mortars hold the desired characteristics and how mortar mix design can be shifted in order to achieve the optimum restoration mortar. In this process, computational and statistical methods can play a decisive role and assist in mortar design, while considering the vast amount

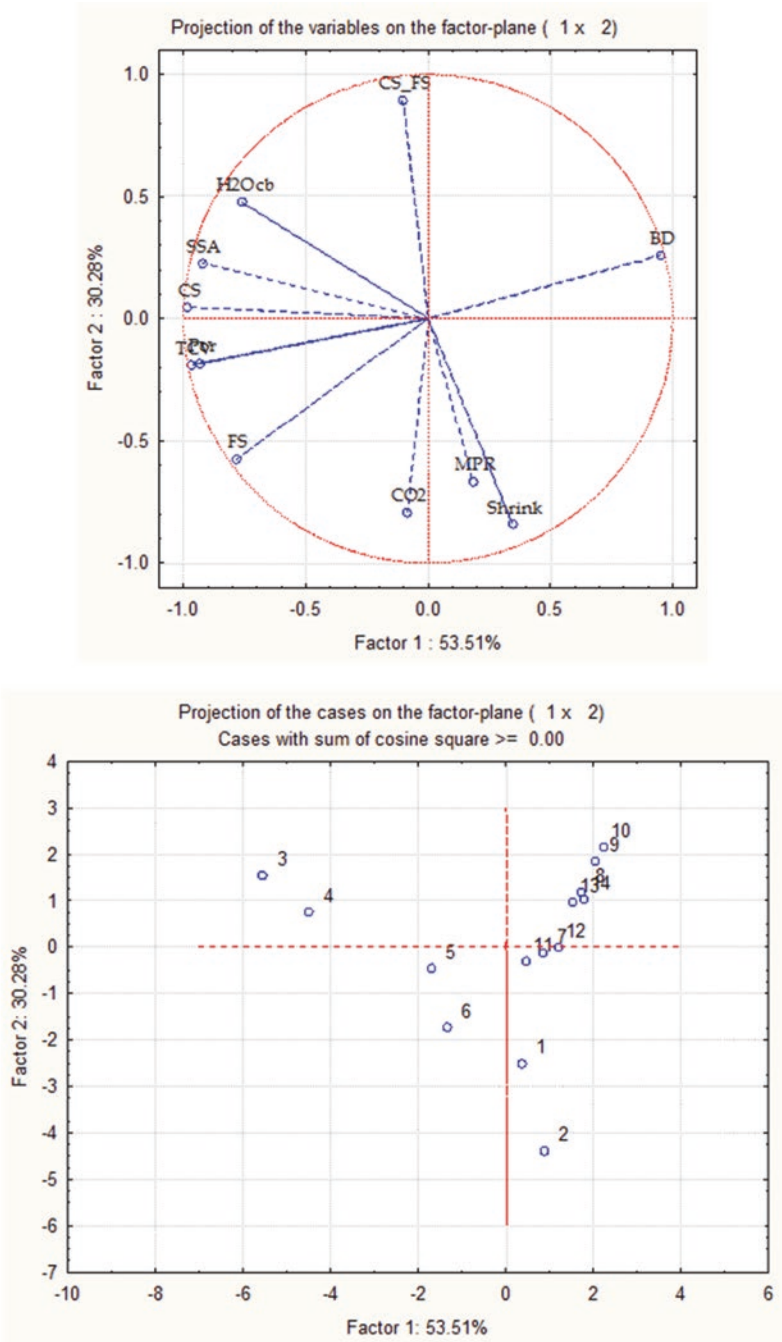

Fig. 6.14 Projection of the variables on the plane of principal components/factors 1 and 2 (top); graphical representation of the PCA scores of the examined restoration mortars (bottom)

of available data. PCA has the ability to incorporate the data and create a lower dimensional space, which includes all crucial information. In this way, it can assist in the classification of different restoration mortars, reveal trends in relation to the influence of mortar mix parameters, as well as common areas, where compatibility and performance are simultaneously achieved.

References

1. Pozo-Antonio JS. (2015). Evolution of mechanical properties and drying shrinkage in lime-based and lime cement-based mortars with pure limestone aggregate. *Construction and Building Materials*, 77, 472–478. doi:https://doi.org/10.1016/j.conbuildmat.2014.12.115
2. Barr, S., McCarter, W. J., Suryanto, B. (2015). Bond-strength performance of hydraulic lime and natural cement mortared sandstone masonry. *Construction and Building Materials*, 84, 128–135. doi:https://doi.org/10.1016/j.conbuildmat.2015.03.016
3. Moropoulou A, Bakolas A, Moundoulas P, Aggelakopoulou E. (2009). Reverse engineering: a proper methodology for compatible restoration mortars. In International RILEM Workshop on Repairs Mortars for Historic Masonry, RILEM Publications SARL, pp. 278–291.
4. Juhasova, E., Sofronie, R., Bairrao, R. (2008). Stone masonry in historical buildings—Ways to increase their resistance and durability. *Eng. Struct.* 30, 2194–2205. doi:https://doi.org/10.1016/j.engstruct.2007.07.008
5. Zhang, D., Zhao, J., Wang, D., Xu, C., Zhai, M., Ma, X. (2018). Comparative study on the properties of three hydraulic lime mortar systems: Natural hydraulic lime mortar, cement-aerial lime-based mortar and slag-aerial lime-based mortar. *Construction and Building Materials*, 186, 42–52. doi:https://doi.org/10.1016/j.conbuildmat.2018.07.053
6. Grist, E. R., Paine, K. A., Heath, A., Norman, J., Pinder, H. (2013). Compressive strength development of binary and ternary lime–pozzolan mortars. *Materials & Design* (1980–2015), 52, 514–523. doi:https://doi.org/10.1016/j.matdes.2013.05.006
7. Aggelakopoulou, E., Bakolas, A., Moropoulou, A. (2011). Properties of lime–metakolin mortars for the restoration of historic masonries, *Appl. Clay Sci.*, 53, 15–19. doi:https://doi.org/10.1016/j.clay.2011.04.005
8. Gomes, M. I., Faria, P., & Gonçalves, T. D. (2018). Earth-based mortars for repair and protection of rammed earth walls. Stabilization with mineral binders and fibers. *Journal of Cleaner Production*, *172*, 2401–2414. doi:https://doi.org/10.1016/j.jclepro.2017.11.170
9. Delgado Rodrigues, J., Grossi, A. Indicators and ratings for the compatibility assessment of conservation actions. *Journal of Cultural Heritage*. 8 (2007) 32–43. doi:https://doi.org/10.1016/j.culher.2006.04.007
10. Groot, C., Bartos, P., Hughes, J. (2000). Characterisation of Old Mortars with Respect to their Repair. In: *12th International Brick/Block Masonry Conference*, Madrid, 815–827.
11. Van Balen, K., Papayianni, I., Van Hees, R., Binda, L., Waldum, A. (2005) Introduction to requirements for and functions and properties of repair mortars. *Mater. Struct.*, 38, 781–785. DOI: https://doi.org/10.1007/BF02479291
12. Schueremans, L., Ö. Cizer, E. Janssens, G. Serré, K.V. Balen. Characterization of repair mortars for the assessment of their compatibility in restoration projects: research and practice. Constr. Build. Mater., 25 (12) (2011), pp. 4338–4350. doi:https://doi.org/10.1016/j.conbuildmat.2011.01.008
13. Ventola, L., Vendrell, M., Giraldez, P., Merino, L., Traditional organic additives improve lime mortars: New old materials for restoration and building natural stone fabric, Constr. Build. Mater., 25 (2011), 3313–3318. doi:https://doi.org/10.1016/j.conbuildmat.2011.03.020
14. Moropoulou, A., Koui, M., Kourteli, Ch., Zezza, F., et al. (1997). Techniques and methodology for the preservation and environmental management of historic complexes – the case

of the Medieval City of Rhodes. In Proceedings of the 4th international symposium on the conservation of monuments in the Mediterranean Basin, A. Moropoulou, F. Zezza, E. Kollias, I. Papachristodoulou (Eds.), vol. 4, Technical Chamber of Greece, Rhodes, 603–634.

15. Moropoulou, A., Bakolas, A., Moundoulas, P., Michailidis, P. (2002). Evaluation of the compatibility between repair mortars and building materials in historic structures by the control of the microstructure of cement-based systems. *Conc. Sci. Engineer.*, 2, 191–195. ISSN: 1295-2826
16. Mosquera, M.J., Benitez, D., Perry, S.H. (2002). Pore structure in mortars applied on restoration – Effect on properties relevant to decay of granite buildings. *Cem. Concr. Res.,* 32, 1883–1888. doi:https://doi.org/10.1016/S0008-8846(02)00887-6
17. Apostolopoulou, M., Aggelakopoulou, E., Siouta, L., Bakolas, A., Douvika, M., Asteris, P. G., Moropoulou, A. (2017). A methodological approach for the selection of compatible and performable restoration mortars in seismic hazard areas. *Construction and Building Materials*, *155*, 1–14. doi:https://doi.org/10.1016/j.conbuildmat.2017.07.210
18. Moropoulou, A., Bakolas, A., Moundoulas, P., Cakmak A.S. (1998). Compatible restoration mortars, preparation and evaluation for Hagia Sophia earthquake protection. In: *PACT, J. European Study Group on Physical, Chemical, Biological and Mathematical Techniques Applied to Archaeology*, 56, 79–118.
19. Moropoulou, A., Aggelakopoulou, E., Bakolas, A. (2006). Earthquakes and monuments – The role of materials in the earthquake protection of monuments. In: *V Int. Conf. on Structural Analysis of Historical Constructions*, eds Lourenço P.B., Roca P., Modena C. and Agrawal S., New Delhi, India, 3, 1625–1631. http://www.hms.civil.uminho.pt/sahc/2006/1625.pdf
20. Palomo, A., Blanco-Varela, M. T., Martinez-Ramirez, S., Puertas, F., & Fortes, C. (2002, February). Historic mortars: characterization and durability. New tendencies for research. In *Advanced Research Centre for cultural heritage interdisciplinary projects, Fifth Framework Programme Workshop*. https://www.semanticscholar.org/paper/Historic-Mortars-%3A-Characterization-and-Durability-Palomo-Blanco-Varela/4c981dea63830434c114ec0688ba3a8a1847845a?p2df
21. Lanas, J., Álvarez-Galindo, J.I. (2003). Masonry repair lime-based mortars: factors affecting the mechanical behavior. *Cem. Concr. Res.,* 33(11), 1867–1876. doi:https://doi.org/10.1016/S0008-8846(03)00210-2
22. Gameiro, A., Silva, A.S., Faria, P., Grilo, J., Branco, T., Veiga, R., et al. (2014). Physical and chemical assessment of lime–metakaolin mortars: Influence of binder: aggregate ratio. *Cem. Concr. Compos.* 45, 264–271. doi:https://doi.org/10.1016/j.cemconcomp.2013.06.010
23. TC 203-RHM (Main author: John J. Hughes) john.hughes@uws.ac.uk. (2012). RILEM TC 203-RHM: Repair mortars for historic masonry: The role of mortar in masonry: an introduction to requirements for the design of repair mortars. *Materials and structures*, 45, 1287–1294.
24. Moropoulou, A., Korres, M., Georgopoulos, A., Spyrakos, C., Mouzakis, C., Lampropoulos, K. C., Apostolopoulou, M. (2018, October). The project of the rehabilitation of Holy Sepulchre's Holy Aedicule as a pilot multispectral, multidimensional, novel approach through transdisciplinarity and cooperation in the protection of monuments. In *International Conference on Transdisciplinary Multispectral Modeling and Cooperation for the Preservation of Cultural Heritage* (pp. 3–25). Springer, Cham.
25. The Venice Charter. International charter for the conservation and restoration of monuments and sites. In: Second international congress of architects and technicians of historic monuments; Venice, Italy, 1964.
26. Moropoulou, A. (2000). Reverse engineering to discover traditional technologies: a proper approach for compatible restoration mortars. *PACT (Rixensart)*, (58), 81–107. ISSN 0257-8727
27. EN 459-1:2015—Building lime. Part 1: Definitions, specifications and conformity criteria. European Committee for Standardisation (CEN): Brussels, Belgium

28. EN 459-2: 2010, Building lime. Part 2: Test methods. European Committee for Standardisation (CEN): Brussels, Belgium.
29. Aggelakopoulou, E., Bakolas, A., Moropoulou, A. (2019). Lime putty versus hydrated lime powder: Physicochemical and mechanical characteristics of lime based mortars. *Construction and Building Materials*, *225*, 633–641. doi:https://doi.org/10.1016/j.conbuildmat.2019.07.218
30. Forster, A. (2004). Hot-lime mortars: a current perspective. *Journal of Architectural Conservation*, *10*(3), 7–27. doi:https://doi.org/10.1080/13556207.2004.10784923
31. Margalha, G., Veiga, R., Silva, A. S., & De Brito, J. (2011). Traditional methods of mortar preparation: The hot lime mix method. *Cement and Concrete Composites*, *33*(8), 796–804. doi:https://doi.org/10.1016/j.cemconcomp.2011.05.008
32. Aggelakopoulou, E. (2006). Criteria and methodology for the evaluation of physico – chemical and mechanical characteristics of restoration mortars addressed to historic masonries restoration interventions (PhD thesis), School of Chemical Engineering, NTUA, supervising professor: A. Moropoulou. (in Greek). DOI: https://doi.org/10.12681/eadd/16788
33. Papayianni, I., Stefanidou, M. (2006). Strength–porosity relationships in lime–pozzolan mortars. *Construction and Building Materials*, *20*(9), 700–705. doi:https://doi.org/10.1016/j.conbuildmat.2005.02.012
34. Figueiredo, C., Lawrence, M., Ball, R. J. (2016). Chemical and physical characterisation of three NHL 2 binders and the relationship with the mortar properties. In *REHABEND 2016, Euro-American Congress: Construction Pathology, Rehabilitation Technology and Heritage Management*. Santander Spain. https://core.ac.uk/download/pdf/161917149.pdf
35. Figueiredo, C., Lawrence, M., Ball, R. J. (2016). Mechanical properties of standard and commonly formulated NHL mortars used for retrofitting. In *International Conference on Integrated Design* (p. 68). University of Bath. https://researchportal.bath.ac.uk/en/publications/mechanical-properties-of-standard-and-commonly-formulated-nhl-mor
36. Lanas, J., Bernal, J. P., Bello, M. A., Galindo, J. A. (2004). Mechanical properties of natural hydraulic lime-based mortars. *Cement and concrete research*, *34*(12), 2191–2201. doi:https://doi.org/10.1016/j.cemconres.2004.02.005
37. Vyšvařil, M., Žižlavský, T., Zimmermann, Š., Bayer, P. (2017). Effect of Aggregate Type on Properties of Natural Hydraulic Lime-Based Mortars. In *Materials Science Forum* (Vol. 908, pp. 35–39). Trans Tech Publications Ltd. doi:https://doi.org/10.4028/www.scientific.net/MSF.908.35
38. Isebaert, A., De Boever, W., Descamps, F., Dils, J., Dumon, M., De Schutter, G., Van Ranst, E., Cnudde, V., Van Parys, L. (2016). Pore-related properties of natural hydraulic lime mortars: an experimental study. *Materials and Structures*, 49(7), 2767–2780. doi:https://doi.org/10.1617/s11527-015-0684-5
39. Sophia, M., Sakthieswaran, N., Babu, G. O. (2016). Gypsum as a construction material-a review of recent developments. *International Journal for Innovative Research in Science Technology*, *2*(12), 1–9.
40. Karni, J. (1995). Gypsum in construction: origin and properties. *Materials and Structures*, *28*(2), 92–100. doi:https://doi.org/10.1007/BF02473176
41. Arizzi, A., Cultrone, G. (2011). Negative effects of the use of white Portland cement as additive to aerial lime mortars set at atmospheric conditions: a chemical, mineralogical and physical-mechanical investigation. *Publisher: Nova Science Publishers, Inc., Editors: S. Manuel Rivera and AL Pena Diaz*, 231–243. ISBN: 978-1-61942-927-7
42. Kalagri, A., Karatasios, I., Kilikoglou, V. (2014). The effect of aggregate size and type of binder on microstructure and mechanical properties of NHL mortars. Construction and Building Materials, 53, 467–474. doi:https://doi.org/10.1016/j.conbuildmat.2013.11.111
43. Lanas, J., Arandigoyen, M., Alvarez, J. I., Bernal, J. L. P., Bello, M. A. (2004). Mechanical behavior of masonry repair mortars: Aerial and hydraulic lime-based mixtures. In *Proceedings of the 10th International Congress on Deterioration and Conservation of Stone, Stockholm, Sweden* (Vol. 27).

44. Silva, B. A., Pinto, A. F., Gomes, A. (2014). Influence of natural hydraulic lime content on the properties of aerial lime-based mortars. Construction and Building Materials, 72, 208–218. doi:https://doi.org/10.1016/j.conbuildmat.2014.09.010
45. Faria, P., Silva, V. (2019). Natural hydraulic lime mortars: influence of the aggregates. In *Historic Mortars* (pp. 185–199). Springer, Cham. doi:https://doi.org/10.1007/978-3-319-91606-4_14
46. Amenta, M., Karatasios, I., Maravelaki-Kalaitzaki, P., Kilikoglou, V. (2017). The role of aggregate characteristics on the performance optimization of high hydraulicity restoration mortars. *Construction and Building Materials*, 153, 527–534. doi:https://doi.org/10.1016/j.conbuildmat.2017.07.134
47. Falchi, L., Varin, C., Toscano, G., Zendri, E. (2015). Statistical analysis of the physical properties and durability of water-repellent mortars made with limestone cement, natural hydraulic lime and pozzolana-lime. Construction and Building Materials, 78, 260–270. doi:https://doi.org/10.1016/j.conbuildmat.2014.12.109
48. Yang, F., Zhang, B., Ma, Q. (2010). Study of sticky rice− lime mortar technology for the restoration of historical masonry construction. *Accounts of chemical research*, *43*(6), 936–944. doi:https://doi.org/10.1021/ar9001944
49. Pahlavan, P., Manzi, S., Sansonetti, A., Bignozzi, M. C. (2018). Valorization of organic additions in restorative lime mortars: Spent cooking oil and albumen. *Construction and Building Materials*, *181*, 650–658. doi:https://doi.org/10.1016/j.conbuildmat.2018.06.089
50. Mydin, M. A. O. (2018). Physico-mechanical properties of lime mortar by adding exerted egg albumen for plastering work in conservation work. *J. Mater. Environ. Sci*, *9*(2), https://doi.org/10.26872/jmes.2018.9.2.41
51. Garijo, L., Zhang, X., Ruiz, G., Ortega, J. J., Wu, Z. (2018). The effects of dosage and production process on the mechanical and physical properties of natural hydraulic lime mortars. *Construction and Building Materials*, *169*, 325–334. doi:https://doi.org/10.1016/j.conbuildmat.2018.03.016
52. Arizzi, A., Martinez-Huerga, G., Sebastián Pardo, E., Cultrone, G. (2015). Mineralogical, textural and physical-mechanical study of hydraulic lime mortars cured under different moisture conditions. *Materiales de Construcción*, 65(318), e053. DOI: https://doi.org/10.3989/mc.2015.03514
53. Van Balen, K., Van Gemert, D. (1994). Modelling lime mortar carbonation. *Materials and structures*, 27(7), 393–398. doi:https://doi.org/10.1007/BF02473442
54. EN1015-11:2007: Methods of Test for Mortar for Masonry—Part 11. Determination of Flexural and Compressive Strength of Hardened Mortars. European Committee for Standardisation (CEN): Brussels, Belgium.
55. EN1015-3:2007: Methods of Test for Mortar for Masonry—Part 3. Determination of Consistence of Fresh Mortar (by Flow Table). European Committee for Standardisation (CEN): Brussels, Belgium.
56. Hanley, R., Pavía, S. (2008). A study of the workability of natural hydraulic lime mortars and its influence on strength. Materials and Structures, 41(2), 373–381. doi:https://doi.org/10.1617/s11527-007-9250-0
57. Apostolopoulou, M., Asteris, P. G., Armaghani, D. J., Douvika, M. G., Lourenço, P. B., Cavaleri, L., Bakolas, A., Moropoulou, A. Mapping and holistic design of natural hydraulic lime mortars. *Cement and Concrete Research*, 2020, 136: 106167. doi:https://doi.org/10.1016/j.cemconres.2020.106167
58. EN 1015-7:1999. Methods of test for mortar for masonry. Part 7: Determination of air content of fresh mortar. European Committee for Standardisation (CEN): Brussels, Belgium.
59. Izaguirre, A., Lanas, J., Alvarez, J. I. (2010). Ageing of lime mortars with admixtures: Durability and strength assessment. *Cement and Concrete Research*, 40(7), 1081–1095. doi:https://doi.org/10.1016/j.cemconres.2010.02.013
60. EN1015-6:2007: Methods of Test for Mortar for Masonry—Part 6: Determination of Bulk Density of Fresh Mortar. European Committee for Standardisation (CEN): Brussels, Belgium.

61. EN1015-8:2007: Methods of Test for Mortar for Masonry—Part 8. Determination of Retained Water of Fresh Mortar. Europ. Commitee for Standardisation (CEN): Brussels, Belgium.
62. Normal 27/88: Caratterizzazione di una malta Rome; Consiglio Nazionale delle Ricerche and Istituto Centrale del Restauro (CNR-ICR): Rome, Italy, 1988.
63. Normal 4/80: Distribution of Pore Volume as a Function of Pore Diameter C.N.R.-I.C.R; Consiglio Nazionale delle Ricerche and Istituto Centrale del Restauro (CNR-ICR): Rome, Italy, 1980.
64. Anovitz, L. M., Cole, D. R. (2015). Characterization and analysis of porosity and pore structures. *Reviews in Mineralogy and geochemistry*, *80*(1), 61–164. doi:https://doi.org/10.2138/rmg.2015.80.04
65. Stefanidou, M. (2010). Methods for porosity measurement in lime-based mortars. *Construction and Building Materials*, *24*(12), 2572–2578. doi:https://doi.org/10.1016/j.conbuildmat.2010.05.019
66. Thomson, M. L., Lindqvist, J. E., Elsen, J., Groot, C. J. W. P. (2004, July). Porosity of historic mortars. In *13th International Brick and Block Masonry Conference Amsterdam*. http://www.hms.civil.uminho.pt/ibmac/2004/232.pdf
67. Thomson, M., Lindqvist, J. E., Elsen, J., Groot, C. J. W. P. (2004). 2.5 Porosity of mortars. *Characterisation of Old Mortars with Respect to their Repair-Final Report of RILEM TC 167-COM*, 77-106.
68. Apostolopoulou, M., Aggelakopoulou, E., Bakolas, A., & Moropoulou, A. (2018). Compatible mortars for the sustainable conservation of stone in masonries. In *Advanced Materials for the Conservation of Stone* (pp. 97–123). Springer, Cham. doi:https://doi.org/10.1007/978-3-319-72260-3_5
69. Figueiredo, C., Ball, R. J., Lawrence, M. (2016). Is BS EN 459-1: 2015 fit for purpose in the context of conservation?. In The Journal of the Building Limes Forum (Vol. 23, pp. 46–52). Building Limes Forum. https://researchportal.bath.ac.uk/en/publications/is-bs-en-459-12015-fit-for-purpose-in-the-context-of-conservation
70. EN 1015-18: 2002. *Methods of test for mortar for masonry-Part*, *18*: Determination of water absorption coefficient due to capillary action of hardened mortar. European Committee for Standardisation (CEN): Brussels, Belgium.
71. Alexakis, E., Delegou, E. T., Lampropoulos, K. C., Apostolopoulou, M., Ntoutsi, I., Moropoulou, A. (2018). NDT as a monitoring tool of the works progress and the assessment of materials and rehabilitation interventions at the Holy Aedicule of the Holy Sepulchre. *Construction and Building Materials*, 189, 512–526. doi:https://doi.org/10.1016/j.conbuildmat.2018.09.007
72. Isebaert, A., De Boever, W., Cnudde, V., Van Parys, L. (2016). An empirical method for the estimation of permeability in natural hydraulic lime mortars. *Materials and Structures*, 49(11), 4853–4865. doi:https://doi.org/10.1617/s11527-016-0829-1
73. Elsen, J. (2006). Microscopy of historic mortars—a review. *Cement and concrete research*, *36*(8), 1416–1424. doi:https://doi.org/10.1016/j.cemconres.2005.12.006
74. Blaeuer, C., Kueng, A. (2007). Examples of microscopic analysis of historic mortars by means of polarising light microscopy of dispersions and thin sections. *Materials characterization*, *58*(11–12), 1199–1207. doi:https://doi.org/10.1016/j.matchar.2007.04.023
75. Stefanidou, M., Pavlidou, E. (2018). Scanning Mortars to Understand the Past and Plan the Future for the Maintenance of Monuments. *Scanning*, *2018*. doi:https://doi.org/10.1155/2018/7838502
76. Moropoulou, A., Zendri, E., Ortiz, P., Delegou, E. T., Ntoutsi, I., Balliana, E., Becerra, J., Ortiz, R. (2019). Scanning Microscopy Techniques as an Assessment Tool of Materials and Interventions for the Protection of Built Cultural Heritage. *Scanning*, *2019*. doi:https://doi.org/10.1155/2019/5376214
77. Stefanidou, M., Papayianni, I., Pachta, V. (2012). Evaluation of inclusions in mortars of different historical periods from Greek monuments. *Archaeometry*, *54*(4), 737–751. doi:https://doi.org/10.1111/j.1475-4754.2011.00645.x

