The Getty Conservation Institute

research in conservation

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An Overview of Current Research

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1996

Publication Coordinator: Dinah Berland
Editor and Production Coordinator: Anita Keys
Designer: Garland Kirkpatrick

Printed in the United States of America

Mailing address:
P.O. Box 2112
Santa Monica, CA 90407-2112

ISBN 0-89236-389-4

Library of Congress Cataloging-in-Publication Data
Price, C. A.
Stone conservation : an overview of current research / C.A. Price.
p. cm.
Includes bibliographical references and index.
ISBN 0-89236-389-4
1. Building stones—Deterioration. 2. Stone buildings—Conservation and restoration.
I. Getty Conservation Institute.
II. Title.
TA426.P75 1996
691′.2—dc20 95-51727
CIP

The Getty Conservation Institute

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Research in Conservation

The Research in Conservation reference series presents the findings of research conducted by the Getty Conservation Institute and its individual and institutional research partners, as well as state-of-the-art reviews of conservation literature. Each volume covers a separate topic of current interest to conservators and conservation scientists. Other volumes in the Research in Conservation series include: *Accelerated Aging: Photochemical and Thermal Aspects* (Feller 1994); *Airborne Particles in Museums* (Nazaroff, Ligocki, et al. 1993); *Epoxy Resins in Stone Consolidation* (Selwitz 1992); *Evaluation of Cellulose Ethers for Conservation* (Feller and Wilt 1990); and *Protection of Works of Art from Atmospheric Ozone* (Cass, Druzik, et al. 1989).

Contents

Foreword

The "sympathetic conservation" of historic or culturally significant stone is a relatively recently recognized practice. In the past, the repair of damaged sculptured stone objects was frequently accomplished using more intrusive means, such as iron dowels, staples, or clamps that often marred the appearance of the object and could lead to further damage. For the patching and filling of defects, lime mortar, cement, plaster of paris, sodium silicate, and various gums and resins were used—materials no longer considered acceptable. Stone-cleaning processes involved harsh acidic treatments followed, at times, by neutralization which resulted in the production of soluble salts that penetrated the stone and increased the potential for future salt-crystallization damage. Damaged architectural stone was either replaced or repaired with little regard to materials compatibility with the stone, appearance matching, or the durability of the treatment. The unsuitability of many of these treatments encouraged research efforts to develop new materials and procedures for the preservation of stone.

Over the past twenty years or so, these studies have resulted in the publication of a vast number of reports and papers, most of which were concerned with case studies and how specific stone substrates were treated. Few were accompanied by details of the research that supported selection of the treatment method or materials used. Fewer yet were those concerned with stone-damage mechanisms and with scientific research studies on stone conservation processes, materials behavior, and environmental effects.

Although research has proliferated, there has not been a recent, concerted effort to evaluate the direction in which research has been progressing and whether or not the current direction is proving fruitful. Should the emphasis on stone conservation research be placed on development of new materials and new application procedures? Has there been significant work on the evaluation of the post-treatment stone property improvements? Are the methods for evaluating stone properties universally accepted? Do we need to conduct research on methods for carrying out and assessing the long-term durability of treatments? Are there problems in the process of conducting stone conservation research that bear on our ability to do the research effectively? Can these problems be defined; and, if so, what can be done to further the effectiveness of stone research?

These are some of the many questions that Clifford A. Price has considered in this review of the current status of stone conservation research. We asked Dr. Price to give us his subjective viewpoint on what is being done right, what areas of current research should be continued or accelerated, and what new directions should be addressed that would promote an increase in the effectiveness of stone conservation. In the course of preparing this review, Dr. Price has had extensive discussions with a number of active participants in the stone conservation community and what has emerged is an engaging account on whither we seem to be going and in which ways, if any, our paths should be altered.

—William Ginell
Head, Architecture and Monuments
The Getty Conservation Institute

Preface

This volume was written over a short period during the summer of 1994, following a systematic study of the major publications of the last five years (see Appendix). Inevitably, the volume reflects my own experience, expertise, and linguistic abilities. An international working party could, no doubt, have produced a more objective and comprehensive report—albeit over a longer span of time. In order that my own prejudices might not shine through too strongly, I have consulted with other conservation scientists and stone conservators, and I am very grateful for the help and advice that they have given me. In particular, I would like to acknowledge the help given by John Ashurst, Norbert Baer, Guido Biscontin, Sue Bradley, Api Charola, Vasco Fassina, John Fidler, William Ginell, Lorenzo Lazzarini, Bill Martin, Antonia Moropoulou, Marisa Laurenzi Tabasso, Jeanne Marie Teutonico, Giorgio Torraca, and George Wheeler. I am also grateful to Sasha Barnes for the help that she has given in rooting out references and to Julie Paranics for help in the final production of the volume.

The emphasis of this publication is on stone as a material. There is little reference to mortars, and no consideration of the structural performance of stone masonry.

This volume is not a detailed, state-of-the-art review, and many of the references I have given are intended as illustrative rather than definitive. It is intended to give a strategic overview of the whole field and to identify areas of strength and weakness where further research should be focused.

—C. A. Price
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Introduction

One of the elder statesmen of conservation, returning from a stone conference, was asked whether there had been anything new and interesting. "No," he replied, and then he paused before adding, "There never is."

Perhaps he was being overly pessimistic, but his attitude reflects a widespread feeling among many people who are involved in stone conservation at present. There is a feeling that research has stagnated; that we are not making any real progress in the way that we care for our historic stone buildings and monuments; that we should be looking for radically new approaches; in short, that research is "on the rocks." And yet this feeling comes at a time when more people than ever before are working in stone conservation, and when the number of publications and conferences is ever increasing.

This volume takes a broad, and sometimes critical, look at the present state of stone conservation and of the way in which research is conducted. It looks first at the deterioration of stone and at ways in which deterioration may be prevented or remedied. It then looks at some of the factors that are limiting the effectiveness of research, and it concludes with recommendations as to how research might be made more effective.

Stone Conservation

An Overview of Current Research

Chapter 1

Stone Decay

The deterioration of stone is all too familiar to anyone who has looked closely at a historic stone building or monument. While there are a few stones that seem to be little affected by centuries of exposure to the weather, the majority of stones are subject to gradual deterioration. This may not matter much if the stone is an undecorated part of a massive wall—in a castle or a cathedral, for example. However, it does not take much deterioration in an intricately carved piece of stone for the sculptor's intention to be lost altogether. A high proportion of the world's cultural heritage is built in stone, and it is slowly but inexorably disappearing.

If we are to do anything to reduce or prevent this loss of our heritage, we must first be able to characterize the many stones involved. We need to be able to describe the decay, and to measure the extent and severity of decay. We then need to understand the causes and mechanisms of decay. Only then can we hope to understand the behavior of any particular stone in a given environment.

Characterizing the Stone

The literature is full of papers concerned with stone characterization. Pick up any set of conference proceedings and you will find numerous papers that describe first the situation and history of some particular monument and then go on to lay out the physical properties of the stones involved. There will be petrological descriptions, followed by measurements of surface hardness, porosity, water absorption, capillarity, pore size distribution, mechanical strength, velocity of sound, resistance to salt crystallization, and so on. There will invariably be some photographs taken on the scanning electron microscope, and probably some energy-dispersive X-ray analyses for good measure. To what end? The information will no doubt be of value to those who are concerned with the care and maintenance of that particular monument, but it is of questionable relevance to a wider audience unless the properties of the stone can be linked to its performance.

Most of the techniques for characterization are well established. Many of them are summarized by E. C. Robertson (1982), and a recent review of pore structure is given by Camuffo (1993). A useful atlas of petrological sections is given by MacKenzie and Adams (1994). Gauri and Yerrapragada (1992) extend the interpretation of mercury porosimetry data in a manner reminiscent of that of W. D. Robertson (1982) and cite a number of the seminal papers on pore structure determination. Meng (1993) proposes "pore fraction distribution" in place of "pore size distribution," and defines it as the proportion of rugged pore spaces accessible for model particles of a certain size. He argues that it correlates more closely with the water transport properties of stone, and he goes on to utilize fractal properties as additional parameters of the characterization of pore irregularity. Rautureau et al. (1994) have also used fractal analysis to describe styolite irregularities in limestone.

Describing Decay

Stone decay takes many different forms. Sometimes the stone weathers away gradually, leaving a sound surface behind; sometimes large scales of stone drop away in one go. Sometimes the surface erupts into blisters; sometimes the stone loses all integrity and simply crumbles away. Sometimes the stone may look perfectly sound to the naked eye, while below the surface it has lost its cohesion.

One of the problems in discussing stone decay is that of finding a common language. Even in English, there are a bewildering number of terms that may mean different things to different people. And even if we can agree on terms to describe the types of decay that we observe, it can be difficult to determine the severity or rate of decay. There have been a number of attempts to write a glossary of decay terms, including those of Ordaz and Esbert (1990) and the Italian Commissione NORMAL (1988).

It is worth noting the current project of Van Balen (1993) to produce an atlas of damage to historic brick structures that will form the basis of an expert system for elucidating environmental effects on brick. Fitzner has also produced a classification of weathering forms that he has used as a basis for mapping the deterioration across a building facade. The classification system is presented in Fitzner et al. (1992), and a further illustration of its use is given by Fitzner and Heinrichs (1994). Similar, but simpler systems have been described by Verges-Belmin (1992) and by Massa, Naldini, and Rorro (1991). Fitzner's classification recognizes nineteen different weathering forms and goes some way toward recording the severity of each, based on visual inspection. Zezza (1990, 1994) has used digital image processing to map different forms of surface weathering. Starting with photographs, false color images are produced that are indicative of particular forms of decay.

How Serious Is It? Measuring the Extent of Decay

As well as describing decay, it is essential that we be able to measure its extent and severity. We need to do so first in order to unravel the various causes of decay. How can we say that pollution, for example, is causing decay unless we have some way of correlating pollution levels with decay? Second, we need to have some objective means of assessing the extent and the rate of decay, in order to decide whether remedial action is necessary and, if so, how urgent it is. Third, we cannot establish whether our remedial actions are having any effect unless we can monitor the condition of the stone afterward.

Visual examination clearly has a place. A single examination can give an indication of the state of the stone at that particular moment, but it cannot give any indication of the rate of decay. For this, a series of inspections is required, usually over a period of several years. Photographs are of immense value here, but even their objectivity can be abused. Winkler (1975:87), for example, constructs an alarming graph of exponentially increasing decay on the basis of just two photographs.

In order to make real progress, we need to put numbers on decay. No one technique can be sufficient, for decay takes many different forms. Some techniques look only at the surface, and they are well suited to decay that consists of a gradual loss of surface, leaving sound stone behind. Other techniques are designed to probe below the surface, and these are ideal where decay consists of a loss of cohesion within the stone, or the development of blisters or internal voids.

Surface Techniques

Quantitative surface techniques include the microerosion meter, line profilometry, close-range Photogrammetry, and laser interferometry. The microerosion meter is a simple micrometer device that measures surface height at a number of predetermined points, relative to datum studs set into the stone. It was used, for example, to monitor the rate of stone decay at St. Paul's Cathedral, London, over a ten-year period, during which sulfur dioxide levels fell by 50 percent (Trudgill et al. 1989).

Line profilometry is a contact-free technique that consists of projecting a grid of lines onto the surface at an angle of 45°. Any irregularities in the surface are immediately evident. Aires-Barros, Mauricio, and Figueiredo (1994) have demonstrated its use, coupled with image analysis, to construct a weatherability index.

