Gravestone Guardians Technical Paper No. 1

Salt Residues and Quaternary Ammonium Compound Cleaners

A Scientific Review of Long-Term Effects on Historic Marble Headstones

---

Prepared by

David Carr
Founder & President
Gravestone Guardians, Inc.

Contributing Organization

Gravestone Guardians, Inc.
A 501(c)(3) nonprofit organization dedicated to the preservation, documentation, restoration, and interpretation of historic cemeteries through education, research, and hands-on conservation.

Technical Paper No. 1

First Edition

August 2026

Table of Contents

Table of Figures

Abstract

The use of quaternary ammonium compound (quat) cleaners has become increasingly common in the preservation of historic cemeteries due to their effectiveness in controlling biological growth on marble, granite, slate, and other monument materials. Despite widespread adoption by preservation organizations, government agencies, and conservation professionals, questions remain regarding the potential long-term effects of residual salts associated with these formulations. Debate within the cemetery preservation community often centers on whether repeated applications may contribute to salt-induced deterioration of porous stone or whether such concerns represent an oversimplification of complex conservation chemistry.

This technical paper critically examines the current body of scientific literature concerning salt weathering, crystallization pressure, moisture transport, porous stone deterioration, and the chemistry of quaternary ammonium compounds. Drawing upon research published by the National Park Service, the National Center for Preservation Technology and Training, the Getty Conservation Institute, and leading conservation scientists, this review distinguishes established scientific evidence from commonly repeated assumptions. Particular emphasis is placed on historic marble headstones, where weathering, sugaring, and increased porosity may influence the interaction between cleaning products and the stone substrate.

Rather than advocating for or against any specific commercial product, this paper evaluates the mechanisms by which soluble salts contribute to stone deterioration, examines the behavior of quaternary ammonium compounds within porous carbonate stone, and reviews the preservation practices currently recommended by conservation authorities. Areas where scientific consensus exists are identified alongside questions that remain unresolved and warrant additional research.

It is the intent of this publication to provide preservation professionals, cemetery stewards, monument caretakers, volunteers, and educators with an objective, evidence-based reference that supports informed decision-making while reinforcing the fundamental principle that has guided responsible conservation for generations: **first, do no harm.**

Disclaimer

This publication is intended solely for educational and informational purposes. It is not a substitute for professional conservation assessment or treatment. The discussion of commercial products is presented to explain current scientific knowledge and published research and should not be interpreted as an endorsement or criticism of any manufacturer or proprietary formulation unless explicitly supported by cited evidence.

Recommendations contained herein reflect the best available published conservation research at the time of writing. As additional studies become available, conclusions and best practices may evolve. Readers are encouraged to consult current guidance from the National Park Service, the National Center for Preservation Technology and Training, the Getty Conservation Institute, and other recognized conservation authorities before undertaking preservation work on historically significant monuments.

Executive Summary

Historic marble headstones are among the most vulnerable cultural resources found in cemeteries throughout North America. Exposure to weather, atmospheric pollutants, biological growth, moisture, freeze-thaw cycles, and previous restoration efforts all contribute to their gradual deterioration. While the biological cleaning of monuments has become an accepted component of preservation practice, debate continues regarding the long-term effects of the cleaning agents themselves.

One area of particular discussion concerns the use of cleaners formulated with quaternary ammonium compounds (commonly referred to as quats). These products have demonstrated considerable effectiveness in removing algae, lichens, mosses, fungi, and biofilms while generally avoiding the aggressive chemical action associated with bleach or acidic cleaners. They have therefore become common tools among preservation organizations, monument conservators, and volunteers engaged in cemetery conservation.

Despite their widespread use, questions persist regarding the possibility that quaternary ammonium cleaners leave residual salts within porous stone. Some preservationists have expressed concern that repeated applications could contribute to salt weathering, a well-documented deterioration mechanism responsible for significant damage to stone monuments worldwide. Others contend that these concerns are based upon an incomplete understanding of conservation chemistry and fail to distinguish between the behavior of inorganic salts traditionally associated with stone deterioration and the organic salts represented by quaternary ammonium compounds.

This technical paper examines the scientific evidence underlying these competing viewpoints.

The objectives of this review are to:

- Explain the physical and chemical mechanisms responsible for salt-induced deterioration of porous stone.
- Examine the mineralogical properties of historic marble that influence moisture movement and chemical transport.
- Review the chemistry and function of quaternary ammonium compounds used in monument cleaning.
- Evaluate published research concerning cleaner residues, including studies conducted by the National Park Service (NPS), the National Center for Preservation Technology and Training (NCPTT), and other conservation organizations.

- Distinguish between established scientific evidence, reasonable scientific interpretation, and areas where insufficient data currently exist.
- Present practical recommendations consistent with accepted conservation principles.

The conclusions reached in this paper can be summarized as follows.

First, salt weathering is unquestionably one of the principal causes of deterioration in porous stone. Numerous decades of conservation research have demonstrated that repeated dissolution and crystallization of soluble salts within a stone's pore network can produce stresses sufficient to fracture mineral grains, weaken surfaces, and ultimately result in granular disintegration, scaling, and loss of carved detail.

Second, the presence of a chemical compound classified as a "salt" does not necessarily imply that it will behave similarly to the inorganic salts responsible for most documented stone deterioration. The term *salt* encompasses an extensive range of chemical compounds possessing widely differing physical properties, including solubility, hygroscopic behavior, crystallization characteristics, and interactions with carbonate minerals.

Third, available research does not support broad generalizations regarding all quaternary ammonium compound cleaners. Performance varies according to complete product formulation rather than solely the active ingredient. Buffers, surfactants, stabilizers, builders, and other proprietary additives may influence residue formation and long-term interaction with stone.

Fourth, NCPTT–National Cemetery Administration comparative testing found that one early formulation of D/2 Biological Solution produced measurable salt residues during accelerated weathering experiments, while a subsequently reformulated product eliminated those residues and became one of the highest-performing cleaners evaluated. This illustrates that residue formation may be formulation-specific rather than inherent to quaternary ammonium chemistry.

Finally, current preservation guidance consistently emphasizes that application technique plays a critical role in minimizing potential long-term impacts. Proper pre-wetting, adherence to manufacturer recommendations, gentle mechanical cleaning, and thorough rinsing remain among the most effective means of reducing residue retention while protecting fragile historic marble.

Although considerable progress has been made in understanding salt weathering, significant knowledge gaps remain. Few long-term field studies have examined repeated applications of quaternary ammonium cleaners over multiple decades under varying climatic conditions. Consequently, preservation decisions should continue to emphasize caution, reversibility where possible, and adherence to practices supported by the best available scientific evidence.

Ultimately, the purpose of this paper is not to advocate for or against any individual cleaning product. Rather, it seeks to encourage informed decision-making rooted in conservation science while reinforcing the ethical obligation shared by all preservationists: to ensure that today's interventions do not become tomorrow's deterioration.

1. Introduction

1.1. The Importance of Historic Cemetery Preservation

Historic cemeteries serve as irreplaceable archives of community history. Every monument represents the intersection of personal remembrance, artistic craftsmanship, genealogy, geology, and local heritage. Collectively, they document patterns of settlement, immigration, military service, public health, religious belief, family structure, and regional stoneworking traditions that often cannot be reconstructed through written records alone (Striegel et al., 2016; National Park Service, 2022b).

Marble headstones erected during the eighteenth and nineteenth centuries are particularly significant. Advances in quarrying and transportation made marble both accessible and desirable throughout much of the northeastern United States, leading to its widespread adoption as a monument material. Today, these stones comprise a substantial portion of the historic cemetery landscape.

Unfortunately, the very mineral composition that makes marble attractive also renders it vulnerable to deterioration.

Marble consists primarily of calcite ($CaCO_3$), a mineral readily affected by acidic precipitation, atmospheric pollution, biological colonization, soluble salts, and natural weathering. As deterioration progresses, once-polished surfaces become granular, inscriptions lose definition, and structural integrity gradually declines. This phenomenon, commonly referred to as *sugaring*, represents one of the greatest preservation challenges encountered in historic cemeteries.

Because deterioration cannot be entirely prevented, preservation efforts frequently focus upon slowing ongoing decay while minimizing additional damage introduced through treatment.

This philosophy forms the foundation of modern conservation practice.

1.2. The Evolution of Headstone Cleaning

Methods employed to clean cemetery monuments have changed dramatically during the past century.

Earlier generations often relied upon household detergents, wire brushes, muriatic acid, bleach, sandblasting, or pressure washing. While many of these methods produced immediate visual improvement, subsequent experience demonstrated that they frequently accelerated deterioration by roughening stone surfaces, introducing soluble salts, removing protective weathered layers, or increasing moisture penetration (Doehne & Price, 2010; American Institute for Conservation, 1994).

As conservation science matured during the latter half of the twentieth century, professional guidance shifted toward substantially gentler approaches emphasizing minimal intervention, compatibility with historic materials, and reversibility whenever practical.

Organizations such as the National Park Service, the National Center for Preservation Technology and Training, the Getty Conservation Institute, and numerous state historic preservation offices began publishing recommendations grounded in laboratory research and field observation. Water, soft natural-bristle brushes, patience, and carefully selected cleaners gradually replaced aggressive cleaning methods (National Park Service, 2022a).

Within this evolving framework, quaternary ammonium compound cleaners emerged as valuable tools for controlling biological growth while generally avoiding many of the drawbacks associated with oxidizing agents such as sodium hypochlorite (McDonnell & Russell, 1999; National Park Service, 2025b).

Their widespread adoption, however, has not eliminated controversy.

1.3. The Central Question

Among preservation professionals and volunteers alike, few topics generate more discussion than the long-term implications of quaternary ammonium compound cleaners (Striegel et al., 2016; National Park Service, 2022b).

Advocates point to decades of successful use by conservation organizations, published NCPTT–National Cemetery Administration research, and the products' demonstrated effectiveness against biological colonization.

Critics raise legitimate questions regarding the persistence of chemical residues, particularly the possibility that repeated applications may introduce soluble salts capable of contributing to future stone deterioration.

The challenge is that these discussions often occur without clearly distinguishing among several fundamentally different questions.

For example:

- Does a cleaner contain a compound that is chemically classified as a salt?
- Does that compound remain within the stone after treatment?
- If residue remains, what is its chemical composition?

- Can that residue crystallize under environmental conditions encountered in historic cemeteries?
- Does repeated treatment result in measurable accumulation?
- Is the resulting deterioration significant compared with natural weathering?

Although these questions are closely related, they are not interchangeable. Scientific evidence addressing one question should not automatically be interpreted as answering another.

The purpose of this paper is therefore to evaluate each question independently, drawing upon published conservation research wherever possible while clearly identifying those areas where current evidence remains incomplete.

1.4. Scope and Methodology

This technical paper uses a structured critical narrative review rather than an experimental or formal systematic-review design. The evidence base emphasizes openly accessible peer-reviewed research, government and institutional conservation guidance, and technical sources that a typical reader c an retrieve through ordinary Internet access. Priority is given to sources that address historic stone, salt weathering, porous-material transport, biological colonization, quaternary ammonium chemistry, monument-cleaner performance, or directly relevant conservation practice (Doehne & Price, 2010; American Institute for Conservation, 1994).

Where open primary research is available, it receives the greatest evidentiary weight. Official conservation guidance and high-quality open reviews are used to connect specialized findings to monument practice, while manufacturer information is limited to product composition, current instructions, and formulation history rather than treated as independent proof of long-term compatibility. Differing interpretations are retained where the available evidence does not resolve them.

Whenever possible, conclusions are based upon original research rather than secondary interpretation. Where differing opinions exist within the preservation community, those viewpoints are presented alongside the available evidence rather than dismissed or accepted without examination.

Particular emphasis is placed upon marble headstones because they represent one of the most chemically sensitive and historically common monument materials encountered in North American cemeteries. Granite, slate, sandstone, and limestone are discussed where their behavior informs broader preservation principles, but they are not the primary focus of this review.

Throughout this paper, the guiding philosophy remains consistent with internationally recognized conservation ethics: preservation decisions should be informed by evidence, proportional to the condition of the resource, and undertaken with the long-term protection of the historic fabric as the highest priority.

2. Marble as a Historic Material

2.1. Introduction

Evaluating how cleaning agents interact with historic marble requires an understanding of the material as it exists today. Marble is commonly perceived as a hard and durable stone, an impression reinforced by the survival of monuments, sculpture, and architecture for centuries. That perception is only partly accurate. Marble possesses substantial compressive strength and can perform exceptionally well under favorable conditions, but its mineral composition, crystalline structure, and response to prolonged environmental exposure make it vulnerable to several forms of progressive deterioration (Doehne & Price, 2010; Ahmad, 2020).

Most historic cemetery marble consists predominantly of calcite, a carbonate mineral that is susceptible to dissolution under acidic conditions. Outdoor exposure also subjects a monument to recurring wetting and drying, temperature fluctuations, freeze-thaw cycling, atmospheric pollutants, biological colonization, soluble salts, ground moisture, and mechanical stress. These processes do not act independently. Over decades or centuries, they may enlarge grain boundaries, create microfractures, alter pore connectivity, increase water uptake, reduce surface cohesion, and change the way the stone interacts with treatment materials.

The marble present in a nineteenth-century cemetery is therefore not simply freshly quarried marble that happens to be older. Its physical and chemical properties may have changed substantially since the monument was installed. Preservation decisions must consequently be based on the monument's present condition rather than on generalized assumptions about marble as a geological material.

This chapter examines the formation, mineralogy, microstructure, moisture behavior, and principal deterioration characteristics of historic marble. Together, these properties establish the material framework needed to evaluate salt transport, cleaner penetration, residue behavior, and treatment compatibility in subsequent chapters.

2.2. Geological Formation of Marble

Marble is a metamorphic rock formed when limestone or dolostone undergoes recrystallization under elevated temperature and pressure within the Earth's crust. During metamorphism, the carbonate grains of the original sedimentary rock reorganize into a more tightly interlocking crystalline fabric. The resulting stone varies in crystal size, mineral purity, texture, color, and structural orientation according to the composition of the parent rock and the conditions under which metamorphism occurred (Pinna, 2014; Striegel et al., 2016).

Historic cemetery marble used in the northeastern United States came from several quarrying regions, including Vermont, western Massachusetts, New York, Georgia, and imported European sources. Quarry availability, transportation networks, regional stoneworking traditions, cost, and consumer preference all influenced where particular marbles were used. Consequently, stones that appear similar in a cemetery may differ significantly in mineral composition and weathering behavior.

Calcite generally forms the dominant mineral phase, although cemetery marble may also contain dolomite, quartz, mica, feldspar, iron-bearing minerals, clay minerals, graphite, and accessory silicates. Even small quantities of these phases can affect color, veining, staining, weathering response, and interaction with treatment solutions. Accessory minerals and environmental deposits may also create surface sites whose chemical behavior differs from that of pure calcite.

Fresh marble is often described as dense, but it is not impermeable. Grain boundaries, microscopic voids, mineral inclusions, and naturally occurring discontinuities provide potential pathways for air and moisture. Weathering can enlarge and connect those pathways, changing both the amount of water the stone can retain and the rate at which dissolved materials move through it.

2.3. Calcite: The Dominant Mineral

Calcite governs much of marble's chemical behavior. It is composed of calcium carbonate, $CaCO_3$, arranged in a crystalline structure that remains stable under many environmental conditions but reacts more readily with acidic solutions than the silicate minerals that dominate stones such as granite (Doehne & Price, 2010; Ahmad, 2020).

Atmospheric carbon dioxide dissolves in rainwater and surface moisture and participates in the carbonate equilibrium system:

CO2 + H2O = H2CO3

Carbonic acid can then contribute to the dissolution of calcite:

CaCO3 + H2CO3 = Ca{2+} + 2HCO3{-}

Under relatively clean atmospheric conditions, this process may proceed slowly, but its cumulative effect becomes meaningful over the service life of a monument. Acidic atmospheric pollutants and biologically produced acids may further increase carbonate dissolution under favorable conditions.

Marble deterioration therefore often develops through the cumulative loss of very small quantities of calcite rather than through a single catastrophic event. Progressive dissolution can soften carved edges, reduce surface polish, enlarge grain boundaries, and diminish the sharpness of inscriptions. Because marble is crystalline, dissolution along grain boundaries also affects the mechanical relationship among adjacent crystals. Chemical alteration at the microscopic scale can therefore contribute directly to the granular deterioration observed macroscopically.

2.4. Microstructure of Historic Marble

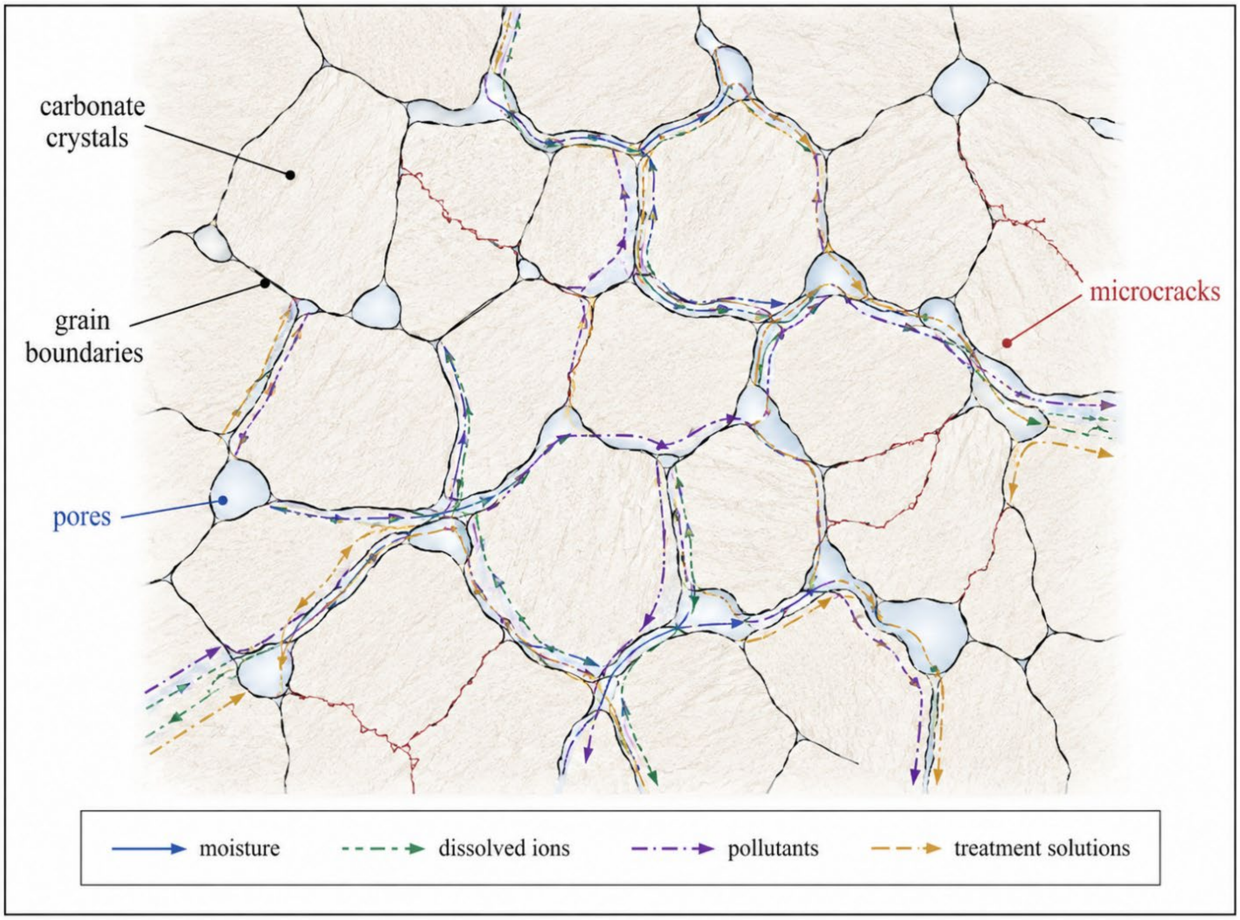
At the microscopic scale, marble consists of interlocking carbonate crystals separated by grain boundaries. In sound stone, this crystalline fabric provides substantial cohesion. The same boundaries, however, also provide pathways through which water, dissolved ions, gases, and treatment solutions can move. Their condition and connectivity strongly influence how weathered marble responds to its environment (Pinna, 2014; Striegel et al., 2016).

Weathering can progressively change this internal structure. Dissolution may widen grain boundaries, while differences in thermal expansion among neighboring crystals can produce microscopic stresses. Freeze-thaw activity, salt crystallization, structural loading, impact, and previous interventions may create or enlarge microfractures. As these features become increasingly connected, pathways for moisture and dissolved materials become more extensive.

Weathering also increases the internal surface area available for chemical interaction. A treatment applied to a deteriorated marble surface may therefore contact not only the visible exterior but also mineral surfaces within pores, open grain boundaries, and fractures. This helps explain why two visually similar monuments can respond differently to the same cleaning solution. One may retain a relatively cohesive and poorly connected pore network, while another may contain substantial subsurface alteration that is not readily apparent during casual examination.

Figure 2.1 provides the microstructural framework for the transport and deterioration mechanisms developed throughout this paper by illustrating how grain boundaries, pores, and microcracks create interconnected pathways within weathered marble.

Figure 2.1: Microstructure of Historic Marble



Note. *Conceptual schematic—not to scale. Historic marble consists of interlocking carbonate crystals separated by grain boundaries and intersected by pores and microcracks. As weathering enlarges and connects these features, they become increasingly important pathways for moisture, dissolved ions, pollutants, and treatment solutions.*

2.5. Porosity and Permeability

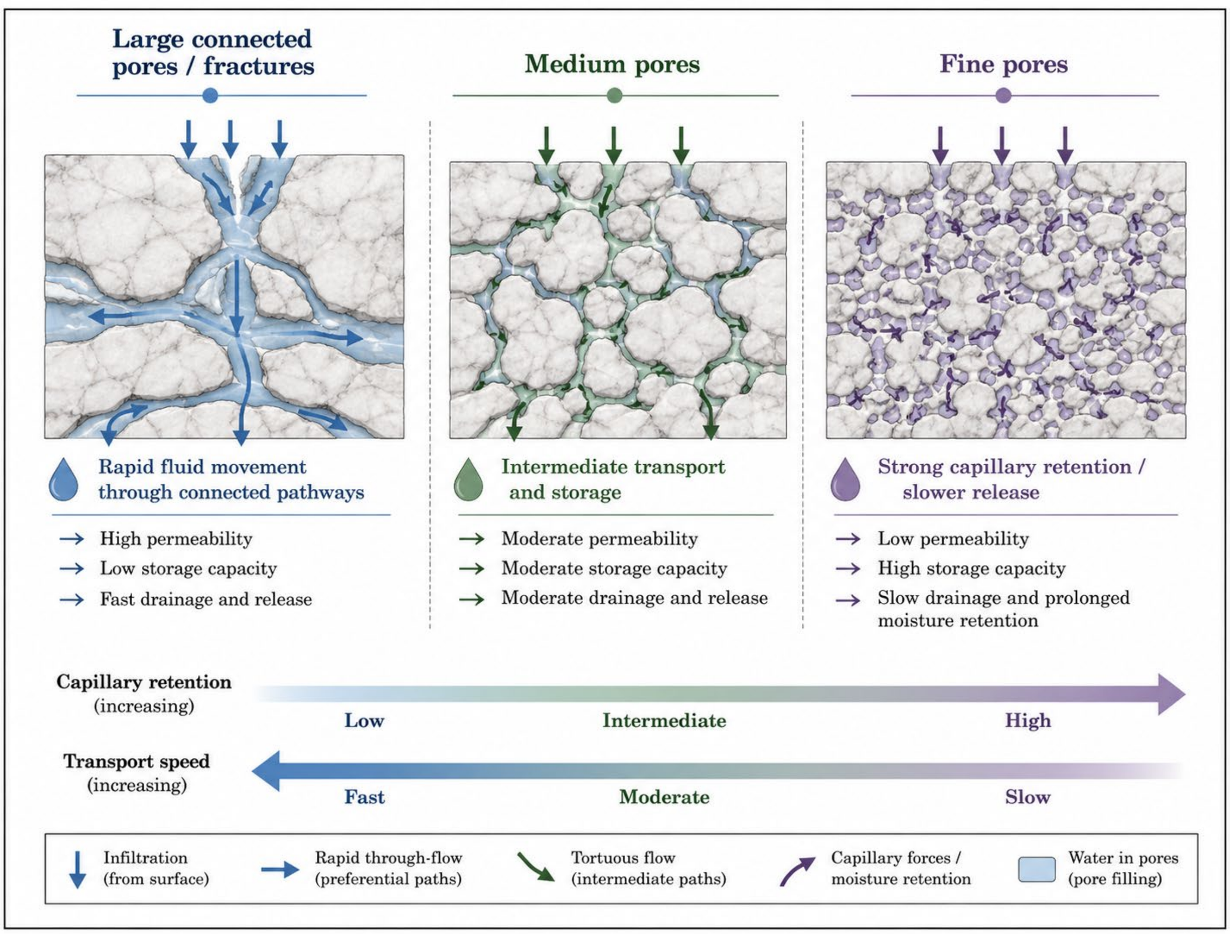
Porosity and permeability describe related but distinct aspects of stone behavior. **Porosity** refers to the proportion of void space within a material, whereas **permeability** describes the ease with which a fluid can move through connected voids. Total pore volume alone does not determine how water behaves. Pore size, geometry, distribution, tortuosity, and connectivity are equally important (Doehne & Price, 2010; Ahmad, 2020).

A marble may contain measurable porosity while remaining comparatively resistant to fluid movement if many of its pores are isolated. Conversely, modest total porosity may permit substantial transport when fractures and grain boundaries form continuous pathways. Weathering commonly increases permeability by enlarging and connecting features that were once less accessible.

Pore size also affects water retention. Larger connected openings may permit relatively rapid movement and drainage, while finer pores can develop stronger capillary forces and retain moisture for longer periods. Historic marble normally contains a distribution of pore sizes rather than a single uniform class, creating complex patterns of wetting, redistribution, and drying.

Building on the pathways illustrated in Figure 2.1, Figure 2.2 shows how differences in pore size and connectivity influence whether moisture is retained within the stone or transported more readily through it.

Figure 2.2: Conceptual Pore-Size Distribution in Historic Marble



Note. *Conceptual schematic—not to scale. Pores of different sizes influence how water is absorbed, transported, retained, and released. Fine pores can sustain strong capillary forces and prolonged moisture retention, while larger connected pores and fractures may provide more rapid pathways for fluid movement. Actual pore distributions vary with marble type, weathering history, and condition.*

As these pathways become more extensive, weathered marble may experience greater water absorption, deeper transport of dissolved compounds, altered drying behavior, increased biological colonization, and greater vulnerability to salt- and freeze-related deterioration. For conservation purposes, connectivity is often as significant as the total amount of void space within the stone.

2.6. Moisture as a Major Deterioration Driver

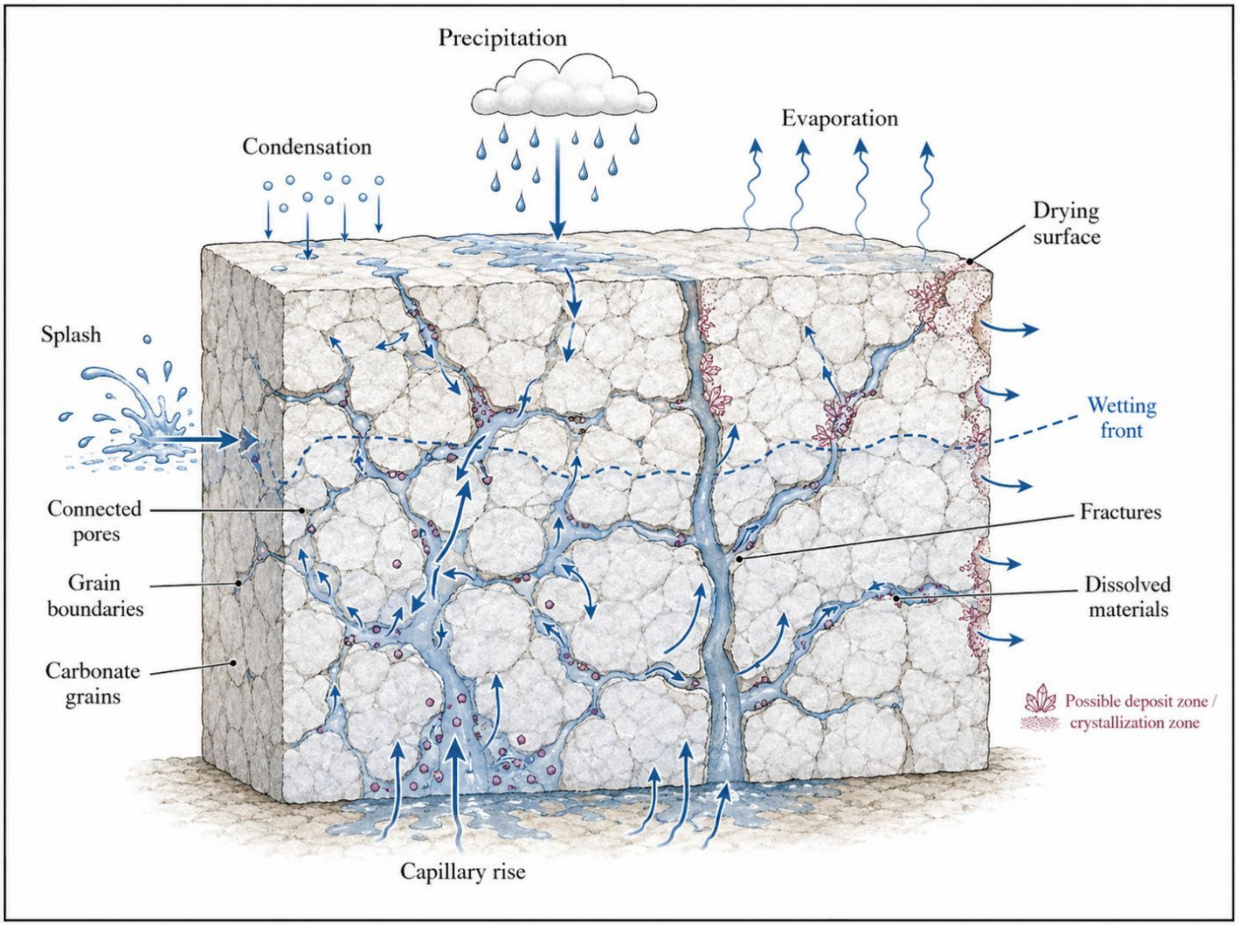
Moisture enables or accelerates many of the processes affecting historic marble. It transports atmospheric pollutants, nutrients, soluble salts, acids, and cleaning materials; supports biological activity; participates in carbonate dissolution; and supplies the liquid phase required for many salt reactions. In cold climates, retained moisture can also contribute to freeze-thaw deterioration (Pinna, 2014; Striegel et al., 2016).

Cemetery monuments receive water from several sources, including rain, snow, fog, dew, condensation, irrigation, splash-back, ground contact, and capillary rise. Their relative importance depends on monument geometry, foundation condition, soil drainage, vegetation, exposure, and local climate. Water may enter directly through an exposed surface, migrate upward from the base, or collect in carved recesses, cracks, joints, and horizontal surfaces.

Once within the pore network, moisture continues to move. Capillary forces redistribute water through fine openings, while evaporation draws moisture toward drying surfaces. Fine pores and sheltered interior zones may remain wet after the exterior appears dry, meaning that visible surface condition is not always a reliable indicator of internal moisture.

Cleaning introduces an additional wetting event into this system. Pre-wetting, cleaner application, dwell time, rinsing, and drying influence how treatment solutions enter, move through, and leave the near-surface pore network. Figure 2.3 connects these pore-scale characteristics to monument-scale moisture movement, illustrating the pathways through which water and dissolved material may enter, migrate through, and leave weathered marble.

Figure 2.3: Moisture Transport Through Marble



Note. *Water may enter marble through precipitation, splash, condensation, or capillary rise. Moisture moves through connected pores, grain boundaries, and fractures and migrates toward drying surfaces during evaporation. Repeated wetting and drying can transport dissolved materials and influence where deposits or crystals form.*

Moisture should not be treated as the sole cause of every form of marble deterioration. Thermal stress, physical impact, structural movement, vandalism, and other processes may act independently or in combination with water. Nevertheless, moisture remains a central transport medium and enabling factor in many of the deterioration mechanisms relevant to historic cemetery marble.

2.7. Sugaring

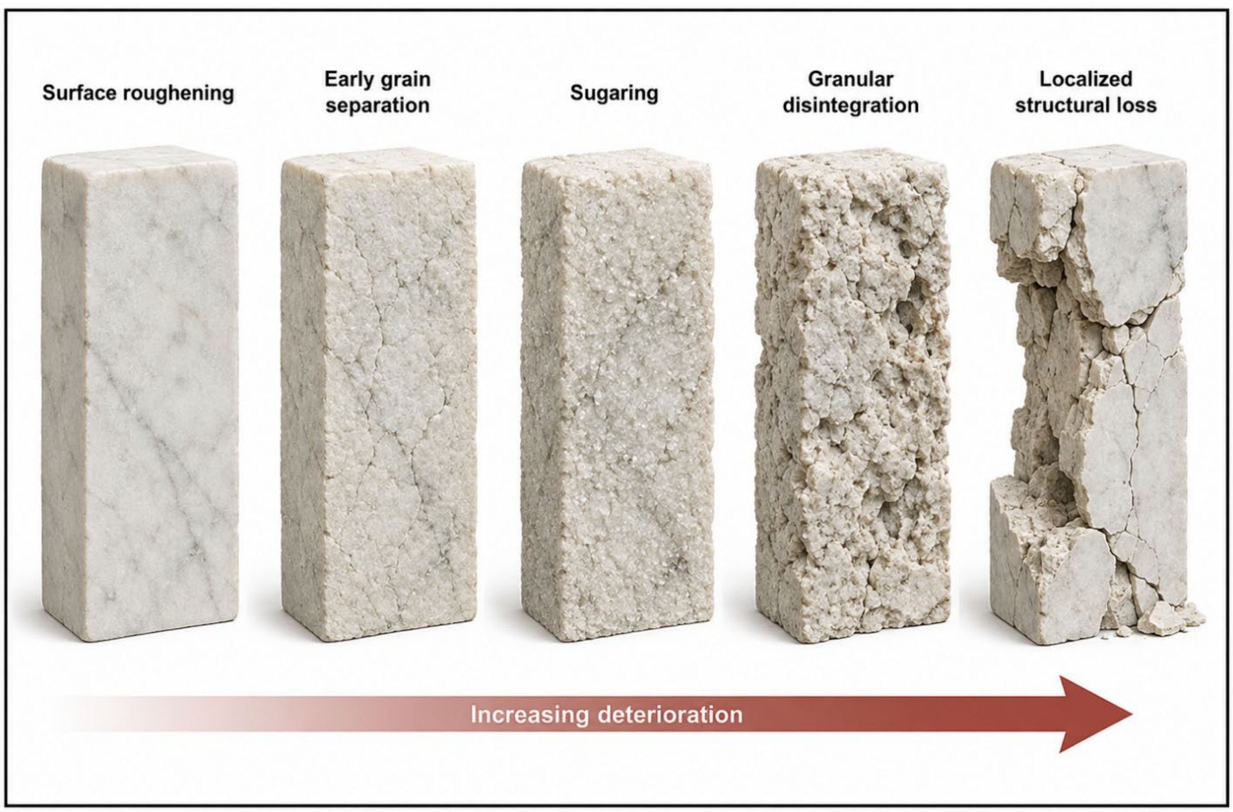
Sugaring is among the most recognizable forms of marble deterioration. It develops when cohesion among adjacent carbonate crystals decreases sufficiently for individual grains to loosen from the surface. The resulting texture can resemble granulated sugar and may range from slight roughening to advanced granular disintegration (Doehne & Price, 2010; Ahmad, 2020).

Early deterioration may appear only as loss of polish or subtle roughness. As grain separation progresses, lettering becomes rounded, carved details lose definition, and loose particles may accumulate at the base of the monument. In advanced cases, the surface can become sufficiently friable that brushing, rubbing, or concentrated water flow removes original stone along with the material being cleaned.

Sugaring is therefore more than an aesthetic condition. Grain separation increases exposed internal surface area, alters moisture movement, and reduces the mechanical resistance of the stone. A treatment acceptable for cohesive marble may impose excessive stress on a severely sugared surface.

Figure 2.4 translates these microscopic changes into observable conservation conditions by illustrating a generalized progression from early surface roughening to increasingly advanced loss of cohesion and historic fabric.

Figure 2.4: Weathering Progression of Historic Marble



Note. *Conceptual progression—not a universal deterioration sequence. Marble weathering may develop from surface roughening and early grain separation to* *pronounced sugaring, granular disintegration, scaling, and localized structural loss. Rate, severity, and expression vary among monuments and across different areas of the same stone.*

The degree of surface cohesion should therefore be considered before any cleaning treatment is selected. Mild deterioration may permit carefully controlled work, while severe granular loss may warrant professional assessment, stabilization, monitoring, or a decision not to clean.

2.8. Freeze-Thaw Weathering

Freeze-thaw deterioration occurs when moisture retained within pores, grain boundaries, or cracks is exposed to freezing temperatures. Water expands by approximately nine percent when it freezes, but the resulting behavior within stone is more complex than simple volumetric expansion. Pore saturation, freezing rate, pore geometry, drainage, pressure generated by moving unfrozen water, and existing microfractures all influence whether damage occurs (Pinna, 2014; Striegel et al., 2016).

A single freezing event does not necessarily damage sound marble. Greater concern exists where a stone remains sufficiently wet and experiences repeated freezing and thawing. Over time, these cycles may enlarge existing discontinuities and contribute to scaling, delamination, crack propagation, and loss of surface cohesion.

Exposure is often uneven across a monument. Bases in contact with damp soil or poorly drained foundations may remain wet longer than upper surfaces. Open cracks, carved recesses, horizontal ledges, and previous repairs can also retain water. As a result, freeze-thaw deterioration may be concentrated in localized areas rather than distributed uniformly.

Dissolved salts can further complicate the system by altering moisture distribution, solution concentration, and freezing behavior. Freeze-thaw action is therefore best understood as one part of the broader relationship among moisture, pore structure, environmental cycling, and preexisting deterioration.

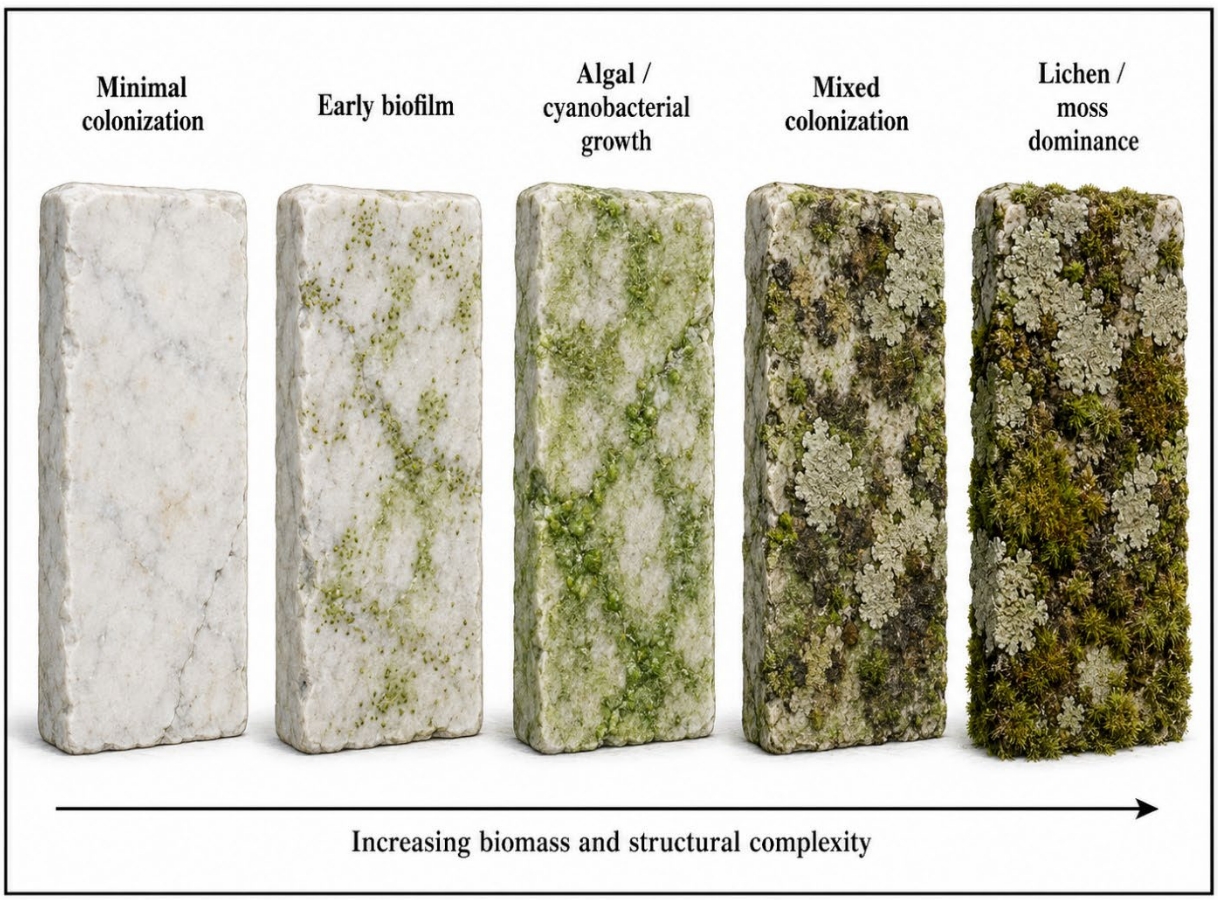
2.9. Biological Colonization

Historic marble provides habitat for bacteria, cyanobacteria, algae, fungi, lichens, mosses, and mixed biofilms. Colonization is influenced by moisture, shade, orientation, surface roughness, atmospheric nutrients, nearby vegetation, air quality, and the physical and chemical characteristics of the stone (Doehne & Price, 2010; Ahmad, 2020).