78. Normal 34/91: Analysis of Clay Materials by XRD Rome; Consiglio Nazionale delle Ricerche and Istituto Centrale del Restauro (CNR-ICR): Rome, Italy, 1991.
79. Middendorf, B., Hughes, J. J., Callebaut, K., Baronio, G., Papayianni, I. (2005). Investigative methods for the characterisation of historic mortars—part 1: mineralogical characterisation. *Materials and Structures*, *38*(8), 761. doi:https://doi.org/10.1007/BF02479289
80. Moropoulou, A., Bakolas, A., Bisbikou, K. (1995). Characterization of ancient, byzantine and later historic mortars by thermal and X-ray diffraction techniques. *Thermochimica Acta*, *269*, 779–795. doi:https://doi.org/10.1016/0040-6031(95)02571-5
81. Bakolas, A., Biscontin, G., Moropoulou, A., Zendri, E. (1998). Characterization of structural byzantine mortars by thermogravimetric analysis. *Thermochimica Acta*, *321*(1–2), 151–160. doi:https://doi.org/10.1016/S0040-6031(98)00454-7
82. Middendorf, B., Hughes, J. J., Callebaut, K., Baronio, G., Papayianni, I. (2005). Investigative methods for the characterisation of historic mortars—part 2: chemical characterisation. *Materials and Structures*, *38*(8), 771–780. doi:https://doi.org/10.1617/14282
83. Moropoulou, A., Bakolas, A., Bisbikou, K. (2000). Investigation of the technology of historic mortars. *Journal of Cultural Heritage*, *1*(1), 45–58. doi:https://doi.org/10.1016/S1296-2074(99)00118-1
84. Fang, S. Q., Zhang, H., Zhang, B. J., Zheng, Y. (2014). The identification of organic additives in traditional lime mortar. *Journal of Cultural Heritage*, *15*(2), 144–150. doi:https://doi.org/10.1016/j.culher.2013.04.001
85. Normal 13/83: Dosage of Soluble Salts Rome; Consiglio Nazionale delle Ricerche and Istituto Centrale del Restauro (CNR-ICR): Rome, Italy, 1983.
86. Gulec, A., Ersen, A. (1998). Characterization of ancient mortars: Evaluation of simple and sophisticated methods. *Journal of Architectural Conservation*, *4*(1), 56–67. doi:https://doi.org/10.1080/13556207.1998.10785207
87. Veiga, M. R., Aguiar, J., Silva, A. S., Carvalho, F. (2001, November). Methodologies for characterisation and repair of mortars of ancient buildings. In *Proceedings of the 3rd International Seminar Historical Constructions* (pp. 353–362). Guimarães, Portugal: University of Minho.
88. Válek, J., Veiga, R. (2005). Characterisation of mechanical properties of historic mortars–testing of irregular samples. *WIT Transactions on The Built Environment*, *83*. Paper DOI: https://doi.org/10.2495/STR050351
89. Moropoulou, A., Polikreti, K., Bakolas, A., Michailidis, P. (2003). Correlation of physicochemical and mechanical properties of historical mortars and classification by multivariate statistics. *Cement and concrete research*, *33*(6), 891–898. doi:https://doi.org/10.1016/S0008-8846(02)01088-8
90. Gkolias I, et al. The bridge of Plaka: the NTUA contribution towards its restoration. Athens: NTUA; 2016. (in Greek)
91. Apostolopoulou, M., Delegou, E. T., Alexakis, E., Kalofonou, M., Lampropoulos, K. C., Aggelakopoulou, E., Bakolas, A. & Moropoulou, A. (2018). Study of the historical mortars of the Holy Aedicule as a basis for the design, application and assessment of repair mortars: A multispectral approach applied on the Holy Aedicule. *Construction and Building Materials*, *181*, 618–637. doi:https://doi.org/10.1016/j.conbuildmat.2018.06.016
92. Moropoulou, A., Bakolas, A., & Anagnostopoulou, S. (2005). Composite materials in ancient structures. *Cement and concrete composites*, *27*(2), 295–300. doi:https://doi.org/10.1016/j.cemconcomp.2004.02.018
93. Moropoulou, A., Bakolas, A. (1998). Range of acceptability limits of physical, chemical and mechanical characteristics deriving from the evaluation of historic mortars. In PACT (No. 56, pp. 165–178). Conseil de l'Europe.
94. Kioussi, A., Karoglou, M., Bakolas, A., Labropoulos, K., & Moropoulou, A. (2013). Documentation protocols to generate risk indicators regarding degradation processes for cultural heritage risk evaluation. *International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences*, *5*, W2. https://core.ac.uk/download/pdf/189121041.pdf

95. Rob van Hees et al (2012). RILEM TC 203-RHM: Repair mortars for historic masonry. From problem to intervention: a decision process. Materials and Structures, 45: 1295–1302.
96. Maravelaki-Kalaitzaki, P., Bakolas, A., Karatasios, I., Kilikoglou, V. (2005). Hydraulic lime mortars for the restoration of historic masonry in Crete. *Cement and Concrete Research*, 35(8) 1577–1586. doi:https://doi.org/10.1016/j.cemconres.2004.09.001
97. Moropoulou, A., Biscontin, G., Bakolas, A., Bisbikou, K. (1997). Technology and behavior of rubble masonry mortars. Construction and Building Materials, 11(2), 119–129. doi:https://doi.org/10.1016/S0950-0618(97)07023-2
98. Moropoulou, A., Bakolas, A., Bisbikou, K. (2000). Physico-chemical adhesion and cohesion bonds in joint mortars imparting durability to the historic structures. *Construction and Building Materials*, *14*(1), 35–46. doi:https://doi.org/10.1016/S0950-0618(99)00045-8
99. EN15801:2010: Conservation of Cultural Property-Test Methods-Determination of Water Absorption by Capillarity; European Committee for Standardisation: Brussels, Belgium, 2010.
100. Isebaert, A., Van Parys, L., Cnudde, V., De Kock, T., & Baele, J. M. (2019). Compatibility assessment for repair mortars: an optimized cement-based mix for Tuffeau de Lincent. In *Historic Mortars* (pp. 169–184). Springer, Cham. https://link.springer.com/chapter/10.1007/978-3-319-91606-4_13
101. Apostolopoulou, M., Keramidas, V., Galanaki, N., Kalofonou, M., Skoula, C., Karoglou, M., Delegou, E.T., Mouzakis, Ch., Bakolas, A., Moropoulou, A., Pikoula, M., Kalagri, A., Farmakidou, E., Michailidou, M. (2019). A study on the historical materials of the Apollo Pythios Temple in Rhodes and the evaluation of potential restoration materials. *Heritage*, *2*(1), 988–1022. doi:https://doi.org/10.3390/heritage2010065
102. Groot, C. (2016). Repair mortars for historic masonry: Effects of the binder choice on durability. Heron, 61(1), 33–56. http://pure.tudelft.nl/ws/files/6982509/3.pdf
103. Spyrakos, C. C., Maniatakis, C. A., Moropoulou, A. (2018, October). Preliminary assessment of the structural response of the Holy Tomb of Christ under static and seismic loading. In *International Conference on Transdisciplinary Multispectral Modeling and Cooperation for the Preservation of Cultural Heritage* (pp. 44–57). Springer, Cham. https://link.springer.com/chapter/10.1007/978-3-030-12957-6_3
104. Asteris, P. G., Chronopoulos, M. P., Chrysostomou, C. Z., Varum, H., Plevris, V., Kyriakides, N., & Silva, V. (2014). Seismic vulnerability assessment of historical masonry structural systems. Engineering Structures, 62, 118–134. doi:https://doi.org/10.1016/j.engstruct.2014.01.031
105. Asteris, P. G., Douvika, M. G., Apostolopoulou, M., & Moropoulou, A. (2017). Seismic and restoration assessment of monumental masonry structures. Materials, 10(8), 895. doi:https://doi.org/10.3390/ma10080895
106. Asteris, P. G., Moropoulou, A., Skentou, A. D., Apostolopoulou, M., Mohebkhah, A., Cavaleri, L., Rodrigues, H., Varum, H. (2019). Stochastic vulnerability assessment of masonry structures: concepts, modeling and restoration aspects. *Applied Sciences*, *9*(2), 243. doi:https://doi.org/10.3390/app9020243
107. Silva, B. A., Pinto, A. F., Gomes, A. (2015). Natural hydraulic lime versus cement for blended lime mortars for restoration works. Construction and Building Materials, 94, 346–360. doi:https://doi.org/10.1016/j.conbuildmat.2015.06.058
108. Moropoulou A, Bakolas A, Moundoulas P, Aggelakopoulou E, Anagnostopoulou S. (2005). Strength development and lime reaction in mortars for repairing historic masonries. Cem Concr, 27:289–94. doi:https://doi.org/10.1016/j.cemconcomp.2004.02.017
109. Aggelakopoulou, E., Bakolas, A., & Moropoulou, A. (2018). Design and evaluation of concrete for restoration interventions on Byzantine monuments. *Journal of Cultural Heritage*, *34*, 166–171. doi:https://doi.org/10.1016/j.culher.2018.05.006
110. Anagnostopoulou, S. (2012). *Methodology for the estimation of aggregate materials influence on the mix design of restoration mortars*. PhD thesis. School of Chemical Engineering, NTUA, supervising professor: A. Moropoulou (in Greek). https://www.didaktorika.gr/eadd/handle/10442/33308

111. Karoglou, M., Bakolas, A., Kouloumbi, N., & Moropoulou, A. (2011). Reverse engineering methodology for studying historic buildings coatings: The case study of the Hellenic Parliament neoclassical building. Progress in Organic Coatings, 72(1–2), 202–209.
112. Nogueira, R., Pinto, A. P. F., & Gomes, A. (2018). Design and behavior of traditional lime-based plasters and renders. Review and critical appraisal of strengths and weaknesses. Cement and Concrete Composites, 89, 192–204.
113. Moropoulou, A., Polikreti, K., Moundoulas, P., Aggelakopoulou, E. (2008). Classification of Restoration Mortars by Principal Component Analysis and Correlation Between Their Properties and Synthesis. In *11DBMC International Conference on Durability of Building Materials and Components*. ISTANBUL, Turkey (11–14 May 2008). https://www.irbnet.de/daten/iconda/CIB13237.pdf

Chapter 7
Repair Mortars/Grouts for Reinstatement of Stone Units in Historic Structures

Ioanna Papayianni

Abstract Stone units (shaped or unshaped) are the components of many historical masonries found in monuments such as archaeological sites, ancient theaters, castles, monasteries, arched bridges, and industrial buildings. A great variety of locally available stones have been used in the past, but nowadays the old quarries/deposits do not often exist. Therefore, there is need to reinstate old stone units with mortars/grouts to produce artificial stone pieces to replace the missing parts in restoration works. These repair mortars/grouts should fulfill conceptual, functional, and technical requirements with respect to their compatibility with old stone (color and texture harmonization, good adhesion to substrate, resistance to environmental conditions, no secondary reaction products, etc.). Furthermore, before the selection or design of a repair material (mortar/grout), a systematic analysis of the original stone pieces and environmental conditions affecting their degradation should be well understood and considered. Improvement to the composition of repair materials should be made by using additives and taking measures for good practice in the execution of old stones reinstatement or replacement works.

Three selected case studies concerning two archaeological sites and an ancient theater are also presented. Problems confronted in practice are recognized, and possibilities to overcome them are suggested.

Keywords Historic masonry · Stone units · Reinstatement · Replacement · Mortars/Grouts · Case studies

I. Papayianni (✉)
Laboratory of Building Materials, Department of Civil Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece
e-mail: papayian@civil.auth.gr

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7.1 Introduction

Stone masonries constitute a great part of worldwide monumental Heritage from the prehistoric up to the post-industrial period. Prominent Historic Structures (HS) with stone units are found in:

- Remains of archaeological sites (Fig. 7.1),
- Ancient theaters (Fig. 7.2),
- Castles and towers,
- Monasteries and churches,
- Arched bridges,
- Industrial buildings and lighthouses, and
- Masons and houses in mountainous areas.

Locally available stones are commonly used for buildings, therefore, a great variety (in terms of geological and mineralogical characteristics) of shaped or unshaped stones, such as limestones, sandstones gneiss, granites, etc., are found in monuments. This means each case of repair should be considered individually. In Table 7.1 the characteristics of common limestone types found in Greek monuments are given. It is obvious that, even of the same origin, limestones are of different porosity and strength.

Heavy stone masonries often suffer from cracking due to subsidence, overloading, lateral push, and loss of adequate tying of the corners, and as a result, stone units are displaced and cracked. In addition, long term exposure to daily and seasonal changes of temperature and relative humidity (RH) provokes weathering

Fig. 7.1 Archaeological site of Pella, northern Greece

Fig. 7.2 Ancient Theater of Plevrona, southwestern Greece

damages, which start from the surface of the stone unit, but go gradually deeper, up to significant loss of mass. The presence of salts accelerates damages, as well as the presence of pollutants in the environment around the HS.

The indicators of weathering effects on stone masonry or stone artworks have been studied extensively for more than a century, and mechanisms such as wetting-drying, physical crystallization, reactions of pollutants on stone surfaces, and the action of extreme temperatures have been detected and very well described [1–3].

A plethora of consolidants have been developed and used. Advanced technological products and techniques are still being produced, which help in the preservation and conservation of stones [4–7].

In the vast field of historic stone unit reinstatement or replacement, some of the problems that are encountered include the reconstruction of missing stones of masonry remnants in archaeological sites and ancient theaters with mortars, and filling voids and cracks with grouts or flowable mortars. Additionally, it is often difficult to replace the old stone pieces with stone of the same origin, since quarries or stone deposits of the past do not exist nowadays. Therefore, there is need to produce artificial stone pieces with mortars based on well documented characteristics of the existing stones.

Stone repair with mortars was carried out in the past, particularly from the period of nineteenth up to twentieth century, in which mostly Portland cement was used as a binder. The strong cement-based mortars caused destructive side effects in the original body of the stones and the surrounding area. Those mortars often included colored cement binder and were called “plastic stone” or “plastic repair”. The inappropriate mortars or technique of mortar application created a bad reputation, though it is a cost-effective solution especially for large projects [8].

Table 7.1 Characteristics of common limestones found in some representative Greek monuments

Monument/ type of limestone	Open porosity (%)	Apparent specific gravity	Compressive strength (MPa)	Soluble salt content, % by mass			Comments
				Cl^-	NO^3	SO^{-2}_4	
Medieval Castle of Rhodes	1.5–2.5	2.01–1.74	0.5–1.0	0.85–2.94	0.13–0.25	0.15–1.20	Intensive weathering due to marine environment
Biogenic limestone							
Pela Ancient Agora	0.5–4.0	2.40–2.58	30–45	Very low	Very low	Low	Sound stone units
-							
Marl limestone							
Edessa Ancient theater	21.4	1.72	1.30–1.95	Low	Low	Low	
-							
Travertine							
Macedonian Tomb Derveni	1: 9.58	2.03	6.05	–	–	–	Two types of different color:
-	2: 6.12	2.14	11.67				1 → yellow
Biogenic limestone (types 1,2)							2 → grey
Oiniades Ancient theater	1.90–9.5	2.4–2.6	14–16	1.6–1.8	Low	Low	The theater is near the sea from an area which salt (NaCl) is present. The mass of stone units is not homogeneous. There are parts with cracks and venules. Biological attack is obvious.
-							
Biogenic limestone							

The replacement of original stone mass/volume with inorganic repair mortars had been commonly used in the past, as referred in literature [9] about old buildings in Glasgow. Taking into account the bad experiences from the failures of the past interventions and the achievements of materials' science and technology in construction, it is feasible to design much more effective stone repair mortars and grouts of lower shrinkage, better adhesion to substrate, and more resistance to weathering.

7.2 About Designing Repair Mortars/Grouts for Historic Stone Units' Reinstatement

Over the last 20 years, much collective work has been produced in the frame of RILEM Technical Committees (CMs) [10–13] and CEN [14] concerning repair interventions on HS with mortars/grouts, apart from Conferences/Workshops devoted to materials [15–17]. Many research centers and university laboratories have promoted research on relevant topics.

It is now widely accepted in the restoration field that a framework of requirements should be fulfilled to avoid failures. They will refer to conceptual (compatibility, retreatability, etc.), which are closely related to functional requirements for each type of material (e.g., repair mortar for stone, bedding, and plaster), as well as to technical requirements. The latter could be referred to as:

– the selection of materials commercially available or to constituents of custom-made mortars/grouts and their mixing;
– the techniques of application; and
– the assessment of their quality and performance, including their long-term resistance to weathering.

In the paper of RILEM TC RHM [18] about performance requirements for mortars for the surface repair of HS, a very good analysis of the aforementioned requirements is given. Although the paper mainly addresses surface repair of external/internal façades and architectural details of HS, the requirements are also valid for mortars used to repair lost parts of stone units, retain their fragments, and fill wide cracks/voids and lacunae. Using these requirements, some key points (as cornerstones) will be mentioned.

7.2.1 Conceptual Requirements

According to Charter of Venice (ICCOMOS 1964), the following principles have been set up for these types of interventions:

– No conjectural repairs;
– Efficiency of materials and techniques used for repair should be documented in scientific data and proven by experience;
– Replacement of missing parts must integrate harmoniously with the whole, but at the same time must be distinguishable from the original (no falsification of the artistic or historic evidence).

Furthermore, literature on understanding the conceptual requirements can be found in some studies [19, 20], where it is simply stated that "compatibility" means that introduced treatment and materials will not have negative consequences, and "retreatability" means that conservation treatments in the present would not preclude or impede further treatment in the future.

7.2.2 Functional Requirements

Closely related to the conceptual are the so-called functional requirements, such as color and texture harmonization of repair mortar with stone substrate and, in particular, how consistent the color hue is without changes due to wetting or weathering cycles. It is also important to avoid secondary reaction products, such as those coming from lime leaching, alkali silica, or alkali carbonate reactions, which create stains in the repair mortar or the original stones. Another important functional requirement in any repair work is the development of good adhesion between the repair mortar and stone. The factors influencing adhesion, such as soundness of the stone substrate, differential thermal expansion, and water/vapor transport properties, are well summarized in the paper of Veiga et al. [21], which is based on experience from practice. Knöfel and Schubert [22] critically comment on the bond and impact of mechanical strength of mortar as compatibility requirements. For the stone substrate's protection, the chances of failure of bond should always be limited in mortar [18].

Furthermore, the resistance of repair mortars in new composite sections (old stone + repair mortar) to environmental conditions is a matter of balancing the properties/characteristics of new mortars, especially in terms of durability and compatibility, with the original stone [23]. A suggestion about the most important characteristics of the mortar and stone substrate to be compared is made by Peroni et al. [24] and by Knöefel and Shubert [22]. The compatibility requirement seems to be the predominant factor to take into account when a new repair mortar is designed [25].

In order to retain large missing parts of stone or their loose fragments, stainless steel rods or even meshes are embedded properly in the stone body before casting of the repair mortar [26].

Preparatory work could be helpful in enhancing adhesion (consolidation or retreatment of stone substrate, splashing with a thin layer of diluted mortar mixture, etc.), as well as in increasing the service life of repair mortar, by evaluating and assessing the climatic conditions and main causes of deterioration, salt content in the substrate, etc.

What could be considered as progress of the last decades is the sound and deep knowledge on influential parameters, and more precise assessment of properties related to functional requirements by employing regulative guidelines. For example, test methods and acceptable limits for testing adhesion can be found in the paper by Veiga et al. [21].

7.2.3 Technical Requirements

Technical requirements refer to mortar/grout mixtures used in the type of repair mortar and selection of appropriate commercial mortars or constituents, such as binders, aggregates, fillers, and admixtures, to develop the targeted physical (i.e., porosity) and mechanical/elastic properties (i.e., strength, elasticity, and deformability).

As it has been pointed out in the introduction that, before any choice of repair material, the systematic analysis of the under-repair stone and environmental conditions that affect the material should be well understood.

Apart from binder selection (i.e., systems based on lime such as lime + pozzolan + cement, or hydraulic lime + cement), various fillers from natural sources (fine limestone, fine sand) or industrial by-products (brick dust, glass particles) can be used if their addition proves advantageous. For example, crushed wastes of original stone could be used as filler, enhancing color harmonization and compatibility of the mixture's composition. Regulative specifications must be followed to test binders and fillers in order to be suitable to repair mortars/grouts.

Besides additives such as superplasticizers, air-entraining and shrinkage-reducing agents, along with other more general additives/admixtures such as pigments, fibers, nanofibers, and nanomaterials offer new chances to improve the quality and extend the service life of repair mortars/grouts.

As seen in Fig. 7.3, the stainless-steel thin rods are encored in the stone substrate after drilling openings and fixing the rods inside with grouts or resins.

The techniques of application and the finishing of mortars or injection of grouts should be defined before execution of the work. The demand is to have the repair mortar match with original stone, and to be distinct at the same time. Specific tools must be used to imitate the stone surface texture.

Fig. 7.3 Stainless steel rods embedded in the stone body before repairing, from [26]

In the case of grouts used for filling existing cracks in the stone body, apart from the aforementioned requirements, specific instruments for fluidity, volume stability, and injectability have to be utilized. In addition, the proper curing regime is necessary to avoid premature failure. Measures for the protection of the mortar while it is still fresh from exposure to low temperatures should be also taken.

Quality control at all stages of the execution of a stone repair project is more feasible nowadays than in the past. A separate part of the project should be comprised of a set of testing methods, the acceptable limit values, technical descriptions for materials selection, and instructions about implementation of the work in practice, including preparatory work.

Technicians should be skilled and have proven experience. The behavior of the repaired parts should be monitored at regular intervals, and should be included in the planning phase of the project, as well as small scale maintenance works.

Quality control, monitoring, and small-scale maintenance works are of great importance, particularly for repairing stone units of archaeological sites, ancient theaters, and castles, where large-scale repair interventions of the stones are needed.

7.3 Case Studies Presentation

The presentation of the selected case studies that follow is of interest because common problems often confronted in practice are recognized. One of them deals with the lack of adequate time to both conduct tests and conclude the new repair materials design. Another problem is related to limitation of the project budget, which hinders any extension of research.

However, it is necessary to make decisions based on a few tests, regarding the most crucial properties for the good functionality/performance of the repair mortar/grouts.

7.3.1 Archaeological Site of Leivethra (Greece): Designing of the Repair Mortars and Grouts for the Repair of Stone Blocks of Its Acropolis

Some examples related to relevant projects in which the Laboratory of Building Materials of the Aristotle University Thessaloniki (LBM, AUTH) has been involved, are mentioned hereinafter. The archaeological site of Leivethra is situated on a hill, low on the southeastern foot of Olympus Mountain, among three river streams. The place is known from mythology as the country of Orpheus, and it was inhabited from the eighth century BC up to the first century BC.

The acropolis is surrounded by stone masonry walls. The geomorphology of the area and the ground characteristics favor landslide phenomena followed by subsidence of the walls and destruction of their stability. Additionally, the local environmental conditions consist of low temperatures, high humidity, and snow which occur often throughout the year. Vegetation is very invasive and has an impact on the surface of stones via biological attack.

The characteristics of the stone units were assessed by taking six large pieces of stone from which a number (3–4) of samples were shaped and tested to find porosity, compressive strength, and salt content. In Table 7.2, some of their characteristics are shown.

Based on microscopic characteristics and other properties, the geologists found a quarry still in service from which samples were taken and tested to see if they would match with the old stone pieces, in order to reconstruct destroyed parts of wall and upgrade the archaeological site.

However, a great number of stone units had to be treated properly and repaired with mortars (to augment the missing parts) or injected with grout or flowable mortar to fill the cracks and voids.

Each stone unit has been registered by Ephorate of Antiquities of Pieria on a map where the damage rate has been recorded. Selected stone pieces with cracks and loss of mass are given and commented on in Fig. 7.4.

It was decided that the repair mortars/grouts be softer and more deformable than the compact and tough matrix of old marble stone. A ternary binding system consisting of aerial lime CL90, ground natural pozzolan, and white cement was used for grouts. Fine sand (0–1 mm or 0–2 mm) was also added in the binding system to fill cracks with openings of ≥0.5 mm or ≤ 10 mm. Polycarbonylic-based superplasticizers were used to reduce the water demanded for required fluidity, volume stability, and penetrability. The aforementioned properties were measured in their fresh state following the standard methods of ASTM C939–87, ASTM C940–87, and NFP 18–89, respectively.

The composition of grouts and their fresh properties, as well as the mechanical strength and porosity of hardened grouts are given in Table 7.3.

For large cracks (2.0–10.0 cm) a flowable mortar was developed to be inserted into the large cracks/voids by gravity or to fill deep lacunae at the stone surface. It was even used with the complete loss of stone by being properly cast into the fragments of the stone body.