A further technique for monitoring surface roughness was utilized by Jaynes and Cooke (1987). It measures irregularities by means of a stylus which is drawn across the surface; movement of the stylus produces an electrical signal in a transducer. Jaynes and Cooke used the technique to monitor the decay of limestone exposed to a range of different pollution environments.

Close-range Photogrammetry has been described by Coe et al. (1991), who demonstrated that the technique was sufficiently sensitive to detect surface loss of 0.1 mm per year over a four-year period.

Asmus and coworkers (1973) were among the first to propose the use of laser interferometry to monitor surface loss in stone. The technique has now been developed to the point where deformations as small as 0.5 μm can be detected. Meinlschmidt et al. (1991) have demonstrated the use of a portable system based on electronic speckle pattern interferometry (ESPI), or video holography. They were able, for example, to monitor deformations that took place during the hardening of a mortar or the growth of efflorescence over a period of just a few days. Paoletti and coworkers (1992) have also described a contouring technique based on the principle of ESPI, although they acknowledged that their results were far from conclusive.

Looking beneath the Surface

Outward appearances may be sufficient in some instances, but they can be deceptive. It is not unusual to find a stone surface that looks perfectly sound, but that sounds hollow as soon as it is tapped. Sooner or later, we need a way of measuring what is going on beneath the surface.

Many techniques are available and some of the more important are reviewed by Facaoaru and Lugnani (1993). Preeminent among them is the use of ultrasonics to detect the presence of cracks, voids, and other inhomogeneities in stone (Mamillan 1991a:17). This may take a variety of forms, using, for example, the longitudinal wave or the transverse component running parallel to the surface. Galan and coworkers (1992) provide a comprehensive case study demonstrating the reliability and cost-effectiveness of the technique.

The transmission of ultrasonic waves in stone depends on many factors, and interpretation of the data is not necessarily straightforward. Valdeon, King, and de Freitas (1992) have recently used digital analysis of the surface wave to demonstrate that wave attenuation can provide a sensitive measure of stone decay. The velocity of the longitudinal wave was a less sensitive measure. Others of this same group (Montoto et al. 1994) have also used ultrasonic tomography to investigate the internal deterioration of megaliths in northwestern Spain. The technique was useful for determining the position of internal fissures, but less good for assessing the condition of the stone immediately below the surface; more research was necessary on this aspect. Simon and coworkers (1994) have used formal concept analysis to optimize the interpretation of ultrasonic velocity measurements, while Zezza (1994) has used digital image processing to map the thickness of weathered layers.

Jacobs, Sevens, and Kunnen (1994) have proposed the use of computerized X-ray tomography to gain further insight into the internal structure of stone and the changes that occur during weathering. Procedures have been developed that bring the resolution down to grain-size level (about 100 µm or less).

Ground-penetrating radar is being used increasingly in archaeological prospecting, and it is natural that its use should be extended to historic buildings (Finzi, Massa, and Morero 1992). While it may prove of value in detecting flaws in stone masonry, it seems unlikely that it will have application in assessing deterioration of the stone itself.

Infrared thermography has been used by Gayo and coworkers (1992) to study moisture movement in stone. Although they did not use the technique specifically to evaluate decay, it could clearly be applied for that purpose.

So far, we have looked only at nondestructive techniques. It is, of course, possible in some instances to remove samples for analysis in the laboratory. These will often consist of core samples, which may then be sliced parallel to the original surface. The slices may be examined using the normal techniques for characterizing stone, and additional techniques may also be applied (Mamillan 1991b). Surface hardness measurements may be useful, and the salt content of the slices may also be determined. Åborg and coworkers (1993) have demonstrated the use of a laser microprobe to determine the depth of weathering, utilizing carbon and oxygen isotope analysis.

All the Information We Need?

With such sophisticated forms of investigation, one might be forgiven for thinking that no problems remain in the measurement of stone decay. There is, however, a long way to go. Stone decay is a complex phenomenon, and several forms of decay may be present together. No one technique can disentangle and quantify them. And a technique that is suitable for one type of stone in one type of environment may not prove satisfactory elsewhere. The techniques that we have looked at are certainly useful pointers, but further development is necessary before they fully meet the objectives set out above.

Causes of Decay

Before we can take any action to prevent or to remedy the deterioration of stone, we must understand what is causing it. Sometimes, the cause is obvious; sometimes there may be several different causes acting at once. Verdel and Chambon (1994) have recently introduced the principles of system dynamics in an attempt to clarify the relative importance and interdependency of individual causes.

Possible causes are very wide ranging and include earthquake, fire, flood, terrorism, vandalism, neglect, tourism, previous treatments, wind, rain, frost, temperature fluctuations, chemical attack, salt growth, pollution, biodeterioration, and . . . the list goes on and on. Some of the causes, like those at the beginning of the list, are sudden and rapid in their effect. Others, like those toward the end, are slow and more insidious.

The literature includes many papers dealing with the causes of decay, and some reviews are available (e.g., Honeyborne 1990a; Amoroso and Fassina 1983). However, recent literature is dominated by three topics: air pollution, salts, and biodeterioration. These are considered in the following sections.

Air Pollution

Air pollution is, to many people, the prime culprit of stone decay. Everybody has heard of acid rain, and it is easy to conjure up an image of old buildings gently flaking away every time it rains. Needless to say, the situation is a good deal more complex in reality.

The effects of air pollution on stone have received enormous attention in the past two decades. This is due, at least in part, to concerns about the effects of pollution on health, agriculture, and the whole global environment. Stone research has been able to ride on the back of these concerns and to benefit from the funding that they have received. Major programs have been coordinated by the European Union through its STEP and Environment initiatives, the NATO Committee for the Challenges of Modern Society, the United Nations Economic Commission for Europe (UNECE), the U.S. National Acid Precipitation Assessment Program (NAPAP), the U.K. National Materials Exposure Programme, and the German Bundesministerium für Forschung und Technologic (BMFT).

There is a general perception that air pollution is a modern problem, but Brimblecombe (1991) has shown that it is a problem that dates from antiquity. By examining the effects of pollution on individual historic buildings over periods of several hundred years, he has also attempted to correlate pollution levels with observed damage. This links in with another widespread perception: that decay rates are accelerating rapidly, despite falling levels of several major pollutants. There are insufficient data to prove conclusively whether this is indeed the case. It is possible that the perception is due largely to an increasing public awareness of the problem, and to the fact that stone loss through pollution is cumulative.

Most research has focused on the "traditional" pollutants: sulfur oxides, nitrogen oxides, and carbon dioxide. All are capable of dissolving in water to give an acidic solution, and so are capable of reacting with calcareous materials such as limestone, marble, and lime mortar. All are naturally occurring, but human activity has greatly increased the amounts that are to be found in urban areas.

The effects of acidic pollutants on calcareous stones depend very much on the immediate environment of the stone. If the stone is in an exposed position where it is regularly washed by rain, the reaction products are washed away and the surface of the stone gradually recedes. If, however, the stone is in a relatively sheltered position, the reaction products accumulate and may form a dense black crust on the surface.

A great deal of research, particularly in Italy, has been concerned with the nature and the origins of the black crust (e.g., Camuffo et al. 1982; Fassina 1991; Del Monte 1991; Ausset et al. 1992). These studies have shown that carbonaceous particles, particularly fly ash (particulate pollution resulting from the combustion of fossil fuels in electrical power generation), are responsible for the blackness of the crust. More important, however, is the discovery that the particles are not passive prisoners in the crust: They contain metal oxides that catalyze the oxidation of sulfur dioxide and hence promote formation of the crust in the first place.

Schiavon (1992) has studied the "stratigraphy" of black crusts, in an attempt to clarify the growth mechanism. He concludes that growth occurs in two directions: inward and outward with respect to the original stone surface, but with inward growth predominating.

Diakumaku et al. (1994) have observed that some black fungi produce small spherical particles that might, under some circumstances, be confused with fly ash. Microflora may also be capable of producing sulfates. In the opinion of these authors, the formation of black crusts in unpolluted environments may be attributable to biological factors. In addition, Ortega-Calvo and coworkers (1994) have demonstrated that sulfate crusts may provide an ideal habitat for some cyanobacteria through the gradual dissolution of the sulfate. Despite the extensive research already carried out on black crusts, there is clearly more to be done in order to gain a full understanding of the mechanisms by which they form.

The studies of black crusts highlight a more general problem: the difficulty of determining the precise mechanisms whereby pollution damages stone. This may sound rather academic, but it is not. Some of the most pressing questions arise here, and clear answers need to be found in order for informed policy decisions to be made on emission controls. For example:

- By what route do air pollutants reach the surface of the stone? Do they dissolve in the water droplets of clouds and rain, and reach the stone already in solution (so-called *wet deposition)?* Or do they reach the surface of the stone in the gas phase, and then dissolve in moisture already present in the stone *(dry deposition)?* The importance of this question lies in the fact that distant pollution sources will be the major contributor to wet deposition, whereas local sources will predominate in dry deposition.
- What is the mechanism by which sulfur dioxide is oxidized to produce sulfuric acid? Does oxidation take place before the pollution reaches the stone, or is it catalyzed by other pollutants on the surface of the stone? Is the oxidation catalyzed by other air pollutants, such as ozone or nitrogen oxides? Do bacteria in the stone play a part? It would be foolish to concentrate all efforts on reducing sulfur dioxide levels if there were no overall reduction in decay rates.
- To what extent are today's decay rates influenced by pollution levels of the past (the *memory effect)?* For example, would the calcium sulfate that is already present in the stone continue to cause damage even if further pollution were eliminated altogether?

Research has fallen into three areas. First, there have been numerous studies carried out on individual buildings, coupled with extensive monitoring of pollution levels. Such studies will typically include analysis of the rainwater striking the building and of the water flowing off it. They have the advantage of being based on the fundamental problem: the decay of historic stonework in today's environment. They are certainly the best way of studying the memory effect.

Second, there are studies based on the exposure of small samples of unweathered stone. Typically, carousels carrying twenty or thirty samples are exposed to a range of different environments. Some of these studies have been very extensive and have been carried out under the auspices of national and international bodies (e.g., NATO 1985). The drawback of these studies is that they only provide direct evidence of the behavior of *new* stone.

Third, there are studies that attempt to simulate pollution effects in the laboratory. Again, they are normally based on new stone, but they offer the advantage of being able to create a wide range of closely defined environments at will. They are well suited to studying interactions between pollutants, as well as the effects of individual pollutants in isolation. Johansson et al. (1986), for example, demonstrated that nitrogen dioxide catalyzed the adsorption of sulfur dioxide by calcareous stones at high relative humidities. His experiments were criticized on the grounds that the concentration of each pollutant was unrealistically high, and Vassilakos and Salta (1993) concluded, on the basis of experiments using reversed-flow gas chromatography, that synergism between the two pollutants was not important. However, Johnson et al. (1991), De Santis et al. (1994), and Cooke and Gibbs (1993) do not rule out the possibility of synergistic effects, and also point out the possible importance of ozone in the oxidation of sulfur dioxide.

Despite the enormous amount of research that has been conducted over the past twenty years, there has been very little effort to pull it all together and to produce a clear statement of findings to date. (One notable attempt is that of Cooke and Gibbs 1993.) Many authors have failed to provide a clear statement of the objectives of their research, nor have they set out the significance of their results in the wider framework. As a result, it is surprisingly difficult to gain a clear overview of the subject. It would be unreasonable to expect that the findings of such extensive and complex research could be summarized in just a few lines, but nonetheless there is a pressing need for state-of-the-art reviews.