Visible biological growth should not automatically be equated with active material damage. Its conservation significance depends on the organisms present and the conditions they create. Some colonization primarily affects appearance, while other growth retains moisture, traps pollutants, produces acids or chelating compounds, penetrates weathered surface irregularities, obscures inscriptions, or contributes to physical detachment. Removal itself can also become damaging where biological material is strongly attached to weakened marble.

Figure 2.5 places biological colonization within this material and environmental framework by illustrating how biomass and structural complexity may increase when local conditions continue to support growth.

Figure 2.5: Generalized Progression of Biological Colonization

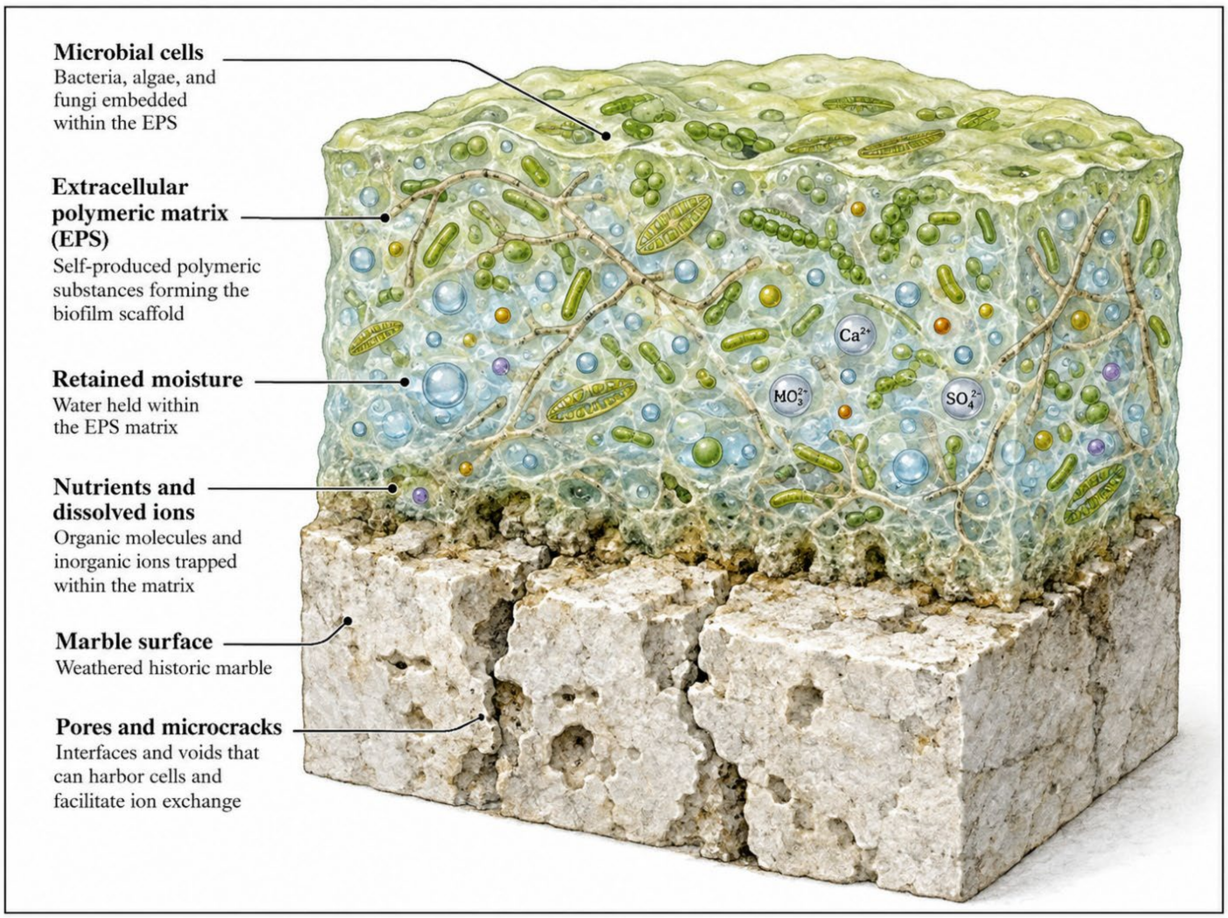


Note. *Conceptual progression rather than a fixed ecological sequence. Biological colonization may increase in biomass and structural complexity over time, although the organisms present and their order of appearance vary with moisture, climate, exposure, surface condition, nutrient availability, and the surrounding environment.*

Biofilms deserve particular attention because they consist of microbial communities embedded within an extracellular polymeric substance, or EPS. This matrix helps organisms adhere to stone, retain moisture, trap nutrients and particulate matter, and establish localized microenvironments. Conditions within a mature biofilm may differ substantially from those of the surrounding atmosphere over very short distances (Pinna, 2014).

Figure 2.6 narrows the discussion from visible colonization to the microenvironment created by a biofilm, helping explain why a biologically occupied surface may retain moisture, nutrients, and dissolved material even when the surrounding stone appears comparatively dry.

Figure 2.6: Biofilm Structure

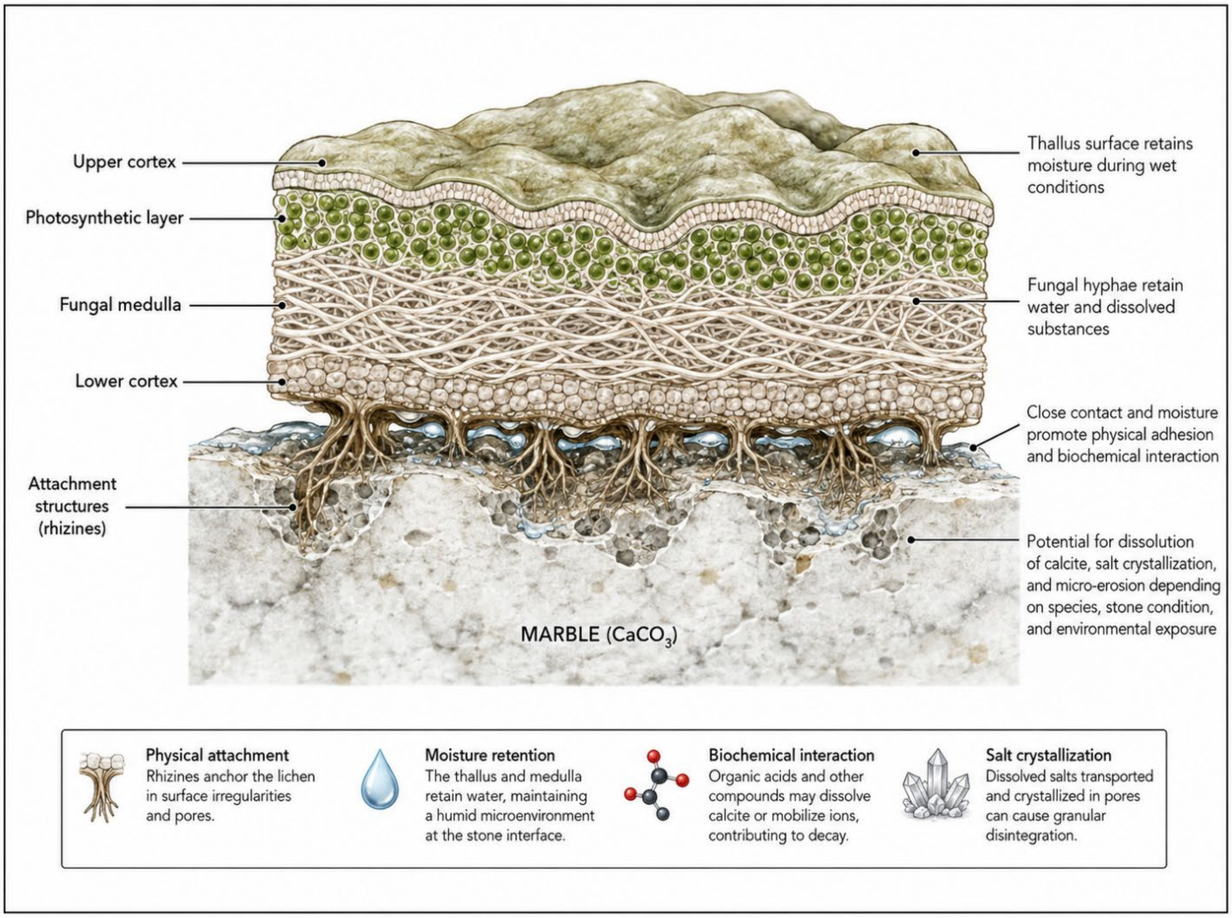


Note. *Conceptual schematic—not to scale. Biofilms consist of microbial cells embedded within an extracellular polymeric matrix. On historic marble, this matrix can retain moisture, collect nutrients, particles, and dissolved ions, and create localized conditions that may contribute to biodeterioration.*

Lichens present an additional conservation challenge because they are composite organisms formed through a symbiotic relationship between a fungal partner and photosynthetic algae or cyanobacteria. Attachment mechanisms vary among lichen forms. Some adhere tightly to the stone and may extend fungal structures into surface irregularities, while others are more loosely attached.

Figure 2.7 illustrates one example of how biological colonization can become physically integrated with a stone surface by showing the principal structural regions and attachment features of a generalized foliose lichen.

Figure 2.7: Generalized Anatomy of a Foliose Lichen on Marble



Note. *Conceptual anatomy—not to scale and not representative of every lichen species or growth form. A foliose lichen may contain an upper cortex, a photosynthetic layer, a fungal medulla, a lower cortex, and attachment structures. Physical attachment, moisture retention, and biochemical interaction may contribute to deterioration depending on species, stone condition, and environmental exposure.*

The presence of biological colonization therefore establishes a need for assessment rather than an automatic requirement for complete removal. The preservation benefit of treatment must be weighed against the condition of the substrate and the mechanical demand required to separate the growth from the historic surface.

2.10. Atmospheric Pollution

Industrial and urban pollution contributed significantly to the deterioration of marble monuments during the nineteenth and twentieth centuries. Sulfur dioxide produced by coal combustion and other sources can participate in atmospheric and surface reactions that ultimately lead to the formation of sulfate compounds on carbonate stone. In the presence of moisture and appropriate oxidizing conditions, calcium sulfate—often occurring as gypsum—may develop on or near the marble surface (Pinna, 2014; Striegel et al., 2016).

Gypsum-bearing alteration layers can behave differently according to their exposure. In sheltered areas, they may retain soot and airborne particulates and develop the dark crusts familiar on many urban monuments and buildings. More exposed surfaces may experience dissolution and runoff, producing gradual recession rather than thick crust formation.

Nitrogen-containing pollutants, acidic precipitation, metals, dust, and other atmospheric materials can contribute additional forms of surface alteration. Biological films may retain some of these pollutants against the stone, while weathered and roughened marble provides a larger effective area for deposition.

Although sulfur dioxide emissions have declined substantially in many parts of North America, historic monuments retain the physical consequences of earlier exposure. Their present condition often reflects cumulative environmental history rather than only the conditions prevailing today.

2.11. Why Historic Marble Behaves Differently from New Marble

The combined effects of dissolution, thermal stress, freeze-thaw cycling, biological activity, atmospheric pollution, salt movement, and mechanical loading can substantially alter marble during its service life. Historic stone may contain enlarged grain boundaries, connected microfractures, increased water absorption, changed pore-size distributions, reduced surface cohesion, sugaring, and heightened sensitivity to mechanical contact (Doehne & Price, 2010; Ahmad, 2020).

These changes are rarely uniform. An exposed upper edge may weather differently from a sheltered inscription panel; the shaded face may support denser colonization than the sunlit side; and the base may remain wet longer because of soil contact or poor drainage.

Previous repairs, bedding orientation, open cracks, carved recesses, and adjacent metals may create additional localized differences.

Material identification is therefore necessary but insufficient. Knowing that a monument is marble does not establish that it can safely tolerate the same treatment used on another marble monument. Condition assessment must determine whether the surface remains cohesive, whether grains are detaching, whether cracks or delamination are present, and whether previous interventions have changed moisture movement or structural behavior.

Conservation does not attempt to reverse centuries of geological and environmental change or restore every surface to its original appearance. Its objective is to retain surviving historic fabric, slow avoidable loss, and select interventions appropriate to the material that remains.

2.12. Summary

Historic marble is a crystalline carbonate stone whose properties change through prolonged environmental exposure. Calcite dissolution, grain-boundary alteration, microfracturing, moisture transport, freeze-thaw cycling, biological colonization, atmospheric pollution, and salt activity may interact to increase permeability and reduce surface cohesion (Pinna, 2014; Striegel et al., 2016).

These changes explain why treatment outcomes vary among monuments and why the behavior of freshly quarried marble cannot be assumed to represent that of an eighteenth- or nineteenth-century headstone. Cleaner compatibility depends not only on the general properties of marble but also on the pore structure, deterioration state, environmental exposure, and treatment history of the individual stone.

Understanding those material characteristics provides the necessary foundation for considering the soluble compounds that may enter, move through, or remain within historic marble.

3. The Chemistry of Salts

3.1. Introduction

The term *salt* is frequently used in preservation discussions as though it describes a single material and a single deterioration process. Chemically, however, the term encompasses a broad range of ionic compounds whose physical behavior may differ substantially. Sodium chloride, calcium sulfate, magnesium sulfate, potassium nitrate, benzalkonium chloride, and didecyldimethylammonium chloride can all be classified as salts, but that classification alone does not determine how they will behave within porous stone (Oguchi & Yu, 2021; Doehne & Price, 2010).

This distinction is central to the evaluation of monument cleaners. A statement that a treatment contains or leaves a salt identifies a chemical category but does not establish the quantity present, its physical state, its mobility, its ability to absorb moisture or crystallize, or whether it can produce measurable damage. Those questions require consideration of the complete compound, the stone in which it occurs, and the environmental conditions to which both are exposed.

This chapter establishes the chemical terminology required for that evaluation. It examines ionic composition, organic and inorganic salts, solubility, hygroscopicity, humidity-dependent behavior, water-mediated transport, surface and subsurface deposition, and the distinction between adsorption and crystallization. Chapter 4 then applies these concepts to the physical mechanisms of salt-induced deterioration.

3.2. What Is a Salt?

In chemistry, a salt is an electrically neutral compound composed of positively charged ions, or cations, and negatively charged ions, or anions. The total positive and negative charges balance even though the individual components remain ionic (Lezzerini et al., 2022; Cappai et al., 2024).

Examples relevant to this paper include:

Salt	**Principal cation**	**Principal anion**
Sodium chloride, $NaCl$	Na^+	Cl^-
Calcium sulfate, $CaSO_4$	Ca^{2+}	SO_4^{2-}
Magnesium sulfate, $MgSO_4$	Mg^{2+}	SO_4^{2-}
Potassium nitrate, KNO_3	K^+	NO_3^-

Salt	Principal cation	Principal anion
Benzalkonium chloride	Quaternary ammonium cation	Cl^-
Didecyldimethylammonium chloride	Quaternary ammonium cation	Cl^-

The complete ionic pairing influences the material's properties. Detection of chloride, for example, does not establish whether the original compound was sodium chloride, calcium chloride, magnesium chloride, a quaternary ammonium chloride, or another chloride-bearing material. Those compounds differ in molecular or ionic size, solubility, hygroscopic behavior, surface activity, crystal structure, and environmental response.

For conservation purposes, chemical identification is therefore only the beginning of the inquiry. The more useful questions concern whether the material dissolves, migrates, adsorbs, precipitates, crystallizes, undergoes hydration or deliquescence, reacts with the substrate, or transforms under environmental exposure.

3.3. Inorganic and Organic Salts

Most salts associated with classical stone-weathering research are inorganic compounds. Sodium sulfate, magnesium sulfate, sodium chloride, calcium nitrate, potassium nitrate, and calcium sulfate are among the materials commonly encountered in conservation literature. When dissolved, their relatively small ions can move with water through pore networks and may participate in precipitation, crystallization, hydration, or humidity-dependent cycles (Oguchi & Yu, 2021; Doehne & Price, 2010).

Inorganic salts can reach monuments through groundwater, soil, marine aerosols, fertilizers, deicing materials, atmospheric pollution, irrigation water, cementitious repairs, biological activity, and previous treatments. Once present, their significance depends on concentration, moisture, pore geometry, phase behavior, and environmental cycling.

Quaternary ammonium compounds belong to a different chemical family. Their positively charged components are comparatively large organic structures built around a permanently charged nitrogen atom. Many also function as surfactants and antimicrobial agents. These structural characteristics influence how they interact with water, mineral surfaces, organic matter, and biological membranes.

The distinction between organic and inorganic salts does not establish a simple division between harmless and harmful compounds. Rather, it identifies why results derived from one chemical system cannot be transferred automatically to another. Quaternary ammonium compounds must ultimately be evaluated according to their own transport, adsorption, residue, phase, and environmental behavior, which are examined more directly in Chapter 5.

3.4. Solubility

Solubility describes the amount of a substance that can dissolve in a particular solvent under specified conditions. In outdoor stone conservation, water is ordinarily the solvent of greatest significance. Temperature, pH, solution composition, competing ions, and the presence of other solid phases can all influence how much material dissolves (Lezzerini et al., 2022; Cappai et al., 2024).

Dissolution makes aqueous transport possible. Once ions enter solution, moving moisture can carry them through connected pores, grain boundaries, and fractures. As water evaporates or solution chemistry changes, the dissolved material becomes more concentrated and may eventually precipitate.

High solubility does not independently predict high deterioration risk. A readily soluble compound may be substantially removed through rinsing or rainfall, whereas a less soluble material may persist as an alteration layer or surface deposit. Likewise, a soluble material produces little crystallization risk if it is not retained in sufficient quantity or does not reach the environmental conditions required for solid-phase formation.

Solubility is therefore one variable within a larger transport and phase-change system. Its significance depends on where the material is located, how often it is mobilized, what concentration develops during drying, and how the resulting solid phase interacts with the stone.

3.5. Hygroscopicity and Deliquescence

Some salts can attract and retain water vapor from humid air. This property is known as **hygroscopicity**. In certain cases, sufficient water is absorbed for the crystalline salt to dissolve into its own saturated solution, a process known as **deliquescence** (Oguchi & Yu, 2021; Doehne & Price, 2010).

Humidity-driven moisture uptake is important because it allows some salts to become active even without direct rainfall. A monument may appear dry while salts within pores or surface deposits absorb atmospheric moisture during humid conditions. If humidity later decreases, the resulting solution can become progressively concentrated and may eventually precipitate or crystallize.

The process is not necessarily reversible at the same humidity. A salt may deliquesce at one relative humidity but remain in a metastable solution during drying until a lower humidity is reached and crystallization begins. This hysteresis complicates attempts to predict behavior from a single environmental threshold.

Hygroscopic compounds may also affect the monument indirectly by prolonging local dampness. Persistent moisture can support biological colonization, alter pollutant reactions, or change the behavior of other dissolved salts. Whether this becomes important depends on compound identity, concentration, temperature, pore conditions, and the composition of the surrounding salt mixture.

3.6. Deliquescence and Equilibrium Relative Humidity

For a pure crystalline salt at a specified temperature, a characteristic relative humidity may describe equilibrium between the solid phase and a saturated solution. The **deliquescence relative humidity** identifies the approximate humidity above which a crystalline salt can absorb enough water to form a solution (Lezzerini et al., 2022; Cappai et al., 2024).

These values should not be treated as universal constants independent of context. Temperature, hydration state, metastable phases, crystal size, pore confinement, impurities, and solution composition can alter observed behavior. During drying, nucleation may also be delayed, allowing a solution to remain supersaturated below the humidity at which the original crystalline salt dissolved.

Historic stone presents an additional complication because its pores commonly contain mixtures rather than pure salts. Mixed systems may remain liquid over broader humidity ranges and may display behavior that differs from any individual component. Environmental salts, repair materials, biological metabolites, and treatment residues may all contribute to such mixtures.

Relative-humidity data are therefore most informative when composition and temperature are known. In field conservation, they provide a framework for understanding potential behavior rather than an exact prediction of when deterioration will occur.

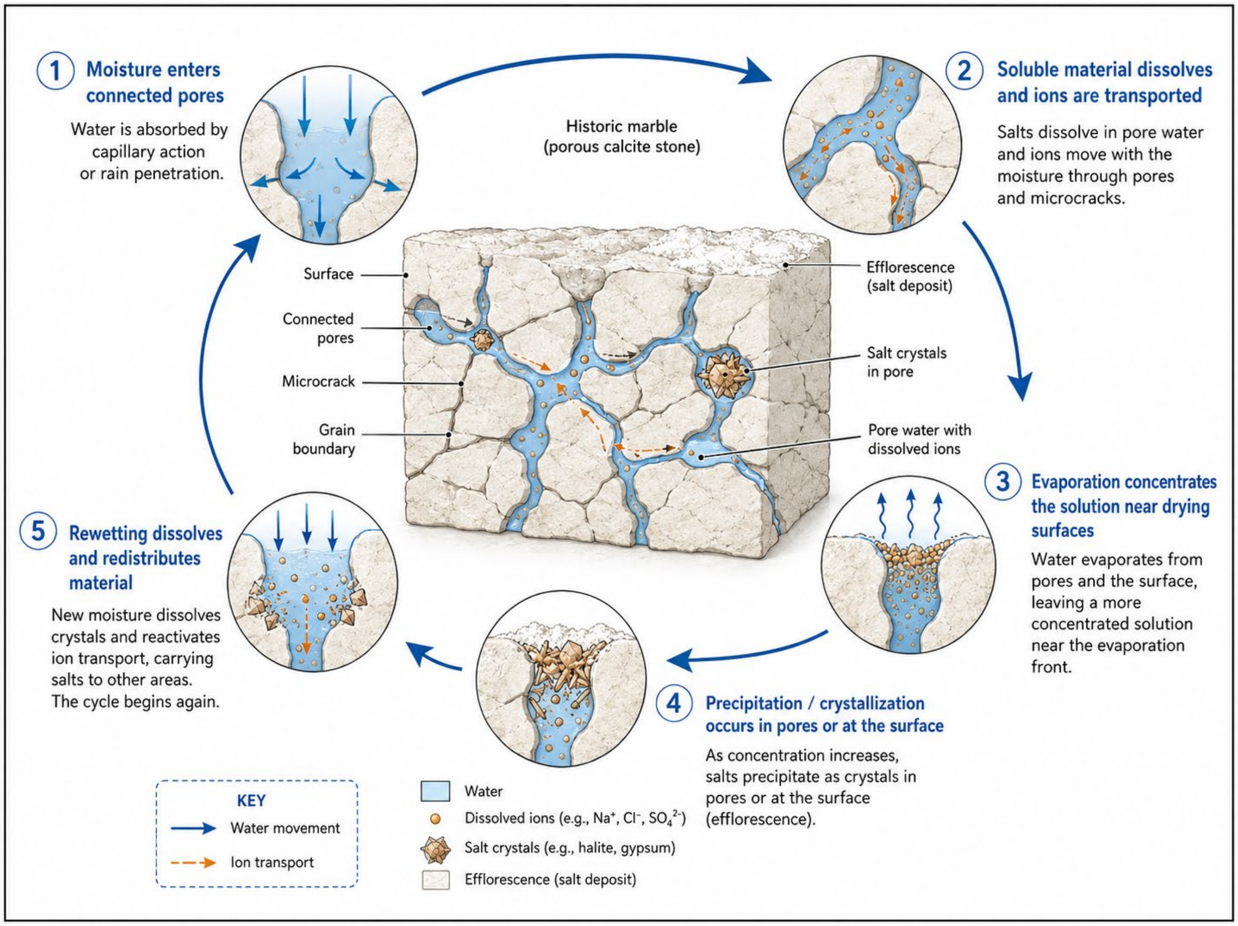
3.7. Water as the Transport Medium

Water carries dissolved ions through marble. The process may begin when rain, dew, irrigation, cleaning water, or rising damp dissolves soluble material already present at or below the surface. Capillary forces then redistribute the solution through connected pores, grain boundaries, and fractures (Oguchi & Yu, 2021; Doehne & Price, 2010).

As drying proceeds, water migrates toward evaporating surfaces. Because the solvent is removed while dissolved ions remain, concentration increases. If the solution becomes sufficiently supersaturated, a solid phase may precipitate. Subsequent wetting can redissolve some of that material and initiate another cycle of transport and concentration.

Building on the moisture pathways illustrated in Figure 2.3, Figure 3.1 shows how dissolved salts can be repeatedly mobilized, concentrated, precipitated, and redistributed as marble undergoes successive wetting and drying cycles.

Figure 3.1: Salt Transport Cycle



Note. *Conceptual transport cycle. Moisture enters connected pores, dissolves soluble material, and transports ions through the stone. Evaporation increases solution concentration and may result in precipitation or crystallization. Rewetting can dissolve and redistribute the material, allowing the cycle to recur.*

The location at which precipitation develops depends on drying rate, pore structure, moisture supply, temperature, relative humidity, and the properties of the dissolved compounds. Material may accumulate at the exterior, immediately below the surface, or deeper within the pore network. That location has important consequences for the form and severity of deterioration.

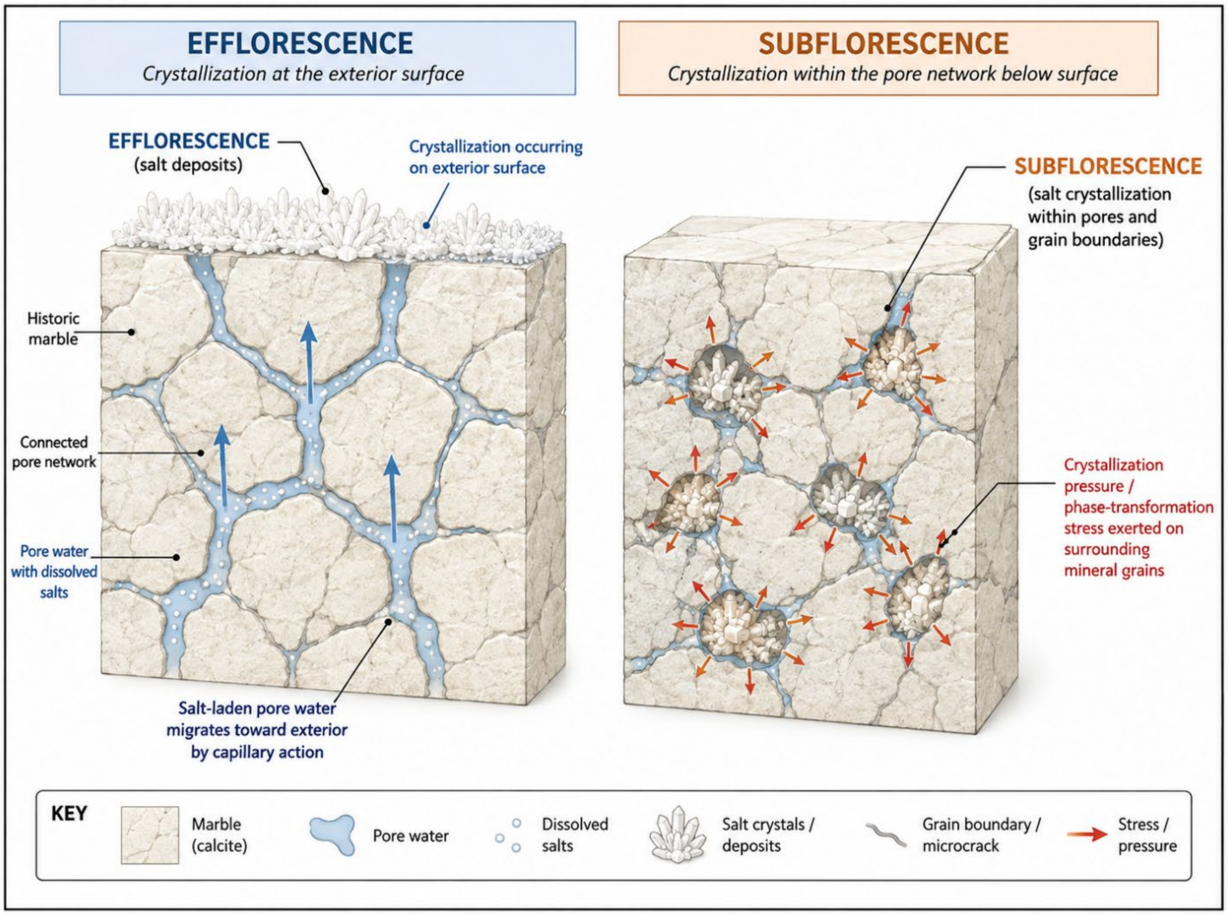
3.8. Efflorescence and Subflorescence

Salt deposition is commonly described according to its position relative to the stone surface. **Efflorescence** forms when dissolved salts migrate to the exterior and precipitate as water evaporates. It may appear as powder, needles, crystalline blooms, films, or crusts. Although visually conspicuous and sometimes associated with other problems, efflorescence frequently functions as evidence of an active moisture-and-salt system rather than as the most damaging expression of that system (Lezzerini et al., 2022; Cappai et al., 2024).

Subflorescence develops beneath the visible surface. Crystals forming within confined pores can interact mechanically with the surrounding mineral framework. Where crystal growth produces stresses greater than the local strength of the stone, repeated cycling can contribute to microfracturing, flaking, scaling, granular disintegration, delamination, or spalling.

Figure 3.2 distinguishes the two principal locations at which this concentration process may become visible or mechanically significant: at the exterior surface as efflorescence or within the pore network as subflorescence.

Figure 3.2: Efflorescence and Subflorescence



> ***Note.*** *Efflorescence forms at or near the exterior surface and is ordinarily visible. Subflorescence develops within the pore network, where crystallization or phase transformation may produce stress against surrounding mineral grains. The location of crystallization is therefore an important determinant of deterioration risk, although that location may shift during successive environmental cycles.*

The distinction is useful but not absolute. Evaporation fronts can move as weather conditions change, and a salt may crystallize at different depths during successive cycles. Surface appearance alone cannot therefore reveal the complete distribution of salts within a monument.

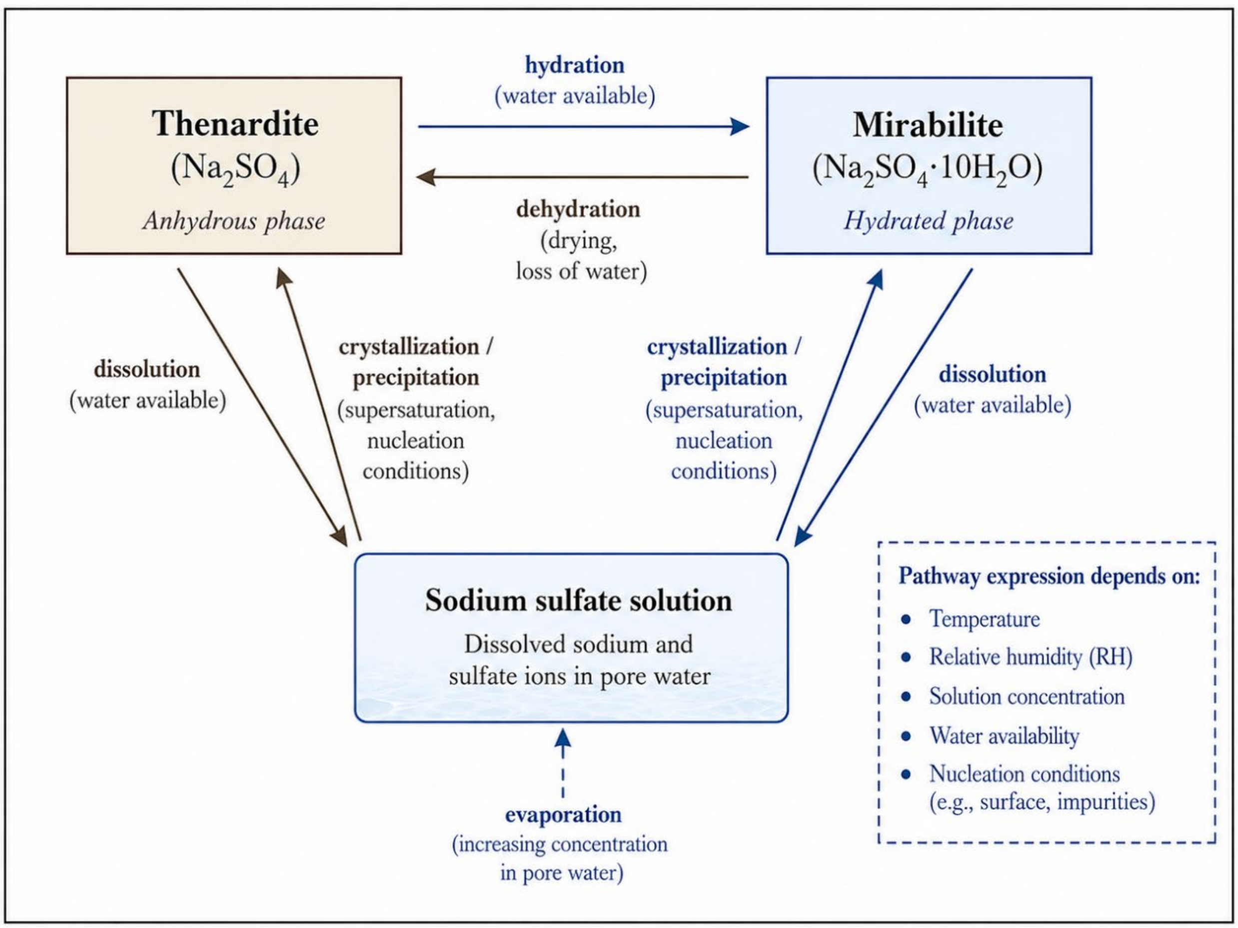
3.9. Why Sodium Sulfate Receives So Much Attention

Sodium sulfate has become one of the most intensively studied salts in porous-material conservation because it can produce severe deterioration under particular conditions. Its behavior involves high solubility, multiple solid phases, delayed nucleation, and the potential for substantial supersaturation during environmental cycling (Oguchi & Yu, 2021; Doehne & Price, 2010).

Two principal phases commonly discussed are thenardite, the anhydrous form Na_2SO_4, and mirabilite, the decahydrate $Na_2SO_4 \cdot 10H_2O$. Their formation and transformation depend on the combined effects of temperature, relative humidity, solution concentration, water availability, nucleation kinetics, and pore confinement. Metastable phases may further complicate the system.

Figure 3.3 illustrates why sodium sulfate cannot be reduced to a simple temperature-controlled transformation: thenardite and mirabilite participate in a system governed jointly by moisture, solution concentration, humidity, temperature, nucleation, and phase stability.

Figure 3.3: Simplified Hydration and Dehydration Pathways of Sodium Sulfate



Note. *Conceptual schematic—not a complete equilibrium phase diagram. Thenardite and mirabilite may dissolve, crystallize, hydrate, or dehydrate as temperature, relative* *humidity, solution concentration, water availability, and nucleation conditions change. Metastable pathways and pore confinement may further influence behavior.*

Sodium sulfate is frequently used in accelerated durability testing precisely because its behavior can produce rapid and measurable damage under controlled conditions. That makes it an important model for studying salt weathering, but not a universal proxy for every ionic compound encountered in conservation (Oguchi & Yu, 2021; Lezzerini et al., 2022).

3.10. Chloride Is Not the Whole Story

Chloride occurs in many materials relevant to historic cemeteries. Possible sources include marine aerosols, groundwater, road and deicing salts, irrigation water, bleach-related chemistry, some cleaning formulations, and naturally occurring environmental contamination (Lezzerini et al., 2022; Cappai et al., 2024).

Analytical detection of chloride identifies only the anion. The associated cation determines many properties of the complete compound. Sodium chloride, calcium chloride, magnesium chloride, benzalkonium chloride, and didecyl dimethyl ammonium chloride (DDAC) differ markedly in size, hygroscopicity, mobility, surface activity, crystallization behavior, and biological function (Gerba, 2015; Kwaśniewska et al., 2020).

Treatment and weathering can complicate identification further. A counterion may become separated from the organic cation with which it was originally associated, older chloride may be mobilized toward the surface during cleaning, and rainfall may redistribute deposits after treatment. Chloride detected at a later date therefore cannot necessarily be assigned to a particular cleaner without supporting chemical and treatment-history evidence.

The broader chemical system—including other ions, organic compounds, mineral phases, location, and environmental setting—must be considered before conservation significance can be inferred.

3.11. Adsorption and Crystallization

Adsorption and crystallization describe fundamentally different forms of material retention.

Crystallization involves the formation and growth of an ordered solid phase from a solution. Under appropriate conditions, growth within confined pores can generate mechanical stress against the surrounding stone (Oguchi & Yu, 2021; Doehne & Price, 2010).

Adsorption involves the association of molecules or ions with a surface or interface. The retained material does not necessarily form a three-dimensional crystal. Electrostatic interactions, hydrophobic effects, van der Waals forces, ion exchange, and other surface processes can all contribute to adsorption.

This distinction becomes important when considering quaternary ammonium compounds. Cationic surfactants may associate with carbonate materials, accessory minerals, environmental deposits, organic matter, or biological films, but the extent and mechanism depend on the particular system. Calcite should not be treated as possessing a uniformly negative surface under every condition; its interfacial behavior varies with pH, ionic strength, dissolved calcium and carbonate, crystal face, impurities, weathering, and surrounding solution chemistry.

Adsorption may reduce mobility and contribute to temporary residual antimicrobial activity, but it does not establish either compatibility or damage. A retained organic layer must be evaluated according to quantity, persistence, environmental transformation, effect on moisture behavior, and interaction with subsequent treatments. Models developed to explain confined crystal growth cannot be transferred directly to an adsorbed organic residue without evidence that an equivalent mechanism occurs.

3.12. Salt Mixtures

Historic marble rarely contains a single pure salt. Its pore network may contain combinations of chlorides, sulfates, nitrates, carbonates, sodium, potassium, calcium, magnesium, environmental contaminants, biological metabolites, and materials associated with previous repairs or treatments (Lezzerini et al., 2022; Cappai et al., 2024).

Mixtures can behave differently from their individual components. One salt may alter the solubility or crystallization of another, extend the range of humidity over which a solution remains liquid, promote or inhibit nucleation, or contribute to the formation of new solid phases. As a result, behavior predicted from a pure laboratory compound may not describe the mixed system encountered in a cemetery monument.

This complexity also complicates the interpretation of post-treatment deposits. Cleaning may introduce new material, but the associated wetting event may simultaneously dissolve and redistribute compounds already present from soil, pollution, irrigation, repairs, or earlier interventions. A deposit appearing after treatment may therefore have more than one source.

Controlled laboratory studies and field observation serve complementary roles in resolving these questions. Laboratory work isolates variables and establishes mechanisms; field monitoring reveals how those mechanisms operate within the heterogeneous chemical environment of actual monuments.

3.13. Why Chemistry Alone Does Not Predict Preservation Outcomes

Chemical properties are necessary to understand treatment behavior, but they do not operate independently of the monument or its environment. The same compound may behave differently in dense marble, severely sugared marble, limestone, sandstone, or a cementitious repair. Differences in concentration, moisture supply, pore connectivity, temperature, humidity, application frequency, and drying conditions may change the outcome even when the chemical itself remains unchanged (Oguchi & Yu, 2021; Doehne & Price, 2010).

A meaningful conservation assessment therefore considers four interacting elements: the material introduced, the condition and mineralogy of the monument, the surrounding environment, and the treatment conditions under which contact occurs. The chemical formulation establishes what processes are possible; the substrate and environment determine which of those processes become significant.

This systems approach is especially important when evaluating cleaner residues. An ingredient name or chemical classification cannot independently establish long-term compatibility. Evidence must address how the material behaves within a real or suitably representative stone system under realistic conditions.

3.14. Summary

Salt chemistry provides the vocabulary needed to describe potential deterioration, but preservation significance depends on behavior rather than classification alone. Solubility enables aqueous transport, hygroscopicity influences moisture uptake, environmental conditions control phase stability, and crystallization location affects the potential for mechanical damage. Adsorption represents a different form of retention whose consequences must be evaluated according to its own mechanisms (Lezzerini et al., 2022; Cappai et al., 2024).