Table 7.2 Characteristics of stones taken from different places in the Leivethra acropolis (Greece)

Sample	Microscopical observation	Porosity (%)/ App. Specific gravity	Compressive strength (MPa)	Content in soluble salts by weight %		
				Cl^-	NO_3^-	SO_4^{-2}
S1	Fine-grained White grey marble of compact matrix*	0.84%/2.62	25.65	<0.01	–	<0.01**
S2		1.26%/2.66	34.96	<0.01	–	<0.01
S3		1.23%/2.68	32.24	<0.01	–	<0.01
S5		0.13%/2.64	39.45	<0.01	–	<0.01
S6		0.60%/2.66	27.56	<0.01	–	<0.01
S7		0.43%/2.66	25.41	<0.01	–	<0.01

*The marble consists of crystalline calcite (98%), trace of quartz (1%) and trace of dolomite (1%)
**Stones are free of salts

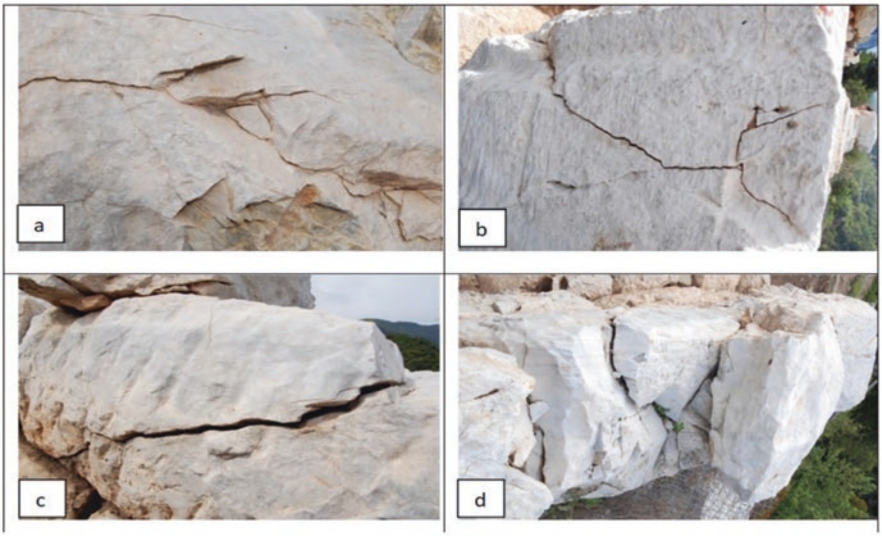

Fig. 7.4 Photos of problematic stones from Leivethra (Greece): (**a**) Cracks and detachment of thick layers of stone; (**b**) Cracks at the end of stone (through its section); (**c**) Transversal cracks of great opening; and (**d**) Loose parts of stone and missing parts

Table 7.3 Composition and properties of two types of grouts for filling stone units of Leivethra acropolis (Greece)

Constituents	Parts by weight	
	Comp. 1	Comp. 3
Aerial lime CL90	0.2	0.2
Ground natural pozzolan	0.3	0.3
White cement	0.5	0.5
Superplasticizer (1% by mass of binders)	√	√
Water/binder ratio	0.75–0.76	1.0
Fluidity time (sec)	12.5	45
Marsh cone ASTM C939–87		
Volume stability settlement (%)	<5%	<5%
ASTM C940–87		
Penetrability (sec)	2–4	2–4
NFP 18–89 sand column 2–4 mm		
28-d Compressive strength (MPa)	10	11.6

(continued)

Table 7.3 (continued)

Constituents	Parts by weight	
	Comp. 1	Comp. 3
28-d Flexural strength (MPa)	1.95	2.35
Porosity (%)	12.18	14.5
Volume change of hardened grout after 15 days	<0.5%	<0.5%

Table 7.4 Composition and properties of flowable mortar

Constituents	Parts by weight
Aerial lime CL90	0.8
Ground natural pozzolan	1.0
White cement	0.5
Limestone filler	0.8
River sand (brown hue) (0–4) mm	3.8
Superplasticizer (1% by mass of binders)	√
Retarder 0.25% by mass of binders	
Water/binder ratio	0.64
Properties	
Fluidity flow table extension (cm)	20–25 cm
28-d Compressive strength (MPa)	20.1
28-d Flexural strength (MPa)	2.5
28-d Porosity (%)	10–11%
28-d Absorption (%)	7–9%
Apparent specific gravity	1.42–1.97

The target characteristics of the type of flowable mortar were:

- adequate fluidity up to 1½ hours from addition of mixing water and penetrability by gravity or slight pressure;
- good cohesiveness of the mortar mixture and volume stability;
- limited shrinkage;
- development of good adhesion with stone substrate; and
- compatibility with original stone (no higher strength and lower porosity compared with of the old stone).

It is also important that the flowable mortar does not react during various environmental conditions with the stone, giving harmful by-products. The coefficient of thermal dilation should be of the same order with that of the existing old stones.

The composition and main properties of the proposed flowable mortar are given in Table 7.4.

7.3.2 Ancient Theater of Kassope (Greece)

The Ancient theater of Kassope was built in the third century BC, on southern foothills of Zaloggo, Preveza, Greece. The *koilon* (auditorium) consists of two seating zones. The upper zone was constructed with limestone pieces, which suffered from intense deterioration.

Three large stones from the upper *koilon* of the theater were cut into shaped samples (2–3 for each stone piece) and tested. LBM, AUTH was asked to estimate only the basic characteristics, as well as to design a mortar for use as an artificial stone to complete the missing seats of *koilon*, and another flowable mortar to fill large voids. In Fig. 7.5 the modified samples from large stone pieces are shown.

The limestone consists of fine grains and was of a very pale brown color hue (10YR 8/2 according to Munsell scale), with intense cracking and many venules inside their mass. Although all the samples were of the same type of limestone, their physical and mechanical characteristics differ greatly because of different deterioration grades and schistosity. When the load is imposed parallel to schistosity direction, compressive strength is very low. In Table 7.5 the physico-mechanical characteristics are shown.

It was decided to keep the target strength level for the newly designed mortars at a value of 20–30 MPa (not as high as sound stone nor too low due to the presence of parts with intense schistosity). In this case a mortar was needed to cast artificial stone for integration of the *koilon*, and a flowable mortar to fill cracks and voids. In addition, it was imperative to keep with the criteria of compatibility, color harmonization, and porosity (slightly higher than the matrix of original stone). Other tests

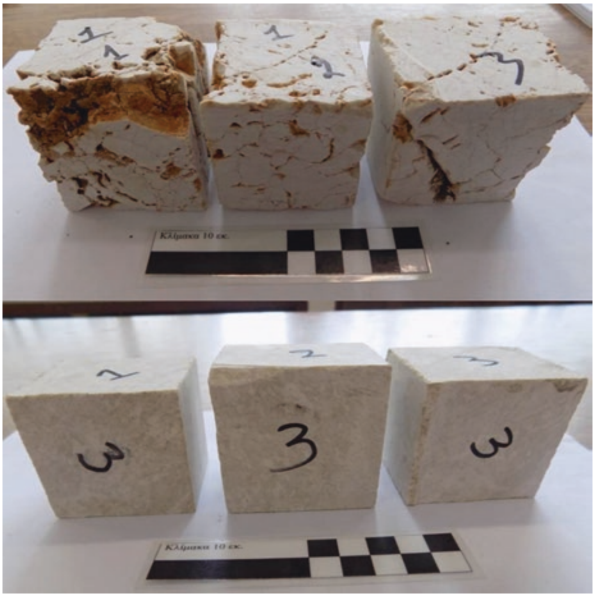

Fig. 7.5 Shaped samples from large stones from Kassope (Greece) of different structure

Table 7.5 Physico-mechanical characteristics of stone samples

Sample mortar	Porosity (%)	Apparent specific gravity	Compressive strength (MPa)	Comments
1	5.53	2.44	9.05	Intensive schistosity
2	7.53	2.40	8.51	Intensive schistosity
3	4.09	2.65	55.74	Sound
4	5.94	2.33	6.62	Intensive schistosity
5	4.20	2.45	32.5	Venules
6	5.30	2.36	22.8	Venules

Table 7.6 Composition of trial mixes for artificial stone seats (1, 2, 3) and flowable mortars (4, 5, 6)

Constituents	1	2	3	4	5	6
White cement, parts by weight	0.5	0.6	0.6	0.5	0.5	0.5
Aerial lime CL90, parts by weight	–	0.2	0.2	–	0.25	–
Ground natural pozzolan, parts by weight	0.2	0.2	0.2	0.2	0.25	0.2
Dry soil <0.25 mm, parts by weight	0.3	–	–	0.3	–	0.3
River sand (0–4 mm), parts by weight	2.0	2.0	1.6	2.0	2.5	2.0
River sand (4–8 mm), parts by weight	–	–	0.4	–	–	0.5
Pigment Ombra 0.5% by mass	–	√	–	–	√	–
Polycarboxylic-based superplasticizer 1% by mass of binder	√	√	√	1.5% by mass of binder	1.5% by mass of binder	1.5% by mass of binder
Water/binder	0.45	0.41	0.36	0.56	0.61	0.56
Flow table expansion (cm)	12–13	12–13	11–12	18	18–19	18–19

concerning durability were difficult to carry out because of the time restrictions of the project. In Tables 7.6 and 7.7 the results of the tested trial mixes are given.

Taking into account that the porosity values of original stone samples range from 4–7.5%, it could be said that the porosity values of mortars are acceptable, as well as the strength development at 28 days. In comparing the color hue of original stone, there are good matches with the compositions No 2 for the artificial stone seats and No 4 and 6 for the flowable mortars.

Table 7.7 Characteristics of hardened trial mixes at 28 days

Trial mixes	Color hue (Munsell scale)	Porosity (%)	App. Spec. gravity	Compressive strength (MPa)	Flex. strength (MPa)
1	10YR 7/3 very pale brown	6.66	2.06	22.75	4.30
2	10YR 8/3 very pale brown	7.14	2.03	32.76	4.40
3	10YR 7/2 light grey	6.36	1.97	34.74	3.95
4	10YR 8/2 very pale brown	10.41	1.69	24.72	3.21
5	10YR 8/1 white	12.93	1.87	16.54	3.40
6	10YR 8/3 very pale brown	8.29	1.90	25.36	4.10

Table 7.8 Physical and mechanical characteristics of old stone units of Agora of Pella

Samples	Absorption (%)	Porosity (%)	Apparent specific gravity	Compressive strength (MPa)
Healthy stone	0.64–1.50	1.5–3.5	2.35–2.60	30–45
Medium deterioration	1.50–2.50	4.0–9.0	2.30–2.40	15–30
Heavily deteriorated	2.50–4.85	9.0–11	2.17–2.27	11.5–15.0

7.3.3 Archaeological Site of Pella (Greece): Survey of Artificial Stones Five Years After Their Manufacture

Pella in Northern Greece was the capital of the Kingdom of Macedonia since the fifth century BC and comprises the largest Agora (70,000 m^2) of Antiquity.

The archeologists responsible for restoration works decided to reconstruct with artificial stones cast in place in the low walls, to highlight the ground plan of the ancient Agora. LBM, AUTH was asked to prepare a mortar composition for superficial repairs and another one for artificial stone.

Following widely applied methodology, the original stones were systematically studied and petrologically characterized. The color was defined as very pale brown 10YR 8/2 on the Munsell scale or white 10YR 8/1. In the calcitic matrix, a small content of gypsum was observed. Stones came from local marl limestone deposits which do not exist nowadays. Pores, nests, and venules of well-crystalized limestone were observed. In the remnants of the walls of the Agora, the stones presented different grades of deterioration. There were compact units and gravel-like pieces. At the surface of the stones there were flakes that had detached and led to loss of mass. Biological attack was also intensive. The physical and mechanical characteristics are given in Table 7.8, while in Fig. 7.6, a photo of compact and deteriorated old stone is provided.

Fig. 7.6 Compact and deteriorated stone units from Pella Agora (Greece)

As shown in Table 7.8 the strength of old sound stones ranges from 30–45 MPa, while for the deteriorated ones, the strength ranges from 11.5–15.0 MPa. For the completion of the unsound stone units the latter strength would be selected as the target strength. For the new artificial stone units, which would not cooperate with the old ones, the former strength level of 30–45 MPa was preferred as target strength.

The addition of cement to a lime-pozzolan combination seemed to be necessary for strength levels ≥20 MPa. White cement is nearer the desirable color and its alkali and sulfate contents are relatively low. Furthermore, sieved dry soil <0.25 mm and inert fine materials coming from recycling old small stone fragments were used for better color harmonization. The morphology of the surface texture of artificial stone units was modified by grooving with a chisel, as shown in Fig. 7.7.

The composition of mortars for surface repair is given in Table 7.9 and artificial stone in Table 7.10.

The characteristics of artificial stones cast on site were checked and found to be significantly lower than the values taken in laboratory, as shown in Table 7.11.

Five years after restoration works, a survey was made. It was observed that the performance of surface mortar repairs was quite good. Color hue was in harmony with that of the old stone. The adhesion to the substrate was very good and resistant to wetting-drying cycles and thermal changes. Salts on the surface were not detected. However, very few repaired stone units have presented visible cracks, due to improper application, such as a thin layer of mortar on a bulging part of stone, or insufficient wetting of the substrate before the mortar's application. The soluble salt content was relatively low, with the content of chlorides at 0.03%, nitrates <0.01%, and sulfates 0.84%.

Several large artificial stone pieces, of sizes ≥100 cm (Fig. 7.8), had presented cracks through their section and were split into smaller compact pieces. At first, it was decided only small size pieces of artificial stone ≤60 cm length would be cast,

Fig. 7.7 Grooving the artificial stone with chisel

Table 7.9 Composition and characteristics of the surface mortar applied to old stones

Materials	Parts by weight
Aerial lime CL90	1
Ground nat. pozz.	0.8
10% retained on 45 μm sieve	
White cement	0.2
River sand (0–2 mm) of light brown color	4.0
Superplasticizer of polycarboxylic base (1% by mass of binders)	√
Water for required workability (flow table extension 15 ± 1 cm)	√
Porosity (%)	15–19
Compressive strength (MPa)	4–7

but later when technicians became familiar with the manufacturing process, they tried to cast larger pieces. They also used a galvanized steel cage and added polypropylene fibers in an effort to avoid cracking. However, cracks continued to appear again (Fig. 7.9), though thinner than in the past. The pattern of cracking seems to be related to shrinkage cracks. Taking into account all these remarks, the mortar's composition was reconsidered and improved by modifying the content in fine materials. Stainless steel fibers were proposed to replace galvanized reinforcement to avoid the corrosion process' activation. The length of artificial stone pieces was limited to 60–80 cm. The improved composition is given in Table 7.12.

A system of checking the quality of manufactured mortar mixtures on site was also suggested, in order to meet the target strength. The cracking tendency was significantly reduced. The reconstructed parts of the walls are shown in Fig. 7.10.

Table 7.10 Composition and characteristics of mortar for artificial stone manufacture

Materials	Parts by weight
White cement CEM II/A-LL 42.5 N	2.8
Sieved dry soil <0.25 mm	0.7
River sand (0–2 mm)	0.65
River sand (2–4 mm)	0.15
Crushed recycled old stone pieces (0–2 mm)	1.2
Superplasticizer polycarboxylic base 1% by mass of binders	√
Water for flow table extension 10 ± 1 cm	√
Porosity (%)	5.78
App. Specif. gravity	2.3
28-d Compressive strength (MPa)	45.8
28-d Dynamic Mod. of Elasticity (GPa)	27.5

Table 7.11 Characteristics of artificial stone cast on site

Sample	Porosity % (mean value of 6)	App. Spec. gravity	Compressive strength (MPa)	Dyn. modulus of elasticity (GPa)
Artificial stone cast on site	1 year: 13	1 year: 1.73	1 year: 24.90	1 year: 11.40
	2 year: 12.35	2 year: 1.78	2 year: 34.12	2 year: 12.42
Authentic natural stone	5.13	2.30	41.25	–

Fig. 7.8 A large artificial stone with severe cracking after 2 years from its manufacture

Fig. 7.9 Thin cracks in the new artificial stone

Table 7.12 Improved composition of mortar for artificial stone

Materials	Parts by weight
White cement CEM II/A-LL 42.5 N	2.8
Sieved dry soil (0–1 mm)	0.7
River sand (2–4 mm)	0.65
River sand (4–6 mm)	0.15
Crushed recycled old stone (0–2 mm)	1.2
Superplasticizer of carboxylic base 1% by mass of binders	√
Stainless steel fibers 1‰ by volume of the mixture	√
Water required for flow table extension 10 ± 1 cm	√

7.4 Conclusions

Repairing stone units of HS with mortars/grouts is a highly specific task, where solutions of commercial mortars/grouts do not often comply with the requirements. A methodology should be applied, including actions such as:

– selecting all data concerning the documentation of stones;
– assessing the grade of their degradation; and
– understanding the changes of the environmental conditions on a daily, seasonal, and annual basis.

Fig. 7.10 A reconstructed part of wall of the Agora in Pella, with greatly reduced cracking

Many trial mixes and a step-by-step process are needed to meet the requirements of good performance. Continuous monitoring of the repaired parts is of great importance and should be established within the project of repair works.

In the last few decades progress has been made in establishing regulative guidelines based on sound research and experience, as well as on advances in science and technology of materials. For instance, significant improvements in designing and applying mortars/grouts in repair works have promoted cost-effective and environmentally friendly alternatives in repairing stone units. A successful repair intervention contributes to the preservation of monumental Heritage closely related to cultural tourism and local economy.

References

1. Charola AE. Stone Deterioration in Historic Buildings and Monuments. In: Kwiatkowski D, Lofvendahi R, editors. 10th International Congress on Deterioration and Conservation of Stone. Stockholm, Sweden: ICOMOS; 2004. p. 3–14.
2. Fassina V, Favaro M, Crivellari F, Naccari A. The Stone decay of monuments in relation to atmospheric environment. Annali di chimica. 2001;91:767–74.
3. Fitzner B. Porosity Properties and Weathering Behaviour of Natural Stones – Methodology and Examples. Stone Materials in Monuments Diagnosis and Conservation, 2nd course CUM Univ, School of Monument Conservation Edited by Mario Adda. Bari, Italy, 1993.
4. Bretti G, Filippo B, Natalini R, Goidanich S, Roveri M, Toniolo L. Modelling the effects of protective treatments in porous materials. MACH 2019 conference 2019.
5. Kapridaki C, Maravelaki P. Titania-silica sol-gel bactericide coatings on marble. 7th International Conference on Nanosciences and Nanotechnologies 2010. p. 192.
6. Laurenzi Tabasso M. Products and Methods for the Conservation of Stone. Problems and Trends. In: Kwiatkowski D, Lofvendahi R, editors. 10th International congress on deterioration and conservation of stone. Stockholm, Sweden: ICOMOS; 2004. p. 269–83.

7. Sassoni E, D'Amen E, Roveri N, Scherer GW, Franzoni E. Photocatalytic hydroxyapatite-titania nanocomposites for preventive conservation of marble. IOP Conference Series: Materials Science and Engineering. 2018;364:012073. doi: https://doi.org/10.1088/1757-899x/364/1/012073.
8. Ashurst J, Ashurst N. Practical Building Conservation. English Heritage Technical Handbook. vol 1, 1988.
9. Hyslop EK. Assessing stone decay and the future repair needs of a sandstone city. A survey of the stone Build Heritage in Glasgow, Scotland. In: Lukas-Zevicz JW, Niencewicz P, editors. 11th International congress on deterioration and conservation of stone. Torun, Poland, 2008. p. 1117–24.
10. TC203-RHM. RILEM TC 203-RHM: Repair mortars for historic masonry. Performance requirements for renders and plasters. Materials and Structures. 2012;45(9):1277–85. doi: https://doi.org/10.1617/s11527-012-9916-0.
11. TC203-RHM. RILEM TC 203-RHM: Repair mortars for historic masonry. The role of mortar in masonry: an introduction to requirements for the design of repair mortars. Materials and Structures. 2012;45(9):1287–94. doi: https://doi.org/10.1617/s11527-012-9847-9.
12. TC203-RHM. RILEM TC 203-RHM: Repair mortars for historic masonry. Repair mortars for historic masonry. From problem to intervention: a decision process. Materials and Structures. 2012;45(9):1295–302. doi: https://doi.org/10.1617/s11527-012-9917-z.
13. TC203-RHM. RILEM TC 203-RHM: Repair mortars for historic masonry. Requirements for repointing mortars for historic masonry. Materials and Structures. 2012;45(9):1303–9. doi: https://doi.org/10.1617/s11527-012-9849-7.
14. Fassina V. CEN TC 346 Conservation of Cultural Heritage-Update of the Activity After a Height Year Period. Springer International Publishing, 2015. p. 37–41.
15. RILEM PRO 12: International RILEM Workshop on Historic Mortars: Characteristics and Tests. Paisley, Scotland, 1999.
16. Historical Mortars. In: Veiga RM, editor. 1st Historical Mortars Conference HMC08. Lisbon, Portugal 2008.
17. Proceedings of 2nd Conference on Historic Mortars – HMC 2010 and RILEM TC 203-RHM final workshop. In: Válek J, Groot C, Hughes JJ, editors.: RILEM Publications, 2011.
18. Válek J, Hughes J, Pique F, Gulotta D, van Hees R, Papayiani I. Recommendation of RILEM TC 243-SGM: functional requirements for surface repair mortars for historic buildings. Materials and Structures. 2019;52(1):28. doi: https://doi.org/10.1617/s11527-018-1284-y.
19. Hayen R, Van Balen K. Thermal Expansion of Historic Masonry, Looking for Physical Compatibility. In: Van Hees R, Naldini S, Van der Klugt L, editors. Maintenance of Pointing in Historic Buildings: Decay and Replacement, Final Report, EC Environment Programme, contract ENV4-CT98–706, 2001. p. 169–74.
20. Teutonico JM, Charola AE, De Witte E, Grasegger G, Koestler RJ, Laurenzi Tabasso M, et al. Group Report 'How Can We Ensure the Responsible and Effective Use of Treatments (Cleaning, Consolidation, Protection)?', Dahlem Workshop on Saving Our Architectural Heritage: Conservation of Historic Stone Structures. In: Baer NS, Snethlage R, editors. Chichester: John Wiley & Sons; 1997. p. 293–313.
21. Veiga MR, Velosa AL, Magalhães AC. Evaluation of mechanical compatibility of renders to apply on old walls based on a restrained shrinkage test. Materials and Structures. 2007;40(10):1115–26. doi: https://doi.org/10.1617/s11527-006-9209-6.
22. Knofel D., Schubert P. Zur Beurteilung von Morteln fur die Instandsetzung von Mauerwerk. Mortel und Stein-erganzungsstoffe in der Denkmalpfledge. Berlin: Verlag Ernst & Sohn; 1993. p. 87–106.
23. van Hees RPJ. Damage diagnosis and compatible repair mortars. International Workshop 'Historic Mortars: Characteristics and Tests', RILEM Technical Committee TC-167COM, University of Paisley, Scotland,1999. p. 1–9.

24. Peroni S, Tersini C, Torraca G, Cevea S, Forti M, Guidobaldi F, et al. Lime based mortars for repair of ancient masonry and possible substitutes. Mortars, cements and grouts used in the conservation of historic buildings Rome, Italy, 1981. p. 63–100.
25. Hughes JJ, Válek J. Mortars in Historic Buildings: A Review of the Conservation, Technical and Scientific Literature. Historic Scotland; 2003.
26. Papayianni I, Stefanidou M, Pachta V. Survey of Repaired and Artificial Stones of the Archaeological Site of Pella Five Years After Application. In: Toniolo L, Boriani M, Guidi G, editors. Built Heritage: Monitoring Conservation Management. Cham: Springer International Publishing; 2015. p. 431–42.

Chapter 8
In situ Assessment of Conservation Treatments and Monitoring of Their Effectiveness

Susanna Bracci and Barbara Sacchi

Abstract In this chapter an overview of the main invasive/non-invasive techniques used *in situ* for the evaluation of conservation treatments is provided. The conservation treatments considered are cleaning, consolidation, and protection of stone, mainly for architectural heritage. After a brief introduction, a paragraph is dedicated to the current process of drafting the standards, starting from previous experiences. In each paragraph dealing with conservation treatments, a reminder of commonly used laboratory tests carried out on stone samples, following either standardized protocols or not, are briefly reported. Details about testing protocols and threshold values for the selection of the best conservation treatment and for the monitoring will be described.

This chapter is not a technical description of each single technique but rather an introduction to the different possibilities of application of *in situ* methods.

Keywords Stone · Conservation treatments · *In situ* evaluation · Monitoring

8.1 Introduction

In conservation, scientific analytical methods are used to evaluate both the materials and the effects of the conservation procedures applied. The aim of this chapter is to review the techniques currently used or potentially usable *in situ* for the evaluation of treatments for stone conservation. There are many different methods to choose from depending on the aim of the analysis, and it is possible to find in the literature several papers or books reporting information about conservation treatment evaluation [1, 2]. Nowadays, a very high number of analytical techniques are available, from very simple ones to those that require large structures, but which can provide information not otherwise obtainable. But which information is needed? According

S. Bracci · B. Sacchi (✉)
Institute for Heritage Science of National Council of Research, ISPC-CNR, Sesto Fiorentino (FI), Italy
e-mail: susanna.bracci@cnr.it; barbara.sacchi@cnr.it

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to Doehne "*One might suppose that the most practical approach to stopping or reducing stone* decay *would be simply to apply a treatment and see if it works. But how can we tell if it is working? What do we really mean by "working"? How long does a treatment need to be left in place? Can things be speeded up a bit? Will it keep on working indefinitely? Will it work on other stones in other environments? What about other* treatments *that come along while a lengthy evaluation of one is being carried out?*" [2]. These are very clear but also very difficult questions to answer. In stone conservation of immovable objects, being a building or a statue, the use of *in situ* analyses, better if non-destructive or micro-destructive, is very important but also very challenging, since the techniques must be portable and able to be used in the field in various conditions, sometimes very difficult ones. It is clear that it is not possible to obtain all the necessary information from one single analytical method and very often, even if a set of techniques that provide complementary information is used, some results are still difficult or impossible to achieve.

Between a completely *in situ* approach and one based only on the analyses of samples, a very efficient diagnostic protocol could be based on the combination of the two with a limited, but very focused, sampling campaign. However, the possibility of using *in situ* diagnostic techniques is not only important for the immediate evaluation of treatments, but also for monitoring them over time, which unfortunately, is not a common practice, mainly due to both logistical and financial problems.

Monitoring is a very important aspect of conservation since it provides the long-term assessment of treatments, thus allowing to evaluate their evolution over time or the need for further interventions.

Literature concerning non-destructive techniques applied to stone conservation is very widely available [3–6]. In the next paragraphs, the different available techniques employed for the evaluation of conservation treatments such as cleaning, consolidation, and protection will be reported, together with some information on drafting specific standards.

8.2 Recommendations & Standards – History and State of the Art at the European Level

Conservation treatments of deteriorated stones date back to nineteenth century. As early as 1861 A. W. von Hoffman suggested the use of alkoxysilanes for the deteriorated limestone on the Houses of Parliament in London [7], and from then, in particular in the second part of twentieth century, a lot of different products have been introduced in the field of conservation. From the mid-70s, methods for examining and evaluating products for conservation began to be developed [8, 9].

Over the years, several scholars have outlined the need for standardised procedures in the field. In 1995, at the end of the International Colloquium ICCROM "Methods of evaluating products for the conservation of porous building materials in monuments" held in Rome [10], six Round Tables were organized, each discussing the data presented, either orally or on poster, on a specific topic and focused on still on-going problems. The summary of each Round Table has been reported in a special issue of Science and Technology for Cultural Heritage [11], and the content will be discussed in more details in the paragraphs dealing with treatments.

Regarding standards, Laurenzi Tabasso stated *"…one point resulted very clearly from the Rome '95 Colloquium: the strong need to define international standards or, at least internationally agreed criteria…*" [10]. Moreover, Rainer Sasse et al. in the conclusions reported "*To conclude it seems evident that international expert groups are necessary to solve the open question concerned with the evaluation of* consolidation treatments" [12].