Damage functions represent a quantitative approach to summarizing results. These are mathematical expressions that attempt to express the rate of stone decay as a function of several different variables. Their value, if reliable, is that they can be used to quantify the benefits of different pollution-control policies. What would be the overall savings in building maintenance costs, for example, if sulfur dioxide levels were reduced by 20%? Several authors have derived damage functions and, although they differ in detail, a fairly consistent overall picture emerges (Lipfert 1989; Benarie 1991; Reddy 1990; Butlin et al. 1992; Livingston 1992a; and Webb et al. 1992). The rate of decay is seen to depend largely on three factors: pollution levels, rainfall acidity, and amount of rainfall. One important corollary of this is that pollution cannot be blamed for all the decay that takes place. Even in the absence of pollution, there would still be some decay. Indeed, some authors argue that sulfur dioxide levels in some cities have now been reduced to the point where sulfur dioxide is not a major contributor to decay. In other words, there may be a "safe level" of around 30 $\mu g/m^3$, below which sulfur dioxide is not a significant problem (Sharma and Gupta 1993). This view, however, is not universally upheld.

Another area where a consensus is beginning to emerge is the relative importance of wet and dry deposition. Where sulfur dioxide levels are high, dry deposition appears to predominate on vertical surfaces; on horizontal surfaces and in rural areas, wet and dry deposition may be of comparable importance (Furlan 1991; Cooke and Gibbs 1993; BERG 1989; Butlin 1991).

Salts

Along with air pollution, soluble salts represents one of the most important causes of stone decay. The growth of salt crystals within the pores of a stone can generate stresses that are sufficient to overcome the stone's tensile strength and turn the stone to a powder. The deterioration of many of the world's greatest monuments can be attributed to salts.

There are many ways in which stonework can become contaminated with salts. Air pollution is a major source of sulfates and nitrates. Other sources include the soil, from which salts may be carried into masonry by rising damp; salts blown by the wind from the sea or the desert; deicing salt; unsuitable cleaning materials; incompatible building materials; and, in the case of some medieval buildings, the storage of salts for meat preservation or even for gunpowder.

Salt damage is largely attributable to two mechanisms: the crystallization of salts from solution; and the hydration of salts. Any salt, in principle, is capable of causing crystallization damage, whereas hydration damage can be caused only by salts that can exist in more than one hydration state. Sodium chloride, for example, is capable only of crystallization damage, while sodium sulfate—which can exist as either the anhydrous salt thenardite (Na_2SO_4) or the decahydrate mirabilite ($Na_2SO_4 \cdot 10H_2O$)—can cause both crystallization damage and hydration damage. A third way in which salts could cause damage is through thermal expansion, but this mechanism has received little attention.

Salt damage does not occur only in an outdoor environment, where the stone is subjected to cycles of rainfall and subsequent drying. It can also happen indoors, through the hygroscopic action of the salts. Severe damage to stonework held in uncontrolled museum environments is not uncommon (Hanna 1984).

On first sight, it appears surprising that salt damage should occur at all. Crystallization, for example, results in the formation of crystals which occupy a smaller volume than the solution from which they were deposited. Is there not ample room for the crystals to develop in the pores, without the necessity of forcing the pore walls apart? However, this simplistic view overlooks the dynamic aspects of stone decay. A stone may be fed constantly with salt-bearing moisture from the soil, for example, so that salts are constantly accumulating at the point of evaporation. A detailed analysis of this situation is provided by Lewin (1982).

Using scanning electron microscopy to supplement macroscopic observation, Zehnder and Arnold (1989) have very elegantly described the crystallization process. They have identified four different stages of crystal growth, which depend primarily on the humidity of the stone, and they have described in detail the process of disruption.

Doehne (1994) has used the environmental scanning electron microscope, together with time-lapse video, to study the hydration and dehydration of sodium sulfate. His work, which complements that of Charola and Weber (1992) and McMahon et al. (1992), demonstrated the breakdown of large crystals of mirabilite during dehydration to form submicrometer aggregates of thenardite. Subsequent hydration-dehydration cycles in the absence of excess water led to the formation of a highly porous salt structure. Dissolution of this structure in liquid water led to the formation of large mirabilite crystals, and this appeared to cause more damage than the previous humidity cycles.

Esbert and coworkers (1991) have used acoustic emission techniques to monitor the development of microfissures during the hydration of sodium sulfate. They adopted a crystallization test which consisted of cycles of immersion in sodium sulfate solution, followed by drying at 60° C and then cooling. They concluded that damage due to hydration occurred rapidly during the cooling cycle and was complete before the next cycle of immersion.

Attempts to quantify the stresses that can be generated through crystallization and hydration have fallen into two distinct areas, with little overlap to date. Some workers have related the stresses to pore structure, following the early work of Honeyborne and Harris (1958) and that of Everett (1961) on frost heave. Rossi-Manaresi and Tucci (1991), for example, have demonstrated a correlation between observed crystallization damage and pore size distribution. On the whole, however, this is an area that has been somewhat neglected.

By contrast, a number of people have used thermodynamic considerations of the salt/solution system to calculate the stresses that can be generated by crystal growth. Lewin (1990) has emphasized that crystallization pressures originate in the release of free energy during the deposition of crystals from a supersaturated solution, and he has demonstrated quantitatively that the energy is sufficient to disrupt stone. One of the earliest studies in this area, however, was that of Thomson, who wrote in 1862:

> [S]tresses tending to change the form of any crystals in the saturated solutions from which they have been crystallized must give them a tendency to dissolve away, and to generate, in substitution for themselves, other crystals free from the applied stresses or any equivalent stresses.

Further studies were undertaken by Correns (1949), whose paper is frequently cited by later researchers, notably Winkler and coworkers (1970, 1972). The essential principle is that a crystal under linear pressure has a greater solubility than an unstressed crystal. Putting it another way, a crystal under pressure is in equilibrium with a solution that is supersaturated for crystals that are not under pressure. Correns derived an equation that relates the pressure to the degree of supersaturation. Although the equation can indeed be used to compute crystal growth pressures far in excess of the tensile strength of stone, Price (1991) has questioned whether the assumed degree of supersaturation is realistic in practice.

Given the importance of salt damage, it is surprising that it has not been studied more thoroughly. Weber (1993) has identified some of the outstanding problems. Among them are the relative importance of hydration and crystallization, a topic studied by Sperling and Cooke (1985) in the case of sodium sulfate. Weber hints that other mechanisms might eventually prove to be more important, such as the swelling of porous salt aggregates by moisture, and he also questions the rate at which hydration and crystallization occur under conditions of varying relative humidity. This is not simply a matter of the physical state of the salt but may also depend on the nature of the substrate (Pique et al. 1992). The crystallization of calcium sulfate is a topic of particular interest, since it is widely held to be ultimately responsible for much of the damage caused to limestones by air pollution. This is perhaps surprising, in view of calcium sulfate's low solubility and its consequently high equilibrium relative humidity. However, recent studies have highlighted the influence of other salts on both the solubility of calcium sulfate and the relative humidities at which it may crystallize (Zehnder 1993; Price and Brimblecombe 1994; Livingston 1994).

Biodeterioration

Biological growths on stone are both a blessing and a blight. Colorful lichens and creepers, such as ivy, can contribute an air of age and romance to a monument, and their removal can leave the stone looking stark and denuded. However, many organisms contribute to the deterioration of stone, and it is necessary to find the right balance between appearance and longevity.

The biological degradation of rocks has been known and studied for a long time: it is one of the weathering mechanisms responsible for the formation of soil. The deterioration of stone in buildings and monuments through the action of biological organisms has also been recognized over a long period, but the topic has received increasing attention over the past few years. Some of the literature is concerned primarily with the influence of organisms on the appearance of stone surfaces, while others deal primarily with the deterioration of the stone itself.

An excellent review is provided by Griffin, Indictor, and Koestler (1991); other useful overviews are given by Caneva, Nugari, and Salvadori (1991), Caneva and Salvadori (1989), and Strzelczyk (1981). Krumbein and Urzi (1992) set out a comprehensive terminology for describing aspects of biodeterioration on stone.

In 1932, in his classic report on *The Weathering of Natural Building Stones,* Schaffer wrote:

> Living organisms also contribute to the decay of stone and similar materials and, although their action is, generally, of somewhat less importance than certain of the other deleterious agencies which have been considered, their study presents numerous features of interest. The effect of certain organisms, such as bacteria, is still a matter of controversy, but the effect of others, such as the growth of ivy, is generally considered to be detrimental.

In this, as in a number of other areas, he is remarkably up-to-date. There is still controversy over the role of bacteria, and we still need to weigh the importance of biodeterioration against the importance of other causes of decay.

Much of the recent research has been centered on algae, lichens, and bacteria. Jones and Wilson (1985) have reviewed the action of lichens, confirming that their effects are both physical and chemical. Mechanical damage is caused by penetration of the hyphae into the stone, and by the expansion and contraction of the thallus (the vegetative part of the fungus) under changes of humidity. Chemical damage, however, is more important, and may arise in three ways: by the secretion of oxalic acid, by the generation of carbonic acid, and by the generation of other acids capable of chelating metal ions such as calcium. The secretion of oxalic acid, which reacts with a calcareous stone to produce calcium oxalate, is of particular interest. A number of authors have noted the presence of calcium oxalate on the surface of stone monuments, where it can form part of a coherent and seemingly protective layer known as *scialbatura.* Del Monte and Sabbioni (1987), for example, have argued that scialbatura is caused solely by lichen activity, whereas Lazzarini and Salvadori (1989) have enumerated other possible causes, including the deliberate application of a protective coating.

The heavyweight controversy is saved for bacteria. They have long been implicated in stone decay, but acceptance of their role has sometimes been hindered by the emotive stance of some researchers, who have appeared determined to see bacteria and nothing else. A troubling number of authors have noted high numbers of bacteria in decaying stone, by comparison with low numbers in sound stone, and have concluded that the bacteria cause the decay. This conclusion is not valid; an alternative explanation could be that decayed stone presents a preferred habitat for the bacteria.

Bacteria attack stone chemically. They fall into two groups: Autotrophic bacteria derive their carbon from carbon dioxide, and may derive their energy from light (photolithotrophs) or from chemical redox reactions (chemolithotrophs). Heterotrophic bacteria, by contrast, utilize organic compounds on the stone to derive their carbon.

Autotrophic bacteria include those that are capable of oxidizing sulfur and nitrogen compounds to produce sulfuric acid and nitric acid, respectively. They are one more means, therefore, of taking air pollutants such as sulfur dioxide and nitrogen oxide and turning them into sulfates and nitrates. This underlines the difficulty of separating out the individual causes of stone decay; several different factors may be part and parcel of the overall decay process. Nobody has come to grips with determining whether bacteria or metal compounds, for example, is the main route of sulfate production, and the question may not be significant in practice. If oxidation by both bacteria and metal compounds is rapid by comparison with the rate at which sulfur dioxide arrives at the stone surface, then the arrival rate will be the rate-determining step.

Heterotrophic bacteria produce chelating agents and organic acids that are weaker than the inorganic acids produced by the sulfur-oxidizing and -nitrifying bacteria. They have received comparatively little attention, but their role in deterioration is well established nonetheless (May and Lewis 1988).

Chapter 2

Putting It Right: Preventive and Remedial Treatments

When confronted with decaying stonework, one's immediate instinct is to "do something about it." Traditionally, this has meant doing something to the stone: perhaps patching it up with mortar, applying some kind of protective coating, or cutting out decayed stone and replacing it with new stone. Now, however, there is an increasing emphasis on doing something *to the environment* in which the stone finds itself. This reflects a growing awareness of the principle of minimum intervention, of the need to limit the use of materials that might prove harmful to either the stone or to the environment, and of the fact that prevention is better than cure.