Sodium sulfate demonstrates how destructive a salt can become when solution chemistry, supersaturation, phase transformation, pore confinement, moisture, and a vulnerable substrate align. It also illustrates why salt behavior must be examined at the level of the complete chemical and physical system (Oguchi & Yu, 2021; Lezzerini et al., 2022).

Chapter 4 builds on these principles by examining the mechanisms through which salt-bearing solutions move, concentrate, crystallize, and contribute to deterioration within porous historic marble.

4. Salt Weathering Mechanisms

4.1. Introduction

Salt weathering is one of the most extensively studied causes of deterioration in porous stone. Its significance arises not simply from the presence of soluble compounds, but from the repeated movement, concentration, precipitation, dissolution, and phase transformation of salts within a vulnerable pore network. When those processes occur beneath the surface, they may generate stresses that weaken grain boundaries, enlarge microfractures, and contribute to powdering, scaling, delamination, and loss of carved detail (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Unlike abrasion or impact, salt-related deterioration can remain concealed during its early stages. Crystallization and phase changes occur within pores too small to observe directly, and cumulative microscopic damage may precede visible surface loss. By the time a monument displays obvious flaking, granular disintegration, or spalling, the underlying moisture-and-salt system may already have operated through many environmental cycles.

Chapter 3 established the chemical properties governing salt behavior. This chapter focuses on the physical mechanisms through which saline solutions move and, under particular conditions, damage porous marble. The distinction is important: Chapter 3 addresses what salts can do chemically, while Chapter 4 examines the circumstances under which that behavior becomes mechanically significant to the stone.

4.2. Development of Modern Salt-Weathering Science

The destructive effects of saline groundwater, sea spray, contaminated soils, and evaporating moisture have been observed for centuries, but early explanations often described salt deterioration as simple crystal expansion or chemical corrosion. Modern research has produced a more rigorous model based on solution transport, supersaturation, nucleation, confined crystal growth, phase transformation, and the mechanical response of the pore network (Lezzerini et al., 2022; Cappai et al., 2024).

Twentieth- and twenty-first-century conservation research increasingly examined salt deterioration at the scale of individual pores and crystal interfaces. This work demonstrated that crystal growth can exert stress when supersaturated solution remains available at a confined growth surface and that the resulting damage depends on more than the identity of the salt. Pore geometry, degree of supersaturation, nucleation behavior, drying rate, temperature, humidity, phase stability, and the strength of the substrate all influence the outcome.

The resulting understanding is more useful to conservation than a simple inventory of harmful salts. It explains why the same salt may be destructive in one stone or climate while producing limited observable change in another, and why a highly weathered marble surface may respond to pressures that a more cohesive substrate can tolerate.

4.3. Conditions Required for Salt Weathering

Damaging salt activity generally requires four interacting conditions:

1. a source of soluble material;
2. sufficient moisture to dissolve or transport that material;
3. a porous or fractured substrate through which the solution can move; and
4. environmental conditions that promote concentration, crystallization, or phase transformation.

The absence or limitation of one component can substantially reduce the potential for crystallization-related damage. Dry salts have limited capacity for aqueous movement until moisture becomes available. Water without soluble material cannot generate salt crystallization, although it may contribute to other deterioration processes. A poorly connected pore network offers fewer locations for internal transport and confinement, while continuously saturated conditions may produce less crystallization than repeated transitions between wet and dry states (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Historic marble often presents a favorable environment for these processes because weathering enlarges grain boundaries and microfractures while outdoor exposure supplies recurring moisture and drying. Susceptibility nevertheless varies among monuments. Mineralogy, pore connectivity, base drainage, environmental exposure, preexisting salt concentration, and surface strength all influence whether the four conditions develop strongly enough to produce measurable deterioration.

4.4. Sources of Salts in Historic Cemeteries

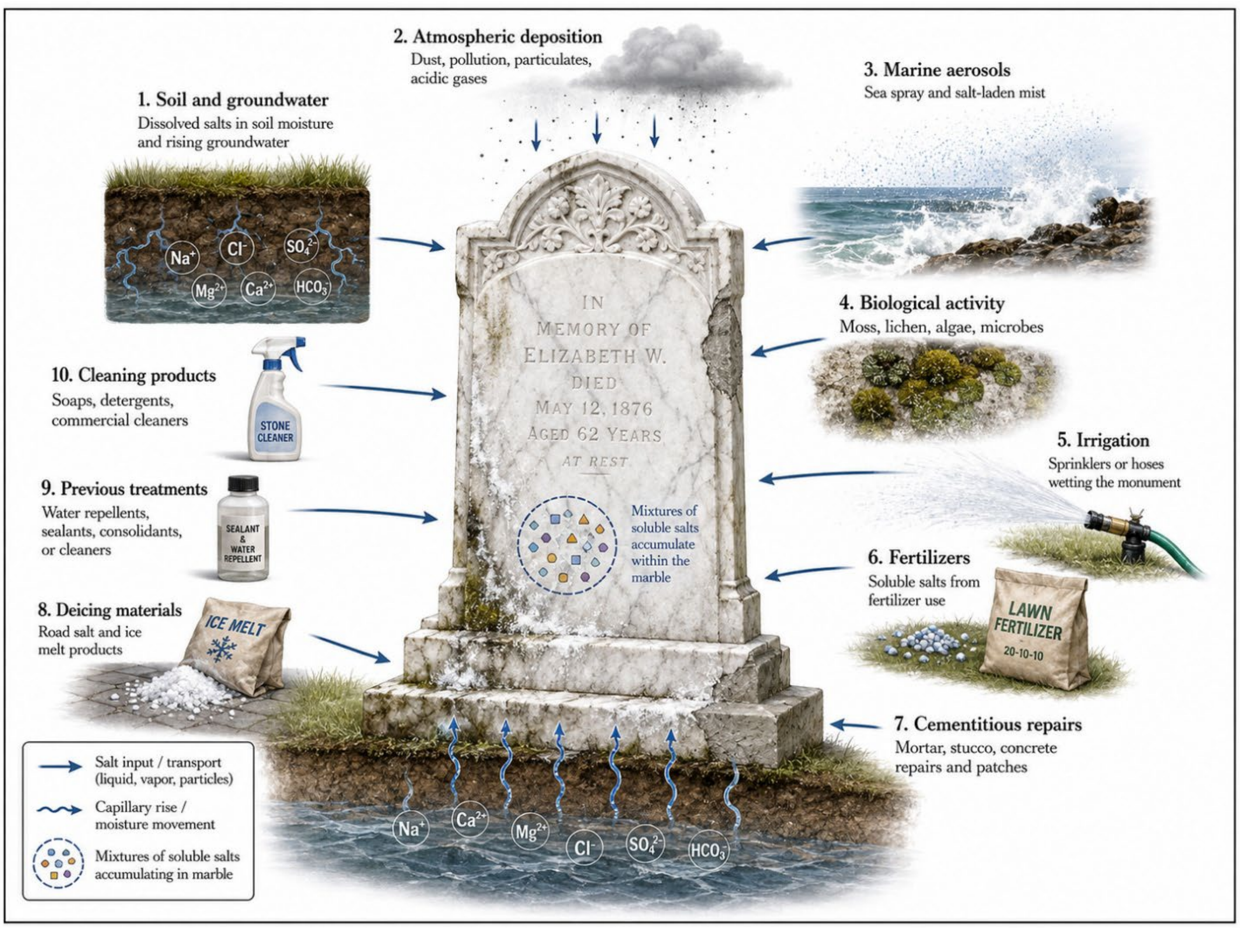
Salts encountered in cemetery monuments may originate from the surrounding environment, form through reactions at the stone surface, or be introduced during construction, repair, maintenance, or cleaning. Because monuments remain outdoors for generations, most accumulate complex chemical histories rather than a single identifiable contaminant (Lezzerini et al., 2022; Cappai et al., 2024).

Soil and groundwater may supply calcium, magnesium, sodium, chloride, sulfate, nitrate, and other dissolved ions through capillary rise. Coastal environments introduce marine aerosols, while windborne dust and atmospheric deposition provide additional mineral material. Pollution can contribute sulfate- and nitrate-bearing compounds, and biological activity may generate or concentrate ammonium, nitrate, phosphate, oxalate, and other species.

Human activity adds further sources. Portland-cement repairs, incompatible mortars, fertilizers, deicing materials, irrigation water, cleaning products, and earlier conservation treatments may all introduce soluble compounds. Some become mobile immediately; others remain within a repair or deposit until a later wetting event releases them.

Figure 4.1 synthesizes the environmental and human sources discussed above and emphasizes why the soluble material detected within a historic monument may reflect a cumulative chemical history rather than a single recent treatment.

Figure 4.1: Sources of Soluble Salts in Historic Cemeteries



Note. *Soluble salts may reach marble from soil and groundwater, atmospheric deposition, marine aerosols, biological activity, irrigation, fertilizers, deicing materials, cementitious repairs, previous treatments, and cleaning products. Historic monuments commonly contain mixtures derived from several sources.*

This diversity is important when interpreting post-treatment deposits. The appearance of salts after cleaning does not establish that the cleaner was their sole source. Treatment water may dissolve older material within the monument and redistribute it toward the surface.

4.5. Capillary Transport

Liquid water moves through porous marble under the influence of capillary forces, pressure gradients, gravity, and evaporation. Narrow interconnected openings can draw water upward or laterally beyond the area of direct wetting, carrying dissolved ions with it. This process helps explain why deterioration or salt deposition may appear well above the ground line or at some distance from an obvious source of moisture (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Capillary behavior is governed by more than pore diameter. Fine pores can generate strong capillary suction but may transmit water relatively slowly, while larger connected pores or fractures can provide rapid pathways with less capillary rise. Historic marble contains many pore sizes and discontinuities, producing a network in which several transport processes can occur simultaneously.

Conditions at the base of a monument often influence capillary transport significantly. Wet soil, poorly drained fill, vegetation, impermeable repair materials, and standing water can maintain a persistent moisture supply. A monument that repeatedly draws saline water from below may remain part of an active transport system even when its exposed surfaces appear dry.

Cleaning solutions enter the same pore network. Pre-wetting may reduce the immediate concentration of cleaner entering accessible near-surface pores, while rinsing can dilute and remove some soluble material. Neither process guarantees uniform distribution or complete removal, particularly where marble is deeply weathered or extensively fractured.

4.6. Evaporation Fronts

Drying does not occur uniformly throughout a wet monument. As evaporation progresses, a transition develops between wetter interior material and the drying exterior. This moving zone is commonly described as the **evaporation front**. Water migrates toward it, carrying dissolved compounds that become increasingly concentrated as the liquid phase is lost (Lezzerini et al., 2022; Cappai et al., 2024).

When solution reaches the exposed surface before substantial evaporation occurs, salts may precipitate externally as efflorescence. If evaporation becomes concentrated beneath the surface, the crystallization zone may instead develop within the pore network. Environmental changes can shift that location repeatedly, causing material deposited during one cycle to dissolve and recrystallize elsewhere during another.

As illustrated in **Figure 3.1 and Figure 3.2**, dissolved salts may migrate toward the surface during drying, but the location of the evaporation front influences whether deposition occurs at the exterior as efflorescence or beneath the surface as potentially damaging subflorescence.

The position of this zone depends on moisture supply, drying rate, pore connectivity, wind, temperature, solar exposure, and relative humidity. It may also vary across a single monument. Sheltered surfaces, carved recesses, repaired joints, bases, and transitions between materials with different permeability can develop distinctly different drying regimes.

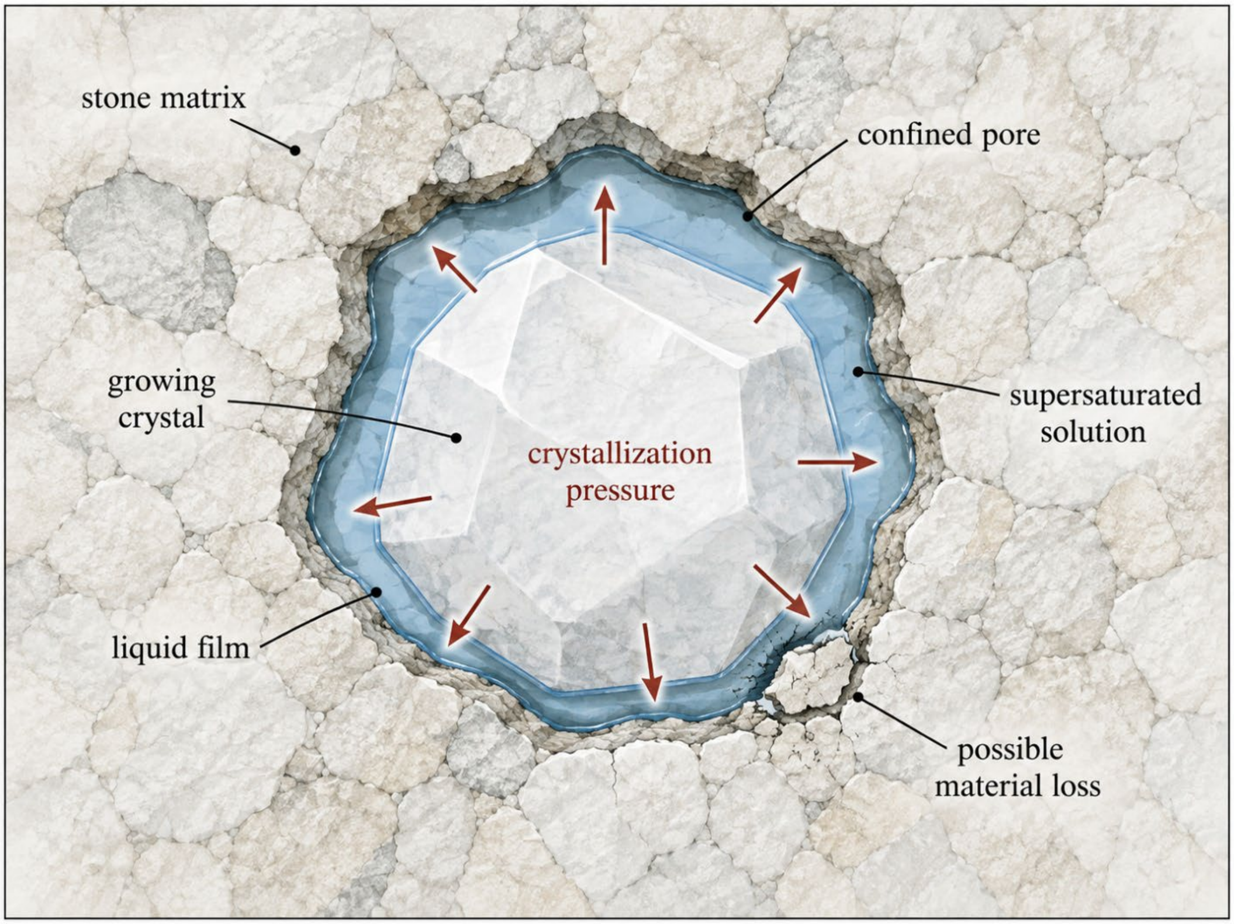
4.7. Crystallization Pressure

Crystallization pressure develops when a crystal grows from a supersaturated solution while confined by surrounding pore walls. The mechanism is more complex than the idea that a solid simply occupies more space than dissolved ions. Continued crystal growth requires a liquid film at the growth interface through which additional dissolved material can reach the crystal (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Under suitable conditions, incorporation of ions into the growing crystal can produce stress against the surrounding pore structure. Whether this stress causes damage depends on the degree of supersaturation, the properties of the crystalline phase, pore geometry, interfacial conditions, and the mechanical strength of the stone. A cohesive stone may tolerate stresses that cause grain detachment in weathered marble whose grain boundaries have already been weakened.

Where Figure 3.2 identifies the location of potentially damaging subflorescence, Figure 4.2 illustrates the pore-scale mechanism by which confined crystal growth can translate supersaturation into mechanical stress on the surrounding stone.

Figure 4.2: Crystallization Pressure Within a Confined Pore



Note. *Conceptual schematic—not to scale. A crystal growing from supersaturated solution may exert stress against surrounding pore walls when liquid remains available at the growth interface. Material loss becomes possible when the resulting local stress exceeds the strength or cohesion of the adjacent stone.*

Salt damage is therefore cumulative as well as local. A single crystallization event may produce little observable change, while repeated dissolution and growth at vulnerable sites can progressively weaken the mineral framework. Over many environmental cycles, microscopic damage may emerge as powdering, scaling, grain loss, or surface recession.

4.8. Hydration, Dehydration, and Phase Transformation

Some salts can exist in several hydrated or anhydrous solid forms, and environmental changes may shift the system from one phase to another. Sodium sulfate provides the most familiar conservation example because thenardite and mirabilite participate in complex cycles involving solution, crystallization, hydration state, temperature, humidity, and water availability (Lezzerini et al., 2022; Cappai et al., 2024).

Earlier explanations sometimes treated this behavior as simple solid-state expansion in which a dry crystal directly absorbs water and increases in volume. Contemporary interpretations are more cautious. In many porous systems, deterioration is better understood as involving dissolution of one phase followed by precipitation of another from supersaturated solution. The resulting stress is therefore closely connected to confined crystal growth and phase selection rather than to volume change alone.

Metastability further complicates the process. A solution may remain supersaturated until an appropriate nucleation site becomes available, after which rapid precipitation can occur. Pore surfaces, existing crystals, impurities, and mixed salts can promote or inhibit particular transformations.

As illustrated in **Figure 3.3**, the formation and transformation of thenardite and mirabilite depend on the combined effects of temperature, relative humidity, solution concentration, and water availability rather than on temperature alone.

These mechanisms are important precisely because they are compound-specific. A phase transformation documented for sodium sulfate cannot be assumed to occur in a chemically unrelated residue that does not possess comparable hydrate phases or crystallization behavior (Oguchi & Yu, 2021; Lezzerini et al., 2022).

4.9. Supersaturation and Nucleation

Crystal growth requires a solution that is supersaturated with respect to the solid phase being formed. Supersaturation can develop as evaporation removes water, as temperature changes alter solubility, as chemical reactions change solution composition, or as dissolution of one phase produces conditions favorable for another (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Supersaturation does not necessarily result in immediate crystallization. Formation of a stable nucleus requires overcoming an energy barrier, allowing some solutions to remain metastable for a period. Pore walls, impurities, preexisting crystals, biological material, and mineral surfaces can influence whether and where nucleation occurs.

This behavior affects the spatial pattern of deterioration. Some very fine pores may inhibit nucleation despite high concentrations, while adjacent larger pores or surface irregularities provide favorable crystallization sites. Once a crystal forms, it may draw material from surrounding solution and alter the distribution of dissolved ions elsewhere in the pore network.

Consequently, total salt concentration is not sufficient to predict where damage will develop. The timing and location of nucleation, the persistence of supersaturated solution, and the geometry of the surrounding pores must also be considered.

4.10. Pore Structure and Confinement

Pore structure influences nearly every stage of salt weathering. It controls water uptake, solution movement, drying, salt concentration, nucleation, crystal confinement, and the transmission of stress into the mineral framework (Lezzerini et al., 2022; Cappai et al., 2024).

A simple relationship in which progressively smaller pores always produce greater damage is inadequate. Fine pores may retain water and develop strong capillary forces, but they may also inhibit formation of particular crystals. Larger pores may provide favorable nucleation sites while permitting comparatively unconfined growth. Particularly complex behavior can occur in networks containing connected pores of several sizes, where solution stored in fine pores supplies growth in neighboring larger voids or at pore transitions.

Weathering alters these relationships. Calcite dissolution, thermal microfracturing, biological penetration, salt activity, and previous interventions may enlarge some openings and connect others. The resulting network can transport greater quantities of water and expose a larger internal mineral surface to dissolved compounds.

Mechanical condition remains equally important. A pore geometry capable of producing stress does not guarantee visible damage unless the surrounding material is weak enough to fail. Severely sugared marble, with reduced grain-boundary cohesion, may therefore be more vulnerable to salt-related stress than dense and relatively intact stone.

4.11. Environmental Controls

Salt weathering is strongly influenced by environmental conditions, but the relevant effects depend on the compounds present. Temperature affects solubility, phase stability, evaporation rate, and crystal growth. Relative humidity determines whether some salts remain crystalline, absorb atmospheric moisture, deliquesce, or precipitate from solution (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Rainfall may dissolve surface and near-surface deposits and redistribute ions, while repeated light wetting can produce a different transport pattern from prolonged saturation. Dew and condensation may activate hygroscopic salts without providing the flushing associated with heavy rain. Wind and solar radiation affect evaporation rates and can create different drying conditions on adjacent surfaces of the same monument.

Orientation and shelter therefore matter. A north-facing surface shaded by vegetation may remain wet longer than a south-facing face exposed to direct sunlight. A recessed inscription may dry differently from an exposed edge, while the base of a monument may receive a continuing moisture supply from the ground. Identical stone types within the same cemetery can consequently develop different salt patterns even when separated by only a short distance.

Seasonal change adds another layer of complexity. Summer heating, autumn rainfall, winter freezing, spring snowmelt, and year-round fluctuations in relative humidity create sequences of exposure rather than isolated environmental events. Long-term deterioration reflects the cumulative effect of those sequences.

4.12. Interacting Deterioration Mechanisms

Salt weathering rarely operates independently of other forms of marble deterioration. Carbonate dissolution can enlarge grain boundaries that later provide pathways for saline moisture. Thermal movement and freeze-thaw cycling may create fractures that become preferential sites for transport and crystallization. Biological films can retain moisture, trap pollutants, and modify local chemistry, while incompatible repairs may introduce soluble material or redirect water into adjacent historic stone (Lezzerini et al., 2022; Cappai et al., 2024).

These processes can reinforce one another. A roughened surface created by granular loss may retain more moisture and support denser biological colonization. Prolonged dampness can increase solution transport, while salt crystallization may produce additional microfractures. A cementitious repair can simultaneously add soluble compounds, restrict evaporation, and create a permeability transition along which deterioration becomes concentrated.

The resulting damage pattern is therefore rarely diagnostic of one mechanism by appearance alone. Scaling, flaking, or granular loss may have several contributing causes. The detection of salts likewise does not establish that salt activity is the dominant deterioration mechanism. Interpretation should consider moisture source, environmental exposure, mineral fabric, repair history, biological condition, and the spatial relationship among damage and deposits.

4.13. Concentration, Distribution, and Repetition

The amount of dissolved material available influences the potential for supersaturation and crystal growth, but total concentration alone does not predict severity. A substantial quantity deposited harmlessly at the surface may produce less mechanical damage than a smaller amount repeatedly concentrated within a vulnerable subsurface zone (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Distribution is therefore as important as mass. Conservation assessment should consider how much material remains, where it is located, whether subsequent moisture can remobilize it, and whether repeated exposure increases the quantity available for future cycling. This is particularly relevant to the evaluation of cleaning materials because repeated treatment can produce different cumulative conditions from a single application.

Treatment interval also matters. If a compound is removed, degraded, desorbed, or environmentally transformed between applications, cumulative retention may remain limited. If material persists and each treatment adds an additional fraction, concentration may increase over time. Establishing which process occurs requires measurement rather than assumption.

These questions provide the scientific bridge between classical salt-weathering research and the later evaluation of cleaner residues. The issue is not simply whether a treatment introduces ionic material, but whether that material can remain in a form, location, and concentration capable of participating in a damaging cycle.

4.14. Interpreting Laboratory and Field Evidence

Laboratory testing is essential because it allows researchers to control variables, compare treatments under identical conditions, characterize residues, and apply analytical methods that would be inappropriate on historic monuments. Accelerated wetting and drying, humidity cycling, temperature control, or salt exposure can reveal potential deterioration mechanisms within a practical research period (Lezzerini et al., 2022; Cappai et al., 2024).

The same control that gives laboratory testing its strength also creates limitations. Fresh marble specimens may lack the enlarged grain boundaries, microfractures, biological films, previous treatments, and mixed salts of historic cemetery stone. Small samples can dry differently from full-size monuments, while deliberately severe cycling may emphasize mechanisms that occur more slowly or less frequently outdoors.

Field observation provides the environmental complexity absent from the laboratory but sacrifices experimental control. Monuments differ in quarry source, age, orientation, previous treatment, soil contact, climate, biological loading, and degree of deterioration. Suitable untreated controls are difficult to maintain, and gradual changes may be difficult to distinguish from natural weathering.

Neither evidence type should be treated as independently decisive. Mechanistic research establishes what can occur; controlled material testing examines whether a particular treatment produces that behavior under defined conditions; analytical characterization identifies what is present; and long-term field monitoring helps determine whether the process becomes meaningful under actual cemetery exposure. Strong conservation conclusions are most defensible when these lines of evidence converge.

4.15. Summary

Salt weathering develops through the interaction of soluble material, moisture, pore structure, environmental cycling, and the mechanical condition of the stone. Dissolved compounds move with water, become concentrated as drying proceeds, and may precipitate or crystallize when solution conditions permit. Where crystal growth or phase transformation occurs under confinement, local stresses can contribute to microscopic fracture and progressive material loss (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

The mechanisms described in this chapter establish criteria for evaluating whether a particular residue presents a credible salt-weathering concern. Relevant questions include whether the material remains mobile, whether it reaches supersaturation, what solid phase forms, where that phase develops, whether repeated environmental cycling occurs, and whether the resulting stress or chemical interaction produces measurable change in the stone.

That framework is particularly important for the next stage of the paper. Quaternary ammonium compounds must be evaluated according to those mechanistic criteria and to their own chemical and interfacial behavior, rather than by assuming that a chemical classification alone determines how they will perform within weathered historic marble.

5. Quaternary Ammonium Compounds: Chemistry, Function, and Conservation Applications

5.1. Introduction

The preceding chapters established the physical and chemical conditions under which soluble materials can contribute to deterioration of porous historic marble. That framework provides the basis for considering the compounds at the center of this paper: quaternary ammonium compounds, commonly abbreviated as quats or QACs (McDonnell & Russell, 1999; Gerba, 2015).

Quaternary ammonium compounds have long been used as disinfectants, sanitizers, algaecides, fungicides, and surface-active cleaning agents. They are found in healthcare, food processing, water treatment, industrial systems, and numerous commercial cleaners. Selected quat-based formulations have also become established tools for controlling biological colonization on monuments, masonry, and architectural stone.

Their use in cemetery preservation has generated understandable questions because quats are chemically classified as salts. That classification has sometimes led to comparisons with sodium sulfate, magnesium sulfate, sodium chloride, and other inorganic salts associated with deterioration of porous stone. At the other extreme, successful professional use has occasionally been interpreted as sufficient evidence that all long-term concerns can be dismissed (Oguchi & Yu, 2021; Lezzerini et al., 2022).

Neither position adequately describes the scientific problem. Quaternary ammonium compounds possess structural, surface-active, and antimicrobial properties that distinguish them from the small inorganic ions central to classical salt-weathering research. Those differences make direct equivalence inappropriate, but they do not eliminate questions concerning adsorption, residue persistence, environmental transformation, complete formulation, or repeated treatment.

This chapter examines quat chemistry and antimicrobial function, their interactions with biological films and mineral surfaces, the significance of residual activity, and the limits of the evidence currently available for historic marble.

5.2. What Is a Quaternary Ammonium Compound?

A quaternary ammonium ion contains a positively charged nitrogen atom bonded directly to four carbon-containing substituents. Its general structure may be represented as: $[R_1R_2R_3R_4N]^+X^-$ (Kwaśniewska et al., 2020; Boyce, 2023).

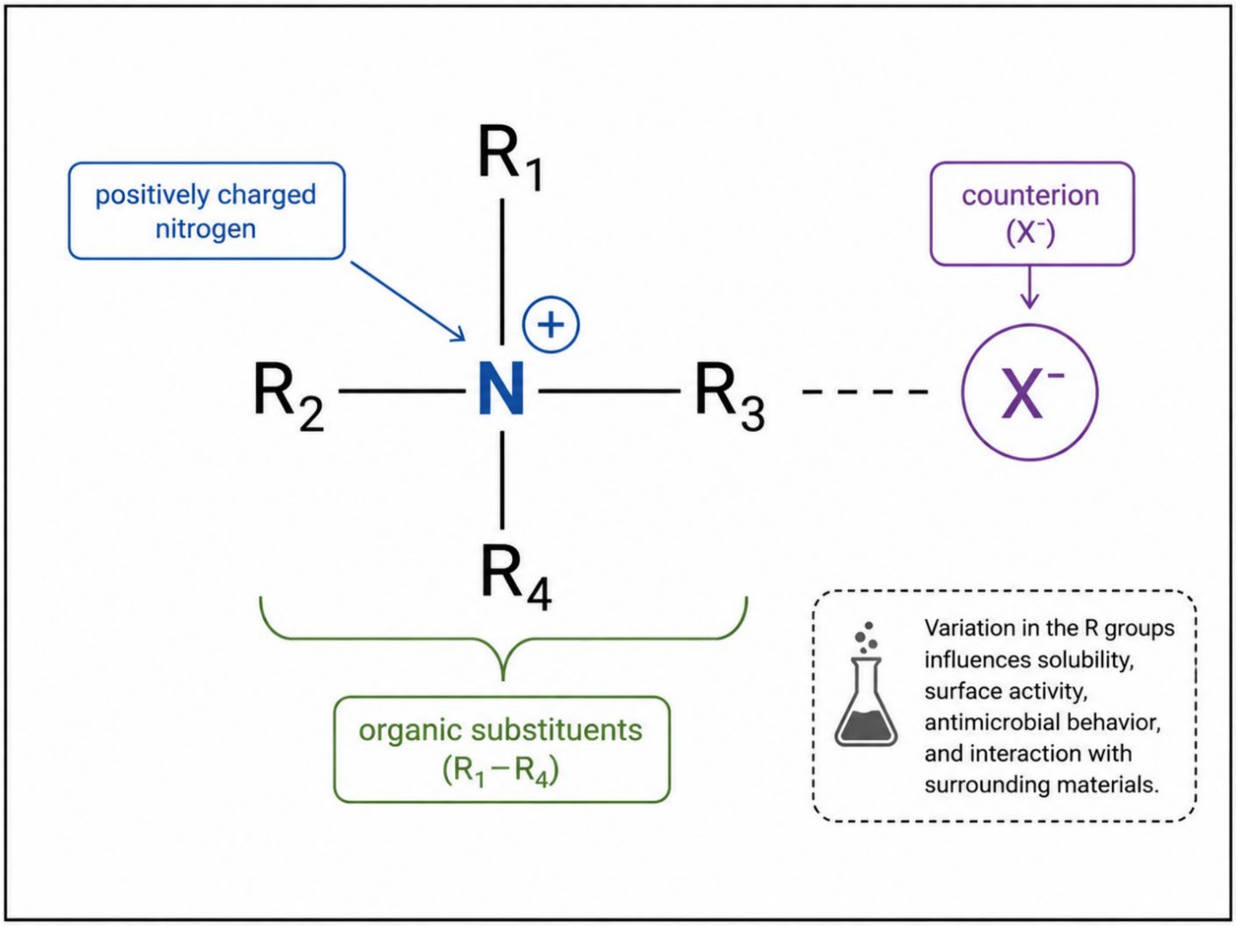
The four organic groups attached to nitrogen may vary in size and structure, while the negatively charged counterion, represented by (X^-), is commonly chloride. Because the positive charge is permanent rather than dependent on temporary protonation, quaternary ammonium ions remain cationic across a broad range of ordinary use conditions.

Many commercially important quats contain both a charged region that interacts readily with water and one or more hydrophobic carbon chains that interact with organic matter and lipid-containing surfaces. This amphiphilic structure gives the compounds surfactant properties and contributes directly to their antimicrobial action.

Quats are therefore more accurately understood as **ionic, surface-active organic compounds** than simply as salts. Their ionic classification is chemically correct, but it does not by itself describe their mobility, adsorption, biological activity, or likely behavior when incorporated into a commercial stone cleaner.

Figure 5.1 establishes the structural characteristic that distinguishes quats from the comparatively small inorganic ions discussed in Chapter 3: a permanently charged nitrogen center bonded directly to four organic substituents.

Figure 5.1: General Structure of a Quaternary Ammonium Compound



Note. *Generalized chemical structure. A quaternary ammonium ion contains a positively charged nitrogen atom bonded directly to four organic substituents and paired with a negatively charged counterion. Variation among the organic groups influences solubility, surface activity, antimicrobial behavior, and interaction with surrounding materials.*

5.3. Quaternary Ammonium Compounds Encountered in Preservation

Several related quaternary ammonium compounds may be found in biological cleaners used on masonry and monuments. Among the most familiar are benzalkonium chlorides and didecyldimethylammonium chloride (Mohapatra et al., 2023).

Benzalkonium chloride, commonly abbreviated BAC, generally refers not to a single pure molecule but to a mixture of alkylbenzyldimethylammonium chlorides containing hydrocarbon chains of different lengths. These related compounds possess broad antimicrobial activity and are widely used in disinfectant and cleaning formulations (Gerba, 2015; Kwaśniewska et al., 2020).

Didecyldimethylammonium chloride, or DDAC, contains two decyl groups and two methyl groups attached to the positively charged nitrogen. It is likewise used as a biocide and may appear alone or in combination with other quaternary ammonium compounds (Gerba, 2015; Kwaśniewska et al., 2020).

Commercial labels may use broader descriptions such as *alkyl dimethyl benzyl ammonium chloride* or simply *quaternary ammonium compounds*. Such language identifies a chemical family but may reveal comparatively little about the precise distribution of homologues, active concentration, supporting surfactants, buffers, or other formulation ingredients.

That distinction is important throughout this paper. Evidence concerning the general chemistry of benzalkonium chloride may help explain a possible mechanism, but it does not automatically establish the behavior of every commercial cleaner that contains a benzalkonium compound. The active ingredient, the specific compound or blend, and the complete finished formulation represent different levels of evidence and should not be treated as interchangeable (Gerba, 2015; Kwaśniewska et al., 2020).

5.4. Antimicrobial Action

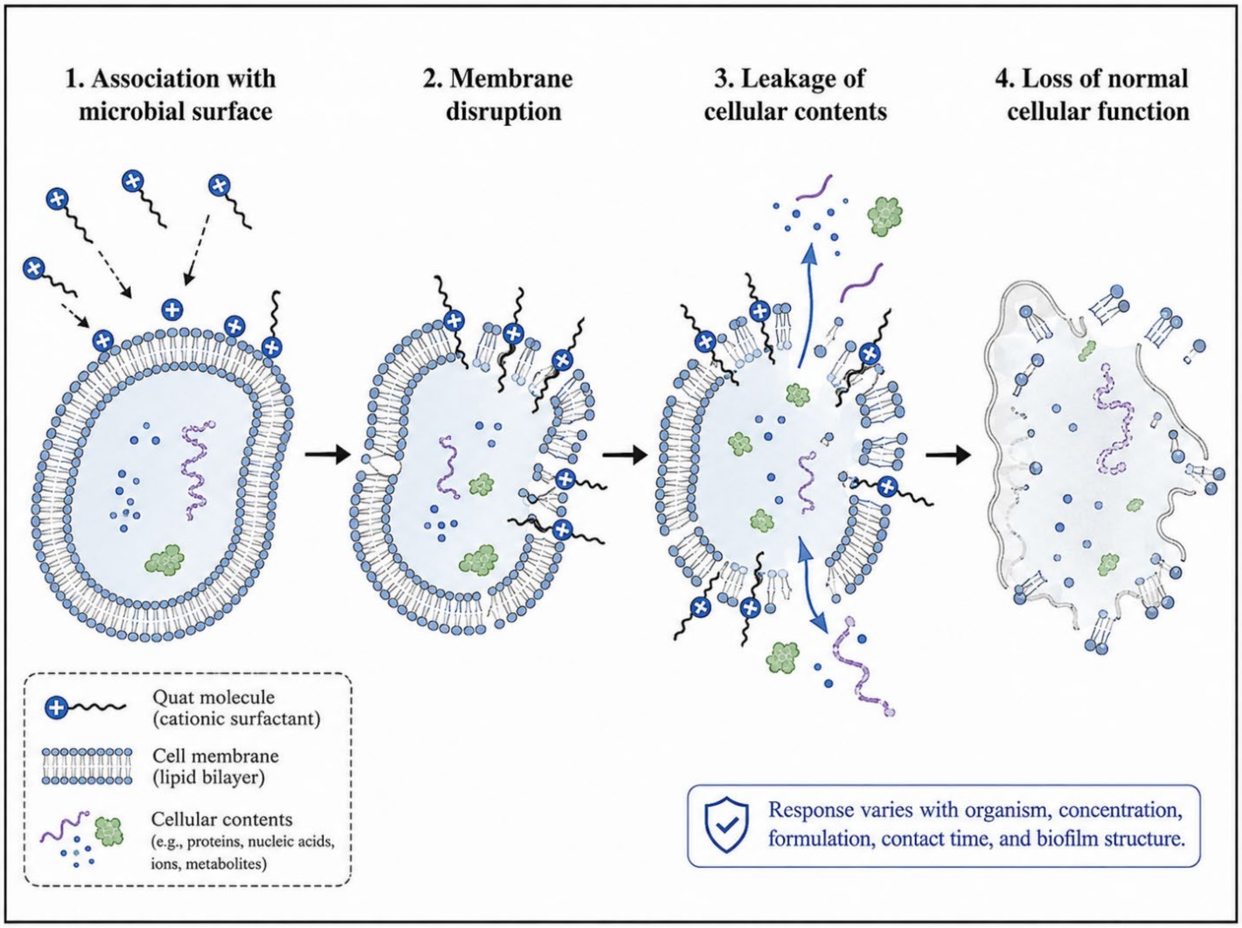
The antimicrobial function of quaternary ammonium compounds arises largely from their interaction with microbial surfaces and cell membranes. The positively charged portion of the molecule can associate with charged or polar components of microbial surfaces, while its hydrophobic groups interact with lipid-containing membrane structures. At an effective concentration and contact time, these interactions can disrupt membrane organization, increase permeability, interfere with essential cellular processes, and lead to leakage of cellular contents and loss of viability (McDonnell & Russell, 1999; Gerba, 2015).

This generalized mechanism is useful for explaining quat activity, but biological response varies considerably. Bacteria, algae, cyanobacteria, fungi, spores, lichens, and organisms embedded within mature biofilms do not respond identically. Concentration, contact time, temperature, water chemistry, pH, organic loading, and formulation all influence efficacy (Pinna, 2014).

Biofilms introduce an additional barrier because microbial cells are embedded within an extracellular polymeric matrix. That material can bind treatment compounds, retain moisture, and reduce direct access to organisms beneath the exterior surface. Successful biological cleaning may therefore involve both microbial inactivation and subsequent removal or weathering of the remaining extracellular matrix and dead biological material (Pinna, 2014).

Figure 5.2 translates this amphiphilic molecular structure into biological function by illustrating the generalized sequence from association with a microbial surface through membrane disruption, increased permeability, and loss of normal cellular function.

Figure 5.2: Mechanism of Quat Antimicrobial Action



Note. *Conceptual antimicrobial mechanism—not a representation of every organism or treatment response. Quaternary ammonium compounds associate with microbial surfaces and disrupt lipid-containing cell membranes. Increased membrane permeability can result in leakage of cellular material and loss of normal cellular function. Actual response varies with organism, concentration, formulation, contact time, environmental conditions, and biofilm structure.*

Biological death and visible cleaning should not be treated as the same outcome. A microorganism may be inactivated while pigments, attachment structures, and dead cellular material remain visible. Conversely, a surface may appear cleaner after physical removal while viable organisms remain in pores or sheltered recesses. Conservation evaluation must therefore distinguish antimicrobial performance from immediate appearance.

5.5. Surfactant Behavior

Quaternary ammonium compounds also function as cationic surfactants. Surfactants accumulate at interfaces and alter the relationship between water and the material being wetted. By reducing interfacial tension, they can improve spreading across irregular stone surfaces and increase contact with hydrophobic biological films (Kwaśniewska et al., 2020; Boyce, 2023).