More recently, Doehne and Price, in their book stated "*Many workers have devised their own procedures for evaluating* treatments*, using a range of tests to build up an overall picture. [….] However, it can be very difficult to compare the findings of one researcher with those of another, and there is a need for standardized procedures"* [2].

During the last 40 years specific groups or national standardization bodies started working on recommendations or national standards for evaluating both conservation materials and procedures. As an example, RILEM (Reunion Internationale des Laboratoires et Experts des Materiaux, systemes de construction et ouvrages) Commissions 25-PEM (Protection et erosion des monuments) Working Groups worked on test procedures [13, 14].

A standard is a document, established by consensus and approved by a recognized body, that provides rules, guidelines, or characteristics for activities or their results, aimed at the achievement of the optimum degree of order in a given context [15]. Standards may include requirements and/or recommendations in relation to products, systems, processes, or services. Standards can also be used to describe a measurement or test method, or to establish a common terminology within a specific sector. Standards, unlike legislation, are voluntary in application, unless called up in legislation or cited as part of a contract.

In Italy, in 1977 the NorMaL (Normativa Materiali Lapidei) Commission was founded thanks to the initiative of a group of conservation scientists from CNR (National Council of Research, in particular, the centres at that time dedicated to works of art) and from the Central Institute for Restoration (ICR, now ISCR). The objective was to publish recommendations (the commission not having the authority to propose standards) for the study of decay of stone materials and for monitoring the effectiveness of conservation treatments of artefacts of historical interest.

The Commission fixed a limitation to its own work: only stone materials (natural stones, plasters, mortars, bricks) were taken into account. The Commission was composed by experts and researchers from the CNR and the Ministry for Cultural Heritage, but also academics, professionals (architects, conservators, and conservation scientists), and representatives of the industries involved in the field, for a total of about 200 members at the time of foundation. From 1977 up to 1993, 44 recommendations were published (copyright CNR-ICR) (Fig. 8.1a). After a twenty-year experience, in 1997 the NorMaL Commission converged in the standardization

Fig. 8.1 (**a**) Image of the cover of NorMaL 11/85 – Assorbimento di acqua per capillarità (Water absorption by capillarity) (1985). (**b**) Image of the cover of the UNI standard 10,859 – Assorbimento di acqua per capillarità (Water absorption by capillarity) (2000)

activities carried out by UNI (Italian Body of Standardization). Therefore, the UNI-Normal Commission "Cultural Heritage" was established and organized into 20 GL (Gruppi di Lavoro, Working groups). Nowadays, the "Cultural Heritage" committee is under the UNI/CT 033 and structured into 8 groups. Since 1997, 64 standards have been published [16]. The first standards that have been revised, updated, and published as UNI standards were the NorMaL recommendations (Fig. 8.1b).

In 2001, UNI, in accordance with other National Standardization Bodies present at CEN (European Committee for Standardization), proposed a request for the Standardization on Conservation of Cultural Property at European level. The Business Plan presented was discussed and approved by nine delegations.[1]

The European Committee for Standardization (CEN) is the European Standardization Body (recognized in Directive 98/34/EC) for the development of standards in all areas except for the telecommunications and the electro-technical fields. CEN Members (with voting rights) are 27 National Standardization Bodies of EU countries, Turkey, and EFTA (European Free Trade Association) countries (Iceland-Switzerland-Norway). There are also other participants (no voting rights)

[1] UNI-Ente Nazionale Italiano di Unificazione-Italy; IBN/BIN-Institut Belge de Normalisation-Belgium; AFNOR-Association Francaise de Normalisation-France; BSI-British Standard Institution-UK; AENOR-Asociacion Espanola de Normalisation-Spain; NEN-Nederlands Normalisatie Instituut-The Netherlands; NSF- Norges Stadardiseringsforbund-Norway; SNV-Switzerland; CSNI-Czech Standards Institute-Czech Republic.

that are associates, such as organizations representing business sectors, SMEs, consumers, and Partner Standardization Bodies (PSBs), i.e., National Standards Bodies that are a member of ISO, but are unlikely to become CEN Members or CEN Affiliates for political or geographical reasons. The CEN is organized with different decisional and working levels. The Technical Board (BT) approves technical policy and strategy. It monitors the technical work and takes decisions about the proposals for new projects. The Technical Committee (TC) is established by the BT to develop standards within a specific scope/area. The Working Groups (WGs) are established by TC, and are in charge of providing draft standards.

The Technical Committee Cultural Property (changed to Cultural Heritage in 2012) (TC346) was initially (2002) organized into 5 WGs, while in 2012, other WGs were added, and nowadays, there are 11 in total [17]. Among the 11 WGs, the one dealing with tests for stone is WG3 (Porous inorganic materials constituting cultural heritage). In WG3, from 2002 to date, experts from 11 European countries (Belgium, Finland, France, Germany, Denmark, Italy, Ireland, Neatherlands, Norway, Sweden, United Kingdom) have contributed to develop several standards on tests procedures for evaluating stone treatments [18, 19].

In order to develop standards within acceptable timeframes and, at the same time, to guarantee sufficient time for consultation and consensus, European Standards (ENs) are developed in a maximum of 3 years. In Fig. 8.2 the scheme of the timeline for publishing an EN standard is reported. The proposal for a new working item (WI) must be presented by at least five experts from five different countries to the Technical Board and acceptance of new proposal is based on: i) technical resources (the subject is sufficiently developed in Europe); and ii) human resources (specific experts available). This timeline starts to run once the Technical Board has taken the decision of registering the new WI submitted by WG, then the 3 years for publication begins.

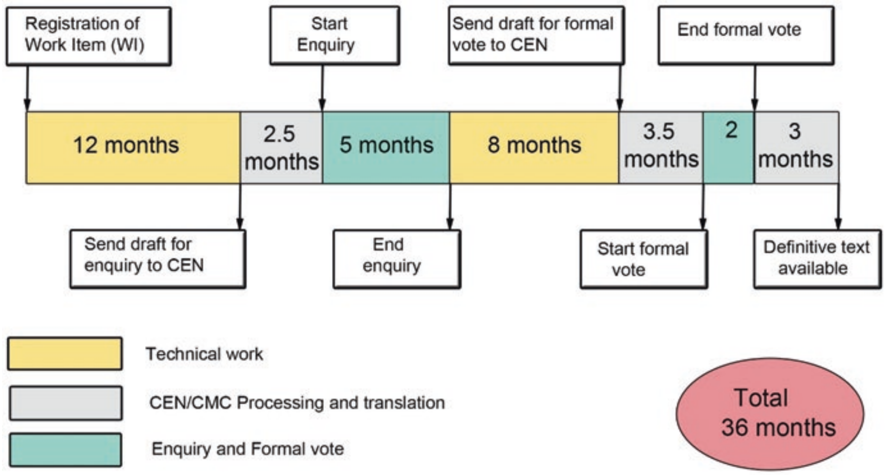

Fig. 8.2 Scheme of the timeline for publishing an EN standard

Once the new WI is approved and the WG starts working on it, the "standstill agreement" comes into effect. This is an agreement between CEN National Members not to publish national standards on the same subject. After 12 months a draft is sent to the enquiry, the comments received during the public consultation are then examined, and the draft is amended in line with the decisions made by the WG. A report of this process is drafted, including the justification for comments not accepted. The new draft is sent to the formal vote and, if this is positive, the standard becomes official and is published in a short time. Once ratified by CEN, a European Standard (EN) must be implemented by CEN members as an identical national standard, and any conflicting national standards must be withdrawn. Up to now, the number of Standards published by CEN/TC346 are 37, and, among these, 11 deal with tests and methods for assessing conservation procedures [20].

Notwithstanding the huge amount of work done up to now, there is still a lot of work to be done, as outlined in the following paragraphs.

8.3 Cleaning

Cleaning is one of the most important treatment for stone conservation. The objective of cleaning is to conserve and preserve the cultural property by removing extraneous materials capable of causing physico-chemical damage or aesthetical modifications, impeding the correct reading of the surfaces. Moreover, cleaning is a treatment that quite often precedes both consolidation and/or protection treatments (when required), and should not create any problems to them.

It is a totally irreversible intervention and, therefore, it should be carefully chosen and conducted, in order to be as much as effective and respectful of the surfaces. Cleaning operations (as well as all the operations conducted on materials belonging to Cultural Heritage) need to take into account the compatibility concept. This concept has been discussed in the papers by Delgado [21, 22]. According to EN 15898 [23] compatibility is defined as the "*extent to which one material can be used with another material without putting significance or* stability *at risk*". Extending the definition of compatibility to the cleaning action, a "compatibility analysis" should therefore ascertain how cleaning actions (in terms of effectiveness and harmfulness) would impact the significance and stability of the heritage object. This concept was further developed in another paper by Delgado focusing on cleaning [24]. In this paper, a sort of risk assessment rating was proposed based on different parameters ranging from the typology of stone, the cleaning method, and other parameters called "quality components", such as skill of operators or budget.

To address all the requirements for choosing the most suitable and least dangerous cleaning procedures, an in-depth knowledge of the substrate, the materials to be removed, and the environmental conditions, is fundamental. These arguments are not discussed here (see Chaps. 2 and 3), but they must be considered when the methodologies aimed at verifing the efficacy and harmfulness of cleaning methods have to be selected.

In the last decades, scholars have published several papers about cleaning methods. In 1996 Vergés-Belmin stated that, at that time, only few authors reported the critical assessment of the evaluation methods [25]. From then, papers focusing on cleaning methods have been published in journals or conference proceedings, but still the focus being on the cleaning procedure, while the methods for assessing it were mostly based on the analyses of mock ups or samples taken from the monument.

The use of *in situ* analyses, better if not invasive, was utilised in the last fifteen to twenty years. This increasing attention to the use of *in situ* analyses was fostered by the arising awareness to preserve as much as possible the integrity of the work of art and, in parallel, by the effort of the industries to develop portable devices with ever better performances.

As already stated, together with the assessment of efficacy, the assessment of the absence of damage that can be potentially caused by cleaning, is of the same importance, and includes: loss of surface, staining, deposition of soluble salts, or making the stone more vulnerable to pollutants or biological growths [2]. However, when evaluating the surface properties after cleaning, it must be taken into account that the stone cannot be considered as the original one, as a series of changes occurred due to interactions with the environment [26, 27]. Some of the techniques that will be quoted in the following paragraphs may be applied also for other purposes, such as the assessment of the state of conservation of untreated stones.

Optical observation with microscope (Fig. 8.3a) is a good and widespread technique to observe the surfaces before and after cleaning [25], and the possibility of acquiring digital images made the method more reliable and quite diffused to monitor cleaning tests [28–32]. Always based on photographs are the close range or ultra-close photogrammetry technique [33–35] (Fig. 8.3b).

Another important parameter is the roughness of the stone surface after treatment. The parameters describing the surface area may be indicators of the susceptibility of the surface to further decay. Roughness can be evaluated by raking light (RL) images, or by using light interferometry [36] and surface roughness meters (profilometer/rugosimeter) [31, 37–39]. The technique was included in standards by

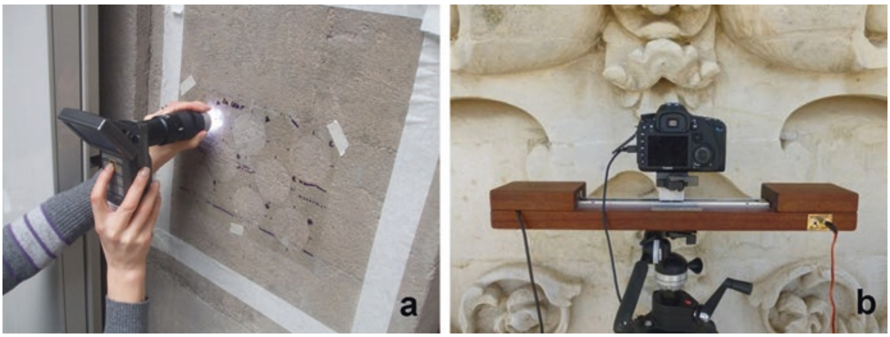

Fig. 8.3 (**a**) Digital portable microscopy, photo by S. Rescic – ISPC-CNR; (**b**) Microphotogrammetry setup, photo by R. Manganelli del Fà – ISPC-CNR [35]

the German Institute for Standardization, such as DIN 4768 [40, 41]. Optical and laser techniques have also been used, such as line profilometry [37, 42] or 3D laser profilometry [43, 44]. Some scholars compared different techniques [45], and Grissom et al. [46] concluded that tactile evaluation was the "*more practical and cost-effective technique*". Some scholars are sceptical on the usefulness of roughness for some types of stone, in particular those that are very "rough" by nature, such as some types of sandstones [3].

UV Fluorescence (or UV Luminescence) is a well-documented photographic technique applied mainly on paintings [47–49]. It has also been used by scholars to rapidly detect the presence of fluorescent materials on stone surfaces [50] and, therefore, it may be used to trace materials to be removed or to assess the residues of the treatment [32]. Another technique based on fluorescence, in terms of spectral and temporal properties and used to map and monitor the cleaning of marble, is fluorescence lifetime imaging spectroscopy (FLIM) [51]. Furthermore, multispectral imaging has also been used to monitor the effects of laser cleaning [52–54].

In addition to image techniques, thanks to the technological development of portable instruments, a wide choice of single spot techniques for evaluating cleaning procedures is available nowadays.

For elemental characterization, it is possible to use portable X-ray fluorescence (XRF). This technique, beyond its intrinsic limits (it is not sensitive to light elements and the data collected may come also from inner layers), is very powerful, relatively fast, easy-to-use, and able to yield information about key chemical elements. It is widely used in the field of CH [55–58]. It has been used to detect gypsum, by mapping sulfur on the surfaces of Michelangelo's David [59, 60], or other marble works of art [61].

Spectroscopy-based analytical techniques include different methods [62]. Fourier-transform infrared spectroscopy (FTIR spectroscopy) is very common in every scientific laboratory [63]. It works in transmission or in other modalities, such as Attenuated Total Reflectance (ATR) or coupled to microscopy (micro-FTIR), and it is widely used to analyse samples taken from the monuments. In the last 20 years, portable instruments, equipped with optical fibres [64] or in total reflectance (TR-FTIR) modality [65, 66], have also become available on the market for *in situ* analyses.

Another important spectroscopic technique is Raman spectroscopy [67, 68]. The presence of fluorescent materials can affect the results obtained with this technique. In such cases, the fluorescence signal may saturate the Raman spectrum, but this problem can be usually overcome by using different laser sources. Portable Raman instruments require high stability and, therefore, their use *in situ* is challenging [69, 70]. Despite this, Raman spectroscopy has been employed to monitor the cleaning agent *in situ* [71] or to assess the cleaning operation [72]. Raman spectroscopy has been also proposed in association with Laser Induced Plasma/Breakdown Spectroscopy (LIPS/LIBS) [73–75], despite the latter being unable to be considered completely non-invasive, since a small amount of material is ablated during analysis.

In literature, it is possible to find many references to other techniques for the monitoring of cleaning methods that can potentially be used *in situ*. Among these, we can mention, Laser induced fluorescence (LIF) for remote monitoring of stone surface [76, 77] or to follow the cleaning in association with LIBS [78, 79], thermography [80, 81], and photoacoustic monitoring of laser cleaning [82, 83].

The presence of salts in masonry is one of the main problems to solve in conservation, and cleaning procedures to remove them are often very complex. The argument would deserve its own specific, large chapter. To address the specific problem of presence of salts and the consequences on conservation, in the last years, dedicated conferences (SWBSS, International Conference on Salt Weathering of Buildings and Stone Sculptures) have been organized [84, 85], and the next will be held in Delft in 2021 [86]. Hence, when severe salt problems exist in a building, it is necessary to map and assess the type of salts, where they come from, and their concentration before and after conservation [87–89]. Moreover, changes in relative humidity (RH) and temperature (T) play a key role in the activation of salt damage, and therefore, monitoring the environment is highly recommended. Several methods are available for identifying salts but most of them are based on sampling and subsequent laboratory analyses (e.g., Infrared and Raman Spectroscopies, X-ray diffraction, Ionic Chromatography) [3]. The method proposed by Borrelli [90, 91] was something in between, because the first part of the analysis may be conducted *in situ,* by measuring the conductivity of the solution obtained through a detailed procedure, while the identification of the salts is made afterwards in the laboratory. For *in situ* screening of the type and location of the salts, it is possible to use semiquantitative test strips. These test strips enable a fast and reliable qualitive determination of salts in solutions through the easy dip-and-read-procedure [92]. A portable *in situ* method that gives results about the "salinity index" and not on the nature of the salts itself, is based on evanescent field dielectrometry and it was proposed by Riminesi et al. [93, 94].

Colorimetry is a technique widely used in almost all areas of conservation [95]. The methods for colour measurement are non-destructive and can be easily used *in situ.* Colour, as perceived by human beings, is the result of three different factors: i) the source illuminating the surface, ii) the reflectance of the surface itself, and iii) the sensitivity of human eyes. Since the description of colour is subjective, a system to objectively communicate colour was necessary. The Munsell system was introduced in the first years of twentieth century [96]. It is based on three parameter descriptors (hue, value, and chroma) which are determined by comparing the object/surface with different sheets with colour samples. The system is still in use. In 1931, the Commission International de l'Eclairage (CIE) created a system for the precise communication of colour through the the Yxy colour space [97]. From then, other systems to express the colorimetric data, always based on the first one, have been developed [98]. More recently, for the total colour difference, a new formula (CIEDE2000) has been introduced, mainly for industrial purposes [99]. However, the most used colour space is the CIELab1976, based on the L*, a* b* parameters, representing a three-dimensional space with achromatic centre. L* describes the luminosity (0, black; 100, white); a* and b* describe the hue of the colour: a* ranges from green (−a*) to red (+a*), and b* ranges from blue (−b*) to yellow (+b*). The higher a* and b* are, in absolute value, the more saturated colour is. To express the total colour variation, the Euclidean distance between two points is calculated as follows: $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [100]. In the case of stones, it is widely used for the evaluation of the aesthetic impact of treatments [101–103], but also for understanding weathering, since alterations in colour might indicate chemical changes [104–107].

However, a distinction must be made when the colour is used for the evaluation of cleaning methods, or of consolidating and/or protective treatments. In the case of consolidating and/or protective treatments, the colour variations must be very limited as the treatment should not affect the aesthetic aspect. On the other hand, in the case of cleaning, the colour variations are often very significant, especially if black crusts or other disfiguring materials are removed. Therefore, the acceptable values are different, according to the treatment to be evaluated. In the case of cleaning methods, the colour also has a function to check the homogeneity of the treatments, since in almost every intervention the areas to be cleaned do not have the same level of dirt and decay, and the cleaning may be differentiated according to the nature and level of dirt [108]. According to Doehne et al. "*Color can be used as criteria for cleaning only when a "reference surface" is defined and taken as a target for the cleaning level to be reached in the intervention*" [2]. Even if it is a quite simple technique, attention must be paid when acquiring the colorimetric data to obtain reliable results. The main drawbacks are the positioning of the instrument on the same area before and after treatment, or during monitoring and the environmental conditions (relative humidity and temperature) that affect the stone surfaces and influence the measures [109]. The problem of repositioning may be overcome by using properly prepared masks (Fig. 8.4). When evaluating the data, it is important to rely not only on the ΔE values, but to also consider the variations of the single parameters. In case of removal of a black crust, the parameter that is expected to contribute most to the ΔE is the increase of L* value (black/white parameter). In the case of laser cleaning with Nd:YAG laser, b* values describe the yellowing effect observed after treatment in some cases [108, 110, 111]. In 2010, the CEN/TC346-WG3 published a specific standard about test methods to measure the surface colour of porous inorganic materials [112].

To evaluate the conditions of the stones after cleaning, it is important to measure the behaviour against water absorption [2, 3]. Several methods that can be used *in situ* to evaluate the water absorption under low pressure or the humidity content are available. Most of them are widely applied not only for monitoring cleaning

Fig. 8.4 Colorimetric measures on different materials (sandstones **a** and **c**, and marble **b**). For each case a mask for repositioning the instrumeent was prepared

treatments, but, even to a greater extent, to evaluate consolidation and/or protection treatments. For this reason, these methods will be described and discussed in the next paragraphs.

Most of the papers cited so far are not based on a single technique but rely on the combinations of two or more techniques, both non-invasive and invasive, to be performed *in situ* or in the laboratory. Very few papers propose protocols to be applied only *in situ* and even fewer are those that propose a rating of the results. The latter is, in fact, a very critical aspect because both the effectiveness and danger are closely related to the situation to which they refer, such as the type of stone, the conditions, the material to be removed, and so on. In 1996 Vergés-Belmin reported some tables where the adequacy (4 levels, from very adequate to inadequate) of several testing methods was estimated, from those to use *in situ*, to the physical and chemical ones used for the evaluation of cleaning methods in laboratory [25]. More recently, Ďoubal proposed a series of analyses (chemical and mineralogical characterization, water uptake, microstructural properties, colour, surface cohesion, and surface roughness), together with criteria for positive assessment of the results [113]. Other scholars have proposed protocols based on a multitechnique approach, very often including sampling and laboratory analyses [114–117]. To have a more objective evaluation with a generation of a "cleaning performance index", a proposal for an integrated decision-making system based on a GIS-based graphical interface and a fuzzy logic model, based on some parameters (to assess by means of *in situ* or laboratory techniques) and their acceptance threshold levels, was made by Delegou et al. [118]. This system was successively integrated with data concerning the environment and other parameters [119, 120].

As already stated, very few scholars proposed cleaning assessment based only on non-destructive, *in situ*, and relatively easy-to-use methods. One of the first protocols to assess and monitor *in situ* cleaning was proposed for the marble statue of David by Michealgelo, by using UV fluorescence, FLIM, XRF, FTIR, and colourimetry [121]. Moreover, all these techniques have been used to monitor the surfaces for the following 10 years after cleaning (data not published).

In the case of buildings, Hauff proposed a combination of visual and optical observations, water uptake and water transport properties, and salt content for eventual residues, also taking into account the cost of the intervention [122].

Recently, the WG 3 of the European Committee for Standardisation (CEN-TC346) developed a standard concerning the evaluation of harmfulness and effectiveness, both *in situ* and in laboratory, for the various cleaning methods for porous inorganic materials (EN 17488) [123]. In the EN 17488:2020 standard, the sequence of fundamental *in situ* tests, which must be carried out before and after cleaning, were as follows: i) optical observations through portable digital microscope, raking light, and fluorescence induced by UV radiation; ii) chemical and physical analyses such as colour measurements, elemental analyses by portable XRF, molecular analysis by portable FTIR, surface ion analysis (ion test strips); and iii) water absorption assessment by means of both pipe and contact sponge method, and water drop test. These *in situ* tests are flanked by other tests in the laboratory, as is also reported in most of the publications concerning the choice and the assessment of cleaning methods.

Once the effects of cleaning have been assessed immediately after the methods have been applied, it would be also important to monitor the consequences in the long-term period. Monitoring is always a problematic aspect due to difficulties in accessing the treated surfaces after the completion of the conservation project. Another problem that arises in the case of monitoring cleaning methods is that often this is not a unique treatment but, generally, it is followed by other treatments such as consolidation and/or protection. For this reason, even if monitoring is performed, it cannot be considered as the monitoring of the cleaning procedure, but of a more complex new "system". For this reason, there are only few cases reported about the long-term monitoring of cleaning. One of these is the paper by Young et al., reporting that the rate of decay of cleaned buildings is higher in respect to uncleaned ones [124, 125]. Unfortunately, the authors do not describe in detail the methodology they have employed to draw their conclusions. Sanmartín et al. reported a medium-term monitoring (1 year) by using colorimetry and chlorophyll-a fluorescence after the removal of biofilms from granite [126]. Colourimetry was used by Perez-Monserrat et al. to monitor the cleaning operations of two façades conducted from 1984–1986 and 2006–2008, respectively, also proposing a model as a tool for planning preventive façade maintenance [127].

8.4 Consolidation

Consolidation of stone surfaces is another important and risky operation [128], often subsequent to cleaning. When a material has become fragile and weak, or has lost its natural compactness, having the tendency to undergo detachment, exfoliation, flaking, or any kind of action that carries away parts of it from the external layers, it needs to be consolidated. As described in Chap. 4, consolidation is the action that is aimed to enhance the mechanical and physical properties of a degraded material, giving back the original solidity, compactness, and structural unit. It is indeed very important to know the characteristics and the properties of the original sound material, because consolidation does not have the aim to enhance physical and mechanical properties absolutely, but just to lead the material back to its original state and aspect. This operation is usually performed by means of consolidant products [2].

These products have to meet several additional requirements to fulfill their tasks, such as to be totally compatible with the stone surface, keep their properties unaltered, penetrate inside the degraded material without occluding the pores, and other requirements extensively reported and discussed in Chap. 4.

Therefore, the choice of the most suitable product for each specific case is of fundamental importance. Equally important is then the subsequent step of evaluation of the performance of the applied treatment. As already underlined for cleaning treatments, in Sect. 8.3, both the assessment of the efficacy of the treatment and the verification of total absence of side effects, potentially harmful ones, are of equal importance.

During the years, some scholars have proposed a sort of rating system for different methods for the evaluation of the consolidation performance [12, 22], but up to now there is nothing that has been agreed upon and commonly applied in the conservation community.

Some of the currently used tests directly measure the mechanical properties of the substrate (treated and untreated), and are often destructive measurements, so it is very difficult to use them *in situ* on historical monuments. Some others are indirect measurements, for example, they try to verify any porosity variations of the treated material. These tests are often used for evaluating the performance of protective treatments, and will be better described in the next paragraphs.