Preventive Conservation

Doing something to the environment in which the stone finds itself (or, more succinctly, preventive conservation) is not simply a matter of temperature and relative humidity. It can embrace a very wide range of topics: legislation to protect individual buildings and monuments, pollution control, traffic control, control of ground water, visitor management, and disaster planning (Baer 1991). Such topics may seem remote from the problems of an individual block of stone, but they are nonetheless of great importance.

Preventive conservation measures of more immediate effect are usually concerned with keeping water out of the stone and with controlling the relative humidity and temperature of the air around the stone. This is relatively easy for stone artifacts within a museum, and it may also be feasible for stone masonry that is exposed on the interior of a building (Price 1993). It is less easy for stonework on the outside of a building, although one may note the proposal to enclose the remains of Hamar Cathedral, Norway, in an air-conditioned envelope of glass and aluminum (Lewis 1992).

The main purpose of relative humidity control is to prevent salt damage. The humidity regime required to prevent damage in a stone that is contaminated with a single salt is well established, but stone is more commonly contaminated with a mixture of salts. The behavior of salt mixtures is described by Price and Brimblecombe (1994), who present a computer program capable of determining the "safe" relative humidity ranges of any given salt mixture.

Protective shelters are frequently used on the outside of a building to protect those features that are particularly important. They may be part of the original design (for example, a canopy protecting a statue in a niche), or they may be a later addition. As an extreme measure, they may enclose the feature altogether. Their purpose is to reduce the amount of rain that reaches the stone and, insofar as is practicable, to stabilize the temperature and moisture content of the stone. If the shelter is a later addition, it is likely to be visually intrusive—unless it is so small as to serve little purpose. Few studies have been undertaken of the design requirements of such shelters, and it is possible that their benefits are more psychological than actual. This needs to be evaluated in practice.

The remainder of this chapter is devoted to aspects of "active conservation": doing something directly to the stone itself. It is not, however, a handbook of repair techniques; practical advice on stone conservation is available elsewhere (e.g., Ashurst and Ashurst 1988).

Active Conservation: Cleaning

Cleaning is often one of the first steps to be undertaken. By removing the dirt, one can better see the condition of the underlying stone and thus judge what further conservation may be necessary. Cleaning may also serve in some circumstances to remove harmful materials from the surface. However, the primary reason for cleaning will often be the dramatic change in appearance that can be achieved. A dirty building or monument does not look well cared for, and the dirt may well obscure both fine detail and major architectural features. Nonetheless, there are those who would argue that cleaning contravenes one of the fundamental principles of conservation—reversibility—and that by removing the dirt one is removing both the sense and the evidence of history.

A wide range of techniques is available for cleaning stone, ranging from those that are intended for use on large facades to those that are intended for meticulous use on finely carved and delicate sculpture. Techniques are reviewed by Ashurst (1990a), Larson (1990), Fassina (1993), and Andrew (1994). This is an area where much progress has been made in the past twenty years, although little of it is reported directly in the literature. The basic techniques have remained largely the same, although they have become more refined. This reflects an increasing awareness of the damage (and consequent litigation) that may be caused by inappropriate or overenthusiastic cleaning, and also of the environmental issues posed by the use of certain chemicals or excessive quantities of water. The developments have largely come about through care and attention on-site rather than in the laboratory.

In most cleaning methods, no attempt is made to collect the dirt and detritus that is instead allowed to run down the stone and pass into the drains. Some attention is now being given to techniques that collect the detritus and, for example, permit recycling of the abrasive (Hoffmann and Heuser 1993).

The effectiveness of a cleaning technique is usually assessed subjectively, although objective procedures have recently been described by Werner (1991), Young (1993), Andrew (1994), and D'Urbano et al. (1994).

A number of authors have emphasized the damage that can be caused by cleaning: loss of surface, staining, deposition of soluble salts, or making the stone more vulnerable to pollutants or biological growths. (They include Maxwell 1992; MacDonald, Thomson, and Tonge 1992; Young and Urquhart 1992; and Andrew 1994.) It is undoubtedly the case that very severe damage can arise, but a degree of skepticism would perhaps be justified over "damage" that is observable only through a scanning electron microscope.

Lasers

The possibility of using lasers to clean stone is attracting increasing attention, and laser cleaning is now available commercially. Its great attraction is that it does not entail any physical contact with the stone and so lends itself ideally to the cleaning of very delicate surfaces. The principle is essentially simple: A laser beam impacts on the surface, and the energy of the beam is dissipated by vaporization of the dirt. While the stone is dirty, the light is absorbed and cleaning proceeds. Once the dirt has been removed, however, the light is reflected by the clean surface, and no more material is removed. The technique is described by a number of authors, including Cooper, Emmony, and Larson (1993); Maravelaki et al. (1992a); and Orial and Riboulet (1993).

At present, the speed of cleaning is comparable to that which can be achieved with a pencil-sized air-abrasive gun, and it is debatable whether the technique can reasonably, or safely, be scaled up for the cleaning of entire facades. Current research is aimed at selecting the optimal wavelength and pulse energy; at examining the effects on the stone, both physical and chemical; at comparing the performance of lasers with other cleaning techniques; and at identifying possible hazards to the operator (Cooper, Emmony, and Larson 1992; Vergès-Belmin, Pichot, and Orial 1993; D'Urbano et al. 1994; Larson 1994a). Further development of equipment is also sure to take place, identifying, for example, the best means of delivering the laser pulse to the surface of the stone.

Biological Cleaning

Hempel (1978) was one of the first to raise the possibility of biological cleaning. He had been surprised by the effectiveness of a clay poultice containing urea and glycerol and proposed that microorganisms were at least partially responsible. Kouzeli (1992) has reported favorably on the technique in comparison with pastes based on EDTA or ammonium bicarbonate.

Biological cleaning, in general, has been little researched. Gauri, however, has demonstrated the use of the anaerobic sulfur-reducing bacterium *Desulfovibrio desulfuricans* in removing the black crust on marble (Gauri et al. 1992). He has argued, moreover, that the bacterium was converting calcium sulfate back to the calcium carbonate from which it was originally formed (Atlas, Chowdhury, and Gauri 1988; Gauri and Chowdhury 1988).

Targeting the Dirt

Gauri's work is interesting because it takes account of the nature of the dirt. It is true that this may be implicit in other cleaning techniques (e.g., the use of complexing agents to increase the solubility of calcium sulfate, or the use of hydrofluoric acid to dissolve silica), but it is disappointing nonetheless that few developments in cleaning techniques have flowed out of the extensive studies on black crusts. Couldn't our knowledge of the crusts be used to facilitate their removal? Livingston (1992b) has studied the solubilities of calcium carbonate and calcium sulfate; Schiavon (1992) has commented on the distribution of calcium sulfate within the pores of stone and on its implications for water washing; and Skoulikidis and Beloyannis (1984) have attempted to convert calcium sulfate back to calcium carbonate by the use of potassium carbonate, blissfully ignoring the potentially harmful effects of the resulting potassium sulfate. Few other researchers, however, have focused directly on the nature of the dirt deposits in an attempt to develop more effective cleaning techniques.

Active Conservation: Desalination

In situations where soluble salts are a major contributor to decay, it makes sense to try to remove the salts. The word try is used deliberately. The removal of water-soluble salts sounds tantalizingly easy, but it can prove difficult in practice. It is relatively straightforward in the case of small artifacts which can, for example, be immersed in water or enclosed completely in a poultice, though even here problems can arise through the frailty of the surface or the presence of pigments. The real problems start when one attempts to remove salts from the masonry of a building or monument. In an early study, Bowley (1975) demonstrated that it was possible to extract a worthwhile quantity of salt from masonry through the repeated use of clay poultices, although little would be gained in the long run unless one could eliminate the source of further salt.

Desalination of masonry is usually attempted through the use of poultices, which may consist of clay, paper pulp, or cellulose ethers. In those instances where calcium sulfate is to be removed, additional materials may be added in order to increase its solubility. Clearly there are overlaps here with cleaning, especially in the removal of black crusts. The additives may include EDTA and its sodium salts, sodium bicarbonate, ammonium bicarbonate, and ammonium carbonate (De Witte and Dupas 1992; Maravelaki et al. 1992b; Alessandrini et al. 1993). A word of warning may be appropriate: If a limestone is heavily sulfated, the calcium sulfate may be all that is holding it together, and removal could be disastrous.

More exotic methods of desalination may invoke the movement of ions and of solutions under the influence of electric fields. Skibinski in particular (e.g., Skibinski 1985) has advocated the use of membrane electrodialysis for artifacts, although it has not gained wide acceptance. Friese (1988) has described a system that can be applied to masonry, although few details are given whereby its effectiveness and potential hazards can be assessed.

Minder-Heng, Berteaud, and Vergès-Belmin (1994) have described the use of microwaves in desalination. An artifact contaminated with a salt solution is placed in a microwave oven. The center of the object gets hotter than the outer surface; and, presumably as a result of surface-tension differences, the solution exudes from the pores. The effectiveness of the technique is strongly influenced by the type of stone and by the presence of the salt, and there are dangers inherent in the high temperature gradients that are generated. Friese (1992) has described the use of a vacuum to draw the solution out.

Finally, the use of bacteria in desalination may merit further attention. Gauri's use of sulfur-reducing bacteria to eliminate the black crust has already been mentioned, and Gabrielli (1991) gives an anecdotal account of the use of cow dung to convert nitrates to elemental nitrogen. One wonders, however, how many other salts are added at the same time.

Active Conservation: Consolidation

Where stone is severely weakened by decay, some form of consolidation may be necessary to restore some strength. Ideally, one might hope to make the stone at least as strong as it was originally, so it might resist further decay; but even the strength to resist the battering of the wind or the wing of a bird may be enough to prolong survival.

It all sounds so easy. One just has to find something that will penetrate the decayed stone, binding it together and securing it onto the sound stone beneath. And why stop there? Why not find something that will also protect the stone from further decay? Perhaps it could embed the salts and prevent further cycles of crystallization or hydration. Or perhaps it could make the surface of the stone water-repellent, so it will resist acid rain. Of course, the treatment will need to be reasonably cheap, easy to apply, and safe to handle. It will need to remain effective for decades at a time, in order to last from one maintenance cycle to the next. The treated stone will need to have much the same moisture expansion, thermal expansion, and elastic modulus as the untreated stone, in order to avoid internal stresses. Ideally, the treatment should work equally well on any type of stone, regardless of the cause of decay. And—I nearly forgot—it must be *completely* invisible.

Put like this, it sounds absurd. It is like trying to find one pill that will cure all the diseases known to humankind. But this has not hindered the search for an all-singing, all-dancing stone consolidant-cum-preservative. It is a wonder we have made as much progress as we have. An enormous variety of materials have been tried since time immemorial, each with its own advocates.

You have to start somewhere, and one of the properties that a consolidant must have is the ability to penetrate the stone. This, in turn, requires a low viscosity and a low contact angle. Next, the consolidant needs to stiffen or set once it is in place in order to strengthen the stone. These requirements can be met in three ways: First, one can apply a wax at elevated temperatures that stiffens as it cools down. In practice, it is hard to get a low enough viscosity without excessive heat, and the wax tends to be sticky and to pick up dirt. The second approach is to use a consolidant dissolved in a solvent. One cannot assume, however, that the consolidant necessarily penetrates as far as the solvent, and there is always a danger of the consolidant being drawn back to the surface as the solvent evaporates. Third, one can use a low-viscosity system that undergoes a chemical reaction in situ to give a solid product.