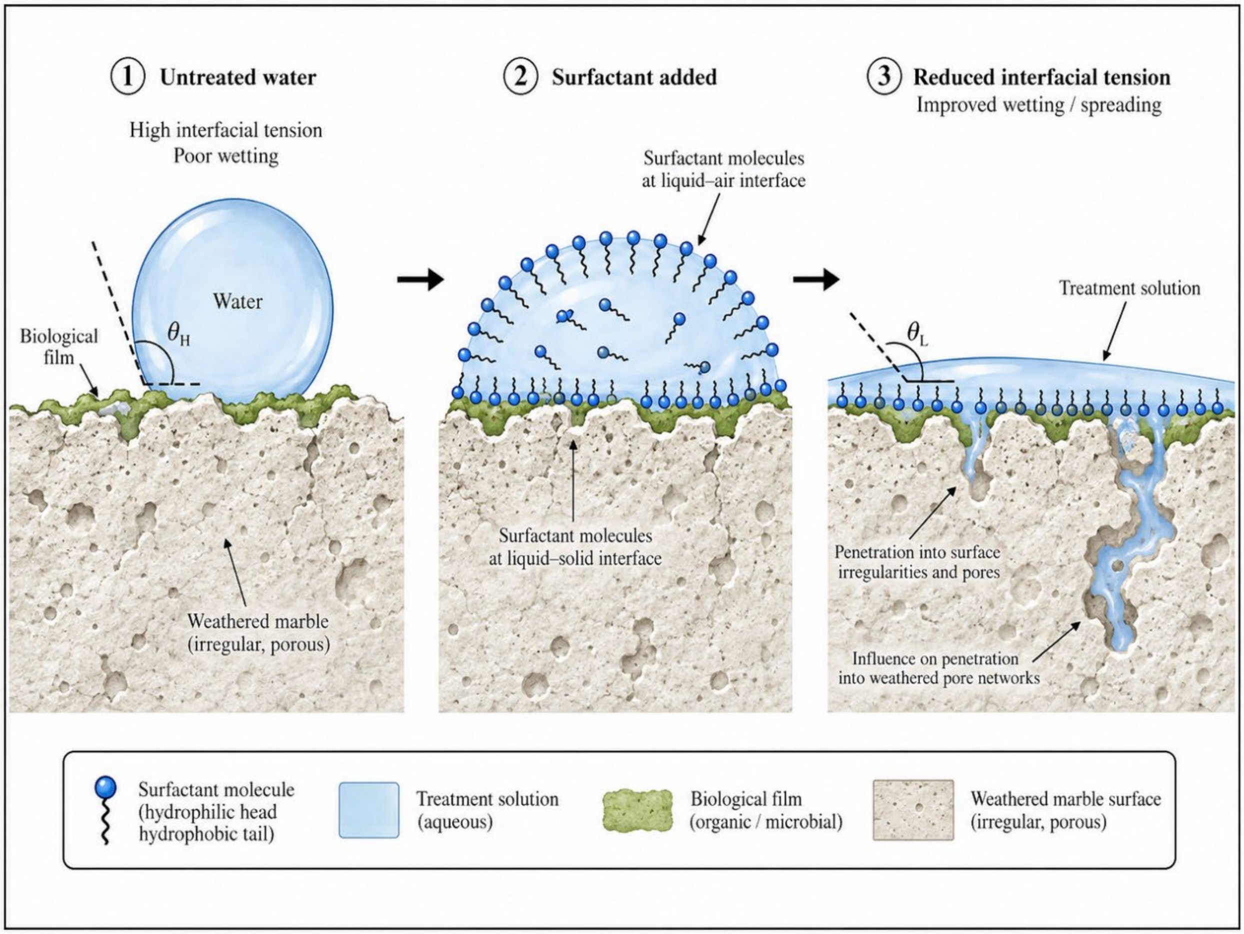
This property contributes to cleaning effectiveness because water alone may bead or move unevenly across some biological deposits. Improved wetting allows the treatment solution to reach a larger portion of the colony and can reduce the mechanical effort required to loosen attached material.

The same property has preservation implications. Improved wetting may also increase access to open grain boundaries, surface irregularities, and pores in weathered marble. Greater penetration is neither automatically beneficial nor automatically harmful; its significance depends on the condition of the substrate, the composition and concentration of the formulation, the duration of contact, and what occurs during subsequent rinsing and drying.

Surfactant behavior also changes with concentration. At sufficiently high concentrations, surfactant molecules can associate into aggregates such as micelles, altering solubilization, detergency, adsorption, and rinsing. Commercial formulations are designed around these relationships, which is one reason arbitrary changes in dilution can change both biological performance and treatment behavior.

Figure 5.3 illustrates a second consequence of quat amphiphilicity: reduced interfacial tension can improve wetting and spreading across biological films and irregular stone surfaces while also influencing penetration into weathered pore networks.

Figure 5.3: Surfactant Action



Note. *Conceptual schematic. Surfactants improve wetting by reducing interfacial tension, allowing treatment solutions to spread more effectively across biological films and irregular stone surfaces. Improved wetting can increase cleaning efficiency while also influencing penetration, retention, and subsequent rinsing within weathered pore networks.*

5.6. Interaction and Adsorption on Carbonate Surfaces

Quaternary ammonium compounds can associate with mineral and organic surfaces rather than remaining entirely in bulk solution. This process is commonly described as adsorption. Depending on the system, adsorption may involve electrostatic interactions, hydrophobic association, van der Waals forces, ion exchange, or interaction with organic matter and mineral impurities (Mohapatra et al., 2023).

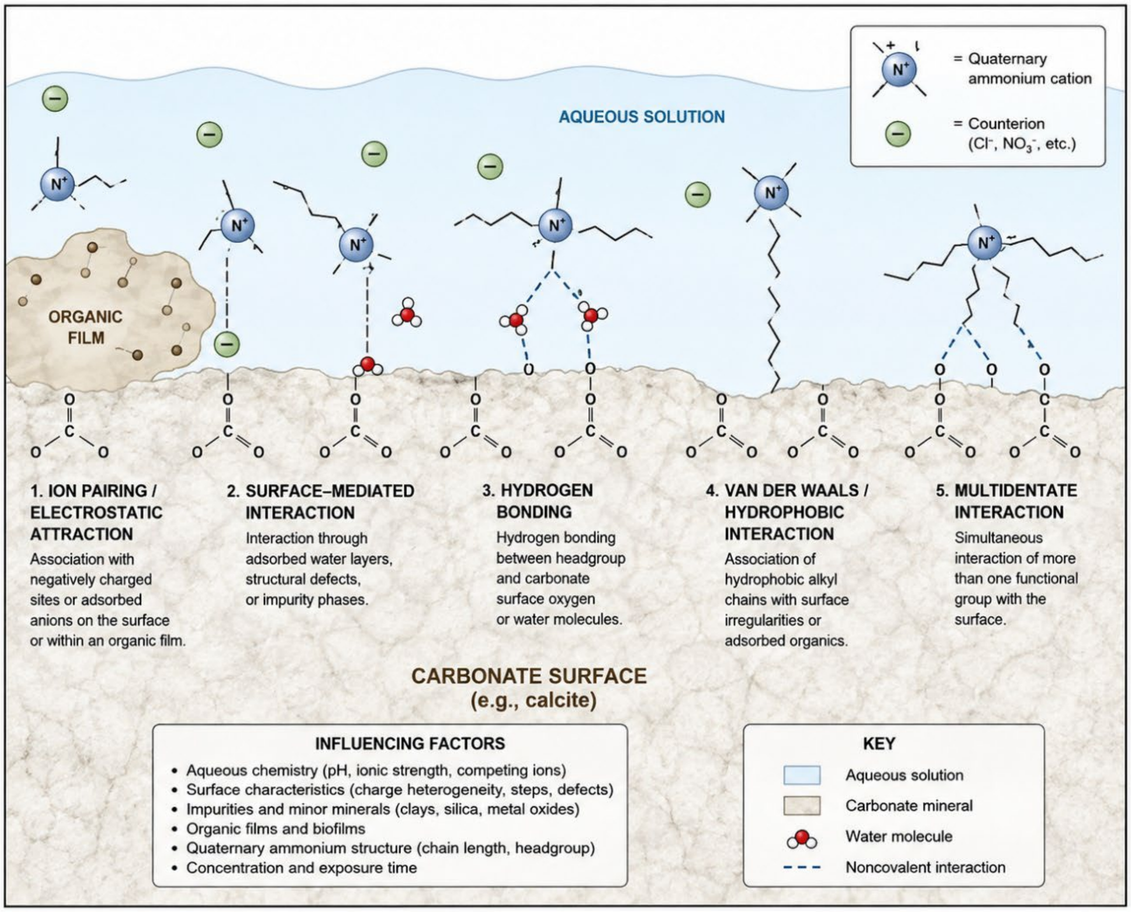
The behavior of calcite should not be simplified to a uniformly negatively charged surface that necessarily attracts every cationic molecule in the same manner. Surface charge and chemical speciation vary with pH, ionic strength, dissolved calcium and carbonate, carbon dioxide, crystal face, and solution history. Natural and weathered marble further complicates the system because it may contain silica, clay minerals, iron-bearing phases, atmospheric deposits, salts, biological films, and previous treatment materials.

A quat applied to historic marble may therefore interact with several different surfaces at once. Some molecular retention may occur on carbonate grains, while other material may associate more strongly with accessory minerals or organic biological matter.

Adsorption can contribute to residual antimicrobial activity by retaining active material near the treated interface, but persistence should not automatically be interpreted as either desirable or damaging. Conservation significance depends on how much remains, where it is located, how strongly it is retained, whether subsequent rainfall or rinsing displaces it, how it changes under ultraviolet and biological exposure, and whether it produces measurable alteration of the stone.

Figure 5.4 should be read in deliberate contrast with Figure 4.2. Whereas Figure 4.2 depicts confined crystal growth, Figure 5.4 illustrates possible interfacial association of quat molecules without assuming either crystal formation or attraction to a uniformly charged calcite surface.

Figure 5.4: Conceptual Interaction of Quaternary Ammonium Compounds with a Carbonate Surface



Note. *Conceptual interfacial model—not a quantitative adsorption model. Association of quaternary ammonium compounds with carbonate materials is influenced by aqueous chemistry, mineral-surface characteristics, impurities, organic films, compound structure, and concentration. Adsorption may occur through several interfacial mechanisms and should not be represented as the inevitable consequence of attraction to a uniformly charged calcite surface.*

5.7. Relationship to Inorganic Deterioration Salts

The distinction developed in Chapters 2 and 3 becomes particularly important when quaternary ammonium compounds are compared with the inorganic salts traditionally associated with stone deterioration (McDonnell & Russell, 1999; Gerba, 2015).

Sodium sulfate, magnesium sulfate, sodium chloride, and related compounds consist of comparatively small ions that can move readily with water when dissolved. Under appropriate conditions, they may become concentrated, crystallize, deliquesce, or undergo phase transitions within the pore network. Their deterioration potential has therefore been examined extensively through salt-weathering research (Oguchi & Yu, 2021; Lezzerini et al., 2022).

Quaternary ammonium cations are much larger organic structures with surface-active and hydrophobic properties. Depending on formulation and environment, they may adsorb at interfaces, associate with organic films, form aggregates in solution, or remain in noncrystalline residues. These behaviors differ substantially from the assumptions underlying classical models of inorganic crystallization pressure (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

The distinction does not mean that quaternary ammonium compounds can never form solid material or that their counterions are irrelevant. It means that a deterioration mechanism established for one chemical system cannot be transferred to another without evidence demonstrating the necessary sequence of dissolution, mobility, supersaturation, solid-phase formation, confinement, and material response.

5.8. Residues and the Crystallization Question

The question of whether quat residues crystallize like traditional deterioration salts lies at the center of the controversy examined by this paper. The answer requires greater precision than a simple yes or no (Kwaśniewska et al., 2020; Boyce, 2023).

After a quat-based formulation is applied to marble, its components may follow several pathways. Some may be removed during rinsing; some may remain dissolved temporarily in pore water; some may adsorb to mineral or biological surfaces; some may persist as dried organic films; and other ingredients may precipitate or become incorporated into mixed environmental deposits. Sunlight, rainfall, oxygen, microorganisms, and subsequent treatments can further alter what remains.

These possibilities should not all be described as crystallization. An adsorbed molecular layer differs fundamentally from a three-dimensional crystal growing from supersaturated solution. Likewise, a dried commercial formulation may contain several substances and cannot automatically be treated as though it were a pure crystalline active ingredient.

The conservation literature reviewed for this paper does not establish a general mechanism in which preservation-use quaternary ammonium compounds repeatedly dissolve, crystallize within marble pores, and generate pressure comparable with the well-documented behavior of sodium sulfate. At the same time, the available evidence is not sufficient to establish the long-term behavior of every quat, concentration, commercial formulation, or repeated-treatment history (Oguchi & Yu, 2021; Lezzerini et al., 2022).

The appropriate conclusion is therefore mechanistic rather than categorical: **classical salt-weathering damage should be demonstrated through evidence of the required physical process rather than inferred solely from the ionic classification of the treatment material.**

5.9. Residual Antimicrobial Activity

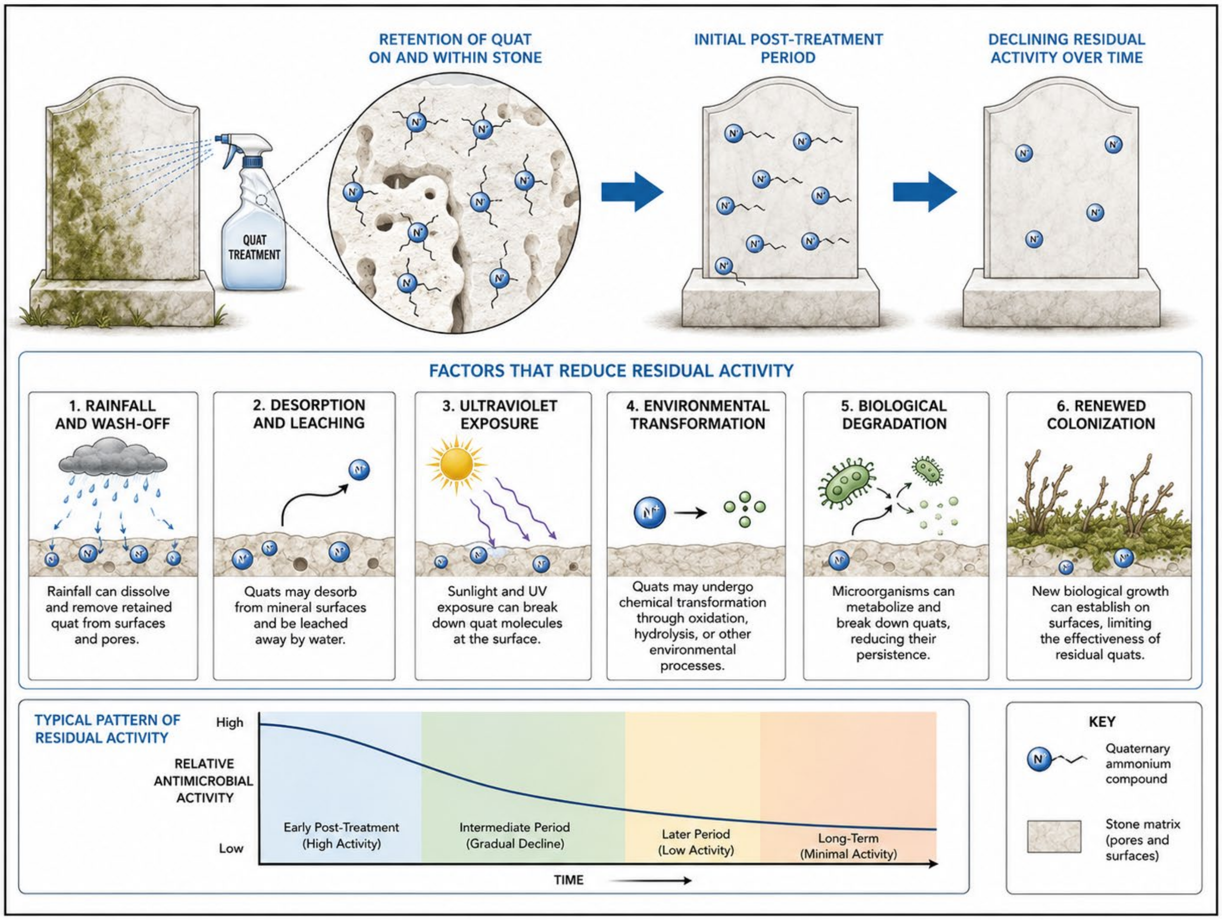
Some quat-based formulations continue to suppress microbial recolonization after the initial treatment period. This residual activity may result from active material retained at surfaces, within remaining biological films, or in near-surface regions accessible to recolonizing organisms (Mohapatra et al., 2023).

Residual control can provide a conservation benefit when it lengthens the interval between necessary treatments. Each cleaning event introduces wetting, mechanical contact, chemical exposure, handling, and the possibility of accidental damage. If biological control can be maintained with fewer interventions, cumulative treatment demands may be reduced.

The duration of residual activity is not fixed. Rainfall, ultraviolet radiation, organic matter, desorption, microbial degradation, environmental chemistry, surface orientation, and biological pressure all influence persistence. A damp, shaded monument surrounded by vegetation may recolonize relatively quickly even when the treatment performed well, while a more exposed stone may remain comparatively clean for longer.

Figure 5.5 extends the adsorption and retention discussion into treatment performance by illustrating how retained active material may temporarily suppress recolonization while environmental processes progressively diminish that effect.

Figure 5.5: Residual Activity of Quaternary Ammonium Compounds



> ***Note.*** *Conceptual representation of residual activity; the curve does not imply a fixed rate or duration. Some retained quat material may continue suppressing biological recolonization after treatment. Residual activity generally declines over time through rainfall and wash-off, desorption, ultraviolet exposure, environmental transformation, biological degradation, and renewed colonization.*

Residual activity should therefore be evaluated as one element of treatment performance rather than as evidence that persistent material is inherently beneficial. Its conservation value depends on the balance between reduced retreatment and the unresolved questions associated with long-term retention.

5.10. Complete Cleaner Formulations

The active biocide is only one component of a commercial cleaning product. Formulations may also contain secondary surfactants, buffers, pH modifiers, solvents, builders, stabilizers, preservatives, chelating agents, antifoaming agents, dyes, fragrances, or other proprietary ingredients (McDonnell & Russell, 1999; Gerba, 2015).

These components influence spreading, penetration, biological efficacy, drying, rinsing, residue formation, product stability, and interaction with the substrate. Two products containing the same nominal active ingredient may therefore perform differently, just as different versions of a product sold under the same name may not be chemically identical.

This distinction is particularly important when interpreting published testing. A study of an isolated quaternary ammonium compound can clarify mechanism, but it does not evaluate a complete commercial cleaner. Conversely, a product-specific performance study may reveal compatibility without identifying which individual ingredient produced the observed result.

Chapter 6 examines formulation chemistry in greater detail, while Chapter 7 considers how formulation-specific testing influenced the development and evaluation of monument cleaners.

5.11. Interaction with Weathered Marble

Historic marble presents a more complex treatment surface than newly cut laboratory stone. Enlarged grain boundaries, microfractures, increased permeability, biological films, atmospheric deposits, salts, previous repairs, and surface roughness can all influence the movement and retention of a cleaning solution (Kwaśniewska et al., 2020; Boyce, 2023).

A highly weathered surface may admit solution more readily while simultaneously possessing less mechanical resistance to brushing. Existing biological films may bind some of the active material before it reaches the mineral surface, while preexisting salts can change ionic strength and alter interfacial behavior. Previous coatings or repairs may further redirect wetting and drying.

These variables help explain why the same product can behave differently on apparently similar monuments. They also define the limits of a small visual test area. A test patch is valuable for identifying immediate staining, etching, discoloration, or surface loss, but it cannot establish how deeply formulation components have penetrated or how retained material will behave after years of environmental cycling.

Treatment decisions must therefore integrate product evidence with the condition of the individual monument rather than treating either factor as sufficient in isolation.

5.12. Interpreting the Published Evidence

Research relevant to quaternary ammonium compounds comes from several disciplines with different objectives. Microbiological and medical studies provide extensive information about antimicrobial mechanisms and organism susceptibility. Environmental research addresses adsorption, degradation, toxicity, and persistence. Mineral-surface studies examine interfacial behavior under controlled conditions, while conservation research evaluates treatments on stone or masonry (Mohapatra et al., 2023).

These forms of evidence are complementary but not equivalent. A disinfectant study may demonstrate antimicrobial efficacy without addressing marble. An adsorption experiment using purified calcite may clarify a possible surface interaction without reproducing weathered marble. A conservation study of a finished cleaner provides greater treatment relevance but may involve proprietary ingredients whose complete composition is unavailable.

Evidence should consequently be interpreted according to how directly it addresses the conservation question. Studies of the actual formulation on representative marble provide the strongest product-specific evidence. Work on related carbonate materials offers useful but more indirect support, while fundamental mineral, chemical, and microbiological studies are most appropriately used to explain mechanisms.

The current body of evidence supports the effectiveness of selected quat-based products for biological control and does not establish them as a recognized class of crystallization-driven deterioration salts. The evidence is considerably less complete regarding multi-decade repeated treatment, residue accumulation, environmental transformation, and behavior in severely weathered historic marble.

5.13. Current Knowledge Gaps

The principal uncertainties are increasingly well defined. Long-term studies are needed to determine how much quat material remains after realistic application and rinsing, whether retained material decreases or accumulates between treatments, and how deeply formulation components penetrate weathered marble (McDonnell & Russell, 1999; Gerba, 2015).

Additional research is also needed on adsorption and desorption under changing environmental conditions, ultraviolet and microbial degradation, behavior of counterions and supporting formulation ingredients, interaction with preexisting environmental salts, and differences among climates and marble types.

These questions should not be treated as evidence that current preservation practice is unsound. Neither should decades of use be interpreted as a substitute for direct long-term study. They identify the boundaries within which current conclusions should remain appropriately cautious.

5.14. Summary

Quaternary ammonium compounds are permanently charged organic surfactants whose structure supports antimicrobial activity and interfacial behavior distinct from that of the small inorganic ions most frequently associated with crystallization damage. Their use in monument conservation therefore cannot be evaluated adequately through the chemical label *salt* alone (Kwaśniewska et al., 2020; Boyce, 2023).

Selected quat formulations have demonstrated useful biological-cleaning performance, and residual activity may reduce the frequency of intervention. Their behavior nevertheless depends on the specific compound, complete formulation, concentration, substrate, environmental setting, and treatment history.

Current evidence does not establish that preservation-use quats generally reproduce the crystallization mechanisms associated with destructive inorganic salts. Important questions remain concerning retention, degradation, repeated application, and long-term interaction with weathered marble. Those uncertainties call for formulation-specific investigation and monitoring rather than categorical assumptions of either safety or harm.

6. Cleaner Formulations: Why Complete Composition Matters

6.1. Introduction

Commercial monument cleaners are formulated systems rather than isolated chemicals. The active antimicrobial ingredient may receive the greatest attention in product labels and preservation discussions, but the behavior of the finished cleaner also depends on the surfactants, buffers, pH modifiers, solvents, stabilizers, preservatives, builders, chelating agents, and other additives with which that active ingredient is combined (National Park Service, 2025c; Gerba, 2015).

These components determine whether the product remains stable in storage, spreads effectively across the stone, penetrates biological films, retains sufficient contact time, responds predictably to dilution, rinses from the surface, or leaves detectable material after treatment. Two products identifying the same active biocide may therefore behave differently, and a product reformulated over time may no longer reproduce the performance of the version originally tested.

A conservation assessment should consequently address the complete product to the extent that reliable information is available. This chapter examines the principal functions performed by formulation components and explains why whole-product testing provides stronger evidence of treatment compatibility than ingredient labels alone.

6.2. What Is a Formulation?

A formulation is a deliberately designed combination of ingredients intended to perform as a single product. In a biological cleaner, the active ingredient must be maintained in a usable form, delivered to the target organisms, retained for an appropriate contact period, and applied under conditions that permit practical field use (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Supporting ingredients may control viscosity, wetting, foaming, pH, solubility, storage stability, evaporation, microbial contamination of the packaged product, and compatibility with application water. Some may be present at low concentrations but still influence treatment behavior substantially.

The function of an ingredient therefore cannot be judged only by its proportion of the final mixture. A buffer present at modest concentration may determine whether the product remains within a useful pH range, while a small quantity of surfactant may change wetting enough to alter penetration. Conversely, fragrances or colorants may provide consumer appeal without contributing to a conservation objective.

Understanding formulation is thus less about identifying a long list of chemicals than about determining what each component contributes to the performance of the finished treatment.

6.3. Active Ingredients

The active ingredient provides the principal antimicrobial or cleaning function claimed by the product. Quat-based monument cleaners may contain benzalkonium chlorides, DDAC, related quaternary ammonium compounds, or combinations of these materials (National Park Service, 2025c; Gerba, 2015).

Active concentration influences biological efficacy, the amount of chemical introduced, worker exposure, environmental loading, and the quantity that may require subsequent removal or degradation. Applying a formulation at a higher concentration than recommended does not necessarily improve conservation performance. Once an effective biological dose has been reached, additional material may offer diminishing benefit while increasing residue and rinsing demands.

Labels and safety data sheets may identify active ingredients as concentration ranges or broad chemical families. Such information is useful but should not be interpreted as a complete formulation description.

6.4. Surfactants

Surfactants improve wetting and spreading by altering interfacial tension. In biological cleaning, this can increase contact with algae, fungi, biofilms, and irregular stone surfaces while helping suspend material loosened during treatment (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Quaternary ammonium compounds can themselves function as cationic surfactants, but commercial products may contain additional surfactants to modify foam, detergency, water compatibility, spreading, or rinsing. Nonionic surfactants are frequently used in formulated cleaners because they can modify wetting without introducing a competing ionic charge.

Improved wetting may reduce the mechanical effort required to remove biological material, which can be beneficial on weathered marble. The same effect may also increase access to open pores and grain boundaries. Surfactant selection must therefore balance biological contact with controllable treatment penetration.

6.5. Buffers

Buffers stabilize pH when a solution is diluted, stored, or exposed to materials capable of changing its acidity or alkalinity. Consistent pH can support product stability and predictable antimicrobial performance (National Park Service, 2025c; Gerba, 2015).

From a stone-conservation perspective, buffer chemistry warrants attention because some buffering systems contain inorganic ions that may remain after drying. A residue identified after treatment may therefore originate from supporting formulation components rather than the active biocide itself.

The conservation significance of a buffer cannot be inferred simply from the fact that it contains an ionic compound. Composition, concentration, solubility, rinsability, and behavior under environmental cycling all matter. The broader implication is that residue findings must be linked to the entire formulation rather than attributed automatically to the most recognizable ingredient on the label.

6.6. pH Modifiers

Marble's calcite content makes it particularly sensitive to acidic solutions. Strong acids can dissolve carbonate minerals directly, roughen surfaces, and accelerate loss of inscription detail. Preservation cleaners intended for marble are therefore generally formulated to avoid strongly acidic conditions (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Strong alkalinity should not be treated as automatically harmless. Highly alkaline products may contain builders or other reactive components and can interact with deposits, metals, paints, previous repairs, and formulation ingredients in ways that require evaluation.

pH also describes only one aspect of solution chemistry. Two products with similar measured pH values may differ substantially in buffering capacity, surfactants, residue, biological efficacy, and interaction with the substrate. A near-neutral or mildly alkaline pH may be reassuring, but it cannot independently establish compatibility.

6.7. Solvents and Carriers

Water is the principal carrier in many monument-cleaning formulations, although water-miscible organic solvents may also be present. These materials influence ingredient solubility, spreading, evaporation rate, contact time, and product stability (National Park Service, 2025c; Gerba, 2015).

A rapidly evaporating carrier may shorten the effective dwell period and concentrate less volatile components at the drying surface. A slower system may extend biological contact but require more careful management of runoff or rinsing. Organic solvents may also introduce worker-safety, odor, or environmental considerations not associated with water alone.

The suitability of the carrier system therefore depends on the purpose of the formulation and the material being treated. A solvent useful in a specialized cleaning treatment may provide no meaningful benefit in routine biological cleaning of porous marble.

6.8. Stabilizers

Commercial formulations must remain sufficiently stable between manufacture and use. Stabilizers can prevent ingredient degradation, phase separation, oxidation, or loss of antimicrobial performance during storage (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

These components may contribute little directly to visible cleaning, but they help ensure that a product applied late in its shelf life behaves similarly to one applied soon after manufacture. Their conservation significance depends on their specific chemistry and on whether they remain on or within the stone after treatment.

Because stabilizers may be proprietary or present below hazard-disclosure thresholds, finished-product testing becomes particularly important when complete composition is unavailable.

6.9. Preservatives

Cleaning formulations may require their own preservatives to prevent microbial growth within the container. These materials can be chemically distinct from the principal antimicrobial active ingredient and are generally included at comparatively low concentration (National Park Service, 2025c; Gerba, 2015).

Their presence illustrates the complexity of commercial formulation even when they do not dominate treatment performance. A safety data sheet may identify the major hazardous active ingredient while omitting other compounds that influence shelf stability or field behavior.

For conservation purposes, preservatives should be considered as part of the complete product rather than assumed either consequential or inconsequential without supporting evidence.

6.10. Fragrances, Dyes, and Other Consumer Additives

Fragrances, decorative dyes, optical brighteners, and similar additives may improve consumer appeal, brand recognition, or the perceived experience of cleaning, but they generally provide little direct preservation benefit (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Colorants are of particular concern on porous light-colored stone because staining may be difficult to reverse once material has entered weathered grain boundaries. Fragrances and other organic additives introduce additional chemical components without necessarily improving treatment performance.

Some products use temporary color indicators for a legitimate application purpose, and such ingredients should be evaluated according to their function and compatibility. The general conservation preference, however, is to avoid unnecessary formulation complexity when an ingredient contributes no meaningful preservation benefit.

6.11. Proprietary Formulations and Safety Data Sheets

Manufacturers commonly protect portions of commercial formulations as proprietary information. Product labels and safety data sheets provide essential information about hazards, active ingredients, required precautions, and regulatory requirements, but they are not intended to disclose a complete chemical recipe (National Park Service, 2025c; Gerba, 2015).

Nonhazardous ingredients, exact concentrations, buffer systems, surfactant blends, stabilizers, and formulation changes may therefore remain undisclosed. Two products that appear similar on their safety data sheets may behave differently, and two versions of the same product name may not be chemically identical.

An SDS remains indispensable for worker safety, storage, disposal, and emergency planning. It should not be treated as a substitute for material-compatibility testing.

Where complete composition is unavailable, treatment records become especially important. Product name, manufacturer, purchase date, lot or batch when available, dilution, and date of use can help future investigators determine which formulation was actually applied.

6.12. Laboratory and Field Testing

Evaluation of a monument cleaner should extend beyond immediate visual improvement. A product may remove biological staining effectively while altering color, roughness, moisture behavior, surface cohesion, or residue distribution. Conversely, a material with excellent laboratory compatibility may prove operationally ineffective if it requires excessive brushing or frequent retreatment (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Useful testing therefore considers several outcomes together: biological efficacy, surface change, material loss, residue, penetration, recolonization, environmental response, and repeated treatment. Controlled laboratory studies allow products to be compared under standardized conditions, while field studies expose them to realistic weather, biological pressure, rainfall, pollution, and seasonal cycling.

Neither form of testing is sufficient alone. Laboratory specimens may not reproduce heavily weathered marble, and short-term field observation may fail to reveal slow changes. Strong product evaluation develops from convergence among controlled testing, analytical characterization, field performance, and long-term monitoring.

6.13. Lessons from NCPTT–National Cemetery Administration Testing

The comparative monument-cleaner research conducted through the National Center for Preservation Technology and Training in cooperation with the National Cemetery Administration provides a particularly useful example of why formulations must be evaluated as finished products (National Park Service, 2025c; Gerba, 2015).

An earlier formulation of one commercial preservation cleaner produced fine surface residues during accelerated-weathering testing. The observation prompted further examination and product reformulation. Subsequent testing of the revised formulation did not reproduce the earlier residue under the test conditions, while biological-cleaning performance remained strong.

The broader significance of this result lies in the formulation change rather than in attaching a permanent judgment to a product name. A concern observed in one version could be modified through changes to the formulation, demonstrating that residue behavior was not adequately explained by identifying the broad active-ingredient class alone.

The case also illustrates why published results should specify the formulation or product version evaluated. Findings associated with an earlier composition should not automatically be applied to later versions, and favorable findings for a revised formulation should not be projected backward onto the original product.

Chapter 7 examines the study and its implications in greater detail.

6.14. Concentration and Dilution

Dilution determines the amount of active ingredient and supporting formulation components delivered to the stone. Application below the effective range may provide inadequate biological control and encourage unnecessary repeat treatment. Application above the recommended range may increase chemical loading, residue, worker exposure, environmental release, and rinsing demand without producing a proportionate improvement (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

Field dilution should therefore be measured rather than estimated. The manufacturer's current instructions for the specific formulation should govern unless a qualified conservation protocol provides a documented alternative.

Application water can also influence the resulting mixture. Hardness, pH, iron, manganese, chloride, sulfate, and other dissolved constituents may affect stability, staining, precipitation, or biological performance. Where local water presents unusual chemistry, it should be treated as another formulation variable rather than assumed to be inert.

6.15. Application Conditions and Product Performance

The performance observed in the field reflects an interaction between the formulation and the conditions under which it is used. Temperature, humidity, wind, sunlight, stone moisture, contact time, and drying rate all influence treatment behavior (National Park Service, 2025c; Gerba, 2015).

Pre-wetting may reduce the initial concentration entering accessible pores and promote more even distribution. Dwell time allows the active ingredients to interact with biological material, while excessive drying may concentrate nonvolatile components. Rinsing removes loosened material and reduces the amount of soluble formulation remaining near the surface, but it does not prove complete molecular removal from weathered marble.

Mechanical action introduces another independent variable. A suitable cleaner can still produce an unacceptable result if brushing removes weakened calcite grains. Conversely, gentle handling cannot make a chemically incompatible formulation appropriate.

Product compatibility and controlled application should therefore be treated as complementary requirements rather than as substitutes for one another.

6.16. Preservation Criteria for Product Selection

A cleaner intended for historic marble should be selected according to a defined conservation objective and the condition of the monument. Relevant questions include whether treatment is necessary, whether the marble is cohesive enough to tolerate wetting and gentle contact, whether the complete formulation has credible compatibility evidence, and whether the product can be applied and managed safely under the available field conditions (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

The expected treatment benefit should also be considered. A formulation that provides effective biological control with limited mechanical effort and reasonable retreatment intervals may impose less cumulative intervention than a product requiring repeated scrubbing or frequent application.

Selection should therefore emphasize documented performance rather than a single marketing claim, ingredient, pH value, or immediate visual result.

6.17. Preservation Products and Household Cleaners

A product developed for historic stone is not automatically compatible with every monument, but it generally provides a more defensible starting point than a household product designed for kitchens, bathrooms, siding, laundry, or general disinfection (National Park Service, 2025c; Gerba, 2015).

Household cleaners may contain oxidants, acids, strong alkalinity, abrasives, fragrances, dyes, thickeners, builders, brighteners, or surfactant combinations optimized for materials very different from weathered marble. Their performance objectives often emphasize speed, appearance, foam, scent, or broad soil removal rather than long-term interaction with historic fabric.

Preservation-specific products are more likely to provide substrate guidance, controlled dilution instructions, treatment limitations, and some form of conservation-oriented evaluation. Those advantages should not be converted into an assumption of universal safety. Product evidence and monument condition remain necessary.

A lightly colonized and cohesive stone may require little more than water and gentle mechanical cleaning, while severely sugared marble may be unsuitable for cleaning regardless of the product selected.

Table 6-1. Functional Components of Monument Cleaner Formulations and Their Conservation Considerations

Component	Principal Function	Potential Conservation Benefit	Potential Conservation Concern
Active biocide	Inactivates or suppresses biological growth	Reduces biological activity and may improve legibility or delay recolonization	Residue, toxicity, persistence, and compatibility vary by compound and concentration

Component	Principal Function	Potential Conservation Benefit	Potential Conservation Concern
Cationic surfactant	Improves wetting and may provide antimicrobial activity	Increases contact with biological films and can reduce mechanical effort	May adsorb or penetrate weathered surfaces; behavior depends on formulation and substrate
Nonionic or secondary surfactant	Modifies wetting, spreading, detergency, and rinsing	Helps loosen biological material and distribute the solution evenly	May remain as a film if excessive or inadequately removed
Buffer	Stabilizes pH	Supports consistent product performance	Some systems may contribute inorganic ions or persistent residues
pH modifier	Adjusts acidity or alkalinity	Helps maintain a range compatible with the intended treatment	Strong acidity can dissolve calcite; strong alkalinity and reactive builders may also create concerns
Solvent or carrier	Dissolves and transports formulation ingredients	Supports uniform delivery and controls contact time	Influences penetration, evaporation, worker exposure, and concentration during drying
Builder or water conditioner	Improves detergency or manages water hardness	May increase performance under difficult water conditions	Can contribute additional ions, deposits, or alkalinity
Chelating agent	Binds selected metal ions	May assist specialized stain or water-hardness treatment	Some chelators can interact with calcium-bearing substrates under unfavorable conditions
Stabilizer	Maintains product integrity during storage	Promotes consistent performance throughout shelf life	Composition may be proprietary and residue behavior incompletely documented
Preservative	Prevents microbial spoilage in the product	Maintains formulation quality	Adds another biologically active compound,

Component	Principal Function	Potential Conservation Benefit	Potential Conservation Concern
			generally at low concentration
Antifoaming or viscosity modifier	Controls handling and application properties	May improve field usability	May add persistent organic material without direct conservation benefit
Dye or colorant	Provides product identification or coverage indication	May have a practical application-control function	Potential staining or unnecessary residue on porous light-colored stone
Fragrance	Modifies odor	Little direct conservation benefit	Adds unnecessary volatile or persistent compounds
Water	Serves as carrier, diluent, and rinse medium	Enables controlled application and removal	Dissolved minerals, iron, manganese, pH, and hardness may influence treatment

The presence of a component in Table 6-1 does not establish either compatibility or harm. Its significance depends on chemical identity, concentration, interaction with the remaining formulation, substrate condition, environmental exposure, and treatment procedure.

6.18. Summary

Commercial monument cleaners should be evaluated as complete chemical systems. The active biocide may determine the principal antimicrobial mechanism, but surfactants, buffers, pH modifiers, carriers, stabilizers, preservatives, and other additives influence how that activity is delivered and how the product interacts with historic marble (Mohapatra et al., 2023; Kwaśniewska et al., 2020).

This systems perspective explains why products containing similar active ingredients can produce different results and why formulation changes can alter residue behavior without changing the broad chemical class of the cleaner.

Whole-product testing, current technical documentation, realistic application conditions, treatment records, and long-term observation therefore provide a stronger basis for conservation decisions than ingredient labels alone.

7. NCPTT–National Cemetery Administration Research: Scientific Evaluation of Monument Cleaners

7.1. Introduction

Modern monument-cleaning guidance in the United States reflects a broader transition from appearance-driven maintenance toward treatment informed by conservation science. Earlier cleaning methods were often judged by how rapidly they removed staining or returned a light-colored surface. As the consequences of abrasion, inappropriate chemicals, high-pressure washing, and repeated intervention became better understood, preservation practice increasingly emphasized retention of original material and long-term compatibility (National Park Service, 2025b, 2025c).

An important contribution to that development came from comparative cleaner research conducted by the National Center for Preservation Technology and Training in cooperation with the Department of Veterans Affairs National Cemetery Administration. NCPTT is part of the National Park Service, while the National Cemetery Administration is responsible for maintaining large numbers of government-furnished headstones and markers. The research discussed in this chapter is therefore most accurately described as **NCPTT–NCA cleaner research** rather than broadly as a National Park Service cemetery-management program.

The significance of the work extends beyond the individual products tested. It demonstrated a method for evaluating monument cleaners according to biological effectiveness, surface change, material compatibility, residues, recolonization, environmental exposure, and the consequences of repeated treatment rather than relying on immediate appearance alone.

7.2. The Preservation Challenge

Government-furnished headstones and cemetery monuments are exposed to widely varying climates, biological communities, pollutants, soils, maintenance histories, and moisture conditions. Marble markers may remain structurally sound for many decades while gradually developing staining, biological growth, granular weathering, cracks, or reduced inscription definition (National Cemetery Administration, n.d.; National Park Service, 2025a).

Routine maintenance must therefore address two competing objectives. Biological colonization and environmental deposits may obscure inscriptions or contribute to undesirable moisture conditions, but the stone itself can be weakened by age and exposure. A method capable of producing a rapid visual result is not a successful preservation treatment if it also removes calcite grains, rounds lettering, corrodes adjacent metal, or creates the need for frequent retreatment.

Historically, cemetery maintenance sometimes relied on household bleach, strong detergents, acidic products, abrasives, wire brushes, or commercial pressure washing. Many of these approaches were accessible and visually effective, but their treatment objectives were not necessarily aligned with conservation of weathered historic surfaces.

The federal research program sought to evaluate cleaner performance using measurable criteria rather than familiarity, speed, or appearance.

7.3. From Visual Cleaning to Conservation Evaluation

Before-and-after photographs are useful documentation, but they cannot establish material compatibility by themselves. A surface may look dramatically cleaner even when some original material has been removed. Conversely, a treatment that leaves modest discoloration may have successfully reduced biological activity while preserving fragile surface fabric (Striegel et al., 2016).

Scientific cleaner evaluation therefore asks several questions simultaneously. Does the formulation control the organisms present? Does it alter color, roughness, tooling, or carved detail? Does measurable material remain after treatment? How rapidly does biological colonization return? Does repeated environmental cycling reveal changes not apparent immediately after cleaning?

This broader definition of performance is important because the desirable outcomes do not always point in the same direction. A product that removes growth very quickly may produce undesirable surface change, while an extremely gentle treatment may require enough brushing or repetition to create its own mechanical burden.

The appropriate objective is not maximum cleaning power. It is sufficient cleaning performance with acceptable material and environmental consequences.

7.4. Accelerated Weathering and Comparative Testing

The long service life of cemetery monuments makes cleaner evaluation difficult. Potential effects may develop gradually over years or decades, far longer than an ordinary research program can observe directly. Accelerated-weathering methods provide one means of comparing products within a practical period (National Park Service, 2025b, 2025c).