In the framework of the IPERION-CH European project [129], among the foreseen activities in the WP9-Networking (Establishing cross disciplinary best practices and protocols), an interesting survey was conducted about type of objects and assessment techniques considered relevant in three main fields of conservation practice: consolidation of stone, protection of metals, and cleaning of paintings. The chosen topics were linked to the Joint Research Activity (JRA1- Innovative instruments and methods for integrated approaches to CH analysis and diagnostics) conducted in the same project. The survey, conducted online, was open to not only project partners, but also to external contributors, such as other researchers, conservation scientists, and conservators. At the end, answers from nine European countries were collected. Analyzing the results about the consolidation of stone, some interesting questions emerged. Most of the contributors stated that they used a set of techniques rather than a single one for the evaluation of the different aspects (efficacy, harmfulness), indicating that the evaluation is usually performed by the combination of the results. Simple techniques are indicated as more frequently used in comparison with less common or more sophisticated ones. Visual observation, optical microscopy, colourimetry, water absorption (by both Karsten tube and contact sponge methods), and drilling resistance measurements were the most used ones. Very few quoted indentation and ultrasonic pulse velocity measurements.

The more interesting result was the answer to the question about the actual situation. The question was: *Do you think that available techniques are sufficient to fully evaluate* consolidation treatments? The answers were NO at 96%. Therefore, the conclusion was clear; the majority of contributors believed that the techniques available up to now for evaluating the consolidation action were not sufficient, even in the best conditions of laboratory tested specimens.

This problem is also discussed, with other interesting aspects, in a recent paper by Praticò et al. [130]. According to the authors, one of the main problems is that "*Despite the large number of publications available on the subject, however, the contribution of scientific research for practical* applications *remains scarce*".

Actually, several studies concerning consolidation and its performance testing make large use of water absorption tests, mostly by capillarity (this latter is carried out only in the laboratory) [131–156]. This test is fundamental to verify the water absorption properties of a porous surface, like the amount of water absorbed per unit of surface, velocity of absorption, depth of penetration reached from water, and so on. It has been widely used for several years and it has been standardized for a long time by EN 15801 [157]. For protective treatments, it is one of the most important tests, in order to verify directly the achievement of the intended purpose (that is, the reduction of the absorption capacity of the stone), and for this reason it will be described in detail in the next paragraphs (Sect. 8.5). In consolidation, this test is a sort of "indirect" evaluation because it highlights the reduction of porosity, but not the true effectiveness of the consolidant.

Another important test regarding the water absorption properties, and that, like the previous one, is carried out only in laboratory, is the determination of static contact angle. This test, standardized by EN 15802 [158], is commonly used in experimentation for both protective and consolidation treatments [135, 149, 154, 159]. Like the water absorption test, for the consolidation assessment, it is an indirect test, aimed to check any variations in the wetting properties of the treated stone, and it will be better described in Sect. 8.5.

An alternative method to be used *in situ*, albeit with some limitations, was conceived and developed some years ago [160]. It is called contact sponge test method, and it is at the moment ruled by a specific UNI Italian Standard [161]. It is already widespread in trials to test protective treatments (see Sect. 8.5), while some scholars introduced it even in consolidation studies [132, 162–164]. The *in situ* sponge test has been applied by the authors in the archeological site of Hierapolis (Turkey) in the framework of a FIRB project called "Marmorae Phrygiae" [165]. The test was conducted to assess and monitor the state of conservation of selected marbles (Fig. 8.5a) and to evaluate and monitor the efficacy of a consolidation treatment done by the conservators on a marble column previously cleaned (Fig. 8.5c and d). The sponge test, together with colour measurements, was also repeated every year for two years to monitor the state of conservation and the efficacy of the treatment. For this purpose, plastic masks (Fig. 8.5a, c and d) were properly prepared in order to exactly reposition the instruments in the same testing areas [166].

Determination of water absorption by pipe method (also known as Karsten tube) is another standardized method [167], that can be performed both in laboratory and *in situ*. It is used for protective (see Sect. 8.5) and, only sometimes, consolidation treatments [164]. Some scholars use the dry index (EN 16322) [168] in order to test the effect of consolidation on stone porosity [148, 149, 152].

As mentioned above, direct methods to verify the efficacy of a consolidation treatment require the use of mechanical tests, since a consolidant should restore hardness and compactness in the treated material.

Compressive strength [134, 140, 169, 170], tensile strength [134, 138], and flexural resistance [152, 171–173] are commonly used laboratory tests. They are destructive tests, as they require work on the specimens, even of considerable size. For this reason, only in few cases is the material extracted from the site [140, 170], while in most cases fresh material from quarries is used.

Elastic modulus and hardness of a material can be obtained by means of (nano-micro) indentation or durometer instruments, for which specimens are needed.

Fig. 8.5 Archeological site of Hierapolis (Turkey). (**a**) and (**b**) Sponge test for evaluation and monitoring of state of conservation of selected marbles; (**c**) and (**d**) sponge test for evaluation and monitoring of a consolidation treatment on a marble column

Several scholars make use of these kinds of methods and carried out studies to develop these tools [132, 154, 170, 173].

In recent years, the need to obtain data on the efficiency of consolidation directly on monuments *in situ* led to the study and the development of new instruments and methods to investigate the mechanical properties of stone surfaces.

Among these, several years ago, a portable system to verify the mechanical resistance of a material to the penetration of a drill bit was developed. The method is called Drilling Resistance Measurements System (DRMS) [174–178], and it was developed, tested, and compared with other mechanical tests in the framework of the European project MCDUR [179]. DRMS allows for the assessment of the "hardness/cohesion" of natural or artificial stone materials both in laboratory and *in situ*. The instrument consists of a modified drill, in which a load cell allows it to measure, in Newtons, the drilling resistance of the material under examination. The drilling resistance of a natural or artificial stone is a function of its compositional, mechanical, and microstructural characteristics and was statistically correlated with the uniaxial compressive strength [177, 180]. The instrument creates a hole in the stone under examination, having a depth that is established by the operator (usually 10 mm). The forward and rotational speeds of the bit are kept constant during the test and selected according to the type of material to be analyzed. The instrument, connected to a PC with specific software, allows for a real-time viewing of a diagram of drilling resistance as a function of the depth of the hole. The DRMS system was applied to assess the performance of both consolidants and protectives in the archeological area of Fiesole, near Florence, in 2004. In addition to DRMS measurements, colour measurements and water uptake, by sponge method, were performed [181]. In this case, the material was sandstone and, since the state of conservation of the stones was very different, it was decided to ideally divide each block in two and leave one part untreated so that the data before and after treatment could be better compared (Fig. 8.6).

The technique has become quite widespread nowadays in Europe and beyond, and many papers report it is a good method to assess consolidation, both in laboratory [137, 141, 148–150, 169, 171, 172, 182, 183] and *in situ* [132, 146]. Very homogeneous materials have been proposed for calibration purposes, as, for example, the artificial reference sample (ARS) [174]. The second is Macor®, produced by Corning (USA), which was proposed in the framework of a European project about Stone Durability Qualification [184].

The method works well for calcareous stones, while for materials that are particularly abrasive, such as sandstones, due to the quartz presence, particular attention should be made to the wear of the drill bits to obtain reliable results [185].

Fig. 8.6 Archeological site of Fiesole (Florence, Italy). (**a**) DRMS system; (**b**) contact sponge test; (**c**) the holes drilled in the treated (below) and not treated (above) stones and the trace leaved by the sponge (just after sponge removal); and (**d**) masks for the colour measurements

Moreover, to overcome the limits of the instrument for particulary hard stones, some modifications have been proposed [186, 187].

Meinhard et al. [188] include the brush abrasion test among a set of fourtheen methods for evaluating and monitoring the effectiveness of conservation measures. For this test, a defined surface area (10 × 10 cm for architectural surfaces, 5 × 5 cm for sculptures) was brushed off with a brush with well-defined dimensions and stiffness. The brush is passed over the surface 10 times vertically and 10 times horizontally across the test surface. The collected material is placed in a sealed box, dried at 60 °C, and weighed. This test, also discussed by Bläuer et al. [189], is a very simple one, with some drawbacks since the results depend on the operator's dexterity and it may vary as a function of relative humidity.

A similar test, widely used *in situ* to evaluate the decohesion of surfaces, is the peel-off resistance test. It is reported as the Power Strip® test [188, 189] or Scotch Tape test, and it has been used for several decades, despite not being supported by any standard or reliably verified recommendations for the application (Fig. 8.7).

Moreover, the results of the tests depended on the manual skills of the operator and led to non-comparable and non-reproducible results. Some scholars [139] use for this test an ASTM Standard [190], that was developed for assessing the adhesion of coating films to metallic substrates. Unfortunately, the application of this method on substrates different from metals has not been validated. For this reason Drdácký et al. [191, 192] proposed a "standard" protocol for testing the cohesion characteristics of brittle and quasi-brittle materials, mainly mortars and stones. In the last years, many papers report the proposed protocol, which is spread among the routine tests to be performed *in situ* in order to evaluate the change in the cohesion of stone surfaces after a consolidation treatment [145, 151, 156, 164, 193–195].

Other methods, that can be performed *in situ*, were developed principally for mortars and are widely used in the building sector. The methods, aimed to measure the hardness of a material, are several and, among them, the Schmidt Hammer or sclerometer [172], durometer [170], and penetrometer [154] are the most used ones.

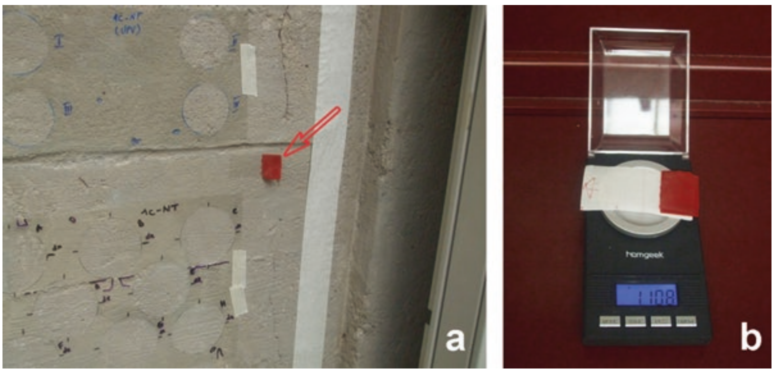

Fig. 8.7 (**a**) Application of scotch tape (red arrow) for the peeling test and (**b**) in situ weighting of the scoth tape after application. (Photo by S. Rescic – ISPC-CNR)

When a sclerometer is used, the width of a scratch made by a diamond or a steel bit under a fixed load is drawn on a stone surface under fixed conditions and accurately measured. It provides a quick and inexpensive measure of surface hardness, that is widely used for estimating the mechanical properties of rock material [196], and it has a direct correlation with the compressive strength of the material [197]. When a durometer is used, what it is measured is the depth of penetration of an indentation in the studied material, made by a given force on a standardized presser foot. (Fig. 8.8). Finally, a penetrometer measures the penetration of a steel needle driven by strikes generated at a constant energy in a stone, giving a curve of the penetration depth versus the number of the applied strikes.

The Equotip is another device used to test the mechanical properties of stone surfaces. In this case, a ball hits the surface with a fixed energy, and the velocity of the ball as it rebounds is recorded. There are different kinds of Equotip devices depending on the material the ball is made of (tungsten carbide, ceramic, and polished diamond), its size, and the impact energy. Viles et al. [198] compared the Equotip with the Schmidt hammer, concluding that each device has its strengths and weaknesses and they recommended using both, since they state that they have high potential to be used together.

Ultrasound pulse velocity (UPV) methods are quite common in stone conservation. They analyse the structure of the material and, thus, only indirectly, the hardness of the material. There are several configurations and possibilities, and their detailed description is beyond the scope of this chapter. What is important to outline is that, notwithstanding the widespread use of the methods, there are few standards dealing with the method, mainly developed for civil applications [199] and applied for the evaluation of consolidant on historical buildings [200], but no specific standard is published for historical monuments. The only one (to the best of our knowledge) is the Normal recommendation of 1986 [201]. Several scholars have used pulse-wave velocity in transmission mode on specimens in laboratory [136, 138, 142, 144, 153–155, 170–172, 202] or, with various configurations *in situ* [203, 204]. The comparison of collected data before and after a consolidation treatment is useful to evaluate the increase in stone cohesion. Ultrasonic Pulse velocity technique is, indeed, effective in detecting any changes in the texture of the stone, that can be

Fig. 8.8 Durometer (Rebound hammer). (Photo by S. Rescic – ISPC-CNR)

related to a decrease of porosity (and therefore, presumably to consolidation), to changes in fissuring and microcracks, and consequently, a decrease of the same after consolidation. Portable ultrasound devices are also available, which allow measurements to be made directly *in situ* (Fig. 8.9).

Becerra et al. [151] suggested its use in a semi-direct transmission or indirect transmission mode (for example, in case of walls). Very recently, Drdácký et al. proposed an immersed ultrasonic probe to assess the penetration depth of the consolidant. The method, even though it can be used *in situ*, is not completely non-invasive because holes must be drilled to position the probes [205].

Once the effectiveness of a consolidant has been verified, as already highlighted for cleaning treatments (see Sect. 8.3), it is of fundamental importance to verify the absence of any side effect (and then damage) that can be potentially caused by the applied product, such as: surface color changes, deposition or development of by-products, or variations of the characteristics of the stone (such as water vapour permeability, thermal expansion, and shrinkage coefficients).

Colour measurements of surfaces are a very popular routine test aimed to verify the changes of aesthetical properties of a stone surface after the application of a conservation treatment. They are usually performed according to the Standard EN 15886 [106]. As already introduced, the methods for colour measurement are non-destructive and can be easily used *in situ*. They are widely used in almost all the areas of conservation. In particular, for consolidation, different from cleaning treatments, the colour variations must be very limited as the treatment should not affect the aesthetic aspect of the stone surface. However, there is no agreement on the limit value of the acceptable total color change (ΔE). In general, ΔE values $\leq 2/3$ are considered as not appreciable by the observer (or just noticeable difference – JND) [206]. Delgado et al. [22] report for both protective and consolidation treatments using the "rating scale of risk" of the different tests. Regarding the total colour variation ΔE, values ≤ 3 are considered as low risk (rating equal to 0), values between 3 and 5 had a rating of medium risk (rating equal to 5), while ΔE values

Fig. 8.9 UPV applied in situ with a portable device. (Photo by O. Cuzman – ISPC-CNR)

higher than 10 are considered of high risk (rating equal to 10). In general, values of ΔE up to 5 are acceptable for treatments of historical building [1, 133, 138].

The application of a consolidant, as already stated, has the hard task of imparting cohesion and mechanical resistance to the stone, without changing either the aesthetic aspect or the intrinsic structure. Most of the papers cited so far for consolidant performance evaluation adopt colour measurements, either in laboratory [133, 134, 136–138, 140, 141, 143, 145, 147–154, 156, 193, 202] or in *in situ* [132, 146, 162, 164, 191, 193].

Another test, used in consolidant testing and validation, takes into account the importance of the maintenance of the water vapour permeability [133, 142, 143, 149, 152, 154, 191, 193]. The determination of this characteristic was standardized several years ago by the standard EN 15803 [207]. The assessment of a possible reduction of water permeability is usually obtained by comparing the water vapour permeability before and after treatment at the equilibrium. Values of such reduction close to zero indicate that the product has a negligible effect on the water vapour flow in the specimen. Unfortunately, this test can be performed only in laboratory on samples specifically prepared in order to meet strict geometric requirements.

Some scholars, mainly for geological applications, have proposed some methods for *in situ* measurement of permeability. Brown and Smith [208] developed a portable syringe air permeameter to be used *in situ*. In this instrument, a chamber, containing a small volume of air in contact with the rock, is suddenly increased in volume, creating a vacuum, causing air to flow from the rock into the chamber. The instantaneous chamber volume and the air pressure within were monitored. The method requires a specific calibration procedure to overcome some geometrical problems. This device is actually commercialized as TinyPerm by New England Research, Inc. The performances have been checked and compared with other systems by several scholars [209, 210]. Another system based on a similar principle is the "Torrent permeability tester method" (Permea-TORR), initially developed for concrete [211]. More recently, Sena da Fonseca et al. [212] measured the permeability of limestones and marbles from Portugal with a Permea-TORR, finding good results. Notwithstanding these few examples, the *in situ* measurements are not very frequently adopted.

Techniques based on spectroscopy are also used by scholars to verify the effective presence of the applied products in the stone. As already introduced in Sect. 8.3, FTIR spectroscopy [62] is widely used to analyze treated stone specimens [133, 144, 151, 159, 163, 212–215] and samples taken from the monuments. FTIR analyses on treated stone surfaces become particularly interesting when the applied product is an organic polymer (like silicon, acryilic, or epoxy resins), and it is necessary to verify its presence and durability over time. Instead, if the consolidant is inorganic, some scholars propose the use of X-ray diffraction (XRD), especially for calcium carbonate precipitation induced by bacteria [216, 217], hydroxyapatite [214, 215], ammonium phosphate [137], or nanomaterials [147, 182].

For inorganic products, μ-Raman spectroscopy is a relatively recent but powerful method to study multi-step reactions and investigate the crystalline phases of the final product, for example, in case of the use of oxalates [218, 219], hydroxyapatite [220], or nanomaterials [193].

Conti et al. compared FTIR and Raman spectroscopies to evaluate synthetic treatments [221]. The work was conducted on specimens but the final goal was the use of the portable instruments *in situ*.

Raneri et al. [149] used a multi-scale approach on classic intrusion methods (mercury intrusion porosimetry) and DRMS, combined with non-invasive imaging techniques (X-ray computed micro-tomography and neutron radiography) and small angle neutron scattering (SANS), to investigate the penetration depth of the consolidant product and the interaction with the substrate.

Finally, Normand et al. proposed a terahertz-based method for determination of consolidation depth [222]. The results were only partially positive, but surely it is worth continuing to study its potentialities.

According to Doenhe, *…It is one thing to find a treatment that performs well in the short run; it is another thing altogether to be sure that it will keep on performing year after year when exposed to the weather* [2]. The monitoring of the efficacy of treatments over time and the assessment of any *delayed* harmfulness [2] are two aspects of paramount importance for a conscious choice of a treatment. On the basis of the considerations made regarding the techniques available to be used *in situ* for the evaluation of a consolidation treatment, it is evident that the monitoring of consolidants also suffers from similar problems. Some institutions proposed guidelines for the choice of different interventions, also considering the monitoring procedures very important, but unfortunately without providing details on specific activities [223]. Few papers proposed protocols for *in situ* monitoring, generally excluding expensive and complex techniques, in order to make the protocol easier and cheaper, as the tests have to be repeated over time. Among these papers, Meinhard et al. [188] proposed fourteen methods, considering capillary water absorption with the Karsten tube, micro-drilling resistance, peel-off resistance (tape test and abrasion test with brush), ultrasonic velocity, resonance sensing bar, and infrared thermography (for the detection of delamination/scaling) as the most important ones. In addition, they also propose a final rating of the long-term performance of conservation materials.

Perez-Ema et al. proposed a testing protocol based on the UPV, roughness test, colorimetry, and microhardness tester methods. They evaluate advantages and limitations of the methods by comparing the data obtained in laboratory and *in situ* in an archaeologial site [224]. More recently, Becerra et al. proposed a very simple *in situ* protocol based on colorimetry, digital microscopy, UPV, and peeling tests. They also suggested to use of laboratory methods, such as scanning electron microscopy (SEM) observations and capillary water absorption, to further confirm the data obtained with the *in situ* methods, despite their belief that they are not essential for the decision-making process [151].

Several papers reported the assessment of the behavior of past treatments over time, and in these cases, the assessment is based on the study of samples analyzed in the laboratory, even if some *in situ* tests are also conducted before sampling [107]. Haake et al. applied UPV and Mirowski pipe as *in situ* tests [225]. Bracci et al. employed UPV, water uptake by sponge method, and DRMS [226], together with the analyses of samples taken at the time of treatment compared with those of the samples collected after 40 years [227]. Fassina et al. measured water uptake [228], while Calia et al. assessed the state of conservation of historical surfaces with *in situ* survey based on visual observation, photographic documentation, and water absorption by sponge method, avoiding sampling [229].

8.5 Protective Treatments

Protection of stone surfaces, especially when placed outdoors, is the final treatment commonly planned in a stone conservation program. As described in Chap. 5, a protective treatment has the main goal to prevent water penetration inside the stone. Water, in fact, may be considered the main medium for physical and chemical weathering of stone materials. As a consequence, it is desirable to avoid or reduce, as much as possible, the penetration of water inside the stone, applying a water repellent product that decreases its surface tension and prevents wetting of the surface. The water repellent treatment is applied to the surface and penetrates into the pores of the material, with the depth of penetration being dependent on the capillary properties of the material, the chemical composition of the product, the type and duration of application, the moisture content of the substrate, and the temperature. On the other side, it is necessary to preserve the permeability of the stone to water vapour, in order to let the evaporation of water present inside the stone through the microstructure of the stone itself. In addition to this, a protective product should meet several requirements, including to not alter the aesthetical properties of substrate, to be reversible or better, to allow subsequent treatments over time, and to be stable over time. For these reasons, the first important step in planning the application of a protective treatment, is the choice of the most suitable product for the specific case under evaluation. The second important step is the evaluation of the performance of the applied treatment. As stated above and underlined in previous paragraphs, together with the assessment of the efficacy of the treatment (the effective hydrophobization imparted to the surface by the applied product), the analysis of possible side effects, which may cause damage, is of primary importance for protective treatments.

Among the standards developed from the WG 3 of the Technical Committee Cultural Heritage (TC346, see Sect. 8.2), EN 16581 [230] specifically describes a methodology for laboratory evaluation of the performance of water repellent products on porous inorganic materials. The main methods listed in the standard include tests directed to verify the reduction of the water absorption capacity of the treated material, such as determination of water absorption by capillarity, determination of static contact angle, determination of water absorption by pipe method, and determination of drying properties. Beside these tests, the determination of water vapour permeability and colour measurements are aimed to verify the absence of side effects due to application of incompatible products that could lead to by-products formation or to changes in the aesthetical appearance of the stone. The standard suggests a specific sequence of steps and gives indications on the number and dimensions of the stone specimens and their preparation. This is a very feasible practice, because for laboratory studies, it is possible to obtain as many stone specimens as needed, of the desired dimensions and characteristics. Unfortunately, when dealing with *in situ* tests, the question is definitely more complicated.

In the last decades, many scholars have published several papers about the experimentation of the application of different protective treatments and relative methods for their performance evaluation [231–251]. Many efforts are spent on application of both commercial and new products for the protection of stone surfaces, but so far very few of them [162, 250–252] are carried out *in situ*, on case studies. Most of them are carried out on stone specimens obtained from quarry materials, or, in some lucky cases, extracted from parts of monuments.

On treated specimens, in almost all cases, tests recommended by EN 16581 [223] are performed. Determination of water absorption by capillarity is a very widespread method in the field of conservation of stone materials [231–233, 236–239, 241–246, 248–250]. It has been employed for several years and it is the subject of a standard published in 2009 [157]. It provides direct "*information about the material transport properties for liquid* water…". Capillarity measurements evaluate the amount of absorbed water at the same time intervals; they are carried out on untreated specimens and repeated after treatments and/or ageing of treated material on the same specimen [230]. Both the shape and inclination, in its linear section, of the obtained curve (amount of water absorbed vs. time) provide important information: untreated samples initially shows a high rate of absorption followed by the rate of uptake rapidly decreasing toward an asymptotic value (maximum amount of water absorbed by a material at atmospheric pressure). After treatment, the inclination of the curve's initial linear section presumably changes, showing a decrease of absorption rate, while the curve's second part gives information about the distribution of the product: on the surface or inside the material (Fig. 8.10). The efficacy of a water repellent is not only based on the water absorption coefficient (AC), but also on the shape of the absorption curve: different protective products can have the same AC, but definitely show different curve shapes after long testing times. The greater the decrease of AC and maximum amount of water absorbed for a treated specimen with respect to the untreated one, the greater the capacity of the treatment to impart water repellent properties to a specimen.

The same applies for the determination of static contact angle: this test, standardized by EN 15802 [158], is commonly used in laboratory experimentation [231, 232, 236, 237, 239, 241–249].

Unfortunately, both these standardized tests can only be performed in a laboratory environment because of the necessity of samples of given dimensions (water absorption by capillarity) or a particular equipment (static contact angle). In 2008, Rius [253] proposed a device for the determination of contact angle *in situ*, but, to the best of our knowledge, no other application of the system have been reported since then. Zendri et al. [6] evaluated *in situ* the wettability of the stone surfaces, before and after the application of protection treatment, by using contact angle and

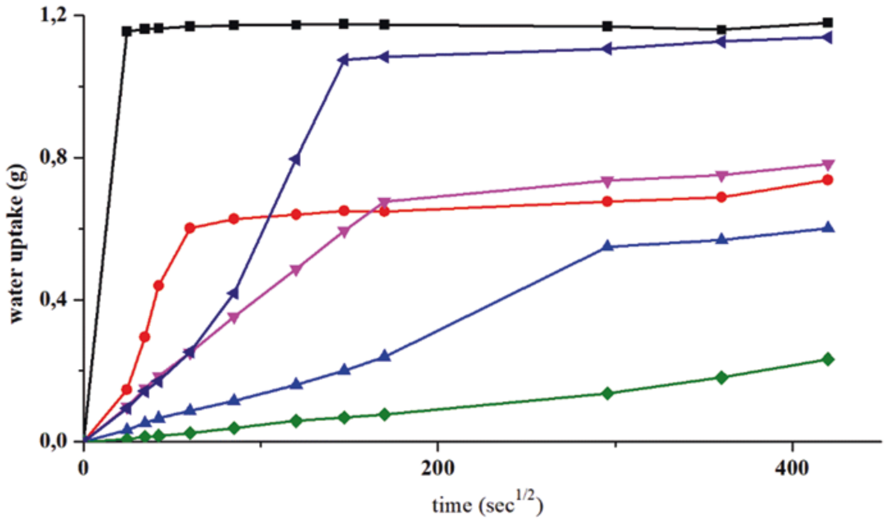

Fig. 8.10 Example of capillary curves of marble specimens (5 × 5 × 2 cm^3), not treated (black curve) and treated with different products (coloured curves). The water uptake (g) is the amount absorbed through the 5 × 5 cm^2 surface

water absorption at low pressure, both soon after the intervention and over the following years.