Consolidants are usually applied to the surface of the stone by brush, spray, pipette, or by immersion, and are drawn into the stone by capillarity. Domaslowski (1969) experimented with a "pocket system" that was intended to hold the consolidant against the stone, and Mirowski (1988) has described a system of bottles for maintaining a steady supply of the consolidant at a large number of points. Schoonbrood (1993) has developed a low-pressure application technique that maximizes capillary absorption. Vacuum systems may also be used to facilitate penetration into movable objects (e.g., Hempel 1976); the vacuum system developed by Balfour Beatty Limited for use on monuments (e.g., Antonelli 1979) did not find extensive application in practice.

The majority of materials that have been tried as stone consolidants have been organic polymers, but two inorganic materials deserve a particular mention, as their mode of operation is rather different: calcium hydroxide (slaked lime) and barium hydroxide.

Lime

Nothing could be more natural than putting lime into limestone. The emotive appeal of lime must account for at least some of its popularity. There is, however, a sound rational basis for its use. If a saturated solution of calcium hydroxide is allowed to penetrate into limestone, subsequent evaporation of the solution will lead to the deposition of calcium hydroxide within the stone. This, in turn, will react with carbon dioxide in the air, to deposit calcium carbonate. This could serve to consolidate the stone, in much the same way as carbonation of calcium hydroxide leads to the hardening of a lime mortar.

This basic chemistry forms the basis of the "lime technique" (Ashurst 1990b), which has been used extensively in England and to a lesser extent elsewhere. The technique, in its entirety, can quite transform the appearance of decayed limestone. However, Price, Ross, and White (1988) demonstrated that the lime was deposited largely in the outer couple of millimeters of the stone and that no deep consolidation of the stone could be attributed to the calcium hydroxide. However, it was conceivable that some consolidation could be attributed to the redeposition of calcium sulfate within the stone, a suggestion supported by the apparent effectiveness of distilled water under some circumstances (Clarke and Ashurst 1972). This being the case, a treatment consisting of ammonium sulfate (to dissolve the calcium sulfate) followed by calcium hydroxide (to reprecipitate it) would be worth investigation. The conclusion of Price, Ross, and White, nonetheless, was that the success of the technique was largely attributable to the subsequent use of well-designed mortars, which filled surface fissures and other defects. An alternative suggestion, put forward by White (1988) and by Anagnostidis et al. (1992), is that the lime is serving to kill bacteria and other organisms, and so reduces decay. A later paper (Krumbein et al. 1993) suggests that the observed sterility of marble treated with lime may be due not to biocidal action but to pore closure, which prevents colonization.

Despite the hope that the lime treatment would lead to the deposition of interlocking calcium carbonate crystals, in the manner of lime mortars, the available evidence suggests that it is deposited in an amorphous form that can have little consolidating effect. Tiano, Addadi, and Weiner (1992), however, have proposed a pretreatment based on glycoproteins derived from marine organisms. The pretreatment is reported to induce the nucleation of calcite, leading to well-formed crystals that adhere strongly to the underlying stone.

Barium Hydroxide

Barium hydroxide is another material with a long pedigree. Chemically, barium compounds and calcium compounds share many of the same characteristics, the one notable difference being the insolubility of barium sulfate as compared with the sparing solubility of calcium sulfate. Barium hydroxide treatments thus have a number of possible objectives, which are not always clearly spelled out. They may serve to convert calcium sulfate to barium sulfate, and thereby reduce damage due to the solution and recrystallization of calcium sulfate; they may serve, after carbonation, to deposit a coating of barium carbonate, which will be more resistant than calcium carbonate to acid rain; and they may serve to consolidate the stone through the formation of solid solutions of barium calcium carbonate (Lewin and Baer 1974).

A number of techniques have been proposed for introducing the barium hydroxide into the stone. Simple application of barium hydroxide solution appears to be ineffective and led Schaffer (1932:84) to dismiss the process in just seven words: "In practice the method proved a failure." Lewin and Baer (1974), by contrast, described a technique that ensured the slow growth of well-formed barium carbonate crystals within the stone, a technique Lewin was still advocating fifteen years later (Lewin 1989). Schnabel (1992) has cast doubt on the effectiveness of the process when applied by capillarity in situ.

The latest development has come from the field of wall paintings, where Matteini (1991) has proposed that barium hydroxide treatment should be preceded by the use of ammonium carbonate to dissolve the calcium sulfate. Use of this procedure on stone has yet to be reported.

Organic Polymers

You name it, somebody has tried it. From naturally occurring compounds, such as linseed oil and cactus oil, to the synthetic polymers of the twentieth century, somebody somewhere will have tried it as a stone consolidant. Generally speaking, such trials have been on a rather hit-or-miss basis. Materials have been selected more on the grounds of availability than of any predetermined qualities. Provided they will penetrate the stone and then set, they have been worth a try.

While it is easy to sound contemptuous about such an empirical approach, it is hard to see how things could have been any different. Our knowledge of decay processes is still incomplete, and our knowledge of how to combat them must necessarily be incomplete, as well. We are having to learn by experience.

The majority of researchers believe that stone needs to "breathe." In other words, stone should remain permeable to water vapor, in order to avoid any buildup of moisture (and consequent shear stresses) at the interface between the treated zone and the untreated stone below. There is some disagreement, however, on even this fundamental issue. Sinner (1991) reports on the continuing success of a commercial process that leads to total filling of the pore space with polymethyl methacrylate, although it should be stressed that this process is used only on stone objects that are not an integral part of a building.

Little attention has been given to the distribution of consolidants within stone at the microscopic level, despite numerous photomicrographs taken with the scanning electron microscope. Many authors have been content simply to state that a treatment "lines the pores." Sasse and Honsinger (1991) have described a "supporting corset" model, consisting of an impermeable layer that coats and protects the internal surfaces of the stone, while imparting mechanical strength. Hammecker, Alemany, and Jeannette (1992) describe the use of mercury porosimetry to monitor changes in pore structure due to treatment, but such studies may be hindered by the change in contact angle following treatment.

Little is known about the bonding, if any, that takes place between a consolidant and the substrate, and much is left to chemical intuition. It is widely argued, for example, that alkoxysilanes will form primary chemical bonds to the Si-OH groups on the surface of sandstones, but that they will not be able to form primary bonds to limestones. Lack of bonding need not necessarily mean failure, however, for an unbonded network of consolidant could still provide strength. There have been very few published studies in this area, although work is in progress in a number of laboratories using Fourier-transform infrared spectroscopy.

Little may be known, either, about the molecular structure of the polymer that is deposited within the stone. We speak glibly, for example, about the network polymer that is formed by the hydrolysis and subsequent condensation of trialkoxysilanes and tetraalkoxysilanes. But how many siloxane bonds are formed, on average, by any one silicon atom? What is the structure of the polymer? How is it influenced by the presence of water, of solvents, of salts, or of particular minerals? How does it affect the strength of the polymer?

Our present knowledge of consolidants may be likened to folk remedies in medicine. We have gained a lot of experience of what is, and what is not, effective, but we have little understanding of *how* they work. Once we have a deeper understanding of the properties that are required of a consolidant, we shall be in a better position to synthesize compounds to meet those properties.

Alkoxysilanes

The alkoxysilanes, or "silanes" for short, have undoubtedly been the most widely used stone consolidants over the past twenty years. Two compounds, in particular, have been dominant: methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS). The silanes are hydrolyzed by water to form silanols, which then polymerize in a condensation reaction to give a silicone polymer. The water may come from the atmosphere or from the stone itself, or it may be added as a deliberate ingredient. In the latter case, a solvent may be required in order to make the mixture miscible. A catalyst may also be added, usually in the form of an organotin or lead compound. The condensation reaction, and often the hydrolysis reaction, also, takes place after the treatment has been absorbed by the stone; and the resulting polymer imparts the required strength to the stone.

The popularity of MTMOS and TEOS is no doubt due in part to their commercial availability, and a number of proprietary products are available that are based on these two compounds. A number of other silanes have also been tried, usually involving substitution of the methyl group for larger alkyl or aryl groups. In an unusual development, Hosek and Sramek (1992) have described the use of a "hydrogensiloxane" for consolidation of arkoses: a long-chain silicone polymer that terminates in a -$Si(CH_3)_2H$ group.

Wheeler, Fleming, et al. (1992) have reported the successful use of silane coupling agents—compounds intended primarily to promote adhesive links between two materials of radically different chemical composition. Wheeler found two coupling agents that gave substantial strength increases to both limestone and sandstone, but at the expense of significant darkening.

Wheeler has also used ^{29}Si nuclear magnetic resonance (NMR) spectroscopy to monitor the polymerization of MTMOS (Danehey, Wheeler, and Su 1992). The technique is valuable because it enables one to follow the gradual disappearance of MTMOS and the emergence of polymers in which a silicon atom is attached (through an oxygen atom) to either one, two, or three other silicon atoms. Wheeler was able to demonstrate that calcite had a dramatic effect on the rate of the condensation reaction, whereas quartz had little effect on either the hydrolysis or condensation reaction. He attributed the effect to surface anticatalytic effects of the calcite crystals and went on to argue that calcitic limestones might therefore prove harder to consolidate with MTMOS than quartz-bearing rocks. This is not an observation that appears to be borne out in practice, however. Butlin et al. (1995), reporting on the performance of silanes in field trials over a period of some fifteen years, states that consolidation of limestones appeared at least as effective as consolidation of sandstones, although this could perhaps be attributable in part to the greater porosity (and hence the greater absorption of consolidant) of the limestones.

Kumar has reported on the influence that soluble salts may have on the hydrolysis and condensation of MTMOS (Kumar and Price 1994). Sodium sulfate, for example, markedly decreased the rate of both hydrolysis and condensation, whereas sodium chloride increased the rate of condensation. Further study is necessary in view of the presence of salts in many practical situations.

Although the literature contains many papers describing the use of silanes on stone, there are very few that even attempt to come to grips with the underlying chemistry or the associated solgel technology. One gets the uncomfortable impression that few conservation scientists have the ability to utilize the extensive chemical literature in this area, and that this is preventing the transfer of valuable knowledge to the conservation field.

Epoxies

Epoxy resins have had a very bad press as far as consolidation is concerned. Many conservators see them as viscous, brittle, yellowing materials that may make admirable adhesives in some circumstances, but which are certainly not to be considered as consolidants.

It is true that there have been some notable failures, but it would be foolish to dismiss epoxy resins entirely on these grounds. Selwitz, in three recent reviews (1991, 1992a, 1992b), has summarized the use of epoxies as consolidants, charting the successes and failures. He highlights the pioneering work of Domaslowski and Gauri, in particular, and emphasizes the two different paths they have adopted in order to treat relatively small objects and large facades, respectively. The choice of solvent, the means of application, and post-application procedures are vitally important to a successful outcome.

Selwitz's major review (1992b) provides an excellent example of something that is badly lacking in conservation: a comprehensive, dispassionate, state-of-the-art review of a well-defined topic. More reviews such as this are urgently needed—something to which we shall return later.

Acrylics

Although in situ polymerization of methyl methacrylate (and other acrylic monomers) has its advocates, the high rigidity and glass transition temperature of polymethyl methacrylate are generally considered to make it unsuitable as a stone consolidant. Far more attention has been given to the use of acrylic resins dissolved in solvents, and the ubiquitous Paraloid B72 (Acryloid B72) inevitably makes its appearance. Many conservators have experimented with B72 dissolved in an alkoxysilane such as MTMOS, the reasoning being that the B72 brings adhesive properties that the alkoxysilane lacks. The B72 is capable of securing pigment or loose flakes, for example, while the alkoxysilane provides deep consolidation. However, Wheeler and coworkers (Wheeler et al. 1991; Wheeler, Wolkow, et al. 1992) have shown that the resulting composite gel is weaker than the polymers derived either from neat MTMOS or from a solution of B72 in a nonreactive solvent.