Test specimens can be exposed repeatedly to controlled wetting and drying, temperature change, relative-humidity variation, ultraviolet radiation, or other environmental stresses.

When similar samples are treated and cycled together, researchers can compare residue formation, color change, biological performance, or material alteration under consistent conditions.

Such testing is most useful for **comparative assessment**. It can reveal that one formulation behaves differently from another under a defined protocol and can identify observations that warrant further study. It does not convert laboratory cycles directly into an exact number of outdoor years or reproduce the full complexity of natural cemetery exposure.

Field monitoring therefore remains a necessary complement. Natural rainfall, sunlight, biological recolonization, pollutants, temperature cycles, soil contact, and monument-scale drying introduce variables that laboratory specimens cannot reproduce fully.

7.5. Evaluation Criteria

The NCPTT–NCA research broadened cleaner evaluation beyond biological removal. Cleaning efficacy remained important, but it was considered alongside changes to the treated material (National Cemetery Administration, n.d.; National Park Service, 2025a).

Biological performance addressed whether the treatment controlled or removed the organisms present. Surface assessment considered color, legibility, texture, and whether the treatment created an appearance inconsistent with the weathered stone. Material compatibility examined changes in roughness, mineral cohesion, polish, carved detail, or other surface characteristics. Residue assessment considered what remained after treatment and whether subsequent weathering changed that material.

Biological recolonization added a longer-term dimension. A treatment that required frequent reapplication might expose the monument to more wetting and mechanical action than a formulation that delayed biological return. Repeated-treatment performance therefore became relevant alongside the outcome of a single cleaning event.

Taken together, these criteria established a preservation-oriented definition of performance: **the cleaner must address the unwanted condition without creating a greater long-term burden on the monument.**

7.6. Findings Across Cleaner Categories

Comparative evaluation reinforced concerns about several traditional maintenance approaches. Mechanical abrasion may remove algae, lichens, or surface deposits efficiently, but the mechanism of removal can also detach weathered carbonate grains.

Wire brushes and hard abrasives are especially incompatible with friable marble because their effectiveness depends in part on cutting or scouring the surface (Striegel et al., 2016).

Commercial high-pressure washing creates a related risk. High-velocity water can detach weakened grains, enlarge existing cracks, round carved edges, and drive moisture into fractures or joints. This should be distinguished from controlled low-pressure water application used by trained practitioners after assessment and testing. The conservation concern is not water delivered through equipment in the abstract, but excessive force applied to a substrate whose surface strength may already be reduced.

Bleach-based products can provide rapid biological inactivation and visible lightening. Their conservation assessment must also consider broad oxidative reactivity, high alkalinity, possible interaction with adjacent metals and vegetation, formulation additives, runoff, and the limited duration of antimicrobial activity after the hypochlorite is consumed or decomposes.

These findings encouraged greater use of treatment systems developed specifically for historic masonry and evaluated according to preservation rather than household-maintenance objectives.

7.7. Evaluation of Quaternary Ammonium-Based Cleaners

Preservation-specific cleaners containing quaternary ammonium compounds demonstrated effective biological control within the federal comparisons. Their surfactant behavior improved contact with biological films, and some formulations continued suppressing recolonization after the initial treatment (National Park Service, 2025b, 2025c).

The possibility of delayed recolonization is relevant because it may reduce the frequency with which a stone is wetted, brushed, and handled. That potential benefit should not be generalized to every quat formulation, however. Residual performance depends on the product, concentration, exposure, rainfall, climate, surface chemistry, organisms present, and the condition of the stone.

Testing also identified an important concern. An earlier formulation of a commercially available preservation cleaner produced fine surface residues during accelerated weathering. Because visible deposits can indicate formulation incompatibility or movement of soluble material, the observation warranted investigation.

The scientific significance of the finding lies in what happened next.

7.8. Reformulation and Retesting

Following identification of the residue, the commercial cleaner was reformulated. When the revised formulation underwent additional testing, the earlier visible residue was no longer observed under the test conditions, while biological-cleaning performance remained favorable (National Cemetery Administration, n.d.; National Park Service, 2025a).

This sequence demonstrates how conservation testing can function constructively. The purpose is not simply to divide products permanently into categories of acceptable and unacceptable. Testing can identify a problem, help isolate formulation characteristics requiring attention, encourage modification, and provide a basis for evaluating the revised product.

The outcome also illustrates why product-specific findings must remain linked to the formulation tested. A cleaner sold under one commercial name may change chemically over time. Results associated with an earlier formulation cannot automatically characterize later versions, just as favorable results for a revised product cannot establish the performance of its predecessor.

7.9. Understanding the Residue Finding

The residue observation has sometimes been interpreted more broadly than the research supports. The test identified a surface deposit associated with a particular commercial formulation under defined accelerated-weathering conditions. It did not demonstrate that every quaternary ammonium compound inherently produces damaging salt crystallization in marble (Striegel et al., 2016).

A formulated cleaner contains more than its active antimicrobial ingredient. Buffers, supporting surfactants, water conditioners, stabilizers, or other components may influence deposit formation. Without identifying the complete residue and its physical behavior, the observation cannot be attributed automatically to the quat cation alone.

The reformulation result reinforces this interpretation. Changing the finished product changed the observed outcome.

The study should therefore be understood as evidence that **formulation-specific residues can occur and should be investigated**, not as proof of a universal crystallization mechanism associated with the entire quaternary ammonium class.

7.10. Best-Practice Implications

Guidance informed by this research emphasizes treatment only when a preservation objective justifies intervention and when the monument remains suitable for cleaning.

Marble that is severely sugared, delaminated, structurally unstable, extensively cracked, or otherwise fragile may require professional assessment rather than routine treatment (National Park Service, 2025b, 2025c).

For suitable monuments, preservation practice favors cleaners developed or credibly evaluated for historic masonry, application within the specified concentration range, soft natural- or synthetic-bristle tools appropriate to the stone, controlled water delivery, and avoidance of unnecessarily aggressive abrasion.

Treatment frequency should respond to condition rather than a desire to maintain a continuously new appearance. Documentation should record the product, dilution, treatment date, tools, environmental conditions, and observations so that future performance can be evaluated against a known treatment history.

The value of these recommendations lies in the system they create rather than in any one procedural step. Treatment need, stone condition, formulation, application, and follow-up observation must remain connected.

7.11. Pre-Wetting and Rinsing in Context

Pre-wetting is commonly used to reduce the concentration gradient between a cleaner and dry porous stone. Clean water already occupying accessible near-surface pores can limit immediate uptake of concentrated solution, promote more even spreading, and provide additional working time (National Cemetery Administration, n.d.; National Park Service, 2025a).

The process should not be described as complete saturation or as an impermeable barrier. Weathered marble contains pores and fractures of different sizes, and water does not fill them uniformly. Treatment solution can still enter the stone.

Rinsing serves a complementary function by diluting and removing loosened biological material and soluble formulation components from accessible surfaces and pores. Its effectiveness depends on rinse volume, water chemistry, stone condition, surface geometry, and the interaction of the cleaner with the substrate.

Neither pre-wetting nor rinsing can compensate for an unsuitable formulation. Their value lies in controlling the exposure associated with an otherwise appropriate treatment.

7.12. Limitations of the Research

The federal cleaner studies provide valuable comparative evidence, but they do not reproduce every condition encountered by historic cemetery monuments (Striegel et al., 2016).

Accelerated weathering compresses selected environmental stresses into a manageable experimental period and may emphasize some processes more strongly than natural exposure. Laboratory specimens may also differ from historic headstones in quarry source, grain size, pore connectivity, biological films, previous treatments, existing salts, and degree of sugaring.

Climate adds further variability. A formulation used in a humid, shaded cemetery may not behave identically in a dry inland environment, a coastal site exposed to aerosols, or a region experiencing repeated freeze-thaw cycling.

Commercial formulations continue to evolve as well. A study describes the product tested at a particular time, not every formulation that may later carry the same name.

The appropriate use of the research is therefore comparative and evidentiary rather than absolute. It informs treatment decisions while leaving room for refinement as longer-term and more representative data become available.

7.13. Influence on Preservation Practice

The significance of the NCPTT–NCA research extends beyond the individual federal markers for which the work was undertaken. Its broader contribution was to demonstrate that monument-cleaning methods can be evaluated using conservation criteria rather than tradition or immediate visual preference (National Park Service, 2025b, 2025c).

That framework has influenced cemetery managers, preservation organizations, professional conservators, historical societies, and volunteer groups. It encourages practitioners to consider whether a monument requires treatment, whether the material is sufficiently sound, whether the selected formulation has relevant evidence, and whether the result will reduce or increase future intervention.

For volunteer organizations in particular, this approach provides an important model of accountability. Unexpected findings are reasons to investigate, not to defend a familiar method. Products can be reformulated, procedures can change, and treatment recommendations can evolve without undermining the larger preservation mission.

7.14. Broader Lessons for Conservation

Several conclusions from the federal cleaner research extend beyond monument cleaning.

Immediate appearance is an incomplete measure of treatment success. Compatibility should be evaluated at the level of the finished formulation rather than from one ingredient. Accelerated testing is useful for identifying differences among products but should be paired with long-term field evidence. Product reformulation can materially change preservation behavior, making formulation dates and treatment records important (National Cemetery Administration, n.d.; National Park Service, 2025a).

The research also demonstrates the value of specifying the desired outcome before selecting a treatment. A cleaning system should not be optimized simply for maximum biological removal. It should achieve sufficient control while limiting material loss, unnecessary residues, environmental exposure, and future treatment demand.

These principles are more durable than any individual product recommendation because they remain applicable as formulations and conservation technologies change.

7.15. Summary

The NCPTT–National Cemetery Administration cleaner research helped establish a more systematic framework for evaluating monument-cleaning products. Biological effectiveness was considered alongside material compatibility, residue formation, surface change, recolonization, and performance after environmental cycling (Striegel et al., 2016).

The observation of residue associated with an earlier commercial formulation was scientifically important because it prompted further investigation and reformulation. Subsequent testing produced a different outcome, illustrating that compatibility may depend on the complete product rather than the broad chemical class of its active ingredient.

The lasting contribution of this work is therefore methodological. Cleaner selection should be based on evidence relevant to the formulation and substrate, treatment should be proportionate to monument condition, and unexpected outcomes should become opportunities for further study and improvement.

8. International and Interdisciplinary Conservation Research

8.1. Introduction

The federal cleaner studies examined in Chapter 7 form only one part of the scientific literature relevant to historic marble preservation. International conservation organizations, universities, research institutes, materials laboratories, microbiologists, geologists, and conservation scientists have spent decades examining moisture transport, salt weathering, crystallization, carbonate deterioration, biological colonization, cleaning, consolidation, and environmental exposure (Doehne & Price, 2010; Oguchi & Yu, 2021).

Institutions such as the Getty Conservation Institute, Historic England and its predecessor organizations, ICCROM, ICOMOS, NCPTT, and academic research programs approach these questions from different perspectives. Some concentrate on fundamental physical chemistry, others on treatment performance, professional guidance, architectural conservation, archaeology, or preventive care.

The value of this literature lies less in identifying a single universal treatment method than in establishing the scientific framework through which treatment should be evaluated. The evidence consistently demonstrates that deterioration develops through interactions among material properties, environment, moisture, biological activity, chemical compounds, and previous interventions.

This chapter synthesizes that broader evidence thematically rather than organizing it as a series of researcher biographies. Individual contributions remain important and should be recognized through the manuscript's final citation system, but the present purpose is to clarify how the major areas of research inform the central question of this paper.

8.2. The International Conservation Evidence Base

Stone-conservation evidence comes from several kinds of research, each answering a different type of question.

Fundamental materials studies examine pore structure, capillary transport, mineral dissolution, crystallization thermodynamics, surface chemistry, and mechanical response. These investigations often use purified minerals or carefully prepared specimens because controlling variables allows individual mechanisms to be isolated (Historic England, 2021; American Institute for Conservation, 1994).

Applied conservation studies examine treatments on stone samples, buildings, sculpture, archaeological material, or monuments. They are more directly relevant to preservation practice but may contain greater variability in substrate, exposure, and treatment history.

Government and institutional guidance translates research and professional experience into field recommendations. Such documents are particularly useful for treatment procedures and risk management, although they often synthesize rather than generate primary experimental evidence.

Microbiological, environmental, and industrial studies provide additional information concerning antimicrobial mechanisms, adsorption, degradation, toxicity, and persistence. Their findings can inform monument conservation when the mechanism is transferable, but they should not be presented as direct stone-compatibility studies when historic marble was not examined.

The strength of a conclusion therefore depends partly on how closely the evidence matches the material, treatment, and outcome under consideration.

8.3. Moisture, Salts, and Environmental Cycling

International research on porous stone has demonstrated that salt-related deterioration cannot be separated from moisture transport and environmental cycling. Dissolved ions move with water, while evaporation, temperature, and humidity influence where solutions become concentrated and when solid phases form (Pinna, 2014).

The amount of salt present is only one variable. Distribution, pore geometry, supersaturation, nucleation, phase behavior, drying rate, and stone strength all influence whether deterioration occurs. A conspicuous efflorescent deposit may indicate substantial salt movement without producing the same mechanical consequences as a smaller quantity repeatedly crystallizing beneath a weakened surface.

Mixed salt systems further complicate prediction. Historic monuments accumulate material from soil, groundwater, atmospheric pollution, marine aerosols, mortars, cementitious repairs, fertilizers, biological activity, and previous treatments. These mixtures may display moisture and phase behavior different from that of their individual components.

Foundational work by researchers such as Scherer, Doehne, Charola, Steiger, Rodriguez-Navarro, and others helped establish this systems-based understanding. Their contribution is most useful to the present paper not as a list of individual authorities but as a body of evidence demonstrating that deterioration depends on physical behavior within a specific stone-and-environment system.

8.4. Crystallization and Pore-Scale Mechanics

Modern crystallization research replaced earlier descriptions of salt damage as simple solid expansion with a more detailed understanding of crystal growth under confinement (Doehne & Price, 2010; Oguchi & Yu, 2021).

A supersaturated solution can support continued crystal growth when dissolved ions reach the growing interface. Where that growth is confined by surrounding pore walls and a liquid film remains available, stress can be transmitted into the mineral framework. Whether the stone fails depends on the magnitude of that stress and the local mechanical strength of the substrate.

Pore geometry influences both nucleation and confinement. Very small pores may inhibit formation of some crystals, whereas large open spaces may permit relatively unconstrained growth. Complex pore networks containing several pore sizes can support transport, solution storage, nucleation, and crystal growth in different locations.

This research explains why sodium sulfate can produce severe deterioration under appropriate conditions. It also establishes the evidentiary standard required when a different material is proposed as a comparable salt-weathering hazard. Similar damage should not be inferred unless the relevant phase behavior, transport, confinement, and stress-generating mechanism can be demonstrated (Oguchi & Yu, 2021; Lezzerini et al., 2022).

8.5. Marble Weathering and Substrate Variability

Research on marble durability demonstrates that historic stone is not a uniform substrate. Quarry source, crystal size, accessory minerals, foliation, thermal history, surface orientation, weathering, previous intervention, and environmental exposure influence how a monument responds to moisture and treatment (Historic England, 2021; American Institute for Conservation, 1994).

Fresh marble specimens offer valuable experimental consistency, but they do not reproduce the open grain boundaries, microfractures, biological films, pollution crusts, salts, repairs, and reduced cohesion encountered in old cemetery monuments. Findings obtained from new marble should therefore be interpreted with that limitation in mind.

Evidence developed from limestone and other carbonate materials may likewise contribute useful mechanisms without reproducing the exact response of marble. Sandstone, granite, concrete, and synthetic porous media offer still more indirect comparisons.

This hierarchy of material relevance is especially important to the central question of this paper. Studies of a quaternary ammonium compound on a purified mineral surface may clarify adsorption, but they cannot alone determine how a complete commercial formulation will behave within severely weathered marble.

8.6. Biological Colonization and Biodeterioration

International conservation research treats biological colonization as a material and ecological condition rather than simply as surface dirt. Bacteria, cyanobacteria, algae, fungi, lichens, mosses, and biofilms can interact with stone through several mechanisms, including moisture retention, physical attachment, pollutant trapping, and production of organic acids or other metabolic compounds (Pinna, 2014).

The extent of deterioration varies with species, substrate, climate, exposure, surface condition, and time. Biological growth that presents a significant moisture or material concern in one setting may be largely aesthetic in another. Strongly attached organisms on a weakened surface may also create a situation in which aggressive removal causes greater immediate loss than continued observation.

The appropriate conservation response is therefore based on assessment rather than automatic eradication. Cleaning is justified when biological colonization threatens material, obscures significant information, interferes with examination, or produces another clearly defined preservation problem.

This distinction is important because the biological effectiveness of a cleaner does not by itself establish that treatment is necessary.

8.7. Cleaning as a Conservation Intervention

Cleaning is an intervention into historic fabric even when the treatment material itself is water-soluble or environmentally degradable. Wetting can redistribute soluble compounds, mechanical action can remove grains, and chemical treatments can alter surface energy, biological communities, deposits, or adjacent materials (Doehne & Price, 2010; Oguchi & Yu, 2021).

Professional conservation consequently evaluates cleaning according to the material retained as well as the material removed. Inscription edges, tool marks, patina, original surface finish, and weathering evidence are part of the monument's historic fabric and should not be sacrificed merely to increase brightness.

The principle of minimum intervention does not mean that water alone is always the most conservative treatment or that the weakest available product is automatically preferable.

An ineffective method requiring extensive brushing or repeated treatment may impose greater cumulative stress than a compatible cleaner that reduces mechanical demand and lengthens retreatment intervals.

The appropriate comparison therefore considers chemical exposure, physical effort, frequency, substrate condition, and long-term outcome together.

8.8. Evaluating Cleaner Residues

Analytical techniques allow conservators to characterize deposits that cannot be identified reliably through visual inspection. Ion chromatography can measure soluble ions; Fourier-transform infrared and Raman spectroscopy can identify many molecular and mineral compounds; X-ray diffraction can identify crystalline phases; and scanning electron microscopy combined with elemental analysis can examine deposit morphology and composition at microscopic scales (Historic England, 2021; American Institute for Conservation, 1994).

The availability of sensitive analytical methods introduces an important interpretive challenge. Detecting a compound establishes that material is present at the sampled location and above the method's detection threshold. It does not independently establish quantity across the monument, original source, mobility, physical state, or preservation significance.

A chloride signal, for example, may arise from environmental salts, groundwater, deicing material, bleach-related chemistry, a quaternary ammonium counterion, or another source. Elemental detection cannot identify an intact organic molecule simply because chlorine is present.

Similarly, material identified on the exterior surface does not establish penetration into deeper pores. Reliable interpretation requires knowledge of sampling location, treatment history, controls, concentration, and the analytical capabilities and limitations of the method employed.

The central conservation question remains whether a detected material participates in a mechanism capable of producing measurable change.

8.9. Evidence Concerning Quaternary Ammonium Compounds

Compared with the extensive literature on inorganic salt weathering and antimicrobial disinfection, direct peer-reviewed research examining long-term, repeated application of preservation-specific quat formulations to naturally weathered historic marble remains limited (Pinna, 2014).

The evidence available comes from several overlapping fields. Microbiological studies explain antimicrobial action. Mineral-surface research provides information about adsorption and interfacial behavior. Environmental studies examine persistence, degradation, toxicity, and transport. Conservation cleaner research provides more direct evidence concerning finished formulations and stone compatibility under defined treatment conditions.

Taken together, this evidence supports the effectiveness of selected quat formulations for biological control and does not establish quaternary ammonium compounds as a recognized class of crystallization-driven marble deterioration agents. The evidence is less complete regarding long-term accumulation, penetration into severely weathered pore networks, environmental transformation, and interaction with complex preexisting salt systems.

This is an important distinction. The absence of a documented classical salt-weathering mechanism is not equivalent to proof that every quat formulation is harmless. It means that uncertainty should be directed toward the questions that remain unresolved rather than filled by analogy to a chemically different system.

8.10. Field Experience as Observational Evidence

Quat-based biological cleaners have been used on monuments and masonry for decades. That history provides useful observational evidence because it represents exposure to real climates, natural rainfall, biological recolonization, varied substrates, and actual maintenance practices (Doehne & Price, 2010; Oguchi & Yu, 2021).

The absence of a substantial published pattern of characteristic marble failure attributable specifically to properly applied preservation quat formulations is reassuring, but it is not a controlled experiment. Treatment histories may be incomplete, products change over time, adverse outcomes may not be reported, and subtle effects can be difficult to distinguish from ordinary weathering.

Field observations become considerably more valuable when they include identifiable formulations, treatment dates, concentration, photographs, condition assessments, and repeated follow-up. In that form, professional and volunteer experience can contribute to long-term evidence rather than remain anecdotal.

Field experience should therefore complement laboratory research, not replace it.

8.11. Limits of Evidence Transfer

A recurring challenge throughout the literature is the transfer of findings from one research context to another.

Antimicrobial performance on a hospital surface does not establish compatibility with marble. Adsorption of an isolated compound on purified calcite does not reproduce a commercial formulation interacting with a weathered gravestone. Results obtained from limestone do not automatically describe marble, and studies of sandstone or concrete require still greater caution (Historic England, 2021; American Institute for Conservation, 1994).

Complete formulation also matters. Research on benzalkonium chloride alone does not evaluate buffers, secondary surfactants, builders, stabilizers, or preservatives included in a finished product. Conversely, a whole-product study may provide useful compatibility evidence without revealing which ingredient controlled the result (Gerba, 2015; Kwaśniewska et al., 2020).

Time presents another limitation. Accelerated aging may reveal a plausible weakness under severe cycling but cannot be translated directly into a guaranteed outdoor service life. Short-term field success likewise cannot exclude changes that require many years or several treatment cycles to become measurable.

A scientifically defensible review identifies these boundaries explicitly rather than allowing a finding to become broader with each citation.

8.12. Areas Requiring Additional Research

The broader conservation literature leaves several questions directly relevant to monument-cleaner evaluation unresolved (Pinna, 2014).

Repeated-treatment studies are needed to determine whether successive quat applications produce measurable accumulation, approach a stable retained concentration, or diminish between treatments. Analytical work should distinguish surface films, adsorbed material, dissolved pore-water constituents, crystalline phases, and environmental transformation products rather than grouping them under the general term *residue*.

Outdoor exposure studies should examine ultraviolet radiation, rainfall, freeze-thaw cycling, humidity, coastal aerosols, groundwater, and biological recolonization across different climates. Research using naturally weathered marble would help establish how open grain boundaries, biological films, previous repairs, and mixed salts alter behavior observed on laboratory specimens.

Formulation-specific studies also require careful version control. Product name, composition date, concentration, treatment method, and rinse procedure should be documented so that results remain interpretable after commercial formulations change.

Long-term treatment registries could eventually link these research approaches by allowing observations from multiple sites to be compared over time.

8.13. Areas of Conservation Consensus

Despite uncertainty surrounding particular cleaners and long-term residue behavior, several principles are well established across the broader conservation literature (Doehne & Price, 2010; Oguchi & Yu, 2021).

Historic stone should be treated as historic fabric rather than restored automatically to a like-new appearance. Cleaning should respond to a defined need and should retain original material wherever possible. Aggressive abrasion and strongly incompatible chemicals are inappropriate for weathered marble, and the condition of the substrate must influence treatment selection.

Complete formulations provide more meaningful evidence than isolated ingredient names. Immediate appearance is an incomplete measure of success, while documentation and long-term observation are necessary to understand treatment performance.

These principles are more useful than a universal list of approved and prohibited products because they provide a framework for evaluating new materials as conservation science evolves.

8.14. Implications for Volunteer Preservation Organizations

Volunteer organizations occupy an increasingly important place in cemetery preservation because the number of historic monuments requiring documentation and care exceeds the capacity of professional conservators and cemetery staff alone (Historic England, 2021; American Institute for Conservation, 1994).

The international literature supports volunteer participation when training, authorization, standardized procedures, and limits of practice are clearly established. Volunteers can make substantial contributions through documentation, routine cleaning of appropriate stones, condition observation, vegetation management, and identification of monuments requiring specialist attention.

Their effectiveness should not be measured simply by the number of stones treated. The ability to recognize severe sugaring, instability, delamination, inappropriate previous repairs, or conditions beyond routine cleaning is itself a preservation skill.

Documentation can also give volunteer work scientific value beyond the individual treatment. Consistent photographs, product records, treatment dates, and follow-up observations can create longitudinal evidence across cemeteries and climates that would otherwise be difficult to obtain.

Responsible volunteer practice therefore extends conservation capacity without lowering the standard applied to the monument.

8.15. Summary

International and interdisciplinary stone-conservation research demonstrates that deterioration emerges from interactions among mineralogy, pore structure, moisture, salts, biological activity, environmental exposure, and previous treatment. No single chemical label provides a complete prediction of performance (Pinna, 2014).

This broader evidence supports the controlled use of selected preservation-specific quat formulations while leaving important questions unresolved regarding repeated treatment, retained organic material, environmental transformation, and behavior in severely weathered marble. Laboratory testing clarifies mechanisms and allows controlled comparisons, while field experience provides real-world context and long-term observation.

The most reliable conservation judgments arise when those lines of evidence are considered together and when conclusions remain proportional to the material actually studied. That approach provides a stronger foundation for treatment decisions than either categorical acceptance or categorical rejection based on chemical classification alone.

9. Sodium Hypochlorite and Quaternary Ammonium Cleaners: A Comparative Assessment for Historic Marble

9.1. Introduction

Sodium hypochlorite and quaternary ammonium compounds can both control biological growth, but they do so through different chemical mechanisms and are commonly encountered in products designed for different purposes. Household bleach is inexpensive, widely available, and capable of producing rapid visible change. Preservation-specific cleaners containing quaternary ammonium compounds are generally formulated for controlled biological treatment of masonry and may produce a slower immediate visual response while, in some formulations, providing continued suppression of recolonization (McDonnell & Russell, 1999; Gerba, 2015).

Public discussion sometimes reduces this comparison to opposing claims: bleach is described as either harmless because it is familiar and effective or inherently destructive because it is chemically aggressive, while quat-based cleaners are portrayed as either universally compatible or dangerous because their active ingredients are chemically classified as salts. Neither position provides an adequate conservation assessment.

The more useful comparison considers biological efficacy, complete formulation, mechanism of action, material compatibility, mechanical demand, residue behavior, environmental exposure, worker safety, retreatment, and the strength of the evidence supporting each use. This chapter evaluates those factors without assuming that every product within either category behaves identically.

9.2. Sodium Hypochlorite Chemistry

Household bleach is typically an alkaline aqueous formulation containing sodium hypochlorite, NaOCl. In water, hypochlorite participates in an acid-base equilibrium with hypochlorous acid: $HOCl\backslash H^{+} + OCl^{-}$ (Boyce, 2023; Mohapatra et al., 2023).

The relative proportions of hypochlorous acid and hypochlorite ion depend strongly on pH. Commercial bleach is maintained under alkaline conditions in part to preserve storage stability, while dilution and contact with surfaces can alter the chemical environment during use.

Hypochlorous acid and hypochlorite are reactive oxidizing species. Their antimicrobial effectiveness derives from reactions with proteins, enzymes, membrane components, pigments, and other cellular constituents. This broad reactivity accounts for both the rapid biological control associated with bleach and its ability to alter the color of organic staining.

Sodium hypochlorite does not simply disappear when a treated surface dries. During use and storage it reacts, decomposes, and forms other dissolved or reaction products. Light, heat, time, metals, dilution, and contact with organic matter all influence this process. Its conservation behavior should therefore be considered in terms of the complete formulation and the reactions occurring during treatment rather than through the simplified idea that bleach ultimately “evaporates.” (McDonnell & Russell, 1999; National Park Service, 2025b).

9.3. Quaternary Ammonium Cleaner Chemistry

Quaternary ammonium compounds contain permanently charged organic cations paired with negatively charged counterions, frequently chloride. Their amphiphilic structures allow them to function both as antimicrobial agents and as cationic surfactants (National Park Service, 2025b).

Rather than acting primarily through oxidation, quats associate with microbial surfaces and lipid-containing cell membranes. At an effective concentration and contact time, these interactions can disrupt membrane organization, increase permeability, interfere with essential cellular functions, and ultimately cause loss of viability.

Commercial quat cleaners may contain a single quaternary ammonium compound, a mixture of related homologues, or several antimicrobial ingredients. Secondary surfactants, buffers, pH modifiers, stabilizers, builders, preservatives, solvents, and other formulation components may further influence how the finished product spreads, penetrates, rinses, persists, and interacts with historic marble.

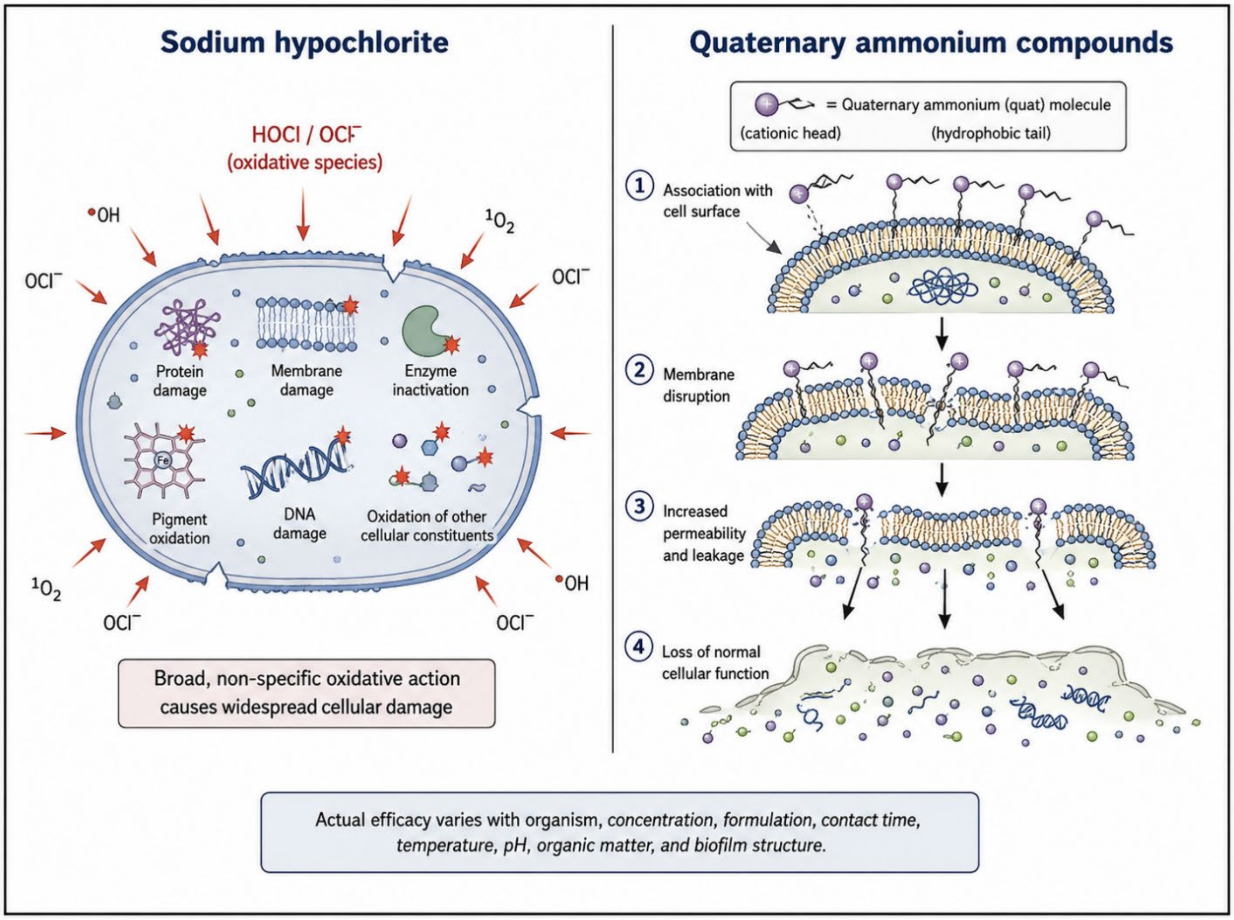
The active biocide therefore explains only part of the treatment system. Compatibility must ultimately be assessed at the level of the finished formulation.

9.4. Modes of Antimicrobial Action

The principal distinction between sodium hypochlorite and quaternary ammonium compounds lies in how they interact with microorganisms. Hypochlorite provides broad oxidative action, while quats act primarily through association with microbial surfaces and disruption of membrane function (McDonnell & Russell, 1999; Gerba, 2015).

Building on the quat mechanism illustrated in Figure 5.2, Figure 9.1 places that pathway beside the generalized oxidative action of sodium hypochlorite so that differences in biological mechanism can be compared without conflating antimicrobial efficacy with compatibility toward historic marble.

Figure 9.1: Sodium Hypochlorite and Quaternary Ammonium Compounds: Generalized Modes of Antimicrobial Action



Note. *Conceptual comparison of antimicrobial mechanisms; the diagram does not represent relative potency, treatment concentration, dose, or conservation compatibility. Sodium hypochlorite produces broad oxidative damage to microbial proteins, membranes, enzymes, pigments, and other cellular constituents. Quaternary ammonium compounds associate with microbial surfaces and disrupt membrane organization and permeability. Actual efficacy varies with organism, concentration, formulation, contact time, temperature, pH, organic matter, and biofilm structure.*

The difference in mechanism helps explain some differences in cleaning behavior, but it does not independently establish compatibility with historic stone. An antimicrobial agent may be highly effective against biological growth and still be poorly suited to a particular substrate. Likewise, a less oxidative mechanism does not guarantee that every supporting ingredient within a commercial formulation is compatible.

Biological efficacy and conservation suitability must therefore remain separate evaluation criteria.

9.5. Biological Efficacy and Visible Cleaning

Sodium hypochlorite often produces rapid visible lightening because it simultaneously inactivates microorganisms and oxidizes organic pigments. This immediate response can make bleach appear especially effective when treatment is judged primarily through before-and-after appearance (Boyce, 2023; Mohapatra et al., 2023).

Quat-based preservation cleaners may produce a different visual sequence. Biological organisms can be inactivated or weakened while pigments, dead cellular material, extracellular polymeric substances, and physical attachment structures remain temporarily visible. Gentle mechanical removal, rinsing, rainfall, sunlight, and subsequent natural weathering may continue changing the appearance after the initial treatment.

Neither response should be interpreted solely through surface brightness. A monument can become lighter because biological pigments have been oxidized, because attached material has been removed, because weathered calcite grains have been abraded away, or through some combination of those processes. Conversely, discoloration remaining after treatment does not necessarily indicate that the organisms remain viable.

A conservation assessment should therefore distinguish biological control, physical removal, inscription legibility, preservation of the original surface, and aesthetic appearance.

9.6. Residual Biological Control and Retreatment

Sodium hypochlorite loses antimicrobial activity as it reacts with organic material, decomposes, and becomes diluted. Once the active oxidizing species have been consumed or removed, little continuing biological suppression is expected from the original treatment. Recolonization then depends primarily on environmental conditions such as moisture, shade, surface roughness, nutrient deposition, and nearby biological sources (National Park Service, 2025b).

Some quat formulations can remain associated with treated surfaces or biological films and temporarily suppress recolonization after the initial application. The duration of that effect depends on formulation, concentration, rainfall, ultraviolet exposure, surface chemistry, environmental transformation, and biological pressure.

When residual control meaningfully lengthens the interval between necessary treatments, it may reduce cumulative wetting, brushing, handling, and chemical application. That can represent a preservation advantage. The benefit should nevertheless be weighed against questions concerning retained material and environmental exposure rather than treated as evidence that persistence is inherently desirable.

Retreatment should be triggered by monument condition and a defined preservation need, not by an expectation that historic marble remain continuously free of visible biological growth.

9.7. Compatibility with Historic Marble

Weathered marble may contain enlarged grain boundaries, microfractures, reduced surface cohesion, soluble salts, pollution deposits, biological films, and previous repair materials. Cleaner compatibility must therefore be evaluated against the condition of historic stone rather than the behavior of fresh carbonate material alone (McDonnell & Russell, 1999; Gerba, 2015).

Sodium hypochlorite is alkaline and does not dissolve calcite through the same direct acid-carbonate reaction associated with acidic cleaners. Its conservation concerns instead include broad oxidative reactivity, formulation additives, possible deposits or reaction products, interaction with organic or pigmented materials, corrosion of nearby metals, effects on vegetation, runoff, and the implications of repeated treatment (McDonnell & Russell, 1999; National Park Service, 2025b).

Selected preservation-specific quat formulations avoid the same hypochlorite oxidation mechanism and have performed favorably in comparative monument-cleaner studies. Their uncertainties lie elsewhere: adsorption, complete formulation, retained films, penetration into weathered pores, repeated treatment, environmental degradation, and interactions with existing salts or earlier treatments.

Neither category should therefore be evaluated solely by the chemistry of its active ingredient. The finished formulation and the condition of the individual monument remain central to compatibility.

9.8. Hypochlorite, Chlorine, and Chloride

Chemical terminology surrounding bleach and quaternary ammonium compounds can create unnecessary confusion. Sodium hypochlorite contains the hypochlorite ion, OCl^-, while benzalkonium chloride and many related quats contain chloride, Cl^-, as a counterion associated with the positively charged organic molecule (Boyce, 2023; Mohapatra et al., 2023).

Hypochlorite and chloride do not have equivalent chemical behavior. Hypochlorite is an oxidizing chlorine-containing species. Chloride is a considerably more stable anion that may occur in many environmental and treatment-related materials.

During use and decomposition, some hypochlorite chemistry can ultimately produce chloride. Quaternary ammonium compounds may also dissociate or exchange their counterions in solution or at surfaces. Detecting chloride on a monument after treatment therefore does not establish its original source, identify an intact treatment compound, or determine whether the detected material is significant.

Interpretation requires knowledge of treatment history, environmental exposure, associated ions or molecular species, concentration, and location.

9.9. Formulation and Application Context

Comparisons between “bleach” and “quats” are frequently made as though each term identifies a single uniform product. In practice, both categories contain formulations that can differ substantially (National Park Service, 2025b).

Household bleach products may contain surfactants, stabilizers, thickeners, fragrances, or other additives according to intended consumer use. Scented, gel, splash-reducing, or multipurpose products introduce formulation characteristics intended for household performance rather than conservation of porous historic stone.

Preservation-specific quat products likewise contain supporting ingredients whose composition and long-term behavior should be evaluated. A preservation label indicates intended use and may reflect relevant testing, but it should not substitute for evidence concerning the particular product.

Application further modifies treatment behavior. Concentration, dwell period, stone moisture, temperature, sunlight, rinsing, and mechanical action determine how much material contacts the stone and how long it remains. Controlled application reduces avoidable exposure but cannot transform an unsuitable formulation into a compatible conservation treatment.

9.10. Environmental and Occupational Considerations

Cleaning decisions affect the surrounding cemetery environment as well as the monument. Sodium hypochlorite is chemically reactive and can injure vegetation, affect aquatic organisms, corrode metals, and react with organic matter. The original active oxidant may degrade relatively rapidly, but short environmental persistence does not mean that no chemical reaction or environmental effect occurred during use (McDonnell & Russell, 1999; Gerba, 2015).

Quaternary ammonium compounds present a different environmental profile. Cationic surfactants can associate strongly with organic matter, soils, sediments, and biological surfaces. At sufficient concentrations, many quats are toxic to aquatic organisms, and environmental research has examined their persistence and the consequences of extensive antimicrobial use. These concerns support careful control of dilution, overspray, runoff, and disposal.

Worker protection is required for both product classes. Sodium hypochlorite can irritate or damage eyes, skin, and respiratory tissues and must never be mixed with acids, ammonia, or other incompatible products. Quat formulations may likewise cause irritation or sensitization and should be handled according to their current labels and safety data sheets (McDonnell & Russell, 1999; National Park Service, 2025b).

Relative chemical aggressiveness should not be confused with absence of hazard. Appropriate personal protective equipment and environmental controls remain necessary regardless of which compatible cleaner is selected.

9.11. Cost and Life-Cycle Preservation Value

Bleach is inexpensive and widely available, while specialized preservation cleaners generally cost more per unit. Purchase price, however, captures only one component of treatment cost (Boyce, 2023; Mohapatra et al., 2023).

A meaningful comparison includes product concentration and coverage, water use, labor, mechanical effort, protective equipment, training, retreatment frequency, environmental controls, and the consequences of accidental or cumulative surface damage. A product that costs less initially may not represent the lower-cost intervention if it requires substantially more labor or more frequent treatment.

Historic marble also contains value that cannot be replaced economically. Loss of an inscription edge, carving, tool mark, patina, or weathered original surface cannot be reversed simply by applying a different product later.

Conservation value is therefore better evaluated across the treatment life cycle than by the price of the container.

9.12. Professional Guidance and Evidence-Based Product Selection

Professional and institutional conservation guidance generally favors treatment methods developed or credibly evaluated for historic masonry. Such guidance emphasizes assessment, minimum necessary intervention, appropriate wetting, gentle mechanical action, controlled water delivery, treatment documentation, and avoidance of unnecessarily aggressive household or industrial methods (National Park Service, 2025b).