Differently, the determination of water absorption by the pipe method is a standardized method [EN 16302 [167], that can be performed both in laboratory and *in situ*. The standard derives from past experiences of similar systems, such as the German Karsten pipe [254–257], the RILEM pipe, the Italian pipetta [258] and the Mirowski pipe, developed and patented by Prof. Ryszard Mirowski. All these systems are very similar, differing only in some operative details, but all of them could be used *in situ*. The test is based on the determination of the amount and rate at which water is absorbed "through a defined surface under low pressure and within a specified time" [230]. It consists of a cylindrical open reservoir in contact with the surface of the wall and connected to a graduated pipe. The reservoir is filled through the pipe until a fixed level. Water starts to move to the porous material, and water height in the pipe is monitored as a function of time. This test can be used to measure vertical and horizontal water transport [212]. During the last decades, the use of this methodology gradually decreased, because of the necessity of a sealing material to prevent water leakage from the edge of the cell (water reservoir). These materials often cause some damage or alteration of the substrate.

Given the great importance of the information related to the amount of water absorbed by a stone surface, alternative methods to be used *in situ*, albeit with some limitations, were proposed. Drdácký et al. [259] developed two devices, one for the laboratory and the other one for the *in situ* measurements, with the possibility of continuous measurement of water, allowing long-term measurements and digital recording. The data obtained were consistent with those obtained with capillary absorption and Karsten tube. However, the available prototypes are still operator-sensitive, and a reliable application requires several measurements to be carried out on the surface, and to calculate the average.

Some years ago another new method, called contact sponge test method was conceived and developed by Tiano [160, 260]. The method is based on the measure of the amount of water that a sponge, soaked with a given amount of deionized water and put in contact with the studied surface for a given time, can supply to the substrate. In order to perform measures *in situ*, the surface to study has to be sufficiently plain and smooth, but, most of all, a balance is needed in order to weigh the sponge during the different steps of the test. Although these small requirements must be taken into account, this method is now used in the Cultural Heritage community, and it is becoming a routine test regarding stone decay and protection [261, 262]. The method has been also compared with others, in particular with the different types of pipes [263, 264], showing that contact sponge gives good results with high precision for the measurements of water uptake in low porosity stones. However, it is less convenient for long time measurements or with high porosity stones due to the small amount of water supply. Like most of the methods to be applied *in situ*, especially outdoors, the results are affected by environmental conditions [265] and this should be kept in mind, especially when the measures are used to monitor the stone over time. The original tests were also made using a calibrated spring, in order to always impart the same pressure to the sponge, and recently this aspect has been investigated and improved by Scrivano and Gaggero [266]. At the time of writing, the WG3 of CEN-TC346 is drafting an EN standard for this test, starting from the UNI Italian Standard (UNI 11432) [161].

Among possible *in situ* techniques for assessing the absorption of water, those based on Nuclear Magnetic Resonance (NMR) deserve some attention [267]. The development of portable, unilateral NMR has made it possible to perform measurements on samples in a non-invasive way [268], with the aim to transfer this method *in situ* [269].

Very recently, ^{1}H-NMR relaxometry has been used, together with colour measurements, to assess the performances of several protectives on stone samples [270].

Regarding the tests that are not directly related to the hydrophobization of a stone surface, most of the studies take into account the importance of the maintenance of the water vapour permeability. As already described, the determination of this property is performed by applying an EN standard [207], and several scholars put this test into the trial of protective products experimentation [232, 236, 238, 242–245]. In the evaluation of protective treatments, the considerations already made for assessing the permeability for the consolidants are the same, and for this reason, please refer to Sect. 8.4. In addition, very recently, a new method has been proposed by Cuzman et al. [271]. The method consists of placing a fixed amount of silica gel with an orange humidity indicator with a diameter of 1–3 mm into a special bag ("Contact Bag"- CB), having a circular opening of 4 cm in diameter. The CB is hermetically attached to the stone samples by plasticine. The WVP (Water Vapor Permeability) is determined by the difference in weight of the CB before and after the time of application. The data obtained were in good agreement with those obtained on the same specimens by using laboratory methods such as permeability by dry cup method [207], but the optimization of the method is still ongoing.

Another test proposed in the protocol of tests for the assessment of protective treatments in the EN 16581 standard [230], with the aim of verifying the absence of side effects which may cause damage, is the colour measurement of surfaces, according to the standard EN 15886 [112]. As already introduced in Sect. 8.3, the methods for colour measurement are non-destructive and can be easily performed *in situ*. They are widely used in almost all the areas of conservation. In particular, for protective treatments, as well as for consolidation, the colour variations must be very limited, as the treatment should not affect the aesthetic aspect of the stone surface. The application of a protective product has the hard task of imparting water repellence to the surface without changing either the aesthetic aspect or the intrinsic structure. Most of the papers cited so far for protective products performance evaluation have adopted colour measurements, either in laboratory [231, 233, 236–239, 241–246, 248, 249, 270] or in *in situ* [162, 250–252].

During the last years, many scholars proposed other methodologies in order to study the behavior of protective treatments during experimentation, most of which are unfortunately only feasible in laboratory. Techniques based on spectroscopy are used by many scholars to verify the effective presence of the applied products on the treated surface. As already introduced in Sect. 8.3, FTIR spectroscopy [63] is widely used to analyze treated stone specimens [235, 236, 238, 244] and samples taken from the monuments. In the last decades portable instruments have also been made available on the market for *in situ* analyses, avoiding sampling [64, 65]. FTIR analyses on treated stone surfaces becomes particularly interesting when the applied product is an organic polymer (like siloxanes, fluoroelastomers, acrylates, and so on), and it is necessary verify its presence and its durability over time (Fig. 8.11).

Torrisi [232] proposed the use of time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) in order to acquire qualitative and quantitative information on the chemical composition of the utmost mono-layers of organic products.

Fig. 8.11 Matera Cathedral (Italy). Total Reflection FTIR instrument positioned on scaffolding to assess the performances of different protective products [252]

If the protective treatment is inorganic, some scholars proposed combinations of μ-Raman and XRF spectroscopies, and XRD, especially for ammonium oxalate treatments [234, 235, 250, 251, 272, 273], where it is important to verify the penetration depth of the treatment [274], and to check the crystalline phase of the newly formed calcium oxalate. Mudronja et al. [275] used most of the quoted techniques (μFTIR, XRD, and SEM), together with synchrotron-based techniques (SR-μXRD and SR-μFTIR), to evaluate different methods of application of a treatment based on ammonium oxalate.

Observations at microscopical level (especially SEM) are nowadays widespread for the study of a treated surface, as they allow the assessment of the morphology of the treatments, their distribution on the stone surface, and the study of the interaction between stone substrates and protective treatments. In particular, nanostructured treatments (nano-silica, nano-titania, and so on) are investigated in depth by SEM, transmission electron microscopy (TEM), and atomic force microscopy (AFM) [237, 243, 248], with the aim to establish a relationship between surface nanostructure, changes in the surface roughness, and degree of hydrophobicity.

Unfortunately, most of the quoted techniques are not applicable *in situ*, but require at least micro-sampling to be performed. Furthermore, even for those techniques for which portable instrumentations, have been available for several years [276–279], their use for the evaluation of conservation treatments *in situ* is extremely limited.

The monitoring of the treated materials assumes a role of fundamental importance, as it allows to control over time the factors that contribute to changes of physical and chemical properties and the progress of their effects. In the case of conservation treatments, the monitoring phase acquires great importance in the study of the effectiveness, the evolution over time, and the assessment of the possibility of repeating conservation interventions. Despite the fact that trial areas to test protective treatments are more frequent compared to consolidation, monitoring is not a common practice.

Indeed, very few papers deal with long-term monitoring and most of them use laboratory techniques applied to samples. This is obvious when we talk about measurements made when the *in situ* techniques were few or not at all developed [280–282]. However, even more recently the choice is oriented towards the laboratory, or, in the best cases, in a combination of both *in situ* and laboratory tests [213]. Moreover, we have to consider some objectives' difficulties in being able to repeat measurements on a working area *in situ* over time. Sometimes, scaffolding, previously availble and then dismantled, is required to access the areas, or there is the need to isolate an area from the public, and it may not be easy. Unfortunately, another important limitation often comes from the lack of adequate funding for monitoring phases.

Furthermore, the preference for laboratory tests is not only due to the greater diffusion of laboratory techniques compared to those applicable *in situ*, but above all, to the complexity of the analytical problems which, in most cases, cannot be solved only with methods applicable *in situ.*

Finally, it is not simple to routinely replace laboratory techniques with *in situ* ones for different reasons. In particular, the need of defining specific indicators, parameters, and threshold values is necessary to individuate suitable methods for specific situations. Moreover, further correlation between traditional laboratory methods and those applicable *in situ* is something that deserves specific attention.

The development of new portable instrumentations and *in situ* methods is a wide sector, open to research and progress. From this point of view, development can range from very simple to high tech, expensive techniques and methods. However, the simpler and less expensive methods have the best chance of being used more widely, especially for long-term monitoring. As a last remark, it must be emphasized that easy and simple must not to be confused with “simplistic”, as outlined in Blauer et al. [189]. The procedure for simple field tests needs to be learned properly, and the quality of the interpretation of the results depends, to a certain extent, on the experience of the operator implementing them, exactly as it does for more complex methods. In this sense, training is an important issue for conservators and conservation scientists. In addition, the drafting of standards shared by the community dealing with Cultural Heritage is an activity that certainly contributes to the dissemination of the correct application of methods and techniques.

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References

1. Sasse HR, Snethlage R. Methods for the evaluation of stone conservation treatments. In Saving Our Architectural Heritage: The Conservation of Historic Stone Structures; Report of the Dahlem Workshop on Saving Our Architectural Heritage, The Conservation of Historic Stone Structures, Berlin, March 3–8, 1996, Baer N. S., Snethlage R. eds., John Wiley & Sons, Chichester and New York 1997; 223–244.
2. Doehne E, Price CA. Stone Conservation – An overview of current research. 2nd ed. The Getty Conservation Institute Los Angeles; 2010.
3. Svahn H. Final Report for the Research and Development Project Non-Destructive Field Tests in Stone Conservation. Literature Study. Riksantikvarieämbetet, Stockholm, Sweden; 2006.
4. Menéndez B. Non-destructive techniques applied to monumental stone conservation. In: Márquez F, Papaelias M, Zaman N, editors, Non-destructive testing, In: Tech. Rijeka: 2016, 173–213. https://doi.org/10.5772/62408.
5. Chastre C, Ludovico-Marques M. Nondestructive testing methodology to assess the conservation of historic stone buildings and monuments. In: Makhlouf ASH, Aliofkhazraei M, editors.. Handbook of Materials Failure Analysis. Butterworth-Heinemann Oxford (UK). 2018. 255–294. https://doi.org/10.1016/B978-0-08-101928-3.00013-6.
6. Zendri E, Falchi L, Izzo FC, Morabito ZM, Driussi G. A review of common NDTs in the monitoring and preservation of historical architectural surfaces, Int J Architect Herit. 11:7, 2017, 987–1004. https://doi.org/10.1080/15583058.2017.1331477.
7. Wheeler G. Alkoxysilanes and the consolidation of stone. Los Angeles, The Getty Conservation Institute, 2005.
8. Laurenzi Tabasso M. Rossi Doria Rota P. Proposte per un metodo di controllo dei trattamenti da effettuare su opere d’arte in pietra. L’ingegnere 1974;4:124–135.

9. Slater GA. Stone preservative: methods of laboratory testing and preliminary performances criteria. NBS Technical Note 941, 1977, Washington D.C.
10. Various Authors, International Colloquium Methods of evaluating products for the conservation of porous building materials in monuments, Rome, 19–21 June 1995, Preprints, ISBN 92-9077-131-3.
11. Laurenzi Tabasso M. Introduction to the results of the round table discussion. Science and Technology for Cultural Heritage. 1996;5(1):53–56.
12. Rainer Sasse H, Snethlage R. Evaluation of stone consolidation treatments. Science and Technology for Cultural Heritage. 1996;5(1):85–92.
13. RILEM Commission 25-PEM. Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods. Materials and Structures 1980;13(3):175–253.
14. Charola AE. De Witte E. Laurenzi Tabasso M. Establishing international standards for the quality control of conservation materials and for qualifying practioners applying them. In Saving Our Architectural Heritage. Berlin, Wiley. 1996;245–254.
15. EN 45020:2006, Standardization and related activities - General vocabulary (ISO/IEC Guide 2:2004).
16. UNI/CT033/SC01 Beni Culturali, http://store.uni.com/catalogo/norme/root-categorie-tc/uni/uni-ct-033/uni-ct-033-sc-01?tpqual[3]=zz. Accessed 01 Oct 2020.
17. CEN TC346- Conservation of Cultural Heritage, https://standards.cen.eu/dyn/www/f?p=204:7:0::::FSP_ORG_ID:411453&cs=11079A55D70F8377E3942E1C6704C7664. Accessed 01 Oct 2020.
18. Fassina V. European Technical Committee 346: Conservation of cultural property: Updating of the activity after a three-year period. In 9th International Conference on Non-Destructive Investigations and Microanalysis for the Diagnostics and Conservation of Cultural and Environmental Heritage: Art, Jerusalem, May 25–30, 2008; 1–9.
19. Fassina V., CEN TC 346 Conservation of Cultural Heritage-Update of the activity after a eight year period. Engineering Geology for Society and Territory. Springer, Cham. 2015;8:37–41. https://doi.org/10.1007/978-3-319-09408-3_3.
20. CEN/TC346 Published standards. https://standards.cen.eu/dyn/www/f?p=CENWEB:84:::NO::: Accessed 01 Oct 2020.
21. Delgado Rodrigues J, Grossi A, Compatibility: building up an operative concept for masonry conservation. In: Delgado Rodrigues J, Mimoso JM, editors. Theory and Practice in Conservation. LNEC, 2006; 139–148.
22. Delgado Rodrigues J, Grossi A. Indicators and rating for the compatibility assessment of conservation actions. J Cult Herit. 2007;8:32–43.
23. EN 15898:2011, Conservation of cultural heritage- Main general terms and definitions, 2011.
24. Revez MJ, Delgado Rodrigues J. Incompatibility risk assessment procedure for the cleaning of built heritage. J Cult. Herit. 2016;18:219–228.
25. Vergés-Belmin V. Towards a definition of common evaluation criteria for the cleaning of porous building materials: a review. Science and Technology for Cultural Heritage. 1996;5(1):69–83.
26. Vergés-Belmin V. Pseudomorphism of gypsum after calcite: A new textural feature accounting for the marble sulphation mechanism. Atmospheric Environment – Part A 1994;28(2):295–304.
27. Smith BJ, Gomez-Heras M. McCabe S. Understanding the decay of stone-built cultural heritage. Prog Phys Geog. 2008;32(4):439–461.
28. Appolonia L. Bertone A. Brunetto A. Vaudan D. The St. Orso Priory: the comparison and testing of cleaning methods. J Cult Herit. 2000:1:S105–S110.
29. Moropoulou A, Labropoulos KC, Delegou ET, Karoglou M, Bakolas A. Non-destructive techniques as a tool for the protection of built cultural heritage. Constr Build Mater. 2013;48:1222–1239.
30. Moropoulou A, Delegou ET, Avdelidis NP, Koui M. Assessment of cleaning conservation interventions on architectural surfaces using an integrated methodology. In: Vandiver P,

Goodway M, Druzik JR, Mass JL, editors. Materials issues in art and archaeology VI, vol. 712. Pittsburgh: Publ. Materials Research Society. 2002; 69–76.
31. Iglesias-Campos MÁ, Prada Pérez JL, Fortes SG. Microblasting cleaning for façade repair and maintenance: Selecting technical parameters for treatment efficiency. Constr Build Mater. 2015;94:605–612.
32. Pozo-Antonio JS, Ramil A, Rivas T, López AJ, Fiorucci MP. Effectiveness of chemical, mechanical and laser cleaning methods of sulphated black crusts developed on granite. Constr Build Mater. 2016, 112, 682–690. https://doi.org/10.1016/j.conbuildmat.2016.02.195.
33. Coe J, Sherwood S, Messerich JA, Andersen A, Mossotti V. Measuring stone decay with close range photogrammetry. In: Delgado RJ, Fernando H, Telmo JF, editors. Proc. of the 7th International Congress on Deterioration and Conservation of Stone;. Lisbon, Laboratorio Nacional de Engenharia; Lisbon, 1992;2:917–926.
34. Tiano P, Tapete D, Matteini M, Ceccaroni F. The microphotogrammetry: a new diagnostic tool for on site monitoring of monumental surfaces. In: Tiano P, Pardini C, editors. In situ monitoring of monumental surfaces. Edifir-Edizioni Firenze, Florence. 2008;97–106.
35. Manganelli Del Fà R, Riminesi C, Tiano P. Monitoring of surface pattern of artistic and architectural artefacts by means of ultra-close range photogrammetry, Kermes Quaderni ESRARC2014, 6th European Symposium on Religious Art, Restoration and Conservation, Proceedings Book, Nardini Editore, 2014;164–167. ISBN: 978-88-404-4365-2.
36. Gaspar P, Hubbard C, McPhail D, Cummings A. A topographical assessment and comparison of conservation cleaning treatments. J Cult Herit. 2003;4:294s–302s.
37. Iglesias-Campos M., Prada Pérez JL., Fortes SG. Spot analysis to determine technical parameters of microblasting cleaning for building materials maintenance. Const. Build. Mater. 2017;132:21–32.
38. Rousset B, Gal G, Girardet F, Béal C, Constantin J. Roughness measurement applied to the monitoring and the follow-up of building cleaning. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;603–610.
39. Vazquez-Calvo C, Alvarez de Buergo M, Fort R, Varas-Muriel MJ. The measurements of surface roughness to determine the suitability of different methods for stone cleaning. J Geophys Eng. 2012;9(4):S108–S117. https://doi.org/10.1088/1742-2132/9/4/S108.
40. DIN 4768:1990, Determination of surface roughness values of the parameters R[a], R[z], R[max] by means of electrical contact (stylus) instruments; terminology, measuring conditions. 1990, German Institute for Standardisation (Deutsches Institut für Normung), Germany.
41. Simon S, Snethlage R. The first stages of marble weathering, preliminary results after short-term exposure of nine months. In Proceedings of the International RILEM/UNESCO Congress Conservation of Stone and Other Materials. Spon, Paris. 2003;51–58.
42. Aires-Barros L, Mauricio A, Figueiredo C. Profilometry and image application to "*in situ*" study of monuments stone decay problems. Fassina V, Ott H, Zezza F, editors. The 3rd International Symposium on The Conservation of Monuments in the Mediterranean Basin. Soprintendenza ai Beni Culturali e Storici di Venezia, Venice. 1994;19–24.
43. Avdelidis NP, Delegou ET, Almond DP, Moropoulou A. Surface roughness evaluation of marble by 3D laser profilometry and pulsed thermography. NDT & E Inter. 2004;37(7):571–575.
44. Colombo C, Daffara C, Fontana R, Gambino MC, Mastroianni M, Pampaloni E, Realini M, Sansonetti A. Evaluation by laser micro-profilometry of morphological changes induced on stone materials by laser cleaning. In: Nimmrichter J, Kautek W, Schreiner M, editors. Proc. of Conference Lasers in the Conservation of artworks: LACONA VI, Vienna, Austria, Sept. 21–25, 2005. Springer Proceedings in Physics 116. Springer, Berlin and New York. 2007;523–526.
45. Charola AE, Grissom CA, Erder E, Washowiak M., Oursrel D. Measuring surface roughness: three techniques. Proc. of the 8th International Congress on the Deterioration and Conservation of Stone. Möller, Druck und Verlag, Berlin.1996;1421–1434.

46. Grissom CA, Charola AE, Washowiak MJ, Measuring surface roughness on stone; back to basics. Stud Conserv. 2000;45:73–84.
47. Mairinger F. UV-, IR-, and X-ray imaging.. In: Janssen K, Van Grieken R, editors. Non-destructive microanalysis of cultural heritage materials. Elsevier, The Netherlands. 2004;42:15–72.
48. Dyer J, Verri G, Cupitt J. Multispectral imaging in reflectance and photo-induced luminescence modes: a user manual. 2013. http://www.britishmuseum.org/pdf/charisma-multispectral-imaging-manual-013.pdf. Accessed 15 January 2020.
49. Warda J, Frey F, Heller D, Kusheld D, Vitale T, Weaver G. Ultraviolet photography. In: Warda J, editor, AIC guide to digital photography and conservation documentation. 2nd edn: American Institute for Conservation of Historic and Artistic Works, Washington DC (USA), 2011.
50. Aldrovandi A, Massi M, Porcinai S. Analysis through photographic documentation of ultraviolet fluorescence. In: Bracci S, Falletti F, Matteini M, Scopigno R, editors. Exploring David-Diagnostic tests and state of conservation, Giunti, Firenze (IT), 2004;150–153. ISBN 88-09-03325-6.
51. Comelli D, Cubeddu R, Valentini G, Toniolo L. Fluorescence lifetime imaging and spectroscopy: a new analytical technique for non-destructive analysis of art surfaces. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;611–618.
52. Pouli P, Zafiropoulos V, Balas C, Doganis Y, Galanos A. Laser cleaning of inorganic encrustation on excavated objects: evaluation of cleaning result by means of multi-spectral imaging. J Cult Herit. 2003;4:338–342
53. Papadakis V, Loukaiti A, Pouli P. A spectral imaging methodology for determining on-line the optimum cleaning level of stonework. J Cult Herit. 2010;11:325–328.
54. Pozo-Antonio JS, Fiorucci MP, Ramil A, Rivas T, López AJ. Hyperspectral imaging as a non destructive technique to control the laser cleaning of graffiti on granite. J Nondestruct Eval. 2016;35–44. https://doi.org/10.1007/s10921-016-0361-9.
55. Janssens K. X-ray based methods of analysis. Comp Anal Chem. 2004;42:129–226.
56. Sianoudis I, Drakaki E, Hein A. Educational X-ray experiments and XRF measurements with a portable setup adapted for the characterization of cultural heritage objects. Eur J Phys. 2010;31(3):419–431. https://doi.org/10.1088/0143-0807/31/3/001.
57. Shugar AN, Mass J., editors. Handheld XRF for art and archaeology. Studies in Archeological Science 3. Belgium: Leuven University Press, 2012. ISBN: 978 90 5867 9345.
58. Bezur A, Lee L, Loubser M, Trentelman K. Handheld XRF in Cultural Heritage, J. Paul Getty Trust and Yale University. 2020
59. Buccolieri G, Castellano., Donativi M, Quarta S, Mapping sulphates on the David using portable EDXRF. In: Bracci S, Falletti F, Matteini., Scopigno R. editors. Exploring David - Diagnostic tests and state of conservation, Giunti, Firenze (IT), 2004;161–164. ISBN 88-09-03325-6.
60. Castellano A, Buccolieri G, Quarta S, Donativi M. Portable EDXRF surface mapping of sulfate concentration on Michelangelo’s David. X-Ray Spectrom. 2006;35:276–279. https://doi.org/10.1002/xrs.907.
61. Diana M, Gabrielli N, Ridolfi S. Sulfur determination on stone monuments with a transportable EDXRF system. X-Ray Spectrom. 2007;36:424–428.
62. Bitossi G, Giorgi R, Mauro M, Salvadori B, Dei L. Spectroscopic techniques in cultural heritage conservation: a survey, Appl Spectrosc Rev. 2005;40(3):187–228.
63. Derrick MR, Stulik D., Landry JM. Infrared spectroscopy in conservation science. The Getty Conservation Institute, Los Angeles (USA). 1999.
64. Ricci C, Miliani C, Brunetti BG, Sgamellotti A. Non-invasive identification of surface materials on marble artifacts with fiber optic mid-FTIR reflectance spectroscopy. Talanta. 2006;69:1221–1226.