Other Materials

Recent accounts of isocyanates, polyurethanes, and polyureas may be found in Hansen and Agnew (1990); Coffman, Agnew, and Selwitz (1991); Zádor (1992); Littmann et al. (1993); and Auras (1993).

Emulsions

Organic consolidants frequently rely on the loss of volatile reaction products or solvents during the curing process. This can make application impracticable in hot climates, and it can pose a hazard both to the conservator and to the wider environment. Some attention is now being given to the development of aqueous emulsions for use as consolidants and as surface coatings (see the following). Snethlage and Wendler (1991) hint at the possible use of an aminoalkylsilane to stabilize a silane emulsion; and Piacenti, Camaiti, Manganelli Del Fà, et al. (1993) report on the development of emulsions based on a hexafluoropropene/vinylidene fluoride elastomer. Further work in this area seems probable.

Surface Coatings

A lot of research in the seventies and eighties was aimed at finding a single treatment that would both consolidate and protect stone. However, the naivete of this approach has become increasingly apparent, and many conservators now accept the need for two treatments: one to consolidate and one to protect. The soundness of the new approach has been borne out by Felix and Furlan (1994) and Alonso et al. (1994), who reported damage to certain stones following treatment with tetraethoxysilane (TEOS) unless the stones were also given a water-repellent coating.

It is a small step to go on and think in terms of renewable protective coatings. The surface coating can be renewed at regular intervals; but the initial consolidation will, it is hoped, last much longer.

The next step, perhaps, is to do away with the consolidant and to rely solely on the protective treatment (Sramek 1993). There may, indeed, be situations where a surface coating alone is sufficient—on a dense, impermeable stone, for example. Nonetheless, the long and disappointing history of surface coatings on the more porous limestones and sandstones should not be dismissed too readily (Honeyborne 1990b).

Water Repellents

The property that has been most sought in surface coatings is water repellency. The logic behind the approach is simple: Since water is involved in most forms of stone decay, a treatment that prevents the ingress of water should help to reduce decay. It has also been argued that water repellents should help to prevent resoiling, although this claim has not been adequately substantiated.

Water repellency has been provided largely by alkoxysilanes, silicones, and fluoropolymers. The development of the fluoropolymers provides an interesting, and regrettably rare, instance of "tailor-made" products. The polymers are close relatives of polytetrafluoroethene (PTFE, or Teflon), renowned for its nonstick properties. The early fluoropolymer coatings worked well, except for a rather poor ability to stick to the stone! Subsequent development has entailed the synthesis of compounds containing functional groups that can adhere to the stone surface, thereby providing more persistent protection (Piacenti, Camaiti, Brocchi, etal. 1993).

Another example of "tailor-making" is provided by Fassina and coworkers (Aglietto et al. 1993; Fassina et al. 1994), who have synthesized a range of fluorinated acrylic polymers. The intention, which was partially achieved, was to improve water repellency and resistance to photooxidation, by comparison with nonfluorinated analogues such as Paraloid B72.

The use of fluorinated polyurethanes has also been reported (Guidetti, Chiavarini, and Parrini 1992).

Emulsions

Aqueous emulsions have been studied by a number of researchers. The emulsions have included acrylics and silicones (Biscontin et al. 1992; Ciabach and Lukaszewicz 1993), silanes (Biscontin et al. 1993), and fluorinated polyurethanes (Guidetti et al. 1992; Chiavarini et al. 1994). Performance varies from stone to stone but is generally promising.

Barriers against Air Pollution

Water-repellent coatings prevent the ingress of liquid water, but they do not prevent the passage of water vapor. Moreover, many surface coatings are also permeable to harmful gases such as sulfur dioxide. Cimitàn, Rossi, and Torraca (1994), for example, have shown that calcium sulfate forms on the surface of calcareous samples that are exposed to sulfur dioxide after treatment with a silicone resin. Drioli, Basile, and Gagliardi (1991), however, have emphasized the potential of polymeric membranes that are permeable to some gases and not others. It is possible, in principle, to deposit on the surface of stone a membrane that is permeable to water vapor, for example, but not to sulfur dioxide. It should also be possible to deposit "directional" membranes, which are more permeable in one direction than in the other (Petropoulos and Sanopoulou 1991). The membranes can be deposited from solution, but further work is required to demonstrate whether the technology can be transferred from the clean conditions of the laboratory to the conditions that are found on the surface of monuments.

Reaction Inhibitors

Cimitàn, Rossi, and Torraca (1994) raise the prospect of treating stone surfaces with compounds that will inhibit the sulfation of calcium carbonate. They report encouraging results with the use of p-nitroaniline, and they suggest that the use of such compounds as "primers" might prolong the service life of silicone coatings.

This is certainly an area that warrants further research: a number of researchers have spoken of schemes to passify specific mineral surfaces. A much deeper understanding of surface catalysis in the context of stone weathering is needed to achieve this.

Crystal Growth Inhibitors

Another possibility is to treat the stone surface with compounds that inhibit the growth of salt crystals. Relevant technology already exists in such diverse fields as anticaking agents for road salt and in underwater oil extraction, where phosphonates are used to prevent the precipitation of barium sulfate and calcium sulfate (Black et al. 1991). Applications in the field of conservation have been proposed from time to time (e.g., Puehringer and Engström 1985), and this too is an area that deserves further research.

Oxalate Formation

Building on the protective properties of scialbatura (see page 10), Matteini, Moles, and Giovannoni (1994) have proposed the use of ammonium oxalate to produce a shallow film of calcium oxalate on calcareous surfaces such as wall paintings. Both calcium carbonate and calcium sulfate react with a poultice containing a solution of ammonium oxalate to produce a cohesive film with unaltered optical and hydrophilic properties.

Lime

The final stage of the lime treatment (see page 17) consists of the application of a very thin coating of lime and fine aggregates rubbed firmly into the surface of the stone. The coating is intended to protect the stone, and it is reapplied as necessary.

Colloidal Silica

Kozlowski, Tokarz, and Persson (1992) have adopted a rather different approach for forming a protective coating on calcareous stones. They have used sols of colloidal silica that deposit silica particles within the outer pores of the stone. The resulting surface is hydrophilic, but the passage of water through the pores is impeded by the presence of the particles. The results of field trials have yet to be reported.

Semiconductors

In an extensive series of papers spanning many years, Skoulikidis has argued that the sulfation of marbles proceeds by a mechanism comparable to the galvanic corrosion of metals (e.g., Skoulikidis 1993; CPAM 1994:20). It is a theory that is much cited by Skoulikidis himself and little by others, although Atzeni et al. (1994) have recently reported supporting evidence from the field of chemical gas sensors.

On the basis of his corrosion model, Skoulikidis has developed protective coatings containing n-semiconductor pigments such as Fe_2O_3, TiO_2, and Al_2O_3 (Skoulikidis and Kritikou 1992; Skoulikidis 1994). It is argued that the coatings not only protect the stone and give it an artificial patina, but that the pigments also serve to protect the polymeric binder against UV degradation.

Biocides

There is a long history of research into surface treatments that will kill biological growths and, if possible, inhibit regrowth. Such treatments must meet a large number of criteria, and this can prove difficult in the outdoor environment, where there is a continual supply of moisture to promote regrowth. They must not only kill the growth in the first place, but they must also be resistant to new strains. They must not have any harmful effect on the stone itself, nor must they change its appearance. They must not be washed out by rainfall or destroyed by ultraviolet light, and they must be safe both to the person applying them and to the wider environment. The last requirement has been applied ever more stringently over the past few years, with the result that a number of proven biocides have been banned by law. It follows that there is still a need for research in this area.

Most of the existing research on biocides has been concerned with algae, lichens, and higher plants like weeds, mosses, and ivy. Some of the research has been based on cultures in the laboratory, while most of it has been based on site trials. Examples of such research are provided by Agarossi, Ferrari, and Monte (1989) and Anagnostidis et al. (1992). The latter also emphasize the need for regular observation and retreatment and they suggest "early warning systems" to indicate the moment for retreatment.

Caneva, Nugari, and Salvadori (1991) provide a valuable account of the many available biocides, which are normally applied to the surface of the stone by brush or spray. Portable objects may also be treated by fumigation: Elmer et al. (1993), for example, report the use of ethylene oxide. Bassier (1989) reports the use of ultraviolet radiation to sterilize mineral surfaces. Caneva et al. (1991:119) mention the possibility of preventive conservation by the deliberate introduction of suitable vegetation in the vicinity.

It is possible that some water repellents may have a biocidal effect. Sorlini, Falappi, and Sardi (1991) report the inhibition of fungal growth by a methyl phenyl silicone resin, but other workers (Koestler and Santoro 1988; Petushkova and Grishkova 1990; Krumbein et al. 1993) have reported the opposite effect: the biodegradation of silicones.

Relatively little research has been conducted on antibacterial treatments for stone. This is surprising, perhaps, in view of the extensive work on the role of bacteria in decay, but it may reflect the difficulty of finding antibacterial treatments with sufficient persistence. Nonetheless, Orial and Brunet (1992) present a satisfying account of the use of streptomycin and kanamycin to eliminate bacteria from stonework at Elne Cathedral for a period of more than seven years, with a resulting cessation of decay.

Chapter 3

Do They Work? Assessing the Effectiveness of Treatments

This chapter is concerned with the evaluation of treatments that are intended to reduce or stop stone decay. It does not deal with the evaluation of cleaning and desalination techniques or with the evaluation of biocides, except insofar as these techniques affect the rate of decay.

One might suppose that the most practical approach would be to simply apply the treatment and see if it works. But how can you tell if it is working? What do you really mean by "working"? How long do you need to leave it? Can you speed things up a bit? Will it keep on working indefinitely? Will it work on other stones in other environments? What about other treatments that come along while you are carrying out your lengthy evaluation?

Price (1982) has reviewed strategic approaches to the evaluation of treatments. It is a subject that is of vital importance, and we cannot afford to get it wrong. We need answers straightaway in order to devise responsible programs for the conservation of monuments that are decaying before our eyes. But if we act too quickly and apply the wrong treatment, we may make matters even worse.

Many workers have devised their own procedures for evaluating treatments, using a range of tests to build up an overall picture (see, for example, De Witte 1992; Galan 1993; Zezza 1993; and Sasse, Honsinger, and Schwamborn 1993). This is both inevitable and understandable, since individual researchers are constrained by the range of techniques that are available to them. It also has the advantage that the procedure can be tailored to suit a particular stone and environment (e.g., Galan and Carretero 1994); it is unrealistic to think that any single procedure could fit all circumstances. However, it can be very difficult to compare the findings of one researcher with those of another, and there is a need for standardized procedures. This was the underlying objective of the Rilem (Reunion Internationale des Laboratoires d'Essais et de Recherches sur les Matériaux et les Constructions) 25 PEM (préservation-érosion-monuments) Working Group, albeit not fully achieved (Rilem 1976; Price 1982). More success has been achieved with the definition of individual test methods (see the following), although the "not invented here" syndrome frequently hinders their widespread adoption.

It is convenient to divide evaluation procedures into two categories: those that characterize the stone shortly after treatment has taken place, and those that are concerned primarily with monitoring long-term performance.

Characterizing the Treated Stone

There are some properties that are helpful in building up an overall picture of the treated stone, even though they may not give any direct indication of the treatment's effectiveness. These include the porosity and pore size distribution of the treated stone, its appearance, and the depth of penetration. The majority of tests, however, are concerned with measuring properties that are known to change as the stone decays, or with assessing the extent to which the treatment has met certain clear objectives.