This preference should not be interpreted as an endorsement of every product marketed for preservation or as a denial that bleach possesses antimicrobial effectiveness. It reflects the difference between demonstrating that a chemical can kill biological growth and establishing that a complete treatment is suitable for weathered historic material.

Several commonly repeated claims illustrate the distinction.

“Bleach evaporates and leaves nothing behind.”
The water carrier evaporates, while sodium hypochlorite reacts, decomposes, and produces other chemical species. Declining odor or antimicrobial activity does not demonstrate the absence of chemical interaction (McDonnell & Russell, 1999; National Park Service, 2025b).

“The whitest result is the best result.”
Brightness may result from pigment oxidation, biological removal, loss of patina, removal of weakened stone, or several mechanisms simultaneously. Conservation success must be evaluated at the material surface.

“Any cleaner described chemically as a salt will cause salt weathering.”
Crystallization damage requires transport, supersaturation, solid-phase formation, confinement, and sufficient stress. Whether a treatment residue participates in that sequence must be demonstrated.

“A preservation-specific label guarantees compatibility.”
Intended use is relevant, but formulation, substrate condition, concentration, exposure, and independent evidence remain necessary.

9.13. Comparative Assessment

Table 9-1. Comparative Considerations for Sodium Hypochlorite and Preservation-Specific Quaternary Ammonium Cleaners

Consideration	Sodium hypochlorite formulations	Preservation-specific quat formulations
Principal antimicrobial action	Broad oxidation of microbial constituents	Association with microbial surfaces and disruption of membrane function

Consideration	Sodium hypochlorite formulations	Preservation-specific quat formulations
Immediate visible response	Often rapid lightening of biological staining	May be more gradual and continue after initial treatment
Residual biological control	Generally limited after reaction and decomposition	May temporarily suppress recolonization, depending on formulation and exposure
Product purpose	Household, institutional, or industrial formulations vary widely	Intended for masonry or biological conservation applications
Principal marble concern	Oxidative chemistry, alkalinity, additives, reaction products, adjacent metals, runoff, repeated treatment	Adsorption, retained formulation components, penetration, repeated application, environmental persistence
Direct acid attack on calcite	Not the principal mechanism; commercial bleach is normally alkaline	Not normally an acid-dissolution mechanism
Formulation variability	Considerable	Considerable; findings remain product- and version-specific
Environmental concern	High initial reactivity; vegetation, metals, aquatic exposure, reaction products	Aquatic toxicity, sorption to soils and sediments, persistence under some conditions
Worker-safety concern	Irritation, corrosivity, dangerous reactions with incompatible chemicals	Irritation, sensitization, aerosol and concentrated-product exposure
Conservation evidence	General bleach formulations usually lack historic-marble-specific compatibility testing	Selected products have relevant monument-cleaner testing and field use
Appropriate routine role	Generally less defensible where better-evaluated preservation alternatives are available	Potentially appropriate when the specific formulation and monument are suitable

Consideration	Sodium hypochlorite formulations	Preservation-specific quat formulations
Principal uncertainty	Formulation-specific reaction products and cumulative effects of repeated treatment	Long-term residue behavior, repeated accumulation, environmental transformation, climate-specific performance

The comparison represents broad treatment characteristics rather than universal properties. Individual formulations should be evaluated according to their current composition, intended use, supporting evidence, and the condition of the monument (McDonnell & Russell, 1999; Gerba, 2015).

9.14. Summary

Sodium hypochlorite and quaternary ammonium cleaners differ in antimicrobial mechanism, formulation purpose, visible response, residual activity, environmental behavior, and conservation evidence. Sodium hypochlorite provides rapid biological oxidation and often produces immediate lightening, but ordinary household formulations are not generally developed around the long-term conservation requirements of weathered marble (Boyce, 2023; Mohapatra et al., 2023).

Selected preservation-specific quat formulations offer effective biological control without relying on hypochlorite oxidation and may reduce recolonization for a period after treatment. Their use nevertheless remains conditional on formulation, substrate condition, environmental setting, application, and the unresolved questions surrounding long-term retained material.

For routine treatment of suitable historic marble, a credibly evaluated preservation-specific formulation provides a more defensible conservation basis than a general-purpose household bleach product. That conclusion rests on formulation-specific evidence and preservation objectives rather than on the assumption that any broad chemical class is universally safe or universally harmful.

10. Residues, Deposits, and Long-Term Compatibility: Separating Evidence from Assumption

10.1. Introduction

The subject of treatment residues has generated substantial discussion within cemetery preservation because it lies at the intersection of legitimate conservation caution and incomplete long-term evidence. Statements that a cleaner “leaves salts,” that any detectable residue must be damaging, or that retained quaternary ammonium compounds will inevitably crystallize often compress several different scientific questions into a single conclusion (Oguchi & Yu, 2021; Doehne & Price, 2010).

Historic marble is never chemically isolated from its surroundings. Over decades or centuries, monuments accumulate atmospheric particles, soil, soluble environmental salts, biological films, corrosion products, hard-water deposits, and materials associated with earlier repairs and treatments. Cleaning may remove some of those substances, mobilize others, and introduce new compounds from the product or application water.

The appearance or detection of material after treatment therefore establishes only that something is present. Its conservation significance depends on composition, quantity, physical state, location, mobility, environmental response, and whether it participates in a mechanism capable of producing measurable change.

This chapter establishes terminology for distinguishing different kinds of retained material and considers how deposits are detected and interpreted. It then places the available evidence concerning quat residues within that broader conservation framework.

10.2. Residue and Related Terminology

The term *residue* is often used informally for anything remaining on a surface. In a technical conservation discussion, that definition is too broad to be useful (National Park Service, 2025c; Mohapatra et al., 2023).

For this paper, an **unintended treatment residue** is material associated with a cleaning or conservation treatment that remains after the intended application and removal process has been completed. It may consist of excess active ingredient, surfactant, buffer, builder, carrier residue, or another formulation component.

An **environmental deposit or accretion** originates primarily through outdoor exposure and may include dust, soot, soil, marine salts, pollution particles, or mineral deposits. A **biological film or remnant** consists of living or dead organisms, pigments, extracellular polymeric substances, and material trapped within them. An **intentional treatment**

material, such as mortar, grout, adhesive, consolidant, or compatible fill, is deliberately left to perform a conservation function and should not automatically be classified as an unwanted residue.

A **reaction or degradation product** is a new material formed through chemical or biological transformation. Such products may differ substantially from the substance initially applied.

These categories can overlap. A biological film may trap environmental salts; cleaning water can mobilize material from an old repair; and an intentional treatment may deteriorate into an unwanted deposit. Distinguishing their likely origins nevertheless prevents the word *residue* from carrying more meaning than the evidence supports.

10.3. Categories and Sources

Table 10-1. Materials Commonly Encountered on or Within Historic Marble

Category	**Examples**	**Principal conservation question**
Environmental deposits	Dust, soot, soil, marine salts, sulfate- or nitrate-bearing deposits	Does the material retain moisture, react chemically, obscure significant features, or supply mobile salts?
Biological colonization and remnants	Algae, fungi, cyanobacteria, lichens, mosses, biofilm, pigments, EPS	Is colonization contributing to deterioration, moisture retention, or loss of legibility, and what is the risk of removal?
Intentional conservation materials	Lime mortar, grout, adhesives, fills, consolidants, coatings	Is the retained material functioning as intended and aging compatibly?
Unintended treatment residues	Excess biocide, surfactant, buffer, builder, cleaner film, minerals from rinse water	What remains, where is it located, and does it persist or participate in harmful processes?
Reaction and degradation products	Gypsum, corrosion products, precipitated minerals, transformed organic compounds	How does the newly formed material behave relative to the original stone and treatment?

These categories are descriptive rather than rankings of risk. Windborne dust may be relatively benign in one setting and moisture-retaining in another. A lime mortar may be intentionally beneficial, while an incompatible cement repair can supply soluble material and redirect moisture. Biological colonization may be actively damaging in one location yet more safely monitored than aggressively removed from a severely deteriorated surface (Oguchi & Yu, 2021; Doehne & Price, 2010).

Source attribution should therefore proceed cautiously. A deposit becoming visible after cleaning may originate from the cleaner, application water, existing material within the marble, an earlier repair, or environmental salts mobilized by the wetting event. Temporal association alone does not establish causation.

10.4. Surface and Internal Distribution

Location influences both preservation significance and the ability to detect or remove material.

Surface deposits occur at the exterior and include dust, soot, efflorescence, biological remnants, mineral films, and dried treatment material. They are comparatively accessible to photography, sampling, and monitoring. Visibility, however, should not be confused with severity. A conspicuous efflorescent deposit may cause less mechanical damage than a smaller quantity of salt repeatedly crystallizing beneath a weakened surface (National Park Service, 2025c; Mohapatra et al., 2023).

Internal material occupies pores, grain boundaries, fractures, joints, or alteration layers beneath the exterior. It may include dissolved ions, adsorbed organic compounds, crystalline salts, environmental contaminants, corrosion products, or intentional conservation materials. Distribution can be highly uneven within weathered marble.

Location also changes over time. Rainfall may dissolve a surface deposit and transport soluble components inward, while evaporation may move material toward the exterior. A substance can therefore occupy several positions during repeated wetting and drying cycles.

Sampling must be interpreted accordingly. A surface swab cannot establish the chemical condition of the interior, while a small extracted sample cannot necessarily represent an entire monument.

10.5. When Retained Material Becomes a Conservation Concern

A retained material becomes significant when its physical, chemical, biological, or environmental behavior creates a credible pathway to deterioration or another unacceptable effect (Oguchi & Yu, 2021; Doehne & Price, 2010).

A soluble and mobile compound may be repeatedly transported as the stone wets and dries. A hygroscopic or deliquescent material can influence local moisture. A crystalline salt may become damaging if it reaches supersaturation and grows under confinement. A chemically reactive substance may dissolve calcite, alter pigments, corrode adjacent metals, or form new mineral phases. An organic film may change wetting, retain particles, affect biological recolonization, or interfere with later treatment.

Quantity is equally important. Modern analytical techniques can detect materials at concentrations far below those required to produce a meaningful material response. Detection therefore establishes presence but not necessarily consequence.

Time also influences interpretation. Some compounds may be removed through rinsing or rainfall, transformed through sunlight or microbial activity, or desorb gradually. Others may persist or accumulate during repeated treatment. A conservation evaluation should therefore consider both the immediate condition and the likely evolution of the material under environmental cycling.

10.6. Assessing Conservation Significance

Table 10-2. Illustrative Assessment of Selected Materials

Material or condition	**Possible significance**	**Important qualifying factors**
Windborne dust	Often limited but may trap moisture and pollutants	Quantity, composition, surface roughness, exposure
Hard-water mineral deposit	Frequently visual but may obscure detail or add ions	Water chemistry, thickness, frequency
Biological film	Highly context-dependent	Organisms, moisture, attachment, stone condition, removal risk
Compatible lime mortar	Intentionally retained and potentially beneficial	Composition, permeability, workmanship, condition
Consolidant	Intentionally retained to improve cohesion	Penetration, compatibility, aging, appearance
Gypsum-rich crust	May retain pollutants and contribute to surface alteration	Exposure, thickness, porosity, pollution history
Sodium sulfate within pores	Potentially damaging under appropriate environmental cycles	Concentration, phase behavior, moisture, confinement, stone strength
Adsorbed biocide	Context-dependent	Compound, quantity, substrate, persistence, transformation

Material or condition	Possible significance	Important qualifying factors
Dried cleaner film	Generally undesirable if unintended	Composition, thickness, solubility, rinsability, environmental response

The table illustrates why material presence cannot substitute for mechanism. Intentionally retained conservation materials and unintended residues may both remain within stone, but they perform different functions and require different evaluation criteria (National Park Service, 2025c; Mohapatra et al., 2023).

10.7. Analytical Detection and Interpretation

Visual examination can identify many deposits but rarely establishes composition. White crystalline material may consist of several different salts or mineral phases, while a thin organic film may be invisible under ordinary light (Oguchi & Yu, 2021; Doehne & Price, 2010).

Analytical methods provide complementary information. Ion chromatography can quantify soluble inorganic ions. Fourier-transform infrared and Raman spectroscopy can identify many organic and inorganic compounds. X-ray diffraction is particularly useful for crystalline phases. Scanning electron microscopy can reveal deposit morphology and relationships among crystals and mineral grains, while energy-dispersive X-ray spectroscopy provides associated elemental information. More specialized surface and chromatographic techniques may assist in characterizing organic residues.

Table 10-3. Selected Analytical Methods for Residue Characterization

Method	Principal information	Important limitation
Ion chromatography	Quantifies extracted soluble ions	Does not reconstruct original physical state or necessarily identify source
FTIR spectroscopy	Identifies many molecular functional groups and materials	Mixed or low-concentration samples may complicate interpretation
Raman spectroscopy	Identifies many crystalline and molecular compounds	Fluorescence and surface condition can interfere
X-ray diffraction	Identifies crystalline mineral phases	Limited for amorphous or very thin organic layers

Method	Principal information	Important limitation
Scanning electron microscopy	Reveals deposit morphology and surface relationships	Morphology alone does not establish chemical identity
EDS	Provides elemental composition at microscopic locations	Elements do not uniquely identify complete compounds
XPS or related surface analysis	Characterizes near-surface elemental and chemical states	Specialized and highly surface-sensitive
ToF-SIMS	Detects and spatially maps molecular and ionic fragments near a surface	Specialized and potentially complex to interpret
Chromatographic/mass-spectrometric methods	Can identify selected organic compounds and degradation products	Often requires targeted extraction and reference standards

No single method fully characterizes a complex commercial cleaner. Chloride detected by ion chromatography or EDS, for example, cannot independently establish that an intact benzalkonium chloride molecule remains. Likewise, elemental calcium and sulfur do not by themselves establish a particular sulfate phase without additional characterization (Gerba, 2015; Kwaśniewska et al., 2020).

Sampling design is therefore part of interpretation. Untreated comparison areas, formulation standards, treatment-water samples, environmental controls, and depth-specific sampling may all be needed to determine whether a detected substance is treatment-related.

10.8. Possible Outcomes Following Cleaning

A cleaning treatment can produce several different residue outcomes.

A substantial proportion of soluble formulation material may be removed during controlled rinsing, leaving quantities below the analytical detection limit or below practical significance. This should be described as substantial removal or non-detection rather than absolute proof that no treatment molecule remains anywhere within the pore network (National Park Service, 2025c; Mohapatra et al., 2023).

Some material may remain temporarily and diminish through subsequent rainfall, desorption, ultraviolet exposure, or environmental degradation. Other compounds may adsorb at mineral or biological interfaces without forming crystalline deposits. Adsorbed material may contribute to residual antimicrobial activity while presenting different questions from those associated with crystal growth.

A treatment can also leave an unintended dried film or contribute material that precipitates during drying. In some cases the remaining substance may be a reaction or degradation product rather than the ingredient originally applied.

These outcomes are not mutually exclusive. A single treated surface may contain small amounts of adsorbed material, environmental salts redistributed during cleaning, and temporary exterior deposits.

10.9. Evidence Concerning Quaternary Ammonium Residues

Available evidence indicates that quaternary ammonium compounds can remain associated with treated surfaces through adsorption and interaction with mineral phases, organic matter, and biological films. Such retention may contribute to temporary residual antimicrobial activity (Oguchi & Yu, 2021; Doehne & Price, 2010).

The extent and location of adsorption are system-dependent. Weathered marble contains carbonate grains, mineral impurities, pollution deposits, salts, microfractures, and biological material, all of which may affect molecular association. A commercial formulation adds still more variables through supporting surfactants, buffers, builders, stabilizers, and other ingredients.

Adsorption should not be equated with crystallization pressure. An adsorbed molecular layer does not automatically participate in the dissolution, supersaturation, confined crystal growth, and phase-transformation mechanisms associated with classical inorganic salt weathering (Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

The conservation literature evaluated in this paper has not established a general pattern in which preservation-specific quat formulations routinely produce crystallization-driven deterioration of historic marble. That conclusion has limits. It does not establish universal safety or resolve questions concerning penetration, repeated accumulation, degradation, desorption, counterion behavior, or interaction with mixed environmental salts.

10.10. Lessons from Accelerated Weathering

The NCPTT–NCA research described in Chapter 7 demonstrates why residue findings should remain tied to the formulation and study conditions from which they were derived. An earlier commercial cleaner formulation produced fine surface deposits during accelerated weathering. The formulation was subsequently changed, and later testing did not reproduce the same visible deposit under the revised conditions (National Park Service, 2025c; Mohapatra et al., 2023).

The appropriate lesson is not that residue concerns were unfounded. The original finding was important precisely because it identified a treatment behavior requiring investigation. Nor does the later result establish that every future version of the product will behave identically.

The sequence instead demonstrates that residue formation can be formulation-specific and that empirical testing can improve treatment materials. It also shows why product name, formulation date, test conditions, and residue characterization should accompany claims about compatibility.

10.11. Application and Residue Retention

The amount and location of retained material are influenced by formulation, dilution, stone condition, moisture content, contact time, drying, and rinsing. A highly weathered surface with open grain boundaries may retain more solution than dense, cohesive marble. Rapid evaporation may concentrate nonvolatile components at or near the surface, while sheltered recesses and joints may retain treatment solution longer than exposed areas (Oguchi & Yu, 2021; Doehne & Price, 2010).

Pre-wetting can reduce the initial concentration gradient between cleaner and dry stone and may limit immediate uptake into accessible pores. It does not create a complete barrier to penetration. Rinsing reduces excess soluble material but does not establish complete molecular removal.

Using more concentrated product than required can increase the amount that must later be removed without providing a proportional cleaning benefit. Allowing a rinse-based cleaner to dry contrary to its instructions may likewise increase local concentration.

Treatment procedure therefore influences residue behavior, but procedure should not be used to explain away formulation-specific concerns. Both must be evaluated.

10.12. Long-Term Field Evidence

Quat-based preservation cleaners have been used on monuments and masonry over extended periods and across varied climates. The absence of a substantial published record documenting a characteristic pattern of widespread marble failure specifically attributable to properly applied preservation quat formulations provides useful practical context (National Park Service, 2025c; Mohapatra et al., 2023).

That observation is reassuring but uncontrolled. Treatment records may be incomplete, formulations may have changed, adverse outcomes may be unreported, and gradual effects may be difficult to distinguish from ordinary environmental deterioration. Most treated monuments also lack directly comparable untreated controls.

Field evidence becomes substantially stronger when product version, concentration, treatment date, monument condition, photographs, and follow-up observations are preserved. Standardized monitoring can convert individual treatment histories into a more useful observational dataset.

Professional experience should therefore be treated as one line of evidence rather than as proof that long-term uncertainty has been eliminated.

10.13. Avoiding False Equivalencies

Several distinctions are necessary for interpreting treatment-residue claims accurately.

Inappropriate equivalence	**More accurate interpretation**
A compound is chemically a salt; therefore, it produces salt weathering	Salt weathering requires the physical sequence necessary for damaging crystallization or other relevant mechanisms
A material is detectable; therefore, it is damaging	Detection establishes presence, not concentration, mechanism, or effect
Something remains after treatment; therefore, treatment failed	Retained material may be temporary, adsorbed, intentional, or below practical significance
Adsorption is crystallization	Adsorption is interfacial association; crystallization is formation and growth of an ordered solid phase
Chloride was detected; therefore, a particular cleaner caused it	Chloride has many environmental and treatment-related sources
No visible film is present; therefore, no material remains	Molecular or internal material may not be visible
The stone became lighter; therefore, treatment was compatible	Immediate appearance does not establish absence of material loss
No published failures have been reported; therefore, safety is proven	Absence of reports is supportive context but not a controlled long-term demonstration

These distinctions apply equally to claims of safety and claims of harm. A scientifically defensible conclusion should be based on the mechanism and evidence actually demonstrated (Oguchi & Yu, 2021; Doehne & Price, 2010).

10.14. Applying the Precautionary Principle

Historic monuments are finite cultural resources, making precaution appropriate when evidence is incomplete. Precaution should not be interpreted as assuming that every uncertain treatment is damaging, nor as requiring that all intervention cease until multi-decade data exist (National Park Service, 2025c; Mohapatra et al., 2023).

A proportionate precautionary approach defines the condition requiring treatment, selects a formulation with the strongest relevant compatibility evidence available, minimizes unnecessary chemical loading and mechanical action, documents the intervention, and monitors the outcome. Where the evidence is weak or the monument unusually vulnerable, additional testing, professional consultation, or postponement may be the more responsible choice.

The same principle applies when new concerns are raised. Unexpected residues should be investigated rather than dismissed, while hypothetical mechanisms should not be represented as demonstrated deterioration without corresponding evidence.

Precaution is most useful when coupled with scientific proportionality.

10.15. Implications for Preservation Practice

Residue uncertainty can be reduced through formulation-specific product selection, measured dilution, appropriate application, controlled rinsing, and careful treatment documentation. Product records should identify the manufacturer, product version or purchase date, lot number when available, dilution, treatment date, water source, dwell period, rinse method, weather conditions, and monument condition (Oguchi & Yu, 2021; Doehne & Price, 2010).

Only the quantity needed to achieve the treatment objective should be introduced. Excessive concentration and unnecessary repeat applications increase chemical loading without necessarily improving preservation.

Unexpected films, crystalline deposits, staining, altered drying, rapid recolonization, or changes in surface condition should be photographed and documented. Where the condition warrants it, analytical characterization can help distinguish treatment-related material from environmental deposits or substances mobilized from within the monument.

The purpose of these practices is not to guarantee that nothing remains. It is to ensure that treatment remains controlled, traceable, and capable of being evaluated over time.

10.16. Summary

Historic marble contains and acquires many kinds of material, including environmental deposits, biological films, intentional conservation materials, treatment residues, and reaction products. These categories differ in origin, function, physical state, and potential effect and should not be collapsed into a single concept of “residue.” (National Park Service, 2025c; Mohapatra et al., 2023).

A retained substance becomes a preservation concern when its quantity, location, mobility, reactivity, moisture response, phase behavior, biological effect, or environmental persistence creates a credible mechanism for measurable change. Analytical detection alone does not establish that mechanism.

Current evidence does not demonstrate that preservation-specific quaternary ammonium cleaners generally produce the crystallization-driven deterioration characteristic of problematic inorganic salts. It also does not resolve every question concerning repeated application, adsorption, environmental transformation, and long-term accumulation. Formulation-specific evaluation, transparent documentation, proportionate treatment, and continued monitoring therefore remain the most defensible approach.

11. Best Practices for Cleaning Historic Marble Headstones: Applying Conservation Science in the Field

11.1. Introduction

The preceding chapters establish that cleaning historic marble is an intervention into a material system already altered by age, moisture, weathering, biological colonization, pollutants, salts, and previous treatment. Cleaning adds water, chemical compounds, physical contact, and another cycle of wetting and drying to that system (Striegel et al., 2016; National Park Service, 2022b).

A compatible cleaner can produce an unacceptable outcome when applied to an unstable monument, used at excessive concentration, permitted to dry improperly, combined with aggressive brushing, or inadequately controlled. Conversely, careful workmanship cannot make an unsuitable formulation appropriate for historic marble.

Responsible cleaning therefore requires a sequence of decisions beginning before any treatment material reaches the stone. The practitioner must determine whether cleaning is necessary, whether the monument is stable enough to tolerate treatment, what material is present, what treatment objective is justified, and how the work will be documented and evaluated afterward.

This chapter provides a field framework for routine cleaning of stable historic marble. Structurally unstable, severely sugared, delaminated, painted, coated, highly carved, unusually significant, or otherwise complex monuments require individualized professional assessment beyond the scope of a general cleaning procedure.

11.2. Preservation Philosophy Before Cleaning

The first treatment decision is whether cleaning should occur at all.

Age, patina, discoloration, and ordinary weathering do not independently justify intervention. Historic marble is not expected to retain the appearance of newly quarried stone and attempts to produce a continuously white or uniform surface can encourage excessive treatment (National Park Service, 2025a, 2025b).

Cleaning is more defensible when biological colonization or deposits obscure an inscription, prevent documentation or examination, contribute to undesirable moisture retention, conceal deterioration, or interfere with another necessary preservation treatment.

Biological growth should nevertheless be evaluated in context. Some colonization may contribute materially to deterioration, while other growth is primarily aesthetic. Strongly attached organisms on a severely weakened surface may present a situation in which complete removal would sacrifice more historic material than careful monitoring.

The treatment objective should therefore be stated before work begins. “Make the stone look new” provides no conservation endpoint. “Improve inscription legibility while retaining the weathered surface” or “reduce moisture-retaining biological growth without removing friable marble” establishes a standard against which the treatment can be evaluated.

11.3. Authorization, Documentation, and Condition Assessment

Cleaning should proceed only with authorization from the cemetery owner, responsible governing body, or other appropriate authority. Public access to a cemetery does not confer permission to treat its monuments. Local requirements may also govern chemicals, water use, runoff, veteran markers, archaeological resources, protected cemeteries, and volunteer activity (National Cemetery Administration, n.d.; Historic England, 2021).

Before treatment, the monument should be examined from all sides and photographed systematically. Documentation should include the inscription, base, biological colonization, visible deposits, repairs, cracks, and areas of deterioration.

The principal condition question is whether the stone can tolerate wetting and gentle physical contact.

Table 11-1. Condition Indicators and Recommended Response Before Cleaning

Observed condition	**Recommended response**
Cohesive surface, stable inscription, no significant structural defects	Candidate for controlled cleaning after authorization and testing
Minor roughness or early sugaring	Proceed cautiously with reduced mechanical action and close observation
Active granular loss or severe sugaring	Defer routine cleaning and seek professional conservation assessment
Scaling, delamination, blistering, or loose surface layers	Do not clean; wetting and brushing may detach original material
Open cracks, displaced fragments, or failed joints	Defer until structural condition is assessed
Leaning, rocking, or otherwise unstable monument	Do not touch or wet until stabilized by qualified personnel

Observed condition	Recommended response
Unidentified coating, paint, gilding, inscription fill, or water repellent	Obtain specialized assessment
Corroding metal, cementitious repair, incompatible mortar, or unidentified adhesive	Document and seek appropriate guidance
Delicate sculpture, complex carving, or exceptionally significant monument	Professional treatment recommended

Stability should never be tested by pushing, pulling, rocking, climbing on, or otherwise loading the monument. Visible movement or instability is sufficient reason to stop.

11.4. Identifying the Stone and Associated Materials

Historic cemeteries contain marble, limestone, sandstone, slate, brownstone, granite, concrete, cast stone, metals, ceramics, and composite monuments assembled from several materials. Each responds differently to water, chemistry, abrasion, and environmental exposure (Striegel et al., 2016; National Park Service, 2022b).

Marble is vulnerable to acidic dissolution and, when sugared, to mechanical grain loss. Slate can delaminate along cleavage planes. Sandstone may be porous and friable. Limestone varies substantially in pore structure and composition. Granite generally resists carbonate dissolution but may contain weathered minerals, open joints, and metal attachments.

A treatment tolerated by one material should not therefore be transferred automatically to another.

Associated materials also matter. Cleaner or rinse water may contact bronze plaques, iron pins, lead lettering, paint, mortar, adhesives, concrete foundations, soil, vegetation, or neighboring monuments. A product considered suitable for marble may be incompatible with one of those adjacent materials.

Where visual stone identification is uncertain, documentation, cemetery records, quarry history, and professional consultation are preferable to destructive field testing.

11.5. Weather and Site Conditions

Environmental conditions affect cleaner concentration, contact time, evaporation, worker exposure, and runoff. Moderate temperatures, shaded or indirect light, limited wind, and adequate water generally provide the most controllable conditions, subject to the requirements of the specific product (National Park Service, 2025a, 2025b).

Cleaning should be postponed when freezing temperatures, excessive heat, strong wind, intense direct sunlight, thunderstorms, or uncontrolled precipitation prevent the treatment from remaining within its intended operating conditions. Rapid drying can shorten the dwell period and concentrate nonvolatile ingredients, while very cold conditions may reduce treatment efficacy or prolong moisture retention.

Site conditions should also be assessed before work begins. Slopes, storm drains, wells, ponds, wetlands, ornamental vegetation, neighboring graves, public traffic, and access routes may influence runoff and safety. Hoses, tools, containers, and work areas should be arranged so that preservation activity does not create hazards or damage surrounding resources.

11.6. Water Quality and Delivery

Water is the principal carrier and rinse medium in most routine monument-cleaning treatments. It can soften biological material, suspend loosened debris, wet accessible pores, dilute cleaning agents, and remove soluble material during rinsing (National Cemetery Administration, n.d.; Historic England, 2021).

Clean potable water provides an appropriate general standard. Highly mineralized water can leave calcium, magnesium, iron, or manganese deposits, particularly where repeated wetting is allowed to dry on light-colored stone. Where local water chemistry is unusual, it should be documented and considered as part of the treatment system.

Adequate supply is important. Beginning treatment without sufficient water can result in inadequate pre-wetting or rinsing after a cleaner has already been applied.

Water delivery should remain compatible with the stone. Pump sprayers, low-pressure hoses, and controlled streams can wet and rinse surfaces without the force associated with commercial pressure washing. Actual force at the stone depends on pressure, flow, nozzle, distance, and surface condition rather than on the equipment label alone.

11.7. Pre-Wetting the Monument

Pre-wetting introduces clean water into accessible near-surface pores before a more concentrated treatment solution is applied. This can reduce the immediate concentration gradient between the cleaner and dry porous stone, improve spreading, and provide additional working time (Striegel et al., 2016; National Park Service, 2022b).

The amount of water required varies with marble condition, weather, orientation, and existing moisture. A cohesive surface may require relatively little water, while weathered marble can absorb repeated applications before remaining visibly damp.

Pre-wetting should not be described as complete saturation of the pore network or as a barrier that prevents cleaner penetration. Historic marble contains openings of different sizes, and water does not occupy every pore or fracture uniformly.

The objective is controlled wetting rather than flooding. Open cracks, failed joints, hollow areas, and poorly drained bases should not be filled indiscriminately with water.

11.8. Preparing and Applying the Cleaning Solution

Products should be selected for their relevance to historic masonry and supported by credible compatibility information. The current product label, technical information, and safety data sheet should be reviewed before work begins because concentrations, temperature limitations, dwell periods, environmental precautions, and application requirements may change when formulations are revised (National Park Service, 2025a, 2025b).

Dilution should be measured rather than estimated. Dedicated and clearly labeled containers reduce variability and help prevent accidental mixing with incompatible chemicals.

Cleaner should be applied evenly and only in the quantity required to maintain appropriate contact with the biological material. Increasing concentration beyond the documented range should not be used as a substitute for adequate dwell time or repeated controlled treatment.

Drying should be managed according to the product's validated procedure. A cleaner designed to be rinsed should not be allowed to dry simply because field conditions made the work difficult, while a documented leave-on protocol should not be altered casually.

Application should minimize overspray, aerosol formation, and runoff onto neighboring materials or vegetation.

11.9. Gentle Mechanical Cleaning

Biological films and loosened deposits often require some physical assistance, but the purpose of mechanical action is to move material that has already been softened or weakened—not to scour the stone until a desired appearance is achieved (National Cemetery Administration, n.d.; Historic England, 2021).

Soft natural- or synthetic-bristle brushes may be appropriate where the surface remains sufficiently cohesive. Tampico brushes are commonly useful because their flexible fibers retain water, while soft nylon detailing brushes can assist within inscriptions and small recesses when their stiffness is compatible with the stone.

A small test area should establish how the surface responds. Light, repeated passes are preferable to forceful scrubbing. Brushes should be rinsed frequently because trapped grit can make otherwise soft bristles abrasive. Hard backs, metal ferrules, staples, and handles should not strike the monument.

Lettering, carved edges, corners, and sugared areas require particular restraint. Grain loss in the rinse water, changing surface texture, powdering, or newly exposed bright stone can indicate that treatment is removing historic material.

Strongly attached biological remnants may need to remain. Allowing dead material to weather gradually can preserve more original marble than insisting on complete removal during one treatment session.

11.10. Rinsing

Rinsing removes loosened biological matter, suspended dirt, soluble formulation components, and material released during brushing. It also reduces the concentration of treatment solution remaining at accessible surfaces (Striegel et al., 2016; National Park Service, 2022b).

The monument should be rinsed systematically using clean water at a force appropriate to its condition. Carved recesses, joints, sheltered edges, and bases require particular attention because they can retain treatment solution. Visible foam may indicate the need for additional rinsing, but absence of foam does not prove complete removal.

Runoff should be controlled to limit concentrated discharge onto neighboring graves, vegetation, waterways, or drainage systems.

Rinsing should likewise not be represented as proof that every treatment molecule has left the stone. Its conservation purpose is to remove unnecessary accessible material without subjecting the monument to excessive water or mechanical force.

11.11. Multiple Cleaning Cycles and Stopping Criteria

Heavily colonized stone may require more than one controlled cleaning cycle. Increasing product concentration or brushing pressure is rarely the appropriate response when the first application does not produce the desired result (National Park Service, 2025a, 2025b).

Additional manufacturer-approved dwell time, a second gentle treatment, or a later return may provide safer results. Natural rainfall and weathering can also continue removing dead biological material after treatment.

The practitioner should stop when the monument begins losing grains, changes texture, develops unexpected staining, reveals scaling or delamination, or cannot be cleaned further without removal of historic material. Work should also stop if the product begins drying uncontrollably, adequate rinse water is no longer available, or previously unseen instability becomes apparent.

Stopping because the stone will not tolerate additional treatment is a successful conservation decision, not a failed cleaning.

11.12. Cleaning Frequency and Recolonization

Historic monuments should not be cleaned on a fixed annual or seasonal schedule. Retreatment should respond to condition and a clearly defined preservation objective (National Cemetery Administration, n.d.; Historic England, 2021).

Recolonization depends on moisture, shade, vegetation, orientation, surface roughness, climate, air quality, nutrient deposition, and nearby biological communities. Cleaning does not remove most of those environmental drivers.

Some preservation-specific quat formulations may delay recolonization and thereby extend treatment intervals. The duration of that effect varies and should not be presumed. The return of a thin biological film also does not automatically justify another intervention.

Retreatment is most defensible when recolonization once again obscures significant information, contributes to a material or moisture concern, or interferes with condition assessment. Otherwise, documentation and observation may be sufficient.

11.13. Practices to Avoid

Table 11-2. Cleaning Practices Generally Inappropriate for Historic Marble

Practice	**Principal concern**
Strong acids	Direct calcite dissolution, etching, increased roughness, loss of carved detail
Commercial high-pressure washing	Grain detachment, rounded inscriptions, crack enlargement, forced water entry
Sandblasting or abrasive blasting	Irreversible removal of original surface material
Wire brushes	Cutting and abrasion of marble; possible metal contamination

Practice	Principal concern
Metal scrapers or chisels	Scratching, chipping, concentrated force on fragile surfaces
Abrasive pads, grinding, or powered brushes	Loss of weathered marble and artificial alteration of surface texture
Household bleach for routine historic-marble cleaning	Broad oxidative chemistry, variable additives, metal and vegetation concerns, limited conservation-specific formulation evidence
Dishwashing liquids, soaps, and household detergents	Undocumented dyes, fragrances, builders, surfactants, thickeners, and other ingredients
Unidentified homemade mixtures	Unknown concentration, reactions, residues, and safety
Dry brushing or aggressive scraping	Abrasion and detachment of weakened grains
Unapproved coatings, sealers, or water repellents	Potential changes to appearance, moisture movement, retreatability, and salt distribution

Commercial pressure washing should be distinguished from carefully controlled low-pressure water delivery. Adjustable equipment is not automatically suitable simply because a low setting is available. Actual force at the monument and the condition of the stone determine whether pressurized water can be used safely (Striegel et al., 2016; National Park Service, 2022b).

Sodium hypochlorite should also be distinguished from acidic cleaners. Bleach is not discouraged because it dissolves calcite through the same mechanism as an acid; its concerns involve a different combination of oxidative reactivity, formulation, adjacent materials, environmental exposure, and repeated use (McDonnell & Russell, 1999; National Park Service, 2025b).

11.14. Monitoring After Cleaning

Cleaning should create a documented treatment history rather than a single before-and-after event. The monument should be examined after drying and at later intervals appropriate to the treatment and site (National Park Service, 2025a, 2025b).

Monitoring should consider biological recolonization, new deposits, staining, surface films, changes in granular loss, scaling, cracking, moisture retention, condition of repairs, metal corrosion, and effects on nearby soil or vegetation.

Photography is most useful when viewpoint, scale, lighting, and image quality remain reasonably consistent. Treatment records should remain associated with the images so later observers know which formulation, concentration, water source, and procedure were used.

Where practical, untreated or less-treated comparison areas can improve interpretation. Such comparisons still require caution because adjacent surfaces may differ in orientation, porosity, and exposure.

11.15. Volunteer Training and Limits of Practice

Volunteer organizations contribute substantially to cemetery documentation and routine preservation, but training must define both what volunteers are expected to do and where their work should stop (National Cemetery Administration, n.d.; Historic England, 2021).

Instruction should cover authorization, material identification, surface assessment, product preparation, water use, brush selection, personal protective equipment, runoff control, treatment documentation, and recognition of instability. Volunteers should also understand that training in routine cleaning does not automatically qualify them to lift, reset, drill, pin, consolidate, repair, or disassemble monuments.

Effective instruction includes examples of stones that should **not** be cleaned. Recognizing severe sugaring, scaling, delamination, unstable fragments, coatings, paint, complex carving, and failed repairs is as important as mastering the cleaning sequence.

The measure of competent volunteer practice is not the number of stones completed during an event. It is the ability to achieve appropriate results while recognizing the limits imposed by the monument.

11.16. Patience as a Treatment Control

Patience has a direct material consequence in conservation. Adequate wetting and dwell time can reduce the force required to loosen biological material. Small treatment areas can be managed without premature drying. Repeated gentle passes reduce the need for forceful scrubbing, while allowing dead biological remnants to weather naturally may prevent unnecessary removal of weakened stone (Striegel et al., 2016; National Park Service, 2022b).

Historic monuments do not require transformation within a single afternoon. A marble headstone that has weathered for generations can tolerate a slower conservation timetable far better than it can recover from excessive intervention.

Restraint therefore functions as a practical treatment control rather than merely a philosophical preference.

11.17. Ethical Stewardship

A historic headstone is both a material object and a memorial. Its significance lies in inscription, craftsmanship, material, family association, community history, cemetery setting, and the evidence of age carried by its surviving surface (National Park Service, 2025a, 2025b).

Those undertaking treatment are temporary stewards of that resource. Their responsibility is not to determine how new the monument should appear but to retain as much original material and information as reasonably possible.

Ethical stewardship includes obtaining permission, respecting cultural and family concerns, documenting treatment accurately, reporting unexpected outcomes, protecting adjacent graves and landscapes, and declining treatment when the anticipated risk exceeds the preservation benefit.

Efficiency, speed, brightness, and the number of monuments completed are secondary to the survival of the historic resource.

11.18. Best-Practices Checklist

Before Treatment

- Confirm authorization from the cemetery owner or responsible authority.
- Define the preservation objective.
- Identify the monument material and associated metals, repairs, coatings, or paint.
- Photograph all sides, inscriptions, biological growth, and existing deterioration.
- Assess surface cohesion, cracks, fragments, joints, stability, and foundation condition.
- Refer unstable, severely sugared, delaminated, coated, painted, highly carved, or unusually significant monuments for professional assessment.
- Review the product's current label, technical information, and safety data sheet.
- Confirm dilution, dwell period, temperature limits, rinsing requirements, and protective equipment.
- Verify an adequate supply of clean water.

- Evaluate weather, shade, runoff, vegetation, waterways, and public safety.
- Prepare clean, dedicated, labeled tools and containers.

During Treatment

- Establish a small test area.
- Pre-wet with clean water without flooding open cracks or unstable joints.
- Measure the cleaner accurately.
- Apply only the quantity required for controlled contact.
- Manage drying according to the product procedure.
- Use soft natural- or synthetic-bristle brushes appropriate to the surface.
- Keep hard brush backs, metal parts, and grit away from the stone.
- Use light, repeated passes rather than force.
- Rinse tools frequently.
- Observe for grain loss, texture change, staining, movement, or unexpected reaction.
- Stop when additional cleaning would require removal of stone.
- Rinse according to the documented product procedure.
- Control runoff and protect adjacent resources.

After Treatment

- Inspect the monument after rinsing and after drying.
- Photograph the same views recorded before treatment.
- Record product, manufacturer, purchase or formulation date, lot number when available, dilution, dwell period, tools, water source, weather, and rinse procedure.
- Document material intentionally left in place or areas not cleaned.
- Record unexpected deposits, staining, grain loss, or other concerns.
- Establish an appropriate follow-up monitoring interval.
- Retain the treatment record as part of the monument's conservation history.

11.19. Summary

Responsible monument cleaning begins with a justified treatment objective, authorization, material identification, and assessment of the stone's ability to tolerate intervention. Stable historic marble may be suitable for controlled wetting, an appropriately evaluated cleaner, gentle mechanical action, and careful rinsing; unstable or severely deteriorated marble may not be suitable for routine cleaning at all (National Cemetery Administration, n.d.; Historic England, 2021).

Pre-wetting, dilution, dwell time, brushing, rinsing, and environmental conditions influence treatment performance, but none should be presented as a guarantee of safety. They are controls used to reduce avoidable exposure and material loss.