65. Rosi F, Cartechini L, Sali D, Miliani C. Recent trends in the application of Fourier Transform Infrared (FT-IR) spectroscopy in Heritage Science: from micro- to non-invasive FT-IR. Physical Sciences Reviews, 4(11) Walter de Gruyter GmbH, Berlin/Boston. 2019. https://doi.org/10.1515/psr-2018-0006.
66. Magrini D, Bartolozzi G, Bracci S, Carlesi S, Cucci C, Picollo M. Evaluation of the efficacy and durability of the "Barium hydroxide method" after 40 years. Multi-analytical survey on the crocifissione by Beato Angelico. J Cult Herit., in press. https://doi.org/10.1016/j.culher.2020.04.006
67. Edwards HGM, de Faria DLA. Infrared, Raman microscopy and fibre-optic Raman spectroscopy (FORS).. In: Janssen K, Van Grieken R, editors. Non-destructive microanalysis of Cultural heritage materials. Elsevier, The Netherlands. 2004;42:359–395.
68. Casadio F, Daher C, Bellot-Gurlet L. Raman Spectroscopy of cultural heritage materials: overview of applications and new frontiers in instrumentation, sampling modalities, and data processing. In: Mazzeo R. editor. Analytical Chemistry for Cultural Heritage. Topics in Current Chemistry Collections Springer, Cham. 2017;161–211. https://doi.org/10.1007/978-3-319-52804-5_5.
69. Vandenabeele P, Castro K, Hargreaves M, Moens L, Madariaga JM, Edwards HGM. Comparative study of mobile Raman instrumentation for art analysis. Anal Chim Acta. 2007;588:108–116.
70. Martìnez-Arkarazo I, Smith DC, Zuloaga O, Olazabal MA, Madariaga JM. Evaluation of three different mobile Raman microscopes employed to study deteriorated civil building stones. J Raman Spectrosc. 2008;39:1018–1029. https://doi.org/10.1002/jrs.1941.
71. Martìnez-Arkarazo I, Sarmiento A, Usobiaga A, Angulo M, Etxebarria N, Madariaga JM. Thermodynamic and Raman spectroscopic speciation to define the operating conditions of an innovative cleaning treatment for carbonated stones based on the use of ion exchangers—A case study. Talanta. 2008;75:511–516.
72. Martínez-Arkarazo I, Sarmiento A, Maguregui M, Castro K, Madariaga JM. Portable Raman monitoring of modern cleaning and consolidation operations of artworks on mineral supports. Anal Bioanal Chem., 2010;397:2717–2725. https://doi.org/10.1007/s00216-010-3610-2.
73. Klein S, Stratoudaki T, Zafiropulos V, Hildenhagen J, Dickmann K, Lehmkuhl Th. Laser-induced breakdown spectroscopy for on-line control of laser cleaning of sandstone and stained glass Appl Phys A. 1999;69:441–444. https://doi.org/10.1007/s003399900102.
74. Siano S, Agresti J, Cacciari I, Ciofini D, Mascalchi M, Osticioli J, Mencaglia AA. Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers. Appl Phys A. 2012;106:419–446. https://doi.org/10.1007/s00339-011-6690-8.
75. Senesi GS, Carrara I, Nicolodelli G, Milori DMBP, De Pascale O. Laser cleaning and laser-induced breakdown spectroscopy applied in removing and characterizing black crusts from limestones of Castello Svevo, Bari, Italy: a case study. Microchem J. 2016;124:296–305.
76. Weibring P, Johansson T, Edner H, Svanberg S, Sunder B, Raimondi V, Cecchi G, Pantani L. Fluorescence lidar imaging of historical monuments. Appl Optics. 2001;40:6111–6120.
77. Cecchi G, Pantani L, Raimondi V, Tomaselli L, Lamenti G, Tiano P, Chiari R. Fluorescence lidar technique for the remote sensing of stone monuments. J Cult Herit. 2000;1:29–36.
78. Gobernado-Mitre I, Prieto AC, Zafiropulos V, Spetsidou Y, Fotakis C. On-line monitoring of laser cleaning of limestone by laser-induced breakdown spectroscopy and laser-induced fluorescence. Appl Spectrosc 1997;51:1125. https://doi.org/10.1366/0003702971941944.
79. Maravelaki PV, Zafiropulos V, Kilikoglou V, Kalaitzaki M, Fotakis C. Laser-induced breakdown spectroscopy as a diagnostic technique for the laser cleaning of marble. Spectrochim. Acta Part B, 1997:52(1): 41–53.
80. Avdelidis NP, Moropoulou A. Applications of infrared thermography for the investigation of historic structures. J Cult Herit. 2004;5:119–127.
81. Delegou ET, Krokida M, Avdelidis NP, Moropoulou A. Assessment of cleaning interventions- on marble surfaces using pulsed thermography. In: Paipetis AS, Matikas TE, Aggelis

DG, Van Hemelrijck D, editors. Emerging technologies in non-destructive testing, London: CRC Press. 2012;31–36. ISBN: 978-0-415-62131-1.
82. Jankowska M, Sliwiński G. Acoustic monitoring for the laser cleaning of sandstone. J Cult Herit. 2003;4:65s–71s.
83. Tserevelakis GJ, Pozo-Antonio JS, Siozosa P, Rivas T, Pouli P, Zacharakis G. On-line photoacoustic monitoring of laser cleaning on stone: Evaluation of cleaning effectiveness and detection of potential damage to the substrate. J Cult Herit. 2019;35:108–115.
84. Various Authors, SWBSS 2014, Proc. of 3rd International Conference on Salt Weathering of Buildings and Stone Sculptures, Brussel (BE), 14–16 October 2014, De Clercq H. ed. ISBN 978-2-930054-24-7.
85. Various Authors, SWBSS 2017, Proc. of 4th International Conference on Salt Weathering of Buildings and Stone Sculptures, Potsdam (GE), 20–22 September 2017, Laue S. ed. ISBN 978-3-934329-88-1.
86. SWBSS 2021, https://www.tudelft.nl/en/architecture-and-the-built-environment/current/events/swbss-2021/. Accessed 26 Feb 2021.
87. Price C, Brimblecombe P. Preventing salt damage in porous materials. In: Ray RA, Smith P, editors. Preventive Conservation: Practice, Theory and Research, The International Institute for Conservation of Historic and Artistic Works, London, 1994;90–93.
88. Charola AE. Salt in the deterioration of porous materials, J Am Inst Conserv. 2000; 39:327–343.
89. Doehne E, Salt weathering: a selective review. In: Siegesmund S, Weiss T, Vollbrecht A, editors. Special Publication, Geol. Soc., 205, Natural Stones, Weathering Phenomena, Conservation Strategies and Case Studies, London 2002;51–64.
90. Borrelli E. Standardizzazione di un metodo di estrazione di sali da supporti porosi e suo utilizzo a scopo diagnostico. 3rd International Symposium on The Conservation of Monuments in the Mediterranean Basin. Venice: Sopraintendenza ai Beni Artistici e Storici di Venezia.1994;163–167.
91. Borrelli E, Urland A. ARC Laboratory handbook: porosity, salts, binders, colour. Conservation of Architectural Heritage, Historic Structures and Materials, ICCROM, International Centre for the Study of the Preservation and Restoration of Cultural Property, Rome, 1999.
92. Vettori S, Bracci S, Cantisani E, Riminesi C, Sacchi B, D'Andria F. A multi-analytical approach to investigate the state of conservation of the wall paintings of Insula 104 in Hierapolis (Turkey). Microchem J. 2016;128:279–287.
93. Manganelli Del Fa R, Riminesi C, Rescic S, Tiano P, Sansonetti A. Non-destructive testing to perform service of the evaluation of conservation works. In: Aggelis DG, Van Hemelrijck D, Vanlanduit S, Anastasopoulos A, Philippidis T, editors., Proc. of the 6th Inter. Conf. on Emerging Technologies in Non-destructive Testing (ETNDT 2016), CRC Press, Boca Raton (USA). 2016;457–463.
94. Riminesi C, Olmi R. Diagnostics and monitoring of moisture and salt in porous materials by evanescent field dielectrometry. In: Laue S, editor. Proc. of SWBSS 2017, 4th International Conference on Salt Weathering of Buildings and Stone Sculptures. Potsdam, Germany. 20–22 September 2017. Verlag der Fachhochschule, Potsdam (DE). 2017;49–56.
95. Johnston-Feller R. Color science in the examination of museum objects: nondestructive procedures. Tools for conservation. The Getty Conservation Institute, Los Angeles (CA, USA). 2001.
96. Munsell AH, Atlas of the Munsell color system. Wadsworth, Howland & Co., Inc. Printers, Malden MA (USA). 1907.
97. Smith T, Guild., The C.I.E. colorimetric standards and their use, Trans. Opt. Soc. XXXIII(3) 1931–1932;73–134.
98. Schanda J. CIE Colorimetry. 25–78. In: Schanda J, editor. Colorimetry: Understanding the CIE system. John Wiley & Sons, Inc., Hobokeny, New Jersey (USA). 2007.
99. Luo M., Cui G, Rigg B. The development of the CIE 2000 colour-difference formula: CIEDE2000. Col Res Appl. 2001;26:340–350.

100. Mokrzycki WS, Tatol M. Color difference Delta E - A survey. Machine Graph Vis. 2011;20(4):383–411.
101. Fort R, Mingarro F, Lopez de Azcona MC, Rodriguez Blanco J. Chromatic parameters as performance indicators for stone cleaning techniques. Color Res Applic. 2000;25:442–446.
102. Labouré M, Bromblet P, Orial G, Wiedemann G, Simon-Boissond C. Assessment of laser cleaning rate on limestones and sandstones. J Cult Herit. 2000;1:S21–S27.
103. Esbert RM, Grossi CM, Rojo A, Alonso FJ, Montoto M, Ordaz J, Pérez de Andrés MC, Escudero C, Barrera M, Sebastián E, Rodríguez-Navarro C, Elert K. Application limits of Q-switched Nd:YAG laser irradiation for stone cleaning based on colour measurements. J Cult Herit. 2003;4:50s–55s.
104. Selwitz C. Epoxy Resins in Stone Conservation. 1992, The Getty Conservation Institute.
105. Melo MJ, Bracci S, Camaiti M, Chiantore O, Piacenti F. Photodegradation of acrylic resins used in the conservation of stone, Pol Deg Stab. 1999;66:23–30.
106. Pastorelli G, Cucci C, Garcia O, Piantanida G, Elnaggar A, Cassar M, Strlič M. Environmentally induced colour change during natural degradation of selected polymers, Pol Deg Stab. 2014;107:198–209. https://doi.org/10.1016/j.polymdegradstab. 2013.11.007.
107. Tesser E, Lazzarini L, Bracci S. Investigation on the chemical structure and ageing transformations of the cycloaliphatic epoxy resin EP2101 used as stone consolidant, J Cult Herit. 2018;31:72–82. https://doi.org/10.1016/j.culher.2017.11.002.
108. Bromblet P, Labouré M, Orial G. Diversity of the cleaning procedures including laser for the restoration of carved portals in France over the last 10 years. J Cult Herit. 2003;4:17s–26s.
109. Vergés-Belmin V, Rolland O, Leroux L. Can we be confident in colour measurements performed outdoors? In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008;539–546.
110. Klein S, Fekrsanati F, Hildenhagen J, Dickmann K, Uphoff H, Marakis Y, Zafiropoulos V. Discolouration of marble during laser cleaning by Nd:YAG laser wavelengths. Appl Surf Sci. 2001;171:242–251.
111. Vergès-Belmin V, Dignard C. Laser yellowing: myth or reality. J Cult Herit. 2003;4:238s-244s.
112. EN 15886:2010, Conservation of cultural heritage - Test methods – Colour measurement of surfaces.
113. Ďoubal J. Cleaning stone - the possibilities for an objective evaluation. In: Hughes J, Howind T, editors. Science and Art: A Future for Stone: Proc. of the 13th International Congress on the Deterioration and Conservation of Stone. University of the West of Scotland. Paisley, UK. 2016;729–736.
114. Fassina V. General criteria for the cleaning of stone: theoretical aspects and methodology of application. In: Zezza F, editor. Stone Material in Monuments: Diagnosis and Conservation. Scuola Universitaria C.U.M. Conservazione dei Monumenti; Heraklion, Crete. Mario Adda Editore (Bari, IT). 1993;126–132.
115. Mossotti VG, Eldeeb AR, Fries TL, Coombs MJ, Naude VN, Soderberg L, Wheeler GS. The effect of selected cleaning techniques on Berkshire Lee marble; A scientific study at Philadelphia City Hall, U.S. Geological Survey, Prof. Paper 1635, Virginia 2002. http://geopubs.wr.usgs.gov/prof-paper/pp1635/. Accessed 2 Oct 2020.
116. Delegou ET, Avdelidis NP, Karaviti E, Moropoulou A. NDT&E techniques and SEM-EDS for the assessment of cleaning interventions on Pentelic marble surfaces. X-Ray Spectrom. 2008;37 (4):435–443.
117. Mecchi AM, Poli T, Realini M, Sansonetti A. A proposal for a common approach in choosing test for the protocol evaluation of cleaning methods. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008; 425–433.

118. Delegou ET, Moropoulou A. Evaluation, criteria and decision making on cleaning interventions of marble surfaces. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008;1179–1188.
119. Delegou ET, Kiranoudis Ch, Sayas J, Moropoulou A. Developing an integrated decision-making system for the assessment of cleaning interventions on marble architectural surfaces. Proc. of the 12th International Congress on the Deterioration and Conservation of Stone Columbia University, New York, 2012. http://iscs.icomos.org/stonecon.html. Accessed 2 Oct 2020.
120. Delegou ET, Ntoutsi I, Kiranoudis CT, Sayas J, Moropoulou A. Advanced and novel methodology for scientific support on decision-making for stone cleaning. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing AG. 2018;299–234. https://doi.org/10.1007/978-3-319-72260-3_14.
121. Matteini M, Bracci S. Results of preliminary cleaning tests. In: Bracci S, Falletti F, Matteini M, Scopigno R, editors. Exploring David - Diagnostic tests and state of conservation. Giunti, Firenze (IT), 2004;234–237. ISBN 88-09-03325-6.
122. Hauff G, Kozub P, D'ham G. Which cleaning method is the most appropriate one? A systematic approach to the assessment of cleaning test panels. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008;381–388.
123. EN 17488:2020, Conservation of cultural heritage - Procedure for the analytical evaluation and selection of cleaning methods for porous inorganic materials used in cultural heritage.
124. Young ME, Ball J, Laing RA. Quantification of the long-term effects of stone cleaning on decay of building sandstones. In: Fassina V, editor. Proc. of the 9th International Congress on Deterioration and Conservation of Stone, 19–24 June 2000, Venice (IT). Elsevier Science BV, Amsterdam, The Netherlands. 2000;179–186.
125. Young ME, Ball J, Urquhartb DCM, Laing RA. Maintenance and repair issues for stone cleaned sandstone and granite building façades. Build Environ. 2003;38:1125–1131.
126. Sanmartín P, Rodríguez A. Aguiar U. Medium-term field evaluation of several widely used cleaning-restoration techniques applied to algal biofilm formed on a granite-built historical monument. Int Biodet Biodegr. 2020;147:104870. https://doi.org/10.1016/j.ibiod.2019.104870.
127. Perez-Monserrat EM, Fort R, Varas-Muriel MJ. Monitoring façade soiling as a maintenance strategy for the sensitive built heritage. Intern J Architec Herit. 2018;12(5):816–827. https://doi.org/10.1080/15583058.2017.1419312.
128. Delgado Rodrigues J. Consolidation of decayed stones. A delicate problem with few practical solutions. Proc. Int. Seminar on Historical Constructions, Guimarães. 2001;1–13.
129. IPERION-CH -Integrated Platform for the European Research Infrastructure ON Cultural Heritage, n. 654028, 2015–2019. www.iperionch.eu. Accessed 01 Aug 2020.
130. Praticò Y, Caruso F., Delgado Rodrigues J, Girardet F, Sassoni E, Scherer GW, Vergès Belmin V, Weiss NR, Wheeler GW, Flatt R.J. Stone consolidation: a critical discussion of theoretical insights and field practice. RILEM Technical Letters 2019;4:145–153. https://doi.org/10.21809/rilemtechlett.2019.101.
131. Dei L, Salvadori B. Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay. J Cult Herit. 2006;7:110–115. https://doi.org/10.1016/j.culher.2006.02.001.
132. Tiano P, Cantisani E, Sutherland I, Paget JM. Biomediated reinforcement of weathered calcareous stones. J Cult Herit. 2006;7:49–55. https://doi.org/10.1016/j.culher.2005.10.003.
133. Maravelaki-Kalaitzaki P, Kallithrakas-Kontos N, Agioutantis Z, Maurigiannakis S, Korakaki D. A comparative study of porous limestones treated with silicon-based strengthening agents. Prog Org Coat. 2008;62:49–60. https://doi.org/10.1016/j.porgcoat.2007.09.020.

134. Karatasios I, Theoulakis P, Kalagri A, Sapalidis A, Kilikoglou V. Evaluation of consolidation treatments of marly limestones used in archaeological monuments. Constr Build Mater. 2009;23:2803–2812. https://doi.org/10.1016/j.conbuildmat.2009.03.001.
135. Kim EK, Won J, Do J, Kimc SD, Kang YS. Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants. J Cult Herit. 2009;10:214–221. https://doi.org/10.1016/j.culher.2008.07.008.
136. López-Arce P, Gomez-Villalba LS, Pinho L, Fernández-Valle ME, Álvarez de Buergo M, Fort R. Influence of porosity and relative humidity on consolidation of dolostone with calcium hydroxide nanoparticles: Effectiveness assessment with non-destructive techniques. Mat Charact. 2010;61:168–184. https://doi.org/10.1016/j.matchar.2009.11.007.
137. Matteini M, Rescic S, Fratini F, Botticelli G. Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage A preliminary research. Int J Architect Herit. 2011;5(6):717–736. https://doi.org/10.1080/15583058.2010.495445.
138. Sassoni E, Naidu S, Scherer GW. The use of hydroxyapatite as a new inorganic consolidant for damaged carbonate stones. J Cult Herit. 2011;12:346–355. https://doi.org/10.1016/j.culher.2011.02.005.
139. Daniele V, Taglieri G. Synthesis of $Ca(OH)_2$ nanoparticles with the addition of Triton X-100. Protective treatments on natural stones: Preliminary results. J Cult Herit. 2012;13:40–46. https://doi.org/10.1016/j.culher.2011.05.007.
140. Pérez NA, Lima E, Boscha P, Méndez-Vivar J. Consolidating materials for the volcanic tuff in western Mexico. J Cult Herit. 2012;15:352–358. https://doi.org/10.1016/j.culher.2013.07.010.
141. Perito B, Marvasi M, Barabesi C, Mastromei G, Bracci S, Vendrell M, Tiano P. A Bacillus subtilis cell fraction (BCF) inducing calcium carbonate precipitation: Biotechnological perspectives for monumental stone reinforcement. J Cult Herit. 2014;15(4):345–351. https://doi.org/10.1016/j.culher.2013.10.001.
142. Sassoni E, Franzoni E, Pigino B, Scherer GW, Naidu S. Consolidation of calcareous and siliceous sandstones by hydroxyapatite: Comparison with a TEOS-based consolidant. J Cult Herit. 2013;14:e103–e108. https://doi.org/10.1016/j.culher.2012.11.029.
143. Licchelli M, Malagodi M, Weththimuni M, Zanchi C. Nanoparticles for conservation of bio-calcarenite stone. Appl Phys A. 2014;114:673–683. https://doi.org/10.1007/s00339-013-7973-z.
144. Naidu S, Liu C, Scherer GW. Hydroxyapatite-based consolidant and the acceleration of hydrolysis of silicate-based consolidants. J Cult Herit. 2015;16:94–101. https://doi.org/10.1016/j.culher.2014.01.001.
145. Natali I, Tomasin P, Becherini F, Bernardi A, Ciantelli C, Favaro M, Favoni O, Forrat Pérez Olteanu JD, Romero Sanchez MD, Vivarelli A, Bonazza A. Innovative consolidating products for stone materials: field exposure tests as a valid approach for assessing durability. Herit Sci. 2015;3(6). https://doi.org/10.1186/s40494-015-0036-3.
146. Delgado Rodrigues J, Ferreira Pinto AP Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. J Cult Herit. 2016;19:467–476. https://doi.org/10.1016/j.culher.2015.10.002.
147. Zornoza-Indart A, Lopez-Arce P, Leal N, Simão J, Zoghlami K. Consolidation of a Tunisian bioclastic calcarenite: From conventional ethyl silicate products to nanostructured and nanoparticle based consolidants. Constr Build Mater. 2016;116:188–202. https://doi.org/10.1016/j.conbuildmat.2016.04.114.
148. Borsoi G, Lubelli B, van Hees R, Veiga R, Santos Silva A. Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties. Constr Build Mater. 2017;142:385–394. https://doi.org/10.1016/j.conbuildmat.2017.03.097.
149. Raneri S, Barone G, Mazzoleni P, Alfieri I, Bergamonti L, De Kock T, Cnudde V, Lottici PP, Lorenzi A, Predieri G, Rabot E, Teixeira J. Efficiency assessment of hybrid coatings for natural building stones: advanced and multi-scale laboratory investigation. Constr Build Mater. 2018;180:412–424. https://doi.org/10.1016/j.conbuildmat.2018.05.289.

150. Sena da Fonseca B, Ferreira Pinto AP, Piçarra S, Montemor MF. The potential action of single functionalization treatments and combined treatments for the consolidation of carbonate stones. Constr Build Mater. 2018;163:586–599. https://doi.org/10.1016/j.conbuildmat.2017.12.126.
151. Becerra J, Zaderenko A.P, Ortiz P. Basic protocol for on-site testing consolidant nanoparticles on stone cultural heritage. Heritage. 2019;2:2712–2724. https://doi.org/10.3390/heritage2040168.
152. Iucolano F, Colella A, Liguori B, Calcaterra D. Suitability of silica nanoparticles for tuff consolidation. Constr Build Mater. 2019;202:73–81. https://doi.org/10.1016/j.conbuildmat.2019.01.002.
153. Pozo-Antonio JS, Otero J, Alonso P, Mas i Barberà X. Nanolime- and nanosilica-based consolidants applied on heated granite and limestone: Effectiveness and durability. Constr Build Mater. 2019;201:852–870. https://doi.org/10.1016/j.conbuildmat.2018.12.213.
154. Vasanelli E, Calia A, Masieri M, Baldi G. Stone consolidation with SiO_2 nanoparticles: Effects on a high porosity limestone. Constr Build Mater. 2019:219:154–163. https://doi.org/10.1016/j.conbuildmat.2019.05.169.
155. Badreddine D, Becka K, Brunetauda X, Chaaba A, Al-Mukhtar M. Nanolime consolidation of the main building stone of the archaeological site of Volubilis (Morocco). J Cult Herit. 2020;43:98–107. https://doi.org/10.1016/j.culher.2019.12.006.
156. Ruffolo SA, Rovella N, Arcudi A, Crupi V, Majolino D, Osanna M, Pace R, Pantuso A, Randazzo L, Ricca M, Ruggieri N, Venuti V, La Russa MF. New insights to assess the consolidation of stone materials used in built heritage: the case study of ancient grafti (Tituli Picti) in the archaeological site of Pompeii. Herit Sci. 2020;8(49). https://doi.org/10.1186/s40494-020-00393-0.
157. EN 15801:2009 - Conservation of cultural property - Test methods - Determination of water absorption by capillarity.
158. EN 15802:2009 - Conservation of cultural property - Test methods - Determination of static contact angle.
159. Liu Y, Liu J. Synthesis of TEOS/PDMS-OH/CTAB composite coating material as a new stone consolidant formulation. Constr Build Mater. 2016;122:90–94. https://doi.org/10.1016/j.conbuildmat.2016.06.069.
160. Tiano P, Pardini C, Valutazione *in situ* dei trattamenti protettivi per il materiale lapideo. Proposta di una nuova semplice metodologia. Arkos. 2004;5:30–36.
161. UNI 11432:2011 - Cultural heritage - Natural and artificial stone - Determination of the water absorption by contact sponge.
162. Gherardi F, Gulotta D, Goidanich S, Colombo A, Toniolo L. On-site monitoring of the performance of innovative treatments for marble conservation in architectural heritage. Herit Sci. 2017;5(4). https://doi.org/10.1186/s40494-017-0118-5.
163. Tesser E, Lazzarini L, Ganzerla R, Antonelli F. The decay of the polysiloxane resin Sogesil XR893 applied in the past century for consolidating monumental marble surfaces. J Cult Herit. 2017;27:107–115. https://doi.org/10.1016/j.culher.2017.03.001.
164. Delgado Rodrigues J, Ferreira Pinto A.P. Stone consolidation by biomineralisation. Contribution for a new conceptual and practical approach to consolidate soft decayed limestones. J Cult Herit. 2019;39:83–92. https://doi.org/10.1016/j.culher.2019.04.022.
165. "Marmora Phrygiae", Metodologie interdisciplinari per la conoscenza e la conservazione. Archeologia del costruito, informatica e scienze chimico-fisiche per la ricostruzione storica dei cantieri dei materiali di una città romana e bizantina dell'Asia Minore, Hierapolis di Frigia". Project founded by Italian Ministry of Culture, 2012–2015.
166. Vettori, S, Riminesi C, Cantisani E, Bracci S, Sacchi S. Marbles from Hierapolis: decay, conservation, monitoring of surfaces and environment, In: Ismaelli T, Scardozzi G, editors. Ancient quarries and building sites in Asia Minor.Research on Hierapolis in Phrygia and other cities in south-western Anatolia: archaeology, archaeometry, conservation. Building

sites of Hierapolis during the Byzantine age, Edipuglia, Bari (IT). 2016;557–573. https://doi.org/10.4475/819.
167. EN 16302:2013 - Conservation of Cultural Heritage - Test methods - Measurement of water absorption by pipe method.
168. EN 16322:2013 - Conservation of Cultural Heritage - Test methods - Determination of drying properties.
169. Ludovico-Marques M, Chastre C. Effect of consolidation treatments on mechanical behaviour of sandstone. Constr Build Mater. 2014;70:473–482. https://doi.org/10.1016/j.conbuildmat.2014.08.005.
170. Chen W, Dai P, Yuan P, Zhang J. Effect of inorganic silicate consolidation on the mechanical and durability performance of sandstone used in historical sites. Constr Build Mater. 2016;121:445–452. https://doi.org/10.1016/j.conbuildmat.2016.06.008.
171. Ferreira Pinto AP, Delgado Rodrigues J Stone consolidation: The role of treatment procedures. J Cult Herit. 2008;9:38–53. https://doi.org/10.1016/j.culher.2007.06.004.
172. Ferreira Pinto AP. Delgado Rodrigues J. Consolidation of carbonate stones: Influence of treatment procedures on the strengthening action of consolidants. J Cult Herit. 2012;13:154–166. https://doi.org/10.1016/j.culher.2011.07.003.
173. Remzova M, Sasek P, Frankeova D, Slizkova Z, Rathousky J. Effect of modified ethylsilicate consolidants on the mechanical properties of sandstone. Constr Build Mater. 2016;112:674–681. https://doi.org/10.1016/j.conbuildmat.2016.03.001.
174. Tiano P, Filareto F, Ponticelli S, Ferrari M, Valentini E. Drilling force measurement system, a new standardisable methodology to determine the "superficial hardness" of monument stones: prototype design and validation. Int J Rest Build Monum. 2000;6(2):115–132.
175. Tiano P, Delgado Rodrigues J, De Witte E, Vergès-Belmin V, Massey S, Snethlage R, Costa D, Cadot-Leroux L, Garrod E, Singer B. The conservation of monuments: A new method to evaluate consolidating treatments. Int J Rest Build Monum. 2000;6(2);133–150.
176. Delgado Rodrigues J, Ferreira Pinto AP, Rodrigues da Costa D. Tracing of decay profiles and evaluation of stone treatments by means of microdrilling techniques. J Cult Herit. 2002;3:117–125.
177. Pamplona M, Kocher M, Snethlage R, Aires Barros L. Drilling resistance: overview and outlook. Z. dt. Ges. Geowiss., 2007;158(3):665–676. https://doi.org/10.1127/1860-1804/2007/0158-0665.
178. Nogueira R, Ferreira Pinto AP, Gomes A, Alexandre Bogas J. Prediction of compressive strength for heterogeneous mortars from Drilling Resistance Data. Int J Architect Herit. 2018;14(3):415–432. https://doi.org/10.1080/15583058.2018.1547800.
179. MCDUR project. Effects of the weathering on stone materials: assessement of their mechanical durability 2001–2005. https://cordis.europa.eu/project/id/G6RD-CT-2000-00266. Accessed 30 Sept 2020.
180. Fratini F, Rescic S, Tiano P. A new portable system for determining the state of conservation of monumental stones. Mater Struct. 2006;39:139–147. https://doi.org/10.1617/s11527-005-9013-8.
181. Bracci S, Fratini F. La diagnostica preventiva In: Sabelli R, editor. L'area archeologica di Fiesole-Conservazione della memoria e innovazioni per la fruizione. Edizioni Polistampa (Firenze-IT) 2014;111–122. ISBN 978-88-596-1385-5.
182. Niedoba K, Slízková Z, Frankeová D, Nunes CL, Jandejsek I. Modifying the consolidation depth of nanolime on Maastricht limestone. Constr Build Mater. 2017;133:51–56. DOI:https://doi.org/10.1016/j.conbuildmat.2016.11.012.
183. Molina E, Rueda-Quero L, Benavente D, Burgos-Cara A, Ruiz-Agudo E, Cultrone G. Gypsum crust as a source of calcium for the consolidation of carbonate stones using a calcium phosphate-based consolidant. Constr Build Mater. 2017;143:298–311. https://doi.org/10.1016/j.conbuildmat.2017.03.155.
184. Tiano P. Annex to deliverable 15 – Draft of recommended methodologies for stone durability qualification. In: The European Commission Project ACOUTHERM – (GRD3-2001-60001)