Properties That Change with Decay

We have already looked at a number of tests that are intended to measure the extent of stone decay. These tests can obviously be applied to stone that has been treated with a consolidant or surface coating in order to determine whether there has been an improvement in performance. Such tests might include surface hardness, surface profile, strength, ultrasonic pulse velocity, or acoustic emission (Esbert et al. 1988). The recent paper by Villegas, Vale, and Bello (1994) illustrates both the approach and the difficulties of interpretation that may arise. If it is difficult to characterize decayed stone, then characterizing treated stone is doubly difficult.

Meeting Objectives

Some tests are designed to assess the extent to which the treatment is meeting certain objectives. If the treatment is intended to impart water repellency, for example, then measurements of contact angle and water absorption are appropriate. Or if it is intended to provide protection against acid rain, then measurements of weight loss or of salt formation may be necessary. The logical outcome of this approach is the definition of a set of performance criteria against which a treatment may be judged. Sleater (1977) provides a good example of this approach. However, Sleater was unable to find any treatment that met all his criteria, and this may account in part for the lack of attention subsequently given to the approach.

Caution must be exercised when using tests intended primarily for untreated stone. For example, a crystallization test that relies on the absorption of a sodium sulfate solution is frequently used to determine a stone's resistance to salt weathering. The test should not be applied unthinkingly, however, to a stone that has been coated with a water repellent. Excellent performance in the test (e.g., Villegas and Vale 1992:1259) would not necessarily indicate increased resistance to salt growth; it could simply indicate that the water repellent had prevented the ingress of salt in the first place.

Standard Test Methods

Standard test methods are essential if one is to compare the results of different laboratories in any meaningful way. Even for a seemingly straightforward property such as water repellency, differing procedures yield differing results (Henriques 1992).

The standardization of test methods has been the objective of both national and international committees. Notable among them are the recommendations of the Rilem 25 PEM and 59 TPM (traitement des monuments en pierre) Working Groups (Rilem 1976; Pien 1991) and the standards published by the Italian Commissione NORMAL (Alessandrini and Pasetti 1991). It is regrettable that details of these test methods are not more readily available and more widely translated.

Long-Term Performance

It is one thing to find a treatment that performs well in the short run; it is another thing altogether to be sure that it will keep on performing year after year when exposed to the weather.

Natural exposure trials provide the only "true" test. They may be carried out in situ on monuments or on small blocks of stone that can be brought into the laboratory at intervals for evaluation. Either way, the trials can only provide information on a limited number of stones, treatments, and environments, and it may be many years before reliable information is obtained. A new range of treatments will inevitably have emerged in the meantime. What is more, one is still confronted with the difficulty of evaluating the effectiveness of the treatment. The surface may look sound on the outside, but what is going on underneath? In situ monitoring relies heavily on the techniques described in Chapter 1.

Accelerated weathering chambers are extensively used to simulate weathering (see, for example, Sasse and Riecken 1993), but they introduce yet another layer of uncertainty. Do they accurately reflect long-term behavior? By what factor do they increase the rate of weathering?

Sramek (1991) has described a technique that is sensitive enough to detect surface loss under simulated conditions that are close to real conditions. It first entails the bombardment of the stone with low energy ^{85}Kr atoms, which become trapped in the surface layers. Subsequent surface loss releases the atoms, and their loss can be monitored by the radioactivity of the sample.

It is noteworthy that most of the literature on long-term performance is concerned with the behavior of the treated stone per se. There have been surprisingly few in-depth studies of the breakdown of the treatment itself. Even in the field of alkoxysilane consolidants, few authors have made systematic studies of the long-term weathering of the resulting silicone polymer. Some authors, however, have recently highlighted the fact that treatments may serve as an energy source for microorganisms (e.g., Koestler and Santoro 1988; Petushkova and Grishkova 1990; Krumbein et al. 1993). This important aspect had been largely overlooked hitherto.

Documentation of Field Trials

There is a regrettable tendency for researchers to set up field trials, to monitor them for a few years, and then to forget about them as further treatments become available. There is a need for systematic, long-term monitoring of trials. This is often hindered, however, by woefully inadequate or missing records.

The availability of sophisticated computer databases offers the possibility of creating good, centralized records, and this possibility has been seized by a number of workers. Fitz (1991) has described the Monufakt database adopted by the German Federal Environmental Agency, and Rosvall and Lagerqvist (1992) have developed EUROCARE DATA. The difficulty will lie in persuading researchers to put reliable, comprehensive information into the system, and in persuading others to use it in future years. This is on top of the difficulty of curating digital records over long time periods, during which both hardware and software will rapidly become obsolete.

Chapter 4

Putting It into Practice: Conservation Policy

Conservation is not immune to the vagaries of fashion—fashion that varies with both time and place. In England, for example, it was fashionable one hundred years ago to replace decayed sculpture with "copies": contemporary interpretations of what the originals might once have looked like. By contrast, the current normal philosophy is to "conserve as found": to keep original material and prevent further deterioration as far as is practicable. A further approach is common in the Far East, where the emphasis is more on preserving the function of a monument than on preserving the materials from which it is constructed.

Numerous attempts have been made to codify conservation principles and to introduce international uniformity. Notable among them are the 1964 International Charter for the Conservation and Restoration of Monuments and Sites (the "Venice Charter") and the more recent Burra Charter (ICOMOS 1988), which deserves to be more widely known. It is beyond the scope of this publication to discuss conservation principles in detail, but it is relevant to note that many parties play a role in shaping conservation policy: the architect, the art historian, the scientist, the archaeologist, the conservator, the owner, and ultimately the general public. The scientist may be convinced of the validity and importance of his or her results, but there are others to be convinced before the results impact on conservation policy.

This chapter focuses on just three aspects of conservation policy: the responsible use of surface coatings, adhesives, and consolidants; the problems posed by multiple treatments; and recording. These three issues have been chosen because they have a common thread, which is the fact that no treatment can be expected to last forever. However much we may be lured into thinking that a treatment will last indefinitely (or, perhaps, until we are no longer accountable for it?), we must accept that all treatments have a finite life. This has direct implications for conservation policy in the three areas indicated.

Responsible Use of Surface Coatings and Consolidants

If a treatment is not going to last forever, should we use it in the first place? As we have seen above, we cannot be one hundred percent sure that the treatment will not lead to some unforeseen problem in the future. At what point should we "take the risk" of applying a treatment to an important stone object/monument?

Conservators invariably pay homage to the principle of reversibility: No treatment should be used unless it can be removed at some future date, should that prove necessary. In the context of stone conservation, however, reversibility may be more idealistic than realistic. It can be extremely difficult, in practice, to remove even the most soluble of treatments. It is wiser, therefore, to assume that a treatment, once applied, cannot ever be totally removed. Succeeding generations are going to have to live with the consequences of our actions.

What should we do? Treatment is irreversible, in practice, but decay through neglect is irreversible too. The dilemma highlights the importance of preventive conservation, but there are instances where preventive conservation is not enough. Ultimately it will be necessary to reach a carefully balanced decision, taking into account all aspects of each individual case. Sometimes we will conclude that treatment is justified; at other times, we may conclude that we can safely defer treatment for the time being.

This polemic is all very well, but sadly it is often irrelevant. In many of the cases with which we are confronted, the stonework has already been treated by previous generations who were perhaps less cautious or more optimistic than we may be. Often we do not know with any certainty the identity of the treatment, and often there may have been more than one treatment. This leads us to the problems of retreatment.

Retreatment

Virtually all research on stone treatment is based on the assumption that the treatment is to be applied to stone that has never been treated before. It is astonishing that so little work has been done on the effects that one treatment might have on another. While we hear much about reversibility, we hear little about "retreatability," even though the latter is a far more important concept in practice.

Any consolidant that blocks the pores of the stone and prevents the subsequent application of another consolidant must clearly be regarded with some caution. The topic that demands research, however, is the physical and/or chemical interaction of one consolidant with another. The swelling of polymers under the influence of solvents is a well-known phenomenon, but little attention seems to have been paid to the swelling of a consolidant when a second consolidant is applied. It is possible that such swelling might cause damage to the stone—which can safely be assumed fragile, or the consolidant would not have been applied in the first place. Moreover, one can imagine that the second consolidant will not be deposited as a coherent layer on top of the previous treatment, but will form an intermingled mixture. It is not an appealing prospect, and it certainly deserves more attention.

There is equally a need to ensure that there are no unforeseen consequences of multiple applications of maintenance coatings.

Recording

If we cannot preserve stone forever, it is imperative that we make the best possible record of it. Indeed, one could argue that recording should have a higher priority than preserving the stone itself—provided, of course, that we are confident that the records can, in turn, be properly maintained and curated indefinitely.

Drawing and photography still have a place in recording, but attention is turning increasingly to techniques of three-dimensional recording. Molding and casting is the traditional technique, but it is not always practicable on very delicate or undercut surfaces. It is accordingly being replaced by techniques that do not entail any physical contact with the stone surface.

Stereophotography has been known for a long time, but provides only an illusion of depth from a single viewpoint. Photogrammetry, a related technique, has been widely used for producing contoured images, but still suffers from the drawback of a single viewpoint. Holography overcomes this problem, and its use for recording sculpture was first proposed by Asmus et al. (1973). Nonetheless, the role of holography has been limited largely to the production of images that, while visually striking, do not really provide a quantitative record. In this respect, laser scanning has taken the lead.

The operation of the laser scanner is described by Taylor et al. (1987) and Wainwright and Taylor (1990). The time taken to scan an object depends upon both its size and the desired resolution: The time required to scan a human head, for example, can range between 30 seconds and 10 minutes (Larson 1994b). The primary output of the scanner is a digital record of the three-dimensional form of the object, and this can be used in a number of ways. It may be used purely as an archival record; it may be used (in conjunction with subsequent scans) to monitor the deterioration of an object; and it may be used to drive a milling machine in order to produce a replica. Further uses are described by Taylor et al.

One of the great advantages of the laser scanner is that it does not entail any physical contact with the object and is hence suitable for even the most delicate surfaces. It has also been developed to the point where it is now capable of providing stereoscopic color images with a resolution of about 25 µm, which may be viewed, sectioned, and measured on the computer screen (Baribeau 1994). Requirements for computer memory are high (in the region of 20 megabytes for a life-size mask), but techniques for data compression may alleviate this problem in the future.

The ability to produce highly accurate replicas of decayed stonework is an attractive proposition that has been seized upon by some conservators (Larson 1992). Original sculpture can be taken indoors to the safety of a museum, while an exact copy can be put in its place. Nonetheless, there are those who argue that it may be inappropriate to put back an exact copy that will be missing features already lost from the original, and that it may be preferable to re-create those features in as sympathetic a manner as possible.

Chapter 5

Doing Better: Increasing the Effectiveness of Research

The purpose of this chapter is to suggest some ways in which our research might be made more effective. The views expressed are unashamedly personal, and not everybody will agree with them. It is hoped, nonetheless, that they will stimulate some serious thought and discussion in order that limited research resources may be put to the best possible use.

What Is Wrong?

Publications

The number of published papers relating to stone is growing relentlessly. On the face of it, this must surely be welcomed. It indicates the growing concern about stone and the growing numbers of researchers who are working on stone. However, the quality of many papers is disappointing. An informal survey conducted while writing this report suggests that many researchers feel that as few as one paper in ten of the published literature was worth publishing. What gives rise to this alarming view?