Successful treatment is therefore measured less by immediate brightness than by the amount of historic fabric retained, the preservation objective achieved, and the quality of the record left for future caretakers.

12. Evidence Synthesis and Recommendations

12.1. Introduction

The central question of this paper concerns whether residues associated with quaternary ammonium compound cleaners present a long-term salt-weathering threat to historic marble headstones. Answering that question requires several bodies of evidence that are related but not interchangeable: marble mineralogy and deterioration, aqueous transport, inorganic salt weathering, quaternary ammonium chemistry, commercial formulation, biological cleaning, treatment residues, laboratory testing, and field observation (Doehne & Price, 2010; Oguchi & Yu, 2021).

Viewed together, these areas support a more qualified conclusion than either categorical acceptance or categorical rejection of quat-based preservation cleaners. The evidence is strongest in explaining the mechanisms by which traditional inorganic salts can damage porous stone and in demonstrating the antimicrobial effectiveness of selected preservation formulations. It is less complete regarding multi-decade accumulation and transformation of organic treatment residues in naturally weathered marble.

This chapter synthesizes those findings according to their evidentiary strength, distinguishes supported conclusions from unresolved questions, and identifies practical recommendations consistent with the limitations of the current evidence. Detailed future-research priorities are reserved for Chapter 13 so that the conclusions of this review remain separate from the research agenda.

12.2. Revisiting the Central Question

The concern surrounding quaternary ammonium cleaners is sometimes expressed through a straightforward chain of reasoning: quaternary ammonium compounds are salts; salts are known to damage porous stone; therefore, quaternary ammonium compounds must present the same form of deterioration risk (National Park Service, 2025c; American Institute for Conservation, 1994).

The first two statements are chemically and conservationally valid in their appropriate contexts, but the conclusion does not follow without additional evidence. Salt-weathering research demonstrates that damaging crystallization depends on a sequence of physical and chemical conditions, including solubility, transport, concentration, supersaturation, formation of an appropriate solid phase, confinement within the pore structure, environmental cycling, and a substrate mechanically vulnerable to the resulting stress.

Quaternary ammonium compounds are ionic materials, but their comparatively large organic structures, surfactant behavior, adsorption, interaction with biological material, and formulation-dependent residues distinguish them from the small inorganic ions that dominate classical salt-weathering studies.

The appropriate conservation question is therefore not whether quats qualify chemically as salts. It is whether a particular quat-containing treatment, under realistic conditions of application and environmental exposure, develops a residue system capable of producing damaging physical or chemical change in weathered marble.

The literature reviewed in this paper does not presently establish that process as a general outcome of properly formulated preservation-specific quat cleaners. It also does not provide sufficient direct long-term evidence to eliminate every concern associated with repeated treatment or persistent residue.

12.3. Principal Scientific Findings

Historic marble is a weathered material system.

The marble encountered in historic cemeteries differs physically from freshly quarried stone. Grain-boundary opening, microfracturing, sugaring, environmental deposits, biological films, previous repairs, and changing pore connectivity influence how water and treatment solutions enter, move through, and leave the stone. Compatibility findings developed from fresh laboratory specimens should therefore be interpreted with appropriate limits (Doehne & Price, 2010; Oguchi & Yu, 2021).

Moisture enables many relevant deterioration processes.

Moisture transports dissolved material, participates in carbonate dissolution, supports biological colonization, contributes to freeze-thaw activity, and allows soluble salts to migrate and become concentrated. It is a major enabling and transport factor rather than the sole cause of marble deterioration. Structural movement, physical impact, thermal stress, and other mechanisms can operate independently or in combination with water.

Classical salt weathering is mechanism-dependent.

Salt deterioration cannot be predicted from the word *salt* alone. Damaging crystallization requires the development of conditions capable of producing crystal growth or phase transformation within a vulnerable pore network. Sodium sulfate provides a well-studied example because its solution and phase behavior can generate severe deterioration under particular conditions. Its behavior should not be transferred automatically to chemically different materials (Oguchi & Yu, 2021; Lezzerini et al., 2022).

Adsorption and crystallization are distinct processes.

Quaternary ammonium compounds may associate with mineral surfaces, environmental deposits, organic films, or biological material. This adsorption can contribute to residual antimicrobial behavior. It does not by itself represent the formation and confined growth of a crystalline phase. Claims of crystallization-driven damage require evidence of that mechanism rather than evidence of adsorption alone.

Complete formulation affects treatment behavior.

The active ingredient does not determine every property of a commercial cleaner. Surfactants, buffers, pH modifiers, builders, stabilizers, carriers, preservatives, and other additives influence wetting, penetration, biological efficacy, residue, drying, and rinsing. Formulation changes can therefore produce materially different treatment outcomes even where the broad active-ingredient class remains unchanged.

The NCPTT–NCA cleaner research demonstrates the importance of formulation-specific testing.

An earlier cleaner formulation produced fine surface residues during accelerated-weathering testing. Reformulation changed the observed result while retaining favorable biological performance. That sequence demonstrates both that residue concerns should be taken seriously and that they should remain tied to the tested formulation rather than generalized automatically to the entire active-ingredient class.

Immediate appearance is an incomplete conservation endpoint.

Rapid whitening can result from biological removal, pigment oxidation, abrasion, loss of weathered surface material, or several processes simultaneously. The conservation objective is preservation of original fabric and significant information, not restoration of a new-stone appearance.

Biological colonization requires condition-based assessment.

Biological growth can retain moisture, trap pollutants, obscure inscriptions, and contribute to deterioration under some circumstances. Its presence does not automatically justify complete removal. Treatment must account for organism attachment and the condition of the stone beneath it.

Field experience provides useful but limited evidence.

Extended professional use of preservation-specific quat cleaners without a widely documented characteristic pattern of marble failure is reassuring. Because treatment histories, formulations, controls, climates, and reporting are inconsistent, this observational evidence does not establish universal long-term compatibility.

Long-term uncertainty remains concentrated in specific questions.

The major unresolved issues concern repeated-treatment accumulation, adsorption and desorption over extended periods, degradation and transformation products, penetration into weathered marble, interactions with mixed environmental salts, formulation changes, and climate-dependent behavior. These are more precise and scientifically useful questions than the generalized question of whether "quats leave salts."

12.4. What the Evidence Supports

The following conclusions represent the principal positions supported by the evidence reviewed in this paper, subject to verification through the final source audit and citation process (National Park Service, 2025c; American Institute for Conservation, 1994).

Conclusion 1. Historic marble should be cleaned only when a defined preservation, documentation, or legibility objective justifies intervention.

Conclusion 2. Monument condition must be assessed before treatment because weathered marble can respond differently from fresh or more cohesive stone.

Conclusion 3. Salt-weathering risk should be evaluated through physical and chemical behavior rather than chemical classification alone.

Conclusion 4. Adsorbed organic treatment material should not be treated as equivalent to a crystalline inorganic salt unless evidence demonstrates the relevant crystallization mechanism.

Conclusion 5. Cleaner compatibility should be evaluated at the level of the complete commercial formulation and version tested rather than inferred solely from its active ingredient.

Conclusion 6. Selected preservation-specific quaternary ammonium formulations can provide effective biological control on appropriate carbonate-stone substrates under the conditions for which they have been evaluated.

Conclusion 7. Current evidence does not establish preservation-use quat formulations as a general cause of the crystallization-driven deterioration associated with classical inorganic salt weathering.

Conclusion 8. That absence of a demonstrated general mechanism does not establish universal compatibility or eliminate the need for continued investigation of residue retention, repeated application, and environmental transformation.

Conclusion 9. Preservation-specific formulations with relevant compatibility evidence provide a more defensible basis for routine historic-marble cleaning than general-purpose household products whose formulations and intended performance objectives are not centered on historic stone.

Conclusion 10. Treatment documentation and long-term monitoring are necessary components of evidence-based cleaning because the consequences of an intervention may extend beyond its immediate visual result.

These conclusions intentionally avoid claims that all quat formulations are safe, that all retained material is benign, or that successful field use constitutes proof of multi-decade compatibility. They also avoid treating the existence of uncertainty as evidence that harm has been demonstrated.

12.5. What Remains Uncertain

The long-term behavior of complete preservation cleaner formulations within naturally weathered historic marble remains less thoroughly documented than the mechanisms of classical inorganic salt weathering (Doehne & Price, 2010; Oguchi & Yu, 2021).

The available literature does not yet provide a sufficiently broad multi-decade dataset to determine whether repeated quat treatment produces measurable accumulation across different marble types and climates. The depth and persistence of adsorbed material after realistic pre-wetting and rinsing also require more direct characterization.

Environmental transformation introduces additional uncertainty. Ultraviolet radiation, rainfall, biological activity, temperature, dissolved salts, and pollutants may change treatment compounds over time, producing species that differ from those initially applied. The behavior of complete formulations is particularly difficult to predict where supporting ingredients are proprietary or have changed between product versions.

Another uncertainty concerns mixed chemical systems. Historic marble may already contain chloride, sulfate, nitrate, calcium, magnesium, sodium, environmental organics, and compounds introduced by earlier repairs. How cleaner residues interact with those preexisting materials remains incompletely characterized.

These gaps define the boundaries of current knowledge. Chapter 13 develops them into a focused research agenda rather than repeating them here as speculative evidence for either compatibility or harm.

12.6. Recommendations for Practice

For professional conservators

Professional treatment should continue to emphasize condition-based decision-making, material identification, formulation-specific evidence, minimum necessary intervention, and comprehensive documentation. Where residue or compatibility concerns arise, analytical characterization should be considered before attributing the effect to a particular ingredient or mechanism (National Park Service, 2025c; American Institute for Conservation, 1994).

Professional reporting of both successful and unexpected outcomes would strengthen the evidence base considerably. Long-term treatment histories are especially valuable because they connect controlled laboratory findings with actual environmental exposure.

For cemetery owners and managers

Cemetery authorities should establish written cleaning standards rather than permitting unrestricted treatment based on individual product preference. Procedures should identify who may clean monuments, which conditions require professional referral, how products are selected, how runoff is controlled, and what treatment records must be retained.

Maintenance goals should prioritize legibility, material stability, and preservation of historic fabric rather than continuous cosmetic uniformity. Cleaning frequency should respond to condition rather than calendar-based expectations.

For volunteer preservation organizations

Volunteer programs should operate within clearly defined limits of practice. Training should address not only how to clean but how to recognize monuments that should not be cleaned. Authorization, documentation, product control, surface assessment, worker safety, and environmental protection should form part of the standard procedure.

Volunteers are particularly well positioned to contribute long-term observations because they frequently return to the same cemeteries over many years. Consistent documentation can transform those repeated visits into useful preservation evidence.

For manufacturers

Manufacturers serving the conservation community should identify formulation revisions clearly, provide current technical and safety documentation, and support independent compatibility testing when possible. Claims concerning historic-stone suitability should distinguish laboratory evidence, field experience, and manufacturer recommendations.

When testing reveals an unexpected residue or other concern, reformulation and transparent retesting represent constructive product development. The goal should be to improve the evidence available to practitioners rather than to defend a formulation simply because it has an established market history.

12.7. Scientific Humility and the Precautionary Principle

Historic conservation requires decisions before every question can be answered with experimental certainty. The appropriate response to that reality is neither complacency nor paralysis (Doehne & Price, 2010; Oguchi & Yu, 2021).

Scientific humility requires distinguishing what has been demonstrated from what is inferred. A plausible deterioration mechanism deserves investigation, but plausibility should not be reported as documented damage. Long-standing field use can provide reassurance, but it should not be elevated to the evidentiary status of a controlled multi-decade study. Laboratory testing may reveal important incompatibilities, but accelerated exposure should not be represented as a precise forecast of service life.

The precautionary principle provides a practical framework within those limits. Treatment should be necessary, proportionate, supported by the best relevant evidence available, and limited to the amount required to achieve its objective. Uncertainty should encourage careful application, documentation, monitoring, and willingness to revise practice.

That willingness to change is fundamental to evidence-based conservation. A treatment considered appropriate today may be refined when better analytical methods, longer monitoring, or new formulation data become available. Revision does not undermine the credibility of preservation practice; it is one of the mechanisms through which that practice improves.

12.8. Summary

The available evidence supports a more precise conclusion than the generalized claim that quaternary ammonium cleaners either do or do not “leave harmful salts.” Quats are chemically ionic compounds, and treatment material may remain on or within stone after application. Those facts alone do not establish a salt-weathering mechanism (National Park Service, 2025c; American Institute for Conservation, 1994).

Classical crystallization damage requires specific conditions involving transport, concentration, solid-phase formation, confinement, environmental cycling, and a vulnerable substrate. Current conservation evidence has not established that properly formulated preservation-specific quat cleaners routinely reproduce that process in historic marble.

At the same time, direct long-term evidence concerning repeated treatment, adsorption, environmental transformation, formulation changes, and naturally weathered marble remains incomplete. The appropriate preservation position is therefore neither unconditional endorsement nor categorical rejection. It is formulation-specific selection, proportionate treatment, careful documentation, long-term observation, and continued willingness to revise conclusions as the evidence develops.

Those unresolved questions form the basis of the research agenda presented in Chapter 13.

13. Research Agenda for Historic Marble Preservation

13.1. Introduction

Conservation research has substantially improved understanding of historic stone deterioration, biological colonization, cleaning materials, salt weathering, and treatment compatibility. Laboratory analysis and field observation have replaced many practices once based primarily on tradition or immediate appearance with methods that can be evaluated according to measurable material behavior (Doehne & Price, 2010; Oguchi & Yu, 2021).

Important limitations nevertheless remain. Historic monuments are expected to survive for generations, while most treatment studies necessarily operate over months or years. Laboratory specimens provide experimental control but do not fully reproduce naturally weathered marble. Field observations capture environmental complexity but often lack consistent controls, treatment records, analytical measurements, or sufficiently long monitoring periods.

The principal need is therefore not simply more research. It is **better-connected research** that links controlled laboratory studies, formulation-specific analysis, naturally weathered marble, realistic application procedures, environmental exposure, and long-term field monitoring.

This chapter translates the uncertainties identified throughout the paper into a focused research agenda. The objective is not to validate or discredit any particular product category, but to improve the evidence available for decisions involving biological cleaning, treatment residues, water movement, mechanical cleaning, and long-term preservation of historic marble.

13.2. Principles for Future Research

Future investigations should be designed around the actual conditions encountered in conservation practice. Studies using purified compounds, fresh marble, or accelerated environmental cycling remain valuable because they allow individual mechanisms to be isolated, but their conclusions should be distinguished from those derived from complete commercial formulations or naturally weathered historic stone (Mohapatra et al., 2023; Pinna, 2014).

Product studies should document the formulation version, concentration, application rate, dwell period, pre-wetting procedure, rinse method, water chemistry, substrate condition, and environmental conditions. Where possible, untreated controls and standardized comparison treatments should be incorporated into the design.

Research should also distinguish **detection** from **conservation significance**. Increasingly sensitive analytical instruments can identify extremely small quantities of retained material, but presence alone does not establish damage. Studies should connect chemical characterization with spatial distribution, physical state, persistence, moisture behavior, surface change, mechanical properties, or another measurable conservation outcome.

Long-term research is particularly valuable when it combines several forms of evidence. Laboratory experiments can establish plausible mechanisms, controlled material testing can assess treatment response, analytical methods can identify retained or transformed substances, and field monitoring can determine whether those effects become meaningful under natural exposure.

13.3. Long-Term Monitoring Programs

One of the clearest gaps in cemetery conservation is the absence of standardized multi-year treatment monitoring. Preservation cleaners have been used for decades, but relatively few monuments have been documented before treatment and then examined systematically over extended periods using consistent methods (Doehne & Price, 2010; Oguchi & Yu, 2021).

A useful monitoring program would begin with detailed baseline documentation of monument material, condition, orientation, biological colonization, previous repairs, environmental exposure, and treatment history. Standardized photography could then be supplemented, where resources permit, by three-dimensional surface documentation, moisture observations, biological assessments, and measurements capable of detecting surface change.

Follow-up intervals should reflect both the research question and the expected rate of change. Early observations can document immediate treatment behavior and recolonization, while later intervals may reveal cumulative effects that are not apparent after one or two seasons. A program capable of maintaining records across ten, twenty, or more years would provide evidence unavailable through short-duration laboratory testing.

The greatest value would come from maintaining comparable treated and untreated surfaces or monuments where ethically and practically possible. Longitudinal datasets could then distinguish treatment-related change more effectively from the environmental weathering that continues regardless of cleaning.

13.4. Comparative Cleaner Evaluations

Comparative product testing should remain a high research priority. Individual studies often examine only a small number of cleaners, making it difficult to distinguish broad treatment patterns from formulation-specific behavior (Mohapatra et al., 2023; Pinna, 2014).

Future comparisons should include preservation-specific quat formulations, alternative biological cleaners, water-only controls, and other treatments that have credible relevance to historic masonry. Products should be applied at documented concentrations and according to realistic field procedures rather than under conditions unlikely to occur in practice.

Evaluation should extend beyond biological removal. Relevant outcomes include surface alteration, material loss, residue composition and distribution, water absorption and drying behavior, recolonization, required mechanical effort, rinse demand, environmental exposure, worker safety, and performance after repeated treatment.

Comparative research would be especially valuable when the same formulations are tested on both fresh reference marble and representative weathered material. Differences between the two could help determine how strongly laboratory compatibility results depend on substrate condition.

13.5. Organic Residue Behavior

The long-term behavior of large organic cationic compounds within weathered marble remains less developed than the literature concerning inorganic salt weathering. This represents one of the most direct research needs arising from the central question of this paper (Doehne & Price, 2010; Oguchi & Yu, 2021).

Studies should characterize how quaternary ammonium compounds and related formulation components adsorb to marble, how much material remains after realistic rinsing, how retention varies with surface condition, and whether subsequent rainfall or environmental exposure promotes desorption or redistribution.

Research should also examine molecular mobility through open grain boundaries and microfractures. Weathered marble cannot be represented adequately as a uniform calcite surface, and interaction with silica, clay minerals, iron compounds, environmental deposits, salts, and biological material may alter retention substantially.

Repeated-treatment experiments are particularly important. They should determine whether successive applications lead to measurable accumulation, whether retained concentrations approach an equilibrium, or whether weathering between treatments removes or transforms much of the previously retained material.

13.6. Residue Characterization

Future residue research should move beyond the binary question of whether a treatment leaves material behind. The more useful objectives are to determine **what remains, how much remains, where it is located, in what physical state it exists, and how it changes with time** (Mohapatra et al., 2023; Pinna, 2014).

Analytical methods such as Fourier-transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, ion chromatography, scanning electron microscopy with energy-dispersive spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry can provide complementary information. No single method should be expected to characterize an entire commercial formulation.

Sampling design deserves equal attention. Surface analysis should be distinguished from depth-specific sampling, and treated areas should be compared with untreated controls, application water, environmental deposits, and formulation standards where practical.

Of particular value would be research capable of distinguishing adsorbed organic compounds from crystalline material, dried formulation films, environmental salts mobilized during treatment, and chemical degradation products. These states have different conservation implications and should not be grouped under a single residue category.

13.7. Environmental Cycling and Climate

Treatment performance cannot be separated from environment. Historic cemeteries range from humid coastal settings to arid inland climates and from regions experiencing frequent freeze-thaw cycles to areas dominated by intense sunlight and prolonged heat (Doehne & Price, 2010; Oguchi & Yu, 2021).

Future studies should investigate how rainfall, relative humidity, temperature, ultraviolet radiation, freeze-thaw cycling, marine aerosols, atmospheric pollutants, groundwater, and drying rate influence cleaner residues and treated marble. The objective should not be to assign a universal climate ranking but to determine which environmental variables materially change treatment behavior.

Climate-specific research may also reveal different dominant mechanisms. A coastal monument may encounter substantial chloride loading independent of cleaning, while a shaded inland monument may remain damp for long periods and experience persistent biological recolonization. A northern monument may undergo repeated freezing while still containing moisture introduced during late-season treatment.

Regional field studies linked to controlled laboratory simulations could provide a stronger basis for adapting general preservation guidance to local conditions.

13.8. Biological Recolonization

Biological recolonization should be studied as an ecological process rather than only as the return of visible staining. Organisms occupying treated marble may differ from those present before cleaning, and the rate of return can be influenced by shade, moisture, orientation, vegetation, surface roughness, nutrient deposition, climate, and the treatment itself (Mohapatra et al., 2023; Pinna, 2014).

Long-term studies should compare recolonization after different cleaning systems while documenting the environmental variables likely to influence growth. Where appropriate, microbiological techniques could characterize changes in community composition rather than relying exclusively on visual coverage.

Such research could clarify the conservation value of residual antimicrobial activity. The relevant question is not simply whether one product keeps a surface visibly cleaner for longer, but whether reduced recolonization meaningfully decreases the frequency of future interventions without creating unacceptable material or environmental consequences.

Understanding biological succession may also improve treatment thresholds by helping conservators distinguish early recolonization that can safely be monitored from conditions that warrant renewed intervention.

13.9. Water Chemistry

Water is introduced during nearly every stage of routine monument cleaning, yet its contribution to treatment behavior is often treated as secondary. In practice, water chemistry may affect formulation stability, surface deposits, rinsing, staining, and the ionic environment within the marble (Doehne & Price, 2010; Oguchi & Yu, 2021).

Comparative research should examine water hardness, pH, alkalinity, chloride and sulfate content, iron and manganese, and differences among municipal water, well water, deionized water, and other sources commonly used in cemetery work.

The objective should not be to establish one universally required water type. Potable water is practical and appropriate for many routine treatments. Instead, research should identify conditions under which local water chemistry becomes significant enough to alter cleaner performance or leave measurable deposits.

This work could also clarify whether repeated use of mineral-rich water contributes more substantially to some observed residues than the cleaning formulation itself.

13.10. Mechanical Cleaning Research

Chemical treatments receive considerable attention because their composition can be analyzed and debated readily, yet the physical tools used during cleaning interact directly with the historic surface (Mohapatra et al., 2023; Pinna, 2014).

Controlled studies comparing Tampico, other natural bristles, nylon, polyester, and appropriate emerging synthetic materials could quantify differences in cleaning efficiency, surface abrasion, grain loss, and required operator force. Brush age and contamination should also be considered because trapped grit may alter the abrasiveness of an otherwise soft tool.

Weathered marble should receive particular emphasis. A brush that produces negligible change on sound laboratory stone may detach grains from a sugared nineteenth-century tablet.

Mechanical research should also consider the interaction between cleaner performance and brushing demand. A formulation that loosens biological material effectively may permit less mechanical work, while an ineffective treatment can encourage repeated or forceful brushing. Chemical and mechanical exposure should therefore be assessed as parts of the same treatment system.

13.11. Digital Documentation Technologies

Rapid advances in digital documentation offer opportunities to monitor historic monuments while reducing physical contact. Structured-light scanning, photogrammetry, LiDAR, Reflectance Transformation Imaging, multispectral imaging, and other techniques can record surface geometry or inscriptions at levels of detail difficult to reproduce through ordinary photography alone (Doehne & Price, 2010; Oguchi & Yu, 2021).

Their most valuable research role may be longitudinal comparison. Repeated three-dimensional surveys could quantify surface recession, inscription loss, displacement, or localized deterioration over time. Imaging techniques may also improve the documentation of inscriptions that are difficult to read under ordinary lighting without requiring aggressive cleaning.

Artificial intelligence may assist with image registration, pattern recognition, inscription enhancement, or identification of change across large photographic datasets. Such applications should support rather than replace expert interpretation, particularly when digital enhancement risks creating details that are not physically present.

Research should determine which technologies provide sufficient conservation value to justify their cost and complexity in routine cemetery settings.

13.12. Citizen Science and Volunteer Contributions

Trained volunteers can contribute to conservation research in ways that extend beyond individual cleaning projects. Their geographic distribution and ability to revisit cemeteries repeatedly make them particularly well suited to standardized documentation and long-term observation (Mohapatra et al., 2023; Pinna, 2014).

A citizen-science framework could use defined photographic protocols, condition categories, treatment records, environmental observations, and biological-coverage assessments that can be applied consistently across many sites. Professional conservators and researchers could then design the protocols, provide training, audit data quality, and analyze the resulting information.

Volunteer participation is particularly promising for questions that require large numbers of observations rather than destructive sampling or specialized analytical equipment. Recolonization, visible deposit formation, treatment longevity, weathering progression, and geographic variation could all benefit from well-designed observational networks.

The scientific value of such work depends on standardization. A large collection of undocumented before-and-after images cannot substitute for a smaller dataset in which monument, treatment, date, formulation, and follow-up conditions are known.

13.13. Establishing a Treatment Registry

Historic monument preservation would benefit substantially from a centralized treatment registry capable of preserving treatment histories across institutions and generations of caretakers (Doehne & Price, 2010; Oguchi & Yu, 2021).

At minimum, a registry could record monument location, material, approximate age, condition, product and formulation information, dilution, treatment date, application procedure, water source, repair history, environmental setting, and follow-up observations. Photographs or links to digital documentation could provide a visual record of change.

Such a system would not replace controlled research. Its value would lie in identifying patterns across a scale that individual experiments cannot achieve. If a particular treatment repeatedly performed differently in coastal environments, on highly sugared marble, or after several applications, a sufficiently large dataset might reveal that relationship.

A registry would also prevent the loss of treatment history when cemetery personnel, conservators, or volunteer organizations change over time. Knowledge of what has already been applied to a monument is itself a conservation resource.

13.14. Interdisciplinary Collaboration

The questions identified in this paper cross conventional disciplinary boundaries. Stone deterioration involves geology, mineralogy, physical chemistry, materials science, microbiology, environmental science, engineering, conservation practice, and cultural-resource management (Mohapatra et al., 2023; Pinna, 2014).

Chemists may characterize treatment residues while materials scientists examine mechanical change. Microbiologists can evaluate recolonization, and geologists can interpret mineral fabric and weathering. Conservators bring knowledge of treatment objectives and ethical constraints, while cemetery managers and volunteers provide access to large numbers of monuments and long-term field observations.

No single discipline can answer the central questions adequately in isolation. Research programs should therefore be designed collaboratively from the outset rather than adding another specialty only after unexpected results appear.

Such collaboration can also improve translation between laboratory research and field practice. A scientifically sophisticated method has limited preservation value if it cannot be implemented safely on an actual cemetery monument, while a practical technique remains difficult to defend if its material consequences have never been measured.

13.15. Funding and Institutional Support

Long-term conservation research presents a funding challenge because meaningful outcomes may extend well beyond ordinary grant periods. A five-year study is substantial by most research standards but represents only a small portion of the expected remaining life of a historic monument (Doehne & Price, 2010; Oguchi & Yu, 2021).

Government agencies, universities, conservation organizations, foundations, cemetery associations, manufacturers, and private donors all have potential roles in supporting this work. Partnerships can distribute cost while allowing laboratory expertise, field access, analytical equipment, and long-term stewardship to be combined.

Continuity deserves particular attention. Multi-decade monitoring programs require durable data-management plans and institutional commitments capable of surviving changes in personnel and funding cycles.

Investment in research should be viewed as preventive conservation infrastructure. Better evidence can reduce unnecessary treatment, improve product selection, identify vulnerable monuments earlier, and prevent avoidable loss of irreplaceable material.

13.16. Prioritized Research Framework

The research needs identified throughout this chapter do not carry equal urgency or direct relevance to the central question of this paper. A prioritized framework helps distinguish those capable of resolving immediate evidence gaps from longer-term developments that primarily improve documentation or management (Mohapatra et al., 2023; Pinna, 2014).

Table 13-1. Prioritized Research Framework for Historic Marble Preservation

Research area	**Principal question**	**Potential conservation value**	**Relative priority**
Long-term treatment monitoring	How do treated and untreated historic marbles change over decades?	Directly evaluates long-term compatibility under real exposure	Very High
Comparative cleaner evaluation	How do complete formulations perform under identical conditions?	Supports evidence-based product selection	Very High
Repeated-treatment residue behavior	Do organic treatment residues accumulate, stabilize, transform, or diminish between applications?	Directly addresses a central unresolved question	Very High
Residue characterization	What material remains, where is it located, and in what physical state?	Distinguishes detection from damaging mechanism	High
Environmental cycling	How do climate and exposure alter treatment performance?	Improves regional applicability of guidance	High

Research area	Principal question	Potential conservation value	Relative priority
Biological recolonization	What controls return of organisms after treatment?	Supports condition-based retreatment and reduced intervention	High
Treatment registry	Can large-scale observational records reveal long-term patterns?	Creates an enduring field-evidence base	High
Water chemistry	When does application or rinse water influence residues or treatment behavior?	Refines practical cleaning protocols	Moderate
Mechanical cleaning	How much surface change results from different brushes and treatment combinations?	Quantifies an important source of direct physical intervention	Moderate
Digital documentation	Which technologies best detect and quantify change without contact?	Improves monitoring and inscription documentation	Moderate
Citizen-science integration	Can trained volunteers generate reliable large-scale monitoring data?	Expands geographic and temporal research capacity	High

The priorities are intended as a strategic framework rather than a fixed hierarchy. Research opportunities may emerge according to available monuments, institutional partners, funding, or analytical capabilities.

13.17. A Vision for the Next Twenty-Five Years

The next several decades could substantially change how historic cemetery monuments are documented and monitored. Noncontact imaging may allow surface loss to be detected before it becomes obvious visually. Environmental sensors may connect deterioration patterns with actual moisture and climate conditions. More sensitive analytical techniques may distinguish treatment materials from environmental contaminants at increasingly small scales (Doehne & Price, 2010; Oguchi & Yu, 2021).

The greatest advance, however, may come from connecting technologies and datasets that presently operate separately. A monument could eventually possess a treatment record linking three-dimensional surface documentation, cleaner formulation, environmental exposure, biological condition, repairs, and repeated inspections over decades.

Such capability would not eliminate the need for human judgment. Improved measurement can tell conservators that a surface has changed; it cannot independently determine whether treatment is ethically justified, which aspects of weathering constitute significant historic fabric, or how much intervention is appropriate.

The enduring principles of conservation are therefore unlikely to become obsolete. Better technology should allow practitioners to understand the material more clearly, intervene more selectively, document more accurately, and recognize deterioration earlier—not encourage more frequent intervention simply because new tools are available.

13.18. Final Reflections

The research questions identified in this chapter arise from the same principle that has guided the broader review: conservation conclusions should remain proportional to the evidence supporting them (Mohapatra et al., 2023; Pinna, 2014).

Questions surrounding quaternary ammonium cleaner residues are appropriate subjects for continued investigation precisely because historic marble must survive far longer than most experimental programs can observe directly. The response to those uncertainties should be carefully designed research capable of determining composition, location, persistence, transformation, and material consequence.

Progress will depend less on proving one side of a preservation debate correct than on asking increasingly precise questions. When an unexpected result is documented, it should be investigated. When a formulation changes, it should be retested. When long-term observations challenge established expectations, recommendations should change accordingly.

The purpose of future research is not to replace professional judgment with laboratory data. It is to give that judgment a stronger foundation. Every improvement in understanding allows preservation decisions made today to carry less avoidable uncertainty into the future.

14. Final Perspective

14.1. Introduction

Historic marble headstones occupy an unusual position among cultural resources. They are objects of material conservation, but they are also genealogical records, works of craftsmanship, markers of community history, and deeply personal memorials. They remain outdoors rather than within controlled collections, exposed continuously to water, temperature change, pollutants, organisms, salts, physical disturbance, and the accumulated effects of time (American Institute for Conservation, 1994; Striegel et al., 2016).

The technical question examined in this paper—whether residues associated with quaternary ammonium compound cleaners present a significant long-term threat to historic marble—therefore exists within a larger responsibility. Cleaning decisions affect material that cannot be replaced once it is lost.

The preceding chapters have addressed the scientific question in detail. Chapter 12 established what the available evidence supports and where uncertainty remains, while Chapter 13 identified the research needed to narrow those uncertainties. The purpose of this final chapter is different. It considers what that evidence means for the way historic monuments should be approached and cared for.

14.2. Preservation Is a Process

No individual product defines good conservation.

Preservation begins with understanding the monument: what it is made from, how it has weathered, what conditions are affecting it, whether intervention is necessary, and what significance must be retained. Product selection follows from that assessment rather than preceding it (Historic England, 2021).

Cleaning occupies only one part of this process. Moisture conditions, unstable foundations, failed repairs, biological colonization, atmospheric exposure, and surrounding vegetation may continue influencing a monument long after a treatment is completed. Removing surface growth without considering those conditions may improve appearance without addressing the processes that will determine the stone's future.

Preservation therefore extends from assessment through treatment, documentation, monitoring, and eventual reassessment. A cleaning event is not an endpoint but one recorded intervention within the much longer life of the monument.

14.3. Caution and Evidence

Historic conservation appropriately favors caution because original material is finite. Once inscription detail, carving, tool marks, or weathered surface fabric are removed, they cannot be restored authentically (American Institute for Conservation, 1994; Striegel et al., 2016).

Caution is most effective when it is disciplined by evidence. A plausible concern should prompt examination, not automatically become a conclusion. Likewise, successful field experience should inform judgment without being treated as proof that every long-term question has been resolved.

The debate surrounding quaternary ammonium compounds illustrates the value of this balance. Their chemical classification raises legitimate questions, but those questions must ultimately be answered by examining how specific compounds and complete formulations behave within actual or representative stone systems. The same standard should apply to claims of compatibility and to claims of harm.

Scientific uncertainty is therefore not a weakness in the preservation process. Clearly defining what remains unknown allows intervention to be proportionate, monitoring to be purposeful, and future research to focus on questions that can change practice.

14.4. Responsibility of Stewardship

Anyone who undertakes work on a historic monument assumes temporary responsibility for a resource that has already survived several generations and may be expected to survive many more (Historic England, 2021).

That responsibility includes respecting original craftsmanship, inscriptions, weathered surfaces, previous historical alterations, cemetery context, and the people commemorated by the monument. It also requires recognizing that visual transformation is not necessarily preservation improvement.

The safest intervention may leave some staining, biological remnants, patina, or evidence of age. Restraint is especially important where complete removal would require greater abrasion, repeated wetting, stronger chemistry, or treatment of already weakened stone.

A monument does not need to look new to be cared for well. Its age is part of its history.

Stewardship therefore asks a different question from ordinary cleaning: not *How much can be removed?* but *How much original material can be retained while accomplishing a justified preservation objective?*

14.5. Role of Volunteers

Historic cemeteries vastly exceed the capacity of professional conservators, municipal employees, and cemetery staffs to document and care for every monument requiring attention. Trained volunteers can therefore play an important role in preservation (American Institute for Conservation, 1994; Striegel et al., 2016).

Their contribution extends beyond cleaning. Volunteers document inscriptions, photograph changing conditions, identify unstable monuments, monitor biological recolonization, maintain treatment histories, educate communities, and draw attention to cemeteries that might otherwise receive little care.

The strength of volunteer preservation lies in combining enthusiasm with defined limits of practice. Knowing when not to clean, when to stop, and when to refer a monument for professional assessment is as important as knowing how to perform a routine treatment.

Volunteer organizations may also become increasingly valuable to conservation research. Consistent records maintained over many years can provide observations that short-term research programs cannot reproduce. When documentation is standardized, the work performed in a small cemetery can contribute to understanding monument behavior far beyond that site.

14.6. A Personal Reflection

The scientific language of this paper—calcite, crystallization pressure, adsorption, surfactants, pore networks, residues, and environmental cycling—is necessary because preservation decisions deserve technical rigor. Yet none of those terms fully explains why the work matters (Historic England, 2021).

Every inscription represents a person whose life once extended far beyond the few lines surviving on a stone. Cemetery monuments record soldiers and farmers, mothers and fathers, children and immigrants, community leaders and people whose stories have otherwise nearly disappeared from the documentary record.

Cleaning an inscription so that it can be read again can reconnect a family with an ancestor or allow a visitor to encounter a story that had been obscured for decades. Stabilizing a vulnerable monument can preserve craftsmanship that no written transcription can replace.

Science provides a means of doing that work more responsibly. Its purpose in cemetery preservation is not to make stewardship impersonal. It helps ensure that good intentions do not inadvertently damage the very material through which remembrance survives.

14.7. Looking Ahead

Conservation practice will continue to change. Analytical instruments will become more sensitive, monitoring will become more precise, commercial formulations will evolve, and longer field studies will provide evidence unavailable today (American Institute for Conservation, 1994; Striegel et al., 2016).

Some current assumptions will undoubtedly be refined. That should be expected rather than resisted.

Evidence-based preservation depends on the willingness to alter practice when better information becomes available. The methods considered responsible today are the product of earlier generations questioning abrasive cleaning, inappropriate chemicals, incompatible repair materials, and other practices once accepted without the benefit of modern conservation science.

The same responsibility now belongs to the present generation. Current methods should be scrutinized with the same seriousness applied to historical ones, while conclusions should remain proportional to what the evidence actually demonstrates.

The goal is not to discover a final preservation method that will never require reconsideration. It is to create a culture of stewardship in which observation, documentation, research, experience, and professional judgment continually inform one another.

14.8. Final Thoughts

The question that initiated this paper concerned cleaner residues, but the investigation ultimately leads to a broader conclusion about historic preservation (Historic England, 2021).

Materials should be evaluated according to their demonstrated behavior. Treatments should be selected according to the condition and needs of the monument. Uncertainty should be acknowledged rather than filled with assumption. Evidence should remain open to revision as better information becomes available.

Above all, the objective is not the cleanest possible stone. It is the longest responsible preservation of the original monument and the information, craftsmanship, memory, and human story it carries.

Historic headstones cannot be replaced once their original fabric is gone. The responsibility of the present caretaker is therefore temporary but consequential: to intervene only as much as necessary, document what was done, learn from the result, and pass the monument forward with as much of its authenticity intact as possible.

Future researchers will have better instruments. Future conservators will have better data. Future volunteers will undoubtedly develop better methods. Their ability to do so depends in part on the condition in which today's caretakers leave these monuments and the quality of the records left behind.

That is the enduring purpose of the work.

We preserve history—one stone at a time.

Appendix A: Glossary of Conservation and Scientific Terms

A.1. Purpose

This glossary defines the principal scientific and conservation terms used throughout Technical Paper No. 1. Definitions are intended to support consistent interpretation of the manuscript and field appendices. They are explanatory rather than exhaustive disciplinary definitions.

Adsorption
Association of molecules or ions with a surface or interface. Adsorption differs from absorption into a bulk material and from crystallization as an ordered solid phase.

Biofilm
A community of microorganisms embedded within an extracellular polymeric matrix that can retain moisture, dissolved ions, nutrients, and particulate material on a stone surface.

Capillary action
Movement of liquid through narrow pores or fractures resulting from surface tension and interaction between the liquid and pore walls.

Carbonate stone
Stone composed substantially of carbonate minerals such as calcite or dolomite. Marble and limestone are common carbonate stones.

Cationic surfactant
A surface-active compound carrying a net positive charge in solution. Many quaternary ammonium compounds function as cationic surfactants.

Cleaner formulation
The complete commercial cleaning product, including active ingredients and supporting components such as surfactants, buffers, carriers, stabilizers, builders, and preservatives.

Crystallization
Formation and growth of an ordered solid phase from a solution, melt, or vapor. In porous stone, crystallization may become damaging when growth occurs under confinement and local stress exceeds material strength.

Crystallization pressure
Stress that may develop when a crystal grows from supersaturated solution against surrounding pore walls while a liquid film remains available at the growth interface.

Deliquescence
Absorption of atmospheric moisture by a crystalline material until sufficient water is present for the solid to dissolve into a solution.

Deliquescence relative humidity (DRH)
The relative humidity, at a specified temperature, above which a particular crystalline salt can deliquesce under equilibrium conditions.

Efflorescence
Visible precipitation of soluble salts at an exterior surface as moisture evaporates.

Environmental cycling
Repeated changes in moisture, temperature, relative humidity, solar exposure, freezing, rainfall, or other environmental conditions that influence material behavior over time.

Freeze-thaw cycling
Repeated freezing and thawing of moisture within or around porous materials. Damage depends on saturation, pore geometry, drainage, freezing conditions, and the material condition of the stone.

Hygroscopic
Describing a material capable of attracting and retaining water vapor from the surrounding atmosphere.

Mirabilite
The hydrated sodium sulfate phase $Na_2SO_4 \cdot 10H_2O$.

Moisture transport
Movement of liquid water or water vapor through pores, grain boundaries, fractures, or along material interfaces.

Patina
A surface condition resulting from age, weathering, use, deposition, or historic treatment that may contribute to the appearance and significance of a historic object.

Permeability
The ease with which a fluid can move through connected pores, fractures, or other pathways within a material.

Porosity
The proportion of void space within a material. Porosity alone does not determine permeability because pore size, connectivity, and geometry also influence fluid movement.

Quaternary ammonium compound (quat or QAC)
An organic ionic compound containing a positively charged nitrogen atom bonded to four organic substituents and paired with a negatively charged counterion.

Residual antimicrobial activity
Continued suppression of microbial recolonization after the initial treatment period as a result of retained or surface-associated active material.

Reaction or degradation product
A material formed when an original treatment, environmental contaminant, or stone constituent undergoes chemical, photochemical, or biological transformation.