Effects of the weathering on stone materials: assessment of their mechanical durability (McDUR), 2005.
185. Delgado Rodrigues J, Costa D. A new method for data correction in drill resistance tests for the effect of drill bit wear, Int J Rest. 2004;10(3):1–18.
186. Mimoso JM, Costa D. The DRMS drilling technique with pilot holes. In Proceedings of the International Conference on Heritage, Weathering and Conservation, Madrid, Spain. 2006;651–655. ISBN 0-415-41273-0.
187. Mimoso JM, Costa D, A new technique for using the DRMS in hard materials. Application to the study of the consolidation action. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008;1171–1178.
188. Meinhardt J,Snethlage R, Auras., Natural stone monitoring - investigation methods for a reliable evaluation of the effectiveness of conservation measures. Proceeding of the 12th International Congress on the Deterioration and Conservation of Stone Columbia University, New York, 2012. http://iscs.icomos.org/stonecon.html. Accessed 2 Oct 2020.
189. Bläuer C, Franzen C, Vergès-Belmin V. Simple field tests in stone conservation. Proceeding of the 12th International Congress on the Deterioration and Conservation of Stone Columbia University, New York, 2012. http://iscs.icomos.org/stonecon.html. Accessed 2 Oct 2020.
190. ASTM D3359-02: Standard Test Methods for Measuring Adhesion by Tape Test, ASTM International, 10 August, 2002.
191. Drdácký M, Lesák J, Rescic S, Slížková Z, Tiano P, Valach J. Standardization of peeling tests for assessing the cohesion and consolidation characteristics of historic stone surfaces. Mat Struct. 2012;45:505–520. https://doi.org/10.1617/s11527-011-9778-x.
192. Drdácký M, Slížková Z. Enhanced affordable methods for assessing material characteristics and consolidation effects on stone and mortar, J Geophys Eng. 2013;10: 064005. https://doi.org/10.1088/1742-2132/10/6/064005.
193. Becerra J, Ortiz P, Martín JM, Zaderenko AP. Nanolimes doped with quantum dots for stone consolidation assessment. Constr Build Mater. 2019;199:581–593. https://doi.org/10.1016/j.conbuildmat.2018.12.077.
194. De Rosario I, Elhaddad F, Pan A, Benavides R, Rivas T, Mosquera MJ. Effectiveness of a novel consolidant on granite: Laboratory and in situ results. Constr Build Mater. 2015;76:140–149. https://doi.org/10.1016/j.conbuildmat.2014.11.055.
195. De Rosario I, Rivas T, Buceta G, Feijoo J, Mosquera MJ. Surfactant-synthesized consolidants applied to a granitic medieval necropolis in NW Spain. Laboratory and in situ effectiveness evaluation. Int J Archit Herit. 2017;11(8):1166–1176. doi.org/10.1080/15583058.2017.1354097.
196. Aydin A, Basu A, The Schmidt hammer in rock material characterization, Eng Geol. 2005;81:1–14.
197. Christaras B. Non destructive methods for investigation of some mechanical properties of natural stones in the protection of monuments. Bull Int Ass Eng Geol. 1996;54:59–63.
198. Viles J, Goudi A, Grab S, Lalley J. The use of the Schmidt Hammer and Equotip for rock hardness assessment in geomorphology and heritage science: a comparative analysis. Earth Surf Proc Land. 2011;36:320–333. https://doi.org/10.1002/esp.2040.
199. EN 14579:2004, Natural stone test methods - Determination of sound speed propagation.
200. Pápay Z, Török Á, Three consolidants and three porous limestones: testing the effectiveness of consolidant on hungarian porous limstones from Sóskút quarry, in terms of physicomechanical properties. In: Lukaszewicz JW, Niemcewicz P, editors. Proc. of the 11th International Congress on Deterioration and Conservation of Stone, 15–20 September 2008, Torun, Poland. Nicolaus Copernicus University Press, Torun, Poland. 2008;717–724.
201. NORMAL 22/86 Misura della Velocità di Propagazione del Suono – ICR-CNR Eds.
202. Murru A, Fort R. Diammonium hydrogen phosphate (DAP) as a consolidant in carbonate stones: Impact of application methods on effectiveness. J Cult Herit. 2020;42:45–55. https://doi.org/10.1016/j.culher.2019.09.003.

203. Myrin M, Malaga K. A case study on the evaluation of consolidation treatments of Gotland sandstone by use of ultrasound pulse velocity measurements. In: Fort R, Alvarez de Buergo M, Gomez-Heras M, Vazquez-Calvo editors. Heritage, Weathering and Conservation. Taylor & Francis Group, London, 2006;749–755.
204. Sebastian EM, de la Torre MJ, Cazalla O, Cultrone G, Rodriguez-Navarro C. Evaluation of treatments on biocalcarenites with ultrasound, The e-Journal of Non-Destructive Testing. 1999;4(12). http://www.ndt.net/article/v04n12/cultrone/cultrone.htm. Accessed 30. Sept. 2020.
205. Drdácký M, Eisler M, Krompholz R. In-situ investigation of stone consolidation effects with immersed ultrasonic double-probe. In: Siegesmund S, Middendorf B, editors. Monument future: decay and conservation of stone. Proc. 14th Int. Congress on the Deterioration and Conservation of Stone. Mitteldeutscher Verlag (DE). 2020;233–237.
206. Sharma G. Digital Color Imaging Handbook C.R.C. Press, U.S.A. 2002.
207. EN 15803:2009 - Conservation of cultural property - Test methods - Determination of water vapour permeability (δp).
208. Brown S, Smith L, A transient-flow syringe air permeameter. Geophysics. 2013;78(5):D307–D313. https://doi.org/10.1190/geo2012-0534.1.
209. Filomena CM, Hornung J, Stollhofen H. Assessing accuracy of gas-driven permeability measurements: a comparative study of diverse Hassler-cell and probe permeameter devices. Solid Earth. 2014;5(1):1–11. https://doi.org/10.5194/se-5-1-2014.
210. Mertz J-D, Colas E, Yahmed A, Lenormand R. Assesment of a non-destructive and portable mini permeameter based on a pulse decay flow applied to historical surfaces of porous materials. In: Hughes J, Howind T, editors. Science and Art: A Future for Stone: Proc. of the 13th International Congress on the Deterioration and Conservation of Stone. University of the West of Scotland. Paisley, UK. 2016;415–422.
211. Torrent R. A two-chamber vacuum cell for measuring the coefficient of permeability to air of the concrete cover on site. Mater Struct. 1992;25(6):358–365. https://doi.org/10.1007/bf02472595.
212. Sena da Fonseca B, Castela AS, Duarte RG, Neves R, Montemor MF Non-destructive and on site method to assess the air-permeability in dimension stones and its relationship with other transport-related properties. Mat Struct. 2015;48:3795–3809. https://doi.org/10.1617/s11527-014-0440-2.
213. Varas-Muriel MJ, Pérez-Monserrat EM, Vázquez-Calvo C, Fort R. Effect of conservation treatments on heritage stone. Characterisation of decay processes in a case study. Constr Build Mater. 2015;95:611–622. https://doi.org/10.1016/j.conbuildmat.2015.07.087.
214. Ma X, Balonis M, Pasco H, Toumazou M, Counts D, Kakoulli I. Evaluation of hydroxyapatite effects for the consolidation of a Hellenistic-Roman rock-cut chamber tomb at Athienou-Malloura in Cyprus. Constr Build Mater. 2017;150:333–344. https://doi.org/10.1016/j.conbuildmat.2017.06.012.
215. Possenti E, Colombo C, Conti C, Gigli L, Merlini M, Rikkert Plaisier J, Realini M, Sali D, Gatta GD. Diammonium hydrogenphosphate for the consolidation of building materials. Investigation of newly-formed calcium phosphates. Constr Build Mater. 2019;195:557–563. https://doi.org/10.1016/j.conbuildmat.2018.11.077.
216. Jimenez-López C, Rodriguez-Navarro C, Pinar G, Carrillo-Rosú FJ, Rodriguez-Gallego M, Gonzalez-Munoz MT. Consolidation of degraded ornamental porous limestone stone by calcium carbonate precipitation induced by the microbiota inhabiting the stone. Chemosphere. 2007;78:1929–1936. https://doi.org/10.1016/j.chemosphere.2007.02.044.
217. Jimenez-López C, Jroundi F, Pascolini C, Rodriguez-Navarro C, Pinar-Larrubia G, Rodriguez-Gallego M, Gonzalez-Munoz MT. Consolidation of quarry calcarenite by calcium carbonate precipitation induced by bacteria activated among the microbiota inhabiting the stone Int Biodeter Biodegrad. 2008;62352–363. https://doi.org/10.1016/j.ibiod.2008.03.002.

218. Conti C, Aliatis I, Casati M, Colombo C, Matteini M, Negrotti R, Realini M, Zerbi G. Diethyl oxalate as a new potential conservation product for decayed carbonatic substrates. J Cult Herit. 2014;15:336–338. https://doi.org/10.1016/j.culher.2013.08.002.
219. Conti C, Colombo C, Festa G, Hovind J, Perelli Cippo E, Possenti E, Realini M. Investigation of ammonium oxalate diffusion in carbonatic substrates by neutron tomography. J Cult Herit. 2016;19:463–466. https://doi.org/10.1016/j.culher.2015.12.005.
220. Possenti E, Colombo C, Bersani D, Bertasa M, Botteon A, Conti C, Lottici PP, Realini M. New insight on the interaction of diammonium hydrogenphosphate conservation treatment with carbonatic substrates: A multi-analytical approach. Microchem J. 2016;127:79–86. https://doi.org/10.1016/j.microc.2016.02.008.
221. Conti C, Striova J, Aliatis I, Colombo C, Greco M, Possenti E, Realini M, Brambilla L, Zerbi G. Portable Raman versus portable mid-FTIR reflectance instruments to monitor synthetic treatments used for the conservation of monument surfaces. Anal Bioanal Chem. 2013;405:1733–1741. https://doi.org/10.1007/s00216-012-6594-2.
222. Normand L, Giovannacci D, Vérges Belmin V, Duchene S, Hénin J. Terahertz time-domain imaging (THZ-TDI): a new non-destructive method for the determination of consolidation depth on stone. In: Siegesmund S, Middendorf B, editors. Monument future: decay and conservation of stone. Proc. 14th Int. Congress on the Deterioration and Conservation of Stone. Mitteldeutscher Verlag (DE). 2020;639–644.
223. Various authors, Criteria for intervening in stone materials. 2013 review. In Coremans Project: Criteria for Working in Stone Materials; Secretaría General Técnica; Subdirección General de Documentación y Publicaciones: Madrid, Spain. 2013;39–108.
224. Perez Ema N, Alvarez De Buergo M, Bustamante R. Integrated studies for the evaluation of conservation treatments on building materials from archaeological sites. Application to the case of Merida (Spain). Int J Cons Sci. 2013;4:693–700.
225. Haake S, Favaro M, Stefan S. The Bologna cocktail - evaluation of consolidation treatments on monuments in France and Italy after 20 years. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;423–430.
226. Bracci S, Cagnini A, Driussi G, Galeotti M, Morabito ZM, Pinna D, Porcinai S, Sacchi B, Santagostino A. Indagini preliminari all'intervento di restauro. In: Improta MC, editor. Il restauro dei portali di San Petronio a Bologna. Studi e approfondimenti.. Edifir, Firenze (IT). 2016;185–191. ISBN 978-88-7970-744-2.
227. Bracci S, Galeotti M, Pinna D, Marble statues and panels of San Petronio façade in Bologna, state of conservation after 40 years since restoration. Proc. of the 12th International Congress on the Deterioration and Conservation of Stone Columbia University, New York, 2012. http://iscs.icomos.org/stonecon.html. Accessed 02 Oct 2020.
228. Fassina V, Benchiarin S, Molin G. Laboratory and in situ evaluation of restoration treatments in two important monuments in Padua: "Loggia Cornaro" and "Stele of Minerva". In: Hughes J, Howind T, editors. Science and Art: A Future for Stone: Proc. of the 13th International Congress on the Deterioration and Conservation of Stone. University of the West of Scotland. Paisley, UK. 2016;1111–1118.
229. Calia A, Lettieri M, Quarta G, Laurenzi Tabasso M, Mecchi AM. Documentation and assessment of the most important conservation treatments carried out on Lecce stone in the last two decades. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;431–438.
230. EN 16581:2014, Conservation of cultural heritage - Surface protection for porous inorganic materials - Laboratory test methods for the evaluation of the performance of water repellent products.
231. Tsakalof A, Manoudis P, Karapanagiotis I, Chryssoulakis I, Panayiotou C. Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. J Cult Herit. 2007;8:69–72.

232. Torrisi A, Evaluation of five fluorinated compounds as calcarenite protectives. J Cult Herit. 2008;9:135–145.
233. Pinna D, Salvadori B, Porcinai S. Evaluation of the application conditions of artificial protection treatments on salt-laden limestones and marble. Constr Build Mater. 2011;25:2723–2732.
234. Vanmeert F, Mudronja D, Fazinic S, Janssens K, Tibljas D. Semi-quantitative analysis of the formation of a calcium oxalate protective layer for monumental limestone using combined micro-XRF and micro-XRPD. X-Ray Spectrosc. 2013;42:256–161.
235. Mudronja D, Vanmeert F, Hellemans K, Fazinic S, Janssens K, Tibljas D, Rogosic M, Jakovljevic S. Efficiency of applying ammonium oxalate for protection of monumental limestone by poultice, immersion and brushing methods. Appl Phys A. 2013;111:109–119.
236. Calia A, Colangiuli D, Lettieri M, Matera L. A deep knowledge of the behaviour of multicomponent products for stone protection by an integrated analysis approach. Prog Org Coat. 2013;76:893–899.
237. Facio DS, Mosquera MJ. Simple strategy for producing superhydrophobic nanocomposite coatings *in Situ* on a building substrate. Appl Mat Interf. 2013;7517–7526.
238. Licchelli M, Malagodi M, Weththimuni M., Zanchi C, Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure. Prog Org Coat. 2013;76:495–503.
239. Tulliani JM, Serra CL, Sangermano M. A visible and long-wavelength photocured epoxy coating for stone protection. J Cult Herit. 2014;15:250–257.
240. Munafò P, Goffredo GB, Quagliarini E. TiO_2-based nanocoatings for preserving architectural stone surfaces: An overview. Constr Build Mater. 2015;84:201–218.
241. Kronlund D, Lindén M, Smått JH. A polydimethylsiloxane coating to minimize weathering effects on granite. Constr Build Mater. 2016;124:1051–1058.
242. Kronlund D, Lindén M, Smått JH. A sprayable protective coating for marble with water-repellent and anti-graffiti properties. Prog Org Coat. 2016;101:359–366.
243. Pedna A, Pinhoa L, Frediani P, Mosquera MJ. Obtaining SiO_2–fluorinated PLA bionanocomposites with application as reversible and highly-hydrophobic coatings of buildings. Prog Org Coat. 2016;90:91–100.
244. Esposito Corcione C, De Simone N, Santarelli ML, Frigione M. Protective properties and durability characteristics of experimental and commercial organic coatings for the preservation of porous stone. Prog Org Coat. 2016;103:193–203.
245. Andreotti S, Franzoni E, Fabbri P. Poly(hydroxyalkanoate)s-based hydrophobic coatings for the protection of stone in cultural heritage. Materials. 2018;11:165. DOI: https://doi.org/10.3390/ma11010165.
246. Roveri M, Gherardi F, Goidanich S, Gulotta D, Castelvetro V, Fischer R, Winandy L, Weber J, Toniolo L. Self-cleaning and antifouling nanocomposites for stone protection: properties and performances of stone-nanomaterial systems. IOP Conf. Series: Materials Science and Engineering 2018;364:012070.
247. Sabatini V, Cattò C, Cappelletti G, Cappitelli F, Antenuccia S, Farina H, Ortenzi MA, Camazzola S, Di Silvestro G. Protective features, durability and biodegration study of acrylic and methacrylic fluorinated polymer coatings for marble protection. Prog Org Coat. 2018;114:47–57.
248. Gherardi F, Goidanich S, Toniolo L. Improvements in marble protection by means of innovative photocatalytic nanocomposites. Prog Org Coat. 2018;121:13–22.
249. Tokarský J, Martinec P, Mamulová Kutláková K, Ovčačíková H, Študentová S, Jirĭ Ščučka J. Photoactive and hydrophobic nano-ZnO/poly(alkyl siloxane) coating for the protection of sandstone. Constr Build Mater. 2019;199:549–559.
250. Dreyfuss T. Interactions on site between powdering porous limestone, natural salt mixtures and applied ammonium oxalate. Herit Sci. 2019;7:5.
251. Dreyfuss T, Artificially induced calcium oxalate on limestone in urban environments - New findings. J Cult Herit. 2020;42:56–63.

252. Sacchi B, Vettori S, Andreotti A, Rampazzi L, Colombini MP, Tiano P. Assessment of water repellent treatments for the stone of the Matera cathedral facade (Italy), Int J Archit Herit. 2020; https://doi.org/10.1080/15583058.2020.1782532.
253. Rius V. How to use static and dynamic contact angles to characterize surface properties with a small portable device. In: Tiano P, Pardini C, editors. In situ monitoring of monumental surfaces. Edifir-Edizioni Firenze, Florence (IT). 2008;255–260.
254. Bärbel A. Investigation of crusts with the Karsten testing tube. In: Proc. of 7th International Congress on the Deterioration and Conservation of Stone. Laboratorio Nacional de Engenharia Civil, Lisbon (PT).1992;601–609.
255. Hendrickx R. Using the Karsten tube to estimate water transport parameters of porous buildings materials. Mat Struct. 2013;46:1309–1320. https://doi.org/10.1617/s11527-012-9975-2.
256. Kozub P, Karsten tube penetration test - new findings and new evaluation method. In: Siegesmund S, Middendorf B, editors. Monument future: decay and conservation of stone. Proc. 14th Int. Congress on the Deterioration and Conservation of Stone. Mitteldeutscher Verlag (DE). 2020;289–292.
257. Quadrizius JM, Wendler E, Meinhardt J. Improved evaluation of Karsten water uptake: visualization of the soaking front by absorption of dye solutions. In: Siegesmund S, Middendorf B, editors. Monument future: decay and conservation of stone. Proc. 14th Int. Congress on the Deterioration and Conservation of Stone. Mitteldeutscher Verlag (DE). 2020;381–384.
258. Rossi-Manaresi R, Rattazzi A, Toniolo L. Long term effectiveness of treatment of sandstone. In: Laenen M, editor. Methods of Evaluating Products for the Conservation of Porous Building Materials in Monuments. ICCROM: Rome. 1995;225–244.
259. Drdácký M, Hasníková H, Lesák J, Zíma P. Innovated water uptake measurements on historic stone surfaces, in: Proc.of the 12th International Congress on the Deterioration and Conservation of Stone, 2012, Columbia University, New York. http://iscs.icomos.org/stonecon.html. Accessed 02 Oct 2020.
260. Pamplona M, Melo MJ, Tiano P. Contact-sponge method for in situ evaluation of water repellent and consolidation treatment. In: Tiano P, Pardini C, editors. In situ monitoring of monumental surfaces. Edifir-Edizioni Firenze, Florence (IT). 2008;247–254.
261. Vandevoorde D, Pamplona M, Schalm O, Vanhellemont Y. Contact sponge method: Performance of a promising tool for measuring the initial water absorption. J Cult Herit. 2009;10: 41–47.
262. Vandevoorde D, Cnudde V, Dewanckele J, Brabant L, de Bouw M, Meynen V, Verhaeven E. Validation of *in situ* applicable measuring techniques for analysis of the water adsorption by stone. Proc Chem. 2013;8:317–327.
263. Vandevoorde D, Cnudde V, Dewanckele J, Boone M, de Bouw M, Meynen V, Lehmann E, Verhaeven E. Comparison of non-destructive techniques for analysis of the water absorbing behavior of stone. Proc. of the 12th International Congress on the Deterioration and Conservation of Stone, 2012, Columbia University, New York. http://iscs.icomos.org/stonecon.html. Accessed 02 Oct 2020.
264. Vandevoorde D, De Kock T, Cnudde V. *In situ* assessment of the stone conservation state by its water absorbing behaviour: a hands-on methodology. In: Hughes J, Howind T, editors. Science and Art: A Future for Stone: Proc. of the 13th International Congress on the Deterioration and Conservation of Stone. University of the West of Scotland. Paisley, UK. 2016;483–490.
265. Vandevoorde D, Cnudde V, Meynen V, de Bouw M, Janssens K. Influence of environmental conditions on water adsorption measurements performed by non-destructive in situ applicable techniques. In: Boriani M, Gabaglio R, Gulotta D, editors. Proc. of Conference Built Heritage - Monitoring Conservation and Management, Milan - Italy, 18–20 November 2013. Centro per la Conservazione e Valorizzazione dei Beni Culturali, Milano (IT). 2013.
266. Scrivano S, Gaggero L. Non-invasive analytical technique to address water uptake on stone surfaces: the implemented Contact Sponge Method (i-CSM). J Cult Herit. 2017;28:9–15.

267. Sharma S, Casanova F, Wache W, Segre A, Blümich B, Analysis of historical porous building materials by the NMR-MOUSE®. Magn Reson Imaging. 2003;21:249–255.
268. Alesiani M, Capuani S, Maraviglia B, Giorgi R, Baglioni P. Effects induced in marbles by water-repellent compounds: the NMR contribution. Appl Magn Reson. 2002;23:63–73.
269. Poli T, Toniolo L. Determination of the water present in building materials by means of a new portable NMR device. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;651–658.
270. Tortora M, Chiarini M, Spreti N, Casieri C. ^{1}H-NMR-relaxation and colorimetry for evaluating nanopolymeric dispersions as stone protective coatings. J Cult Herit. 2020;44:204–210.
271. Cuzman OA, Rescic S, Tiano P. A new portable technique to evaluate the compatibility of protective treatments applied on monumental stones. In: Siegesmund S, Middendorf B, editors. Monument future: decay and conservation of stone. Proc. 14th Int. Congress on the Deterioration and Conservation of Stone. Mitteldeutscher Verlag (DE). 2020; 339–344.
272. Vanmeert F, Mudronja D, Fazinic S, Janssens K, Tibljasd D. Semi-quantitative analysis of the formation of a calcium oxalate protective layer for monumental limestone using combined micro-XRF and micro-XRPD. X-Ray Spectrom. 2013;42:256–261.
273. de Ferri L, Lottici PP, Lorenzi A, Montenero A, Salvioli-Mariani E. Study of silica nanoparticles – polysiloxane hydrophobic treatments for stone-based monument protection. J Cult Herit. 2011;2(4):356–363.
274. Conti C, Colombo C, Dellasega D, Matteini M, Realini M, Zerbi G. Ammonium oxalate treatment: evaluation by μ-Raman mapping of the penetration depth in different plasters. J Cult Herit. 2011;12:372–379.
275. Mudronja D, Vanmeert F, Hellemans K, Fazinic S, Janssens K, Tibljas D, Rogosic M, Jakovljevic S. Efficiency of applying ammonium oxalate for protection of monumental limestone by poultice, immersion and brushing methods. Appl Phys A. 2013;111:109–119.
276. Bezur A, Lee L, Loubser M, Trentelman K, Handheld XRF in Cultural Heritage - A practical workbook for conservators. J. Paul Getty Trust. Los Angeles (USA). 2020.
277. Nakai I, Abe Y. Portable X-ray powder diffractometer for the analysis of art and archaeological materials. Appl Phys A. 2012;106:279–293.
278. Mendoza Cuevas A, Bernardini F, Gianoncelli A, Tuniz C. Energy dispersive X-ray diffraction and fluorescence portable system for cultural heritage applications. X-Ray Spectrom. 2015;44:105–115.
279. Vandenabeele P, Castro K, Hargreaves M, Moens L, Madariaga JM, Edwards HGM. Comparative study of mobile Raman instrumentation for art analysis. Anal Chim Acta. 2007;588:108–116.
280. Meinhardt-Degen J, Snethlage R. Durability of hydrophobic treatment on sandstone facades - investigations of the necessity and effects of retreatment. In: Kwiatkowski D, Löfvendahl R, editors. Proc. of 10th Int. Congress on deterioration and conservation of stone, ICOMOS Sweden, Stockholm (SE), 2004;347–354.
281. Varas MJ, Alvarez de Buergo M, Fort R. The influence of past protective treatments on the deterioration of historic stone façades: a case study studies in conservation. 2007;52(2):110–124.
282. Doherty B, Pamplona M, Miliani C, Matteini M, Sgamellotti A, Brunetti B. Durability of the artificial calcium oxalate protective on two Florentine monuments. J Cult Herit. 2007;8:186–192.

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