The following criticisms are often made:

- The same material is published on more than one occasion. While it is acceptable to publish interim reports on a major piece of work, there is no excuse for publishing the same material, with only minor variations, time and time again.
- Many papers consist of the application of well-tried procedures to a specific building or monument. The results are of interest only to a limited audience and should be written up as an internal report of the organization carrying out the research. They do not warrant full publication in journals or conference proceedings.
- Many papers fail to set the research into context. They are essentially descriptive; they describe the work that was undertaken, but they do not say *why* it was done.
- Many papers fail to indicate the significance of the results. Having failed to say why the work was done, they give insufficient discussion of the results and so fail to indicate what, if anything, was achieved. The reader is left wondering whether any advance was made and, if so, what it was.
- Few papers identify promising avenues for further research.
- Underlying the previous problems is the frequent neglect of the scientific rigor of hypothesis → experiment → conclusion.

Conferences

Conferences provide unparalleled opportunities for meeting fellow researchers: for making new contacts, finding new collaborators, comparing notes, sharing ideas, and keeping up to date. They also provide a much-needed opportunity to stop and think, and to see one's research in a broader context.

On the negative side, however, conferences often provide an opportunity for publishing substandard, nonrefereed work. The proliferation of conferences, however desirable it may be, can all too easily lead to a proliferation of poor-quality papers.

Standards

The lack of internationally agreed-upon standards, be they for nomenclature or for testing procedures, hinders the interpretation, understanding and evaluation of research. There is no "common language."

Conduct and Quality of Research

Research into stone conservation demands an interdisciplinary approach. Many researchers, however, find themselves working alone or in relatively small teams. As a result, research can become too narrow, failing to take into account factors that might seem self-evident to somebody trained in another discipline. At worst, researchers can become so introspective that they take little or no account of work being undertaken elsewhere; the researcher whose citations are solely to his or her own work is clearly falling into this trap.

A lot of research into stone is conducted at a rather superficial level. Much of the work on consolidants, for example, is very empirical. A particular material will be evaluated simply because it is available, not because there are sound theoretical reasons for believing that it will be effective. Some work on decay mechanisms is equally superficial: We are content, for example, to demonstrate that salts are capable of causing damage to stone, and our research is not at a deep enough level to explain *how* the damage occurs. However, there is always a danger that research can become so theoretical that it loses sight of its main purpose. The researcher needs to be fully aware of what is desirable and practicable from a conservation standpoint, while conducting research at a level that is deep enough to solve the fundamental problems.

Some of these issues were summarized succinctly by Chamay (1992) in his closing remarks at a recent conference:

> Je m'inquiète un peu de constater que vos recherches sont menées sans concertation organisée, chacun travaillant de son côté, l'echange d'information restant très limité. . . . J'ai aussi le sentiment que la tendance générale parmi les chercheurs est de rester confiné dans sa spécialité . . . Attention à l'arbre qui cache la forêt! Avant d'entrer dans le détail, une appréciation d'ensemble est nécessaire. [I am a bit worried to notice that you are carrying out your research without organized dialogue, each person working in his or her own corner, the exchange of information remaining very limited. ... I also have the feeling that the general tendency among researchers is to remain confined to one's own specialty. . . . Beware of the tree that hides the forest! Before going into detail, an assessment of the whole is necessary.]

Getting the Message Across

There is no point in doing research unless the outcome can be applied in practice. This does not mean that there is no place for long-term, strategic research, but that any worthwhile research must contribute ultimately to the care and conservation of the heritage.

There are many ways of getting the message across, including lectures, publications, personal contacts, and advice on specific problems. The message needs to reach other researchers; but it must also reach, for example, conservators, architects, archaeologists, and administrators. It does not follow automatically that a good researcher is a good communicator, and all researchers should ask themselves whether their research is achieving the impact it deserves.

Putting It Right

What can be done to make our research more effective? There are no simple solutions. While some steps may be taken by individual researchers, other solutions lie with research administrators, conference organizers, editors, publishers, training institutions, and with funding bodies. The following proposals deserve consideration.

Quality, Not Quantity

Any institution that funds research may reasonably expect to see some return for its money. This necessitates some means of measuring research output. How else may the institution be sure that its money is being well spent? The simplest indicator, and one that appeals to many administrators, is the number of papers that result from the research. It is an objective, quantitative indicator; but it is one that undermines quality. Individuals find themselves under immense pressure to produce a certain number of publications each year, and it is no wonder that quality suffers. Publishing the same thing several times is an easy way of meeting the target. Other tactics include the publication of a string of interim reports, the publication of material that warrants no more than an internal report, publishing papers that report on what one *proposes* to do in the future, and publishing papers with a long and unjustified string of authors.

An ingenious alternative is to look at the number of times that an individual's work is cited by others. Ideally, this gives an objective measure of the worth of the work, as perceived by the researcher's peers. Unfortunately, this system, too, is open to abuse.

Assessment of quality in research is not a simple matter of numbers. It entails a high degree of subjective judgment, both by research managers and by other researchers. Funding bodies must be prepared to appoint research managers whose judgment they trust, and then be prepared to accept that judgment concerning the quality of research being conducted under those managers' supervision. They must be seeking *value for money,* which entails both quality and quantity, rather than quantity alone.

Conference Papers

It is a common practice for employers not to fund an individual's attendance at a conference unless he or she is presenting a paper or a poster. It is a practice that makes the research administrator's life much simpler, but one that again encourages the production of superfluous publications. This is another area where research managers must be prepared to make their own judgments on the value that will accrue from an individual's attendance, whether or not a paper or poster is to be presented.

Selection of Conference Papers

Another important way of preventing the publication of substandard conference papers lies with the conference's technical committee. All too often, papers are selected on the basis of an abstract submitted some eighteen months or more before the conference. At that time, the research will almost certainly not have been completed; indeed, it may not even have begun. The prospective author, therefore, makes a guess as to the likely outcome of the research and writes an abstract that strikes a delicate balance between the specific and the noncommittal. The technical committee reviews the abstracts and, on this flimsy evidence, decides which papers to accept. By this time, the author has twelve months or less in which to complete a paper—regardless of how the research is going. And the technical committee and the editors, when they finally receive the paper, have little option but to publish it much as it stands.

Not all conferences operate this way, but many do. It means that much of the literature of conservation has been subjected to the very minimum of refereeing, if any. Quality assurance is all but nonexistent.

If preprints are to be issued at the time of the conference, there may be insufficient time for full refereeing. Nonetheless, a significant step forward could be made if technical committees were to insist on seeing the full text of a paper before deciding whether to accept it for presentation and publication. It is true that it takes longer to read a paper than it takes to read an abstract, and that technical committees are comprised of people who do not have time on their hands. However, it does not take long to decide whether a paper consists largely of previously published material, or whether it is of local interest only. A lot of substandard papers could be weeded out very quickly. Another problem is that authors may not be prepared to take the time to write a full paper if there is a risk that it may not be accepted. Too bad—if poor papers were weeded out, there would be correspondingly more space for good papers, so the author who has something worthwhile to say need not fear rejection.

Refereeing

Ideally, *all* published material should be subjected to peer review. It is a process that is open to criticism in that it slows down publication and can fall foul of an ill-informed or prejudiced referee. It is, however, the fairest way of ensuring that papers are of sufficient quality to merit publication. Conservation has suffered greatly from the fact that so much of its literature is in unrefereed publications. As one conservation scientist observed recently: "Why try harder, when you can get away with being sloppy?"

Collaborative Programs

The time has long passed when a well-educated individual might have a working knowledge of the whole of science and the humanities. We are all highly specialized in our individual fields, and we need to collaborate with specialists in other disciplines if we are to solve the very broad problems posed by stone conservation. Not only do we need to collaborate with other conservation scientists from different disciplines, but we also need to draw in talented researchers who are not involved in conservation. Such collaboration is not without dangers (Torraca 1991), but is essential nonetheless.

Some funding bodies are in a position to enforce collaboration. An example is to be found in the Environment Programme operated by the European Union. Research projects are not funded unless they entail genuine collaboration between partners in more than one member state, with each partner making a clearly defined contribution based on a particular expertise. In a relatively short time, the Environment Programme has brought about a much greater degree of collaboration between relevant European research institutions.

Training

Good research requires good researchers. To be a good researcher in the scientific aspects of stone conservation, one needs a thorough grounding in science, training in research, and a sound appreciation of conservation issues. These qualifications are not readily found in any one individual, and a significant proportion of "conservation scientists" do not have sufficient knowledge of science to enable them to undertake research at a fundamental level. They may, for example, have trained primarily as conservators; although their training may well have included some science, they are conservators first and scientists second. As a result, a good deal of research is rather superficial.

Much attention has been paid to the training of conservators, and lists of training courses are readily available (e.g., *International Directory of Training in Conservation of Cultural Heritage* 1994). By contrast, little attention has been paid to the training of conservation scientists. There are very few training programs with such an objective, and a worldwide survey of current training opportunities would be advantageous. A number of possible pathways can be envisaged: doctoral research followed by a fellowship in a major conservation institution or museum, for example, or a master's degree in a particular aspect of conservation science. A first degree in a scientific subject should be a prerequisite, in any event.

Some attention also needs to be given to ways of attracting high-caliber students to conservation. The subject does not, on the whole, attract the outstandingly capable researcher. Such individuals are more likely to be found, for example, in medical research, in nuclear physics, or in military research, where they will benefit from better funding and from the stimulus of working in large, highly focused teams. This situation is unlikely to change, although the recent formation of large, well-funded conservation institutions is a welcome development. Ways must be found of bringing conservation to the attention of science students during the course of their first degree, and of presenting stimulating and challenging career opportunities.

Reviews

The conservation literature is remarkable for its lack of scholarly review articles. In all the mainstream scientific disciplines, the need for state-of-the-art reviews is well recognized, and the authors highly acclaimed. The conservation literature, by contrast, is full of isolated pieces of work, with very little effort being made to pull the information together. It is quite astonishing, for example, that there appears to be no recent, comprehensive review of stone consolidation. True, there are many articles on stone consolidation, but there is no review in which all the information is brought together in an orderly and critical manner, so that the reader may rapidly gain a full and thorough overview of the subject. Similarly, there is no such review of salt damage, even though it is a major cause of decay and the literature contains numerous disconnected pieces of information. Review articles would enable researchers to put their work in context, and to see where further work was worthwhile.

Reviews are not easy to write. They require a lot of time and a high degree of competence in the author. It is likely they would have to be specifically commissioned and funded. There is no current publication that is an ideal vehicle for such major articles, and it is probable that a new journal would be necessary. The effort would be considerable; but the benefits would be immense.

Conclusion

This volume opened with the suggestion that research on stone conservation had stagnated. It has demonstrated, however, that a great deal of activity is occurring and advances are being made in many different areas.

The volume has also shown that some research is poorly focused and that resources are not being used to the best effect. The resources available for stone research are small by comparison with the magnitude of the problem, and we cannot afford to waste them.

Appendix

The following publications were scrutinized during the writing of this book, and use was also made of the Conservation Information Network, operated by the Canadian Heritage Information Network. It must be emphasized, however, that stone conservation is a multidisciplinary subject and that relevant publications are to be found in many other sources.

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About the Author

Clifford Price was born in 1948 and earned his M.A. and Ph.D. in chemistry at St. Catharine's College, Cambridge. He worked first at the Building Research Establishment, where he undertook research in stone conservation. In 1983 he was appointed Head of the Ancient Monuments Laboratory with English Heritage, and in 1990 he began a readership in archaeological conservation at the Institute of Archaeology, University College London, where he is Director-designate of the proposed Centre for Conservation and Museum Sciences.
He has been involved in the conservation of several major cathedrals, notably the west front of Wells Cathedral from 1974 to 1985. His research is concerned primarily with the decay and conservation of stone.

ISBN 0-89236-389-4

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