Residue
Material remaining after treatment. This paper uses the more precise term unintended treatment residue when referring to cleaner-derived material remaining after the intended application and removal process.

Sodium hypochlorite
NaOCl, the principal active ingredient in many bleach formulations. In aqueous systems it participates in equilibrium with hypochlorous acid and functions as a broad oxidizing antimicrobial agent.

Sodium sulfate
Na_2SO_4, a highly studied inorganic salt capable of existing in anhydrous and hydrated phases and of producing severe deterioration in porous materials under particular environmental conditions.

Subflorescence
Salt precipitation or crystallization beneath the visible surface of a porous material. Subsurface crystallization can be mechanically consequential when stress is generated within confined pores.

Sugaring
Granular deterioration of marble in which reduced cohesion among carbonate crystals causes individual grains to loosen or detach, producing a friable texture.

Surfactant
A compound that accumulates at interfaces and alters interfacial tension, thereby affecting wetting, spreading, detergency, foaming, and related solution behavior.

Thenardite
The anhydrous sodium sulfate phase Na_2SO_4.

Treatment residue
Material associated with a cleaning or conservation treatment that remains on or within the substrate after the intended application and removal process has been completed.

Weathered marble
Marble whose mineral surfaces, grain boundaries, pores, fractures, cohesion, or surface condition have been altered through long-term environmental exposure.

Appendix B: Historic Marble Cleaning Condition Assessment and Treatment Screening Form

B.1. Purpose

This form supports consistent pre-treatment assessment of historic marble headstones considered for routine biological or surface cleaning. It is intended to help document observable conditions and identify circumstances in which routine cleaning should be deferred. It does not replace professional conservation judgment or structural assessment. NPS and related federal guidance emphasize condition assessment, documentation, and use of methods appropriate to the individual marker before treatment (Striegel et al., 2016; National Park Service, 2022b).

Monument Identification

Cemetery: ____

Section / lot / plot: _____________________________________

Monument or marker ID: __________________________________

Name(s) represented: ____________________________________

Approximate date of monument: ___________________________

Assessment date: _______________________________________

Assessor(s): ____

Authorization / responsible custodian: _______________________

Material and Construction

☐ Marble confirmed

☐ Marble probable; identification should be verified before treatment

☐ Monolithic tablet

☐ Tablet in slotted base

☐ Die-on-base or multi-piece monument

☐ Associated metal, paint, gilding, inscription fill, coating, or repair material present

☐ Material or construction uncertain

Surface and Structural Condition

☐ Surface generally cohesive

☐ Minor roughening or early sugaring

☐ Active granular loss / severe sugaring

☐ Scaling, blistering, or delamination

☐ Open crack(s)

☐ Loose or displaced fragment(s)

☐ Failed or moving repair

☐ Leaning, rocking, loose, or otherwise unstable monument

☐ Unidentified coating or surface treatment

☐ Complex carving or sculpture

☐ Corroding metal or staining associated with metal

☐ Previous cementitious, adhesive, or other repair affecting treatment area

Biological and Deposit Condition

☐ Light biological film

☐ Moderate algae / cyanobacteria / fungal growth

☐ Moss or heavy biomass

☐ Lichen, loosely attached

☐ Lichen, strongly attached to weathered stone

☐ Environmental dirt or soil deposits

☐ White crystalline or powdery deposit present

☐ Unidentified colored or translucent film / residue present

Environmental Conditions

☐ Adequate clean water available

☐ Weather within product limits

☐ Shade or manageable drying conditions available

☐ Runoff can be controlled

☐ Nearby vegetation requires protection

☐ Nearby waterway / drain / well / sensitive area present

☐ Freezing, extreme heat, strong wind, or severe weather expected

Routine Cleaning Eligibility

Condition	Field interpretation	Recommended response
Cohesive, stable marble with routine biological growth	Ordinary candidate for controlled cleaning	Proceed after authorization, product review, and a small test area.
Minor roughness / early sugaring	Reduced surface tolerance	Use minimal mechanical action and stop at first evidence of grain loss.
Active granular loss, scaling, delamination, or loose fragments	Routine wet cleaning may remove original material	Defer routine cleaning; seek professional conservation assessment.
Open structural crack, displaced component, rocking, or instability	Cleaning may introduce water or movement into an unsafe system	Do not clean until structural condition has been evaluated.
Paint, gilding, coating, complex sculpture, or unidentified surface treatment	Cleaning chemistry may alter significant historic material	Seek specialized assessment before treatment.
Strongly attached lichen on friable marble	Removal may detach stone	Consider limited treatment, monitoring, or professional assessment rather than complete removal.

B.2. Stop-Work Principle

Routine cleaning should stop when treatment begins removing marble rather than unwanted material. Grain loss, powdering, newly exposed bright stone, scaling, movement, unexpected staining, or a condition materially different from the original assessment should trigger reassessment rather than escalation of force or chemical concentration.

Appendix C: Recommended Cleaning Procedure for Stable Historic Marble

C.1. Scope

This procedure operationalizes Chapter 11 for stable historic marble judged suitable for routine cleaning. It is not intended for severely sugared, delaminated, unstable, painted, coated, structurally complex, or exceptionally significant monuments. The product-specific label, technical information, and safety data sheet remain controlling for concentration, contact time, personal protective equipment, and environmental restrictions (National Cemetery Administration, n.d.; National Park Service, 2022b, 2025b).

1. Confirm authorization and define the treatment objective. Document why cleaning is being undertaken. Improving legibility, reducing a material concern, or enabling examination is a more appropriate objective than attempting to make historic marble appear new.

2. Document existing condition. Photograph all sides, inscription, base, biological growth, repairs, cracks, and visible deposits before treatment.

3. Confirm the monument is suitable for routine cleaning. Use Appendix B. Defer treatment where severe sugaring, scaling, instability, open structural defects, significant coatings, or other complex conditions are present.

4. Review the current product information. Confirm formulation, dilution, temperature range, dwell period, rinse requirement, personal protective equipment, and environmental precautions.

5. Prepare clean water, dedicated tools, and runoff controls. Use sufficient clean potable water for wetting, tool cleaning, and rinsing. Avoid beginning treatment when an adequate water supply is uncertain.

6. Establish a small test area. Evaluate immediate color change, surface response, grain loss, staining, or other unexpected behavior before expanding treatment.

7. Pre-wet the marble where appropriate. Wet accessible near-surface pores with clean water to reduce the initial concentration gradient and improve treatment control. Do not flood cracks, failed joints, or hollow areas.

8. Measure and apply the cleaner. Use the documented concentration and only the quantity needed for even contact. Do not increase concentration merely to accelerate visual change.

9. Allow the documented contact period. Manage sun, wind, and working area so a rinse-based formulation does not dry contrary to its intended procedure.

10. Use gentle mechanical action only as needed. Use soft natural- or synthetic-bristle tools appropriate to the surface. Rinse brushes frequently so trapped grit does not become an abrasive.

11. Rinse according to the product procedure. Remove loosened biological material and reduce excess soluble formulation without using damaging water force.

12. Reassess before repeating treatment. A second controlled cycle or later return may be preferable to stronger chemistry or greater brushing pressure. Stop when additional cleaning would require removal of historic material.

13. Document the completed treatment. Record product, purchase or formulation date, lot number when available, dilution, dwell period, water source, tools, weather, rinse method, unexpected observations, and photographs.

14. Monitor rather than cleaning on a fixed schedule. Recolonization should trigger reassessment, not automatic annual retreatment. Use Appendix F to maintain a longitudinal record.

C.2. Practices Outside This Routine Procedure

Strong acids, abrasive blasting, wire brushes, hard scraping tools, uncontrolled commercial pressure washing, unidentified homemade mixtures, and unapproved coatings or sealers are outside the routine procedure described here. General-purpose household bleach and household detergents are likewise less defensible for routine historic-marble conservation where better-evaluated preservation-specific alternatives are available (National Park Service, 2025a, 2025b; Striegel et al., 2016).

Appendix D: Cleaning Methods and Treatment-System Comparison

D.1. Comparative Framework

This appendix compares common treatment approaches according to their principal function, potential conservation value, and major limitations. It is not a product-approval list. Compatibility remains dependent on the complete formulation, concentration, monument condition, environmental setting, and treatment objective.

Method / treatment	Primary function	Potential conservation value	Principal concern / limitation	General role
Clean water + soft-bristle tools	Loosens light soil and some biological material	Minimal chemical introduction; useful for limited soiling on cohesive stone	May provide inadequate biological control and encourage excessive brushing if used beyond its effective range	Appropriate first-line option where it achieves the treatment objective.
Preservation-specific quat cleaner with relevant compatibility evidence	Biological control plus surfactant-assisted wetting	Effective biological treatment; may reduce mechanical effort and delay recolonization	Formulation-specific residue, adsorption, environmental exposure, and repeated-treatment questions remain	Potentially appropriate on suitable marble when current instructions and evidence support use.
Sodium hypochlorite / general household bleach	Broad oxidative antimicrobial and pigment-lightening action	Rapid biological inactivation and visible lightening	Broad oxidative reactivity, high alkalinity, variable additives, metals/vegetation/runoff concerns, limited historic-marble-	Generally less defensible for routine historic-marble cleaning where better-evaluated alternatives exist.

Method / treatment	**Primary function**	**Potential conservation value**	**Principal concern / limitation**	**General role**
			specific formulation evidence	
Acidic cleaners	Dissolve mineral deposits or react with soils	May be effective on acid-resistant substrates in specialized contexts	Direct calcite dissolution and irreversible etching of marble	Inappropriate for routine historic-marble cleaning.
Commercial high-pressure washing	Rapid removal by water force	High productivity on robust modern surfaces	Can detach weakened grains, round inscriptions, enlarge cracks, and drive water into defects	Inappropriate for weathered historic marble.
Abrasive blasting / grinding / powered abrasive tools	Mechanical removal	Rapid removal of coatings or deposits on some nonhistoric substrates	Removes original surface material and tooling; irreversible texture change	Inappropriate for historic marble.
Household soap / dish detergent / multipurpose cleaner	General soil removal	Readily available	May contain fragrances, dyes, builders, thickeners, surfactants, or salts not evaluated for historic marble	Avoid as a default preservation treatment.

Method / treatment	Primary function	Potential conservation value	Principal concern / limitation	General role
Leave-on biological treatment	Continued biological suppression without immediate full removal	Can reduce mechanical work when a specific product is designed and validated for this use	Cannot be generalized from one formulation to another; runoff and residue behavior remain product-specific	Use only when supported by the current formulation instructions and relevant conservation evidence.

D.2. Interpretation Principle

Treatment categories should be compared as complete systems rather than by active ingredient or immediate visual result alone. A method that appears chemically mild may become mechanically aggressive if it requires extensive brushing, while a more effective compatible formulation may reduce cumulative intervention by decreasing mechanical demand and retreatment frequency.

Appendix E: Field Treatment Documentation Form

E.1. Purpose

This form records the treatment conditions necessary for later interpretation. Treatment documentation is especially important where product formulations can change over time and where future observers may need to distinguish treatment effects from environmental weathering (American Institute for Conservation, 1994; National Park Service, 2022a, 2022b).

Monument and Treatment Identification

Cemetery: ____

Section / lot / plot: ____

Monument / marker ID: ____________________________________

Name(s): ____

Treatment date: ____

Treatment lead / team: ____________________________________

Authorization: ____

Product and Water

Product name: ____

Manufacturer: ____

Product purchase date / formulation date if known: _____________

Lot / batch number if available: ______________________________

Dilution / concentration used: ________________________________

Water source: ____

Known water-quality concern: _________________________________

Application Conditions

☐ Stone pre-wet

☐ Test area completed

☐ Surface kept damp during active treatment as required

☐ Cleaner prevented from drying contrary to instructions

☐ Runoff controlled

☐ Adjacent vegetation protected

☐ Adjacent metal / other materials protected

Air temperature: ______________________

Approximate relative humidity if known: ______________________

Sun / shade condition: ______________________________________

Wind condition: ____

Dwell / contact time: ____

Number of treatment cycles: __________________________________

Tools and Mechanical Action

☐ Tampico or other soft natural-bristle brush

☐ Soft synthetic-bristle brush

☐ Detail brush

☐ Low-pressure pump sprayer

☐ Controlled hose rinse

☐ Other: ____

Mechanical action / pressure observations:

____

______

Treatment Outcome

☐ Biological material reduced / removed as intended

☐ Some biological remnants intentionally left in place

☐ Inscription legibility improved

☐ No observable grain loss

☐ Grain loss or surface change observed - work stopped

☐ Unexpected staining or deposit observed

☐ Structural or material condition changed the treatment plan

Narrative treatment notes:

____
____

____
____

Photographic Record

☐ Overall front before / after

☐ Overall back before / after

☐ Side views

☐ Inscription details

☐ Existing damage

☐ Treatment-in-progress

☐ Unexpected condition / residue

☐ Scale and orientation included where useful

Photo file / folder reference:

____
____

Appendix F: Post-Treatment Monitoring Form

F.1. Purpose

This form establishes a repeatable record after cleaning. Immediate appearance is not a sufficient measure of long-term compatibility. Monitoring should document recolonization, deposits, surface condition, moisture behavior, and any changes affecting the stone or adjacent materials.

Time-Zero Record

Monument / marker ID: ____

Treatment date: ____

Time-zero inspection date: ____________________________________

Product / dilution: ____

Primary photograph reference: ___________________________________

☐ Surface dry and visually stable

☐ No unexpected film or deposit

☐ No observable grain loss

☐ No new staining

☐ No new cracking or movement

☐ Adjacent metal unchanged

☐ Adjacent soil / vegetation unaffected

☐ Other observation: ____

Follow-Up Observation

Observation date	Interval since treatment	Biological recolonization	Deposits / films	Surface condition	Moisture / drying notes	Photo reference
_____________ ____	_____________ ____	None / slight /	None / white / colored /	Stable / grain loss / scaling	_____________ ____	_____________ ____

Observation date	Interval since treatment	Biological recolonization	Deposits / films	Surface condition	Moisture / drying notes	Photo reference
		moderate / heavy	translucent / other	/ cracking / other		
_________________	_________________	None / slight / moderate / heavy	None / white / colored / translucent / other	Stable / grain loss / scaling / cracking / other	_________________	_________________
_________________	_________________	None / slight / moderate / heavy	None / white / colored / translucent / other	Stable / grain loss / scaling / cracking / other	_________________	_________________
_________________	_________________	None / slight / moderate / heavy	None / white / colored / translucent / other	Stable / grain loss / scaling / cracking / other	_________________	_________________

F.2. Conditions Warranting Further Evaluation

☐ New crystalline or powdery deposit

☐ Persistent or unusual surface film

☐ Accelerated granular loss or scaling

☐ Unexpected staining

☐ Change in moisture retention or drying pattern

☐ Corrosion or staining at adjacent metal

☐ Repeated rapid recolonization suggesting unresolved environmental drivers

☐ Other: ____

Follow-up action / referral:

____

____

Appendix G: Residue and Deposit Assessment Framework

G.1. Purpose

This appendix translates Chapter 10 into a diagnostic framework for unexpected material observed after cleaning. It is intended to prevent premature conclusions based solely on appearance, timing, or detection of a single ion. Material should be classified, located, and characterized before a deterioration mechanism is assigned.

G.2. First-Level Classification

Observed material	Possible category	Initial questions
Loose dust, soil, soot, or particulate film	Environmental deposit / accretion	Was it present before treatment? Is deposition continuing from the surrounding environment?
Green, dark, orange, gray, or gelatinous material	Biological film or remnant	Is the material living, dead, pigment, EPS, trapped particulate matter, or a mixture?
White powder, bloom, needles, or crystalline crust	Efflorescence or other precipitated material	What ions or crystalline phases are present? Did treatment water mobilize preexisting salts?
Transparent, glossy, tacky, or patchy film	Possible organic or formulation residue	Does the product formulation contain nonvolatile surfactants, polymers, builders, or other film-forming components?
Material deliberately introduced during repair	Intentional treatment material	Is the material functioning as intended and aging compatibly?
New color or corrosion adjacent to metal	Reaction / corrosion product	Is treatment chemistry, moisture, or galvanic / environmental exposure involved?

G.3. Questions Required Before Assigning Conservation Significance

1. What is the material chemically or mineralogically?

2. How much is present and how reproducible is the observation?

3. Is it located at the surface, within near-surface pores, or deeper within the stone?

4. Is it dissolved, adsorbed, amorphous, crystalline, or part of a mixed deposit?

5. Was it present before treatment or could cleaning have mobilized pre-existing material?

6. Can the source be distinguished among cleaner, application water, environment, biological activity, previous repairs, or the stone itself?

7. Does the material remain mobile during wetting and drying?

8. Does it alter moisture retention, surface chemistry, biological recolonization, or mechanical behavior?

9. Is there measurable material change associated with the deposit?

10. Does the evidence establish causation, or only temporal association?

G.4. Analytical Method Selection

Analytical method	Most useful for	Important limitation
Ion chromatography	Quantifying extracted soluble ions such as chloride, sulfate, nitrate, sodium, or ammonium	Does not reconstruct the original physical state or independently identify source.
FTIR spectroscopy	Many organic compounds, polymers, carbonates, sulfates, and treatment materials	Mixed samples and low concentrations can complicate interpretation.
Raman spectroscopy	Many crystalline and molecular compounds, sometimes in situ	Fluorescence, surface roughness, and weak signal can limit analysis.

Analytical method	Most useful for	Important limitation
X-ray diffraction	Identification of crystalline mineral phases	Limited for amorphous materials and very thin organic layers.
SEM with EDS	Deposit morphology plus associated elemental composition	Elements do not uniquely identify complete molecular compounds.
XPS / ToF-SIMS	Near-surface elemental states or molecular fragments	Highly specialized and surface-sensitive; interpretation may be complex.
Chromatography / mass spectrometry	Selected organic compounds and degradation products	Requires targeted extraction, standards, and specialized laboratory methods.

G.5. Interpretive Guardrails

Observation	What it establishes	What it does not establish
Chloride detected	Chloride is present above the method detection threshold	Which chloride-bearing source produced it or whether an intact quat remains.
Material detected after treatment	A post-treatment sample contains the detected material	That the treatment caused the material to form or that it is damaging.
Adsorbed organic material identified	An organic compound is associated with a surface or interface	Crystallization pressure or a classical inorganic salt-weathering mechanism.
No visible residue	No macroscopic deposit is apparent	That no molecular or internal treatment material remains.

Observation	What it establishes	What it does not establish
Visible whitening after cleaning	The surface appearance changed	That biological control was complete or that the historic surface was unaltered.
No published failures identified	No characteristic failure pattern has been established in the reviewed literature	Universal long-term safety for every formulation and treatment history.

G.6. Escalation

Unexpected material should be documented before attempted removal. Persistent crystalline deposits, accelerating stone loss, new staining, altered moisture behavior, or a repeatable association with a specific treatment warrants professional or laboratory evaluation. Analytical detection should be interpreted alongside untreated controls, treatment history, environmental context, and measurable condition change whenever those data are available (Doehne & Price, 2010; Oguchi & Yu, 2021).

Appendix H: Comprehensive Literature Review Methodology and Evidence Matrix

H.1. Purpose and Review Design

The literature review supporting Technical Paper No. 1 was designed as a structured critical narrative review rather than a formal systematic review or meta-analysis. Its purpose was to identify, compare, and synthesize evidence relevant to historic marble cleaning across several overlapping fields: stone conservation, marble weathering, moisture transport, salt crystallization, biodeterioration, quaternary ammonium chemistry, antimicrobial action, environmental fate, monument-cleaner evaluation, professional conservation ethics, and cemetery-specific practice.

The evidence base for this edition was intentionally limited to a compact set of retrievable sources rather than a maximal citation count. Priority was given to open peer-reviewed articles, freely available scholarly publications, and current government or professional guidance that a reader using ordinary home Internet access can reasonably obtain. The final References section contains 21 sources. This source set is intended to provide a transparent and usable scholarly foundation, not to claim exhaustive coverage of every publication in the broader literature.

A single disciplinary literature is insufficient for the central question. Salt-weathering studies provide detailed physical mechanisms but often do not involve commercial cleaners. Microbiology and environmental studies describe quaternary ammonium compounds but usually do not examine historic marble. Cemetery-specific cleaner studies provide the most direct treatment evidence but cover a limited number of formulations and exposure conditions. The review therefore distinguishes direct applicability from mechanistic transferability rather than treating every source as equivalent.

Source verification for the present edition was current through August 24, 2026.

H.2. Research Questions

1. How does naturally weathered historic marble differ from fresh marble in ways relevant to cleaning and residue behavior?

2. Under what physical and chemical conditions do soluble salts damage porous stone?

3. How should sodium sulfate and other classical inorganic salt mechanisms be interpreted when evaluating chemically different treatment materials?

4. How do quaternary ammonium compounds function as antimicrobials and surfactants, and what is known about their adsorption, persistence, environmental fate, and resistance concerns?

5. What evidence directly evaluates complete monument-cleaner formulations on marble or closely related carbonate stone?

6. How does sodium hypochlorite differ from preservation-specific quat systems in antimicrobial mechanism, formulation context, and conservation implications?

7. What can current analytical methods establish about residues, deposits, and treatment-derived material?

8. Where does the evidence justify firm conservation recommendations, and where should conclusions remain conditional or explicitly uncertain?

H.3. Source Domains

Cemetery-Specific and Government Conservation Guidance

Primary emphasis was placed on National Park Service and National Cemetery Administration materials addressing preservation of grave markers, cleaning methods, abrasive cleaning, cleaner comparison, and care of government-furnished headstones. These sources provide the most direct connection between scientific evaluation and cemetery practice (National Cemetery Administration, n.d.; National Park Service, 2022a, 2022b, 2025a, 2025b, 2025c; Striegel et al., 2016).

Stone Conservation and Marble Deterioration

Open scholarly conservation literature was used to establish the material behavior of weathered stone, marble condition, deterioration terminology, and the relationship among moisture, pore structure, material loss, and treatment compatibility (Ahmad, 2020; Doehne & Price, 2010; Historic England, 2021).

Salt Weathering and Crystallization Mechanics

Peer-reviewed salt-weathering sources were used to establish transport, supersaturation, crystallization pressure, pore confinement, phase behavior, and the special role of sodium sulfate without extending those mechanisms automatically to unrelated compounds (Cappai et al., 2024; Lezzerini et al., 2022; Oguchi & Yu, 2021; Shahidzadeh-Bonn et al., 2010).

Biodeterioration and Biological Colonization

Biological literature was used to characterize biofilms and lichens as context-dependent components of stone weathering rather than uniformly damaging surface contaminants. The review therefore distinguishes biological presence from a demonstrated need for removal (Pinna, 2014).

Quaternary Ammonium Chemistry, Microbiology, and Environmental Fate

Microbiological and environmental studies were used to explain antimicrobial mechanism, efficacy, persistence, toxicity, and antimicrobial-resistance concerns. Because these studies generally do not involve historic marble, they are treated as mechanistic or contextual evidence rather than direct proof of stone compatibility (Boyce, 2023; Gerba, 2015; Kwaśniewska et al., 2020; McDonnell & Russell, 1999; Mohapatra et al., 2023).

Professional Conservation Ethics

The American Institute for Conservation Code of Ethics and Guidelines for Practice was used for principles concerning examination, treatment planning, proportional intervention, documentation, professional competence, and consideration of future treatment (American Institute for Conservation, 1994).

H.4. Search Approach

Searches were iterative rather than restricted to a single predefined database string. Broad conceptual searches were combined with author, title, DOI, and institution-specific searches. Where current professional practice or agency recommendations were material to a conclusion, current official webpages were verified rather than assuming that older guidance remained operative.

Representative search concepts included:

- historic marble weathering and sugaring;
- marble pore structure moisture transport;
- salt crystallization porous stone;
- crystallization pressure stone heritage;
- sodium sulfate marble deterioration;
- efflorescence subflorescence marble;
- quaternary ammonium compounds antimicrobial mechanism;

• benzalkonium chloride adsorption carbonate / calcite;

• quaternary ammonium environmental fate toxicity resistance;

• historic monument biological cleaning;

• grave marker cleaner comparative study;

• NCPTT monument cleaning;

• National Cemetery Administration headstone cleaning;

• sodium hypochlorite historic stone cleaning;

• biofilm lichen stone deterioration;

• cleaner residue stone analysis;

• FTIR Raman XRD residue characterization stone conservation.

H.5. Inclusion Criteria

Sources were retained when they met one or more of the following conditions:

• directly addressed cleaning, care, or preservation of grave markers or cemetery monuments;

• constituted current official conservation or cemetery guidance;

• provided open peer-reviewed evidence concerning marble deterioration, pore behavior, salt transport, crystallization, or sodium sulfate;

• provided peer-reviewed evidence necessary to explain quat antimicrobial behavior, environmental fate, toxicity, or antimicrobial-resistance concerns;

• provided a documented comparison of cleaners or treatment performance relevant to carbonate stone;

• provided professional conservation principles directly relevant to treatment selection, proportionality, documentation, or future retreatment;

• could be verified bibliographically and retrieved openly or through ordinary public Internet access.

H.6. Exclusion and Limitation Criteria

The review avoided relying substantively on:

• unsourced blogs, anonymous web posts, and social-media commentary;

• commercial marketing claims presented as independent scientific evidence;

• general household-cleaning advice lacking conservation relevance;

• paywalled or difficult-to-obtain sources when an open and adequately authoritative source supported the same proposition;

• studies of unrelated substrates where the transfer mechanism could not be justified;

• antimicrobial efficacy studies recast as proof of stone compatibility;

• detection of an ion or residue recast as proof of a deterioration mechanism;

• older agency guidance when a current official version could be verified.

Manufacturer documentation may be appropriate for current composition, dilution, safety, or application instructions, but manufacturer claims should not be recast as independent proof of long-term compatibility. The present edition minimizes reliance on manufacturer documents because the principal conclusions can be supported through open scientific and institutional sources.

H.7. Evidence Classification

Each substantive source was interpreted according to the degree to which it directly answers the paper's conservation question.

E1 — Direct Cemetery / Monument Cleaning Evidence
Research or official guidance directly involving grave markers, cemetery monuments, government-issued headstones, or cleaning treatments used on them.

E2 — Historic Stone / Marble Conservation Evidence
Evidence involving historic marble, carbonate stone, or closely related outdoor heritage materials relevant to weathering, condition, and treatment.

E3 — Mechanistic Salt / Porous-Material Evidence
Laboratory or theoretical research establishing moisture transport, supersaturation, crystallization pressure, pore confinement, phase behavior, or related deterioration mechanisms.

E4 — Quat / Antimicrobial / Environmental Mechanistic Evidence
Research establishing quaternary ammonium antimicrobial action, efficacy, adsorption or persistence context, toxicity, environmental fate, or resistance concerns outside a direct marble-treatment experiment.

E5 — Professional Conservation Principle
Professional ethical or methodological guidance concerning examination, proportional intervention, documentation, competence, preventive conservation, and future treatment.

E6 — Contextual / Observational Evidence
Field or review evidence that provides real-world context but lacks the controls necessary for direct causal attribution.

H.8. Rules for Evidence Transfer

Evidence was transferred across disciplines only when the underlying mechanism remained relevant and the limits of transfer could be stated explicitly. For example, the physical requirement that crystallization pressure involve supersaturated solution, crystal growth, confinement, and a vulnerable substrate is relevant to porous stone generally. The numerical outcome of a particular laboratory salt test, however, should not be converted directly into a prediction of field damage from a chemically different cleaner residue.

Similarly, microbiological research can establish how quaternary ammonium compounds disrupt membranes, but it cannot independently establish long-term compatibility with weathered marble. Environmental research can establish aquatic toxicity or persistence concerns without proving that a cemetery application creates the same exposure magnitude as institutional or industrial use. This distinction between mechanism and direct treatment evidence is central to the review.

H.9. Claim-Strength Convention

The manuscript uses language intended to keep rhetorical certainty proportional to evidentiary certainty. Direct agency recommendations are described with formulations such as “NPS recommends” or “NCA advises.” Strong peer-reviewed mechanisms are described as established within the conditions studied. Cross-disciplinary transfer is introduced with formulations such as “the same physical principle is relevant” or “this provides a mechanistic basis.” Where direct long-term evidence remains limited, the manuscript uses conditional language including “may,” “can,” “is consistent with,” and “warrants further study.”

H.10. Evidence-Extraction Fields

For each retained source, the review sought to identify the following information where available:

• complete APA 7 citation and retrievable URL or DOI;

• source type and publication authority;

• material or substrate studied;

• treatment or chemical system studied;

• study design or guidance purpose;

• principal mechanism or finding;

• limitations relevant to historic marble;

• evidence classification;

• manuscript chapters or claims supported.

H.11. Core Evidence Matrix

Source	Evidence class	Principal contribution	Principal limitation	TP1 application
Ahmad (2020)	E2	Non-destructive condition assessment and marble deterioration; supports weathered-marble variability.	Not cleaning-specific; classification and ultrasonic focus.	Ch. 2; condition assessment.
American Institute for Conservation (1994)	E5	Professional ethics: examination, treatment planning, proportional intervention, documentation, competence.	Ethical framework rather than experimental evidence.	Chs. 1, 11–14; Apps. B, E.
Boyce (2023)	E4	Current review of quat tolerance, resistance, and relationship to antibiotic-resistance concerns.	Healthcare/disinfectant context; not stone compatibility.	Chs. 5, 8, 9.

Source	Evidence class	Principal contribution	Principal limitation	TP1 application
Cappai et al. (2024)	E3	Recent chemomechanical treatment of salt crystallization in limestone.	Limestone and modeled/experimental conditions differ from cemetery marble.	Chs. 3–4, 10.
Doehne & Price (2010)	E2/E3	Open GCI synthesis of stone deterioration, salts, moisture, cleaning, and conservation research.	Broad stone scope; not product-specific.	Chs. 1–4, 8, 10–14; App. G.
Gerba (2015)	E4	Quat efficacy and application mechanisms.	Microbiological application context rather than historic stone.	Chs. 5, 8, 9.
Historic England (2021)	E2/E6	Current practical guidance for historic cemetery and graveyard monuments; condition and intervention context.	Professional guidance; not a controlled cleaner study.	Chs. 2, 8, 11–14.
Kwaśniewska et al. (2020)	E4	Open review of biological activity of quaternary ammonium salts and derivatives.	Biological review; limited direct stone relevance.	Ch. 5; comparison framework.
Lezzerini et al. (2022)	E3	Direct sodium-sulfate crystallization	Accelerated/laboratory exposure does not reproduce all cemetery conditions.	Chs. 3–4.

Source	**Evidence class**	**Principal contribution**	**Principal limitation**	**TP1 application**
		effects on marbles and other stones.		
McDonnell & Russell (1999)	E4	Foundational review of antiseptic/disinfectant mechanisms, including quats and oxidants.	Medical/microbiological context; older but foundational.	Chs. 5 and 9.
Mohapatra et al. (2023)	E4	Comprehensive review of QAC classification, occurrence, fate, toxicity, and antimicrobial resistance.	Environmental exposure scales differ from cemetery use.	Chs. 5, 8, 9, 12.
National Cemetery Administration (n.d.)	E1	Current federal guidance for cleaning government-furnished headstones and markers.	Applies specifically to government-furnished markers and NCA context.	Chs. 7, 9, 11; App. C.
National Park Service (2022a)	E1	NCPTT cemetery-conservation program orientation and preservation context.	Program-level guidance rather than experimental detail.	Chs. 1, 7, 8, 11–14.
National Park Service (2022b)	E1	Cemetery-preservation course guidance on	General instructional guidance; product and substrate limitations still apply.	Ch. 11; Apps. B–E.

Source	Evidence class	Principal contribution	Principal limitation	TP1 application
		cleaning grave markers.		
National Park Service (2025a)	E1	Current federal warning regarding abrasive cleaning of grave markers.	Focused on abrasive methods rather than full cleaner chemistry.	Chs. 7, 11; App. D.
National Park Service (2025b)	E1	Current best-practice recommendations for cleaning government-issued headstones.	Government marker context; not universal to all monument materials and conditions.	Chs. 7, 9, 11; Apps. C–D.
National Park Service (2025c)	E1	Comparative study of commercially available cleaners used on federally issued headstones; formulation-specific residue and performance evidence.	Limited products, specimens, and accelerated-test conditions; formulation versions matter.	Chs. 6–7, 9–12.
Oguchi & Yu (2021)	E3	Open review of theoretical salt-weathering mechanisms for stone heritage.	Mechanistic review; not cleaner-specific.	Chs. 3–4, 8, 10; App. G.
Pinna (2014)	E2/E6	Balanced open review of whether biofilms and lichens damage or protect stone.	Broad stone and organism scope; site-specific effects vary.	Chs. 2, 8, 11.

Source	Evidence class	Principal contribution	Principal limitation	TP1 application
Shahidzadeh-Bonn et al. (2010)	E3	Experimental evidence of crystallization damage in porous media.	Model porous systems do not reproduce full historic-marble complexity.	Chs. 3–4, 10.
Striegel et al. (2016)	E1/E2	NPS Preservation Brief 48: comprehensive grave-marker conservation, condition, maintenance, and treatment guidance.	Broad interdisciplinary guidance rather than product-specific long-term study.	Overall conservation framework; Chs. 1, 7, 11–14; Apps. B–E.

H.12. Synthesis by Evidence Domain

Historic Marble and Moisture

The stone-conservation literature strongly supports treating weathered marble as a heterogeneous, moisture-responsive material whose pore connectivity, grain cohesion, and surface condition change over time. This evidence supports the paper's emphasis on condition assessment and limits the direct transfer of findings from fresh laboratory marble to severely weathered cemetery stone.

Classical Salt Weathering

The salt-weathering literature strongly supports a mechanism involving dissolved transport, concentration, supersaturation, crystallization or phase transformation, confinement, and material response. Sodium sulfate provides a particularly important model because its phase behavior can generate severe damage. The literature does not support using the chemical category "salt" alone as a sufficient predictor of deterioration.

Quaternary Ammonium Compounds

The microbiological literature strongly supports quat antimicrobial activity and membrane-disruption mechanisms, while environmental literature identifies persistence, sorption, aquatic toxicity, and resistance-related concerns under some exposure conditions. Direct evidence connecting those properties to multi-decade deterioration of historic marble remains substantially more limited.

Cleaner Formulations

The most directly relevant federal cleaner research demonstrates that complete formulation matters. A residue observed in an earlier commercial formulation was not reproduced after reformulation under the subsequent test conditions. This supports formulation-specific rather than chemical-class-wide interpretation.

Cleaning Practice

Government and professional conservation guidance consistently favors condition assessment, minimum necessary intervention, avoidance of aggressive abrasion, controlled water and mechanical action, documentation, and selection of treatment according to the individual monument. These recommendations form the practical framework in Chapter 11 and Appendices B–F.

H.13. Principal Evidence Gaps

The review identified five evidence gaps that materially limit stronger conclusions:

1. Multi-decade repeated-treatment studies on naturally weathered historic marble are scarce.

2. The depth, quantity, and persistence of retained quat material after realistic treatment and environmental exposure are not well characterized across marble conditions.

3. Complete commercial formulations change over time and may contain supporting ingredients not represented in studies of isolated active compounds.

4. Interactions among cleaner residues, preexisting mixed environmental salts, biological films, and local climate remain incompletely characterized.

5. Field treatment records are rarely standardized enough to support strong retrospective causal analysis.

H.14. Review Limitations

This review was not prospectively registered and does not claim the completeness of a formal systematic review. Search methods were iterative, the source base spans disciplines using different terminology and experimental designs, and emphasis on open accessibility necessarily excludes some paywalled literature. The compact reference set was selected deliberately to improve transparency and reader access rather than to maximize citation count. Direct studies of complete preservation-specific cleaner formulations on naturally weathered historic marble remain limited, and proprietary formulation information may be incomplete.

H.15. Relationship of the Review to Manuscript Conclusions

The paper's principal conclusions are intentionally calibrated to this evidence structure. Firm statements are reserved for well-established mechanisms and current agency guidance. Formulation-specific cleaner findings are not generalized automatically to an entire chemical class. Biomedical and environmental QAC research is used to explain mechanism and environmental context rather than as direct proof of marble behavior. Where direct long-term evidence remains limited, the manuscript identifies uncertainty and defines the research needed to reduce it.

The methodological standard adopted throughout the review is therefore the same one used in Technical Paper No. 4: where the evidence establishes a mechanism, the paper explains the mechanism; where it supports a treatment principle, the paper states that principle; and where it does not support a universal conclusion, the paper does not invent one.

References

Ahmad, A. (2020). Investigation of marble deterioration and development of a classification system for condition assessment using non-destructive ultrasonic technique. *Mediterranean Archaeology and Archaeometry, 20*(3), 75–89. https://doi.org/10.5281/zenodo.3930410

American Institute for Conservation. (1994). *Code of ethics and guidelines for practice*. https://www.culturalheritage.org/conservation-at-work/uphold-professional-standards/code

Boyce, J. M. (2023). Quaternary ammonium disinfectants and antiseptics: Tolerance, resistance and potential impact on antibiotic resistance. *Antimicrobial Resistance & Infection Control, 12*, 32. https://doi.org/10.1186/s13756-023-01241-z

Cappai, M., Casti, M., & Pia, G. (2024). Salt crystallization in limestone: Materials decay and chemomechanical approach. *Materials, 17*(16), 3986. https://doi.org/10.3390/ma17163986

Doehne, E., & Price, C. A. (2010). *Stone conservation: An overview of current research* (2nd ed.). Getty Conservation Institute. https://www.getty.edu/conservation/publications_resources/pdf_publications/stone_cons_2nd_edit.html

Gerba, C. P. (2015). Quaternary ammonium biocides: Efficacy in application. *Applied and Environmental Microbiology, 81*(2), 464–469. https://doi.org/10.1128/AEM.02633-14

Historic England. (2021, February 19). *Caring for historic cemetery and graveyard monuments*. https://historicengland.org.uk/advice/caring-for-heritage/cemeteries-and-burial-grounds/monuments/

Kwaśniewska, D., Chen, Y.-L., & Wieczorek, D. (2020). Biological activity of quaternary ammonium salts and their derivatives. *Pathogens, 9*(6), 459. https://doi.org/10.3390/pathogens9060459

Lezzerini, M., Tomei, A., Gallello, G., Aquino, A., & Pagnotta, S. (2022). The crystallization effect of sodium sulfate on some Italian marbles, calcarenites and sandstones. *Heritage, 5*(3), 1449–1461. https://doi.org/10.3390/heritage5030076

McDonnell, G., & Russell, A. D. (1999). Antiseptics and disinfectants: Activity, action, and resistance. *Clinical Microbiology Reviews, 12*(1), 147–179. https://doi.org/10.1128/CMR.12.1.147

Mohapatra, S., Lin, Y., Goh, S. G., Ng, C., You, L., Tran, N. H., & Gin, K. Y.-H. (2023). Quaternary ammonium compounds of emerging concern: Classification, occurrence, fate, toxicity and antimicrobial resistance. *Journal of Hazardous Materials, 445*, 130393. https://doi.org/10.1016/j.jhazmat.2022.130393

National Cemetery Administration. (n.d.). *Cleaning government-furnished headstones and markers*. U.S. Department of Veterans Affairs. Retrieved August 17, 2026, from https://www.cem.va.gov/hmm/cleaning.asp

National Park Service. (2022a, March 21). *Cemetery conservation*. https://www.nps.gov/subjects/ncptt/cemetery-conservation.htm

National Park Service. (2022b, March 16). *Cleaning grave markers*. https://www.nps.gov/articles/000/cemetery-preservation-course-cleaning-grave-markers.htm

National Park Service. (2025a, April 7). *Abrasive cleaning of grave markers*. https://www.nps.gov/articles/000/abrasive-cleaning-of-grave-markers-cemetery-conservation.htm

National Park Service. (2025b, April 7). *Best practice recommendations for cleaning government issued headstones*. https://www.nps.gov/articles/000/best-practice-recommendations-for-cleaning-government-issued-headstones.htm

National Park Service. (2025c, April 7). *Comparative study of commercially available cleaners for use on federally-issued headstones*. https://www.nps.gov/articles/000/comparative-study-of-commercially-available-cleaners-for-use-on-federally-issued-headstones.htm

Oguchi, C. T., & Yu, S. (2021). A review of theoretical salt weathering studies for stone heritage. *Progress in Earth and Planetary Science, 8*, Article 32. https://doi.org/10.1186/s40645-021-00414-x

Pinna, D. (2014). Biofilms and lichens on stone monuments: Do they damage or protect? *Frontiers in Microbiology, 5*, 133. https://doi.org/10.3389/fmicb.2014.00133

Shahidzadeh-Bonn, N., Desarnaud, J., Bertrand, F., Chateau, X., & Bonn, D. (2010). Damage in porous media due to salt crystallization. *Physical Review E, 81*(6), 066110. https://doi.org/10.1103/PhysRevE.81.066110

Striegel, M. F., Gale, F., Church, J., & Dietrich-Smith, D. (2016). *Preserving grave markers in historic cemeteries* (Preservation Brief 48). National Park Service. https://www.nps.gov/articles/000/preserving-grave-markers-in-historic-cemeteries-preservation-brief-48.htm