

ARCHITECTURAL CONSERVATION AND APPLIED MINERALOGY

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ABSTRACT

The field of architectural conservation concerns the restoration and protection of buildings and other structures from environmental agents of deterioration such as climate, air pollution and acid rain. Although usually thought of only in relation to historic buildings, the principles of architectural conservation can also be applied to contemporary structures. Applied mineralogy is an essential part of architectural conservation. It is used to study the mechanisms of deterioration, to diagnose the problems of individual buildings and to develop methods of dealing with the problem. Typical uses of applied mineralogy include characterization of building materials, identification of altered surface-layers, and the prediction of the durability of both the original material and the alteration products as a function of environmental conditions. Several applications are reviewed including: inherent vice, air-pollution attack on limestone and marble; failure of iron reinforcements in masonry, damage by soluble salts to masonry, corrosion of bronze and the performance of weathering steel.

Keywords: architecture, building materials, air pollution, corrosion, marble, bronze, reinforced concrete, salt damage, steel, acid rain.

SOMMAIRE

Le domaine de la conservation architecturale porte sur la restauration et la protection d'édifices et autres structures des agents dans l'environnement qui contribuent à leur détérioration, tels que le climat, la pollution atmosphérique et les pluies acides. Quoique l'on étudie généralement ces facteurs pour les édifices d'intérêt historique, les principes de la conservation architecturale s'appliquent aussi bien aux structures contemporaines. La minéralogie appliquée en forme une part essentielle. Elle s'adresse aux mécanismes de détérioration, au diagnostic de problèmes dans des cas particuliers et au développement de méthodes pour remédier aux problèmes. Par exemple, on s'en sert pour caractériser les matériaux de construction, identifier les couches altérées à leur surface, et prédire la durabilité des matériaux originels et des assemblages d'altération en fonction du milieu. On discute de plusieurs applications, dont les défauts cachés, l'attaque du calcaire et du marbre par la pollution atmosphérique, la déconfiture des renforts de fer dans les pierres taillées, le dommage dû aux sels solubles, la corrosion du bronze et le rendement de l'acier traité pour l'environnement.

(Traduit par la Rédaction)

Mots-clés: architecture, matériaux de construction, pollution atmosphérique, corrosion, marbre, bronze, béton armé, dommage par les sels, acier, pluies acides.

INTRODUCTION

The field of architectural conservation concerns the study of the deterioration of buildings and methods of preventing this damage. Historic buildings have received the most attention, but the principles of architectural conservation can also be applied to modern buildings as well. Since many of the problems addressed by architectural conservators could have been prevented by more enlightened construction and maintenance practices, a knowledge of architectural conservation could be used to advantage at the stage of the specification of materials and architectural design.

The fundamental problem of architectural conservation concerns the failure in some way of building materials to perform as intended. Usually, the situation is the accelerated weathering or corrosion of the material, to the point where the building's structural integrity may be compromised. However, aesthetic considerations can also be important. These include the loss of details in sculpture, the staining of a surface or the loss of a polished finish.

The practice of architectural conservation involves several aspects of applied mineralogy. The durability of inorganic building-materials is determined largely by the physical properties of the individual mineral phases of the materials, such as crystal structure, molar volume and hydration states, as well as petrographic considerations concerning the physical relationships among the phases, including grain morphology and porosity. The materials and their alteration products are thus usually studied by the methods of optical and electron microscopy and X-ray analysis. Occasionally, infrared absorption spectroscopy, differential thermal analysis and other scientific tools are also employed (Rossi Manaresse 1982). The actual rates of weathering and deterioration are usually determined by kinetics rather than thermodynamic equilibria, and involve some difficult problems in applied geochemistry. These are beyond the scope of this paper. Nevertheless, simply from a study of the mineral assemblages found in and on building materials, the architectural conservator can make reasonably accurate inferences about the major causes of deterioration.

The causes of deterioration can be grouped into several major categories, beginning with the use of inferior materials in the original construction, or inherent vice. The failure of protective surface-layers

or the formation of deleterious alteration-layers are two more categories. The presence of soluble salts is another. Interactions between building materials is a separate category, as is biological attack. Finally, measures taken to protect a deteriorating building can sometimes introduce additional problems.

INHERENT VICE

The original choice of building materials is obviously a major determinant in the durability of the structure. Materials that fail because of intrinsic shortcomings are said to suffer from *inherent vice*. This is especially prevalent in stone, and the importance of choosing durable stone has been emphasized since antiquity. The Roman author Vitruvius, writing in the first century A.D. (Morgan 1914), described the relative durability of building stones from quarries in the vicinity of Rome. This is typical of the body of conventional wisdom that has built up over the centuries concerning the suitability of stones from a given region for use in construction.

Unfortunately, this type of classification depended primarily on geography rather than mineralogy itself, in the sense that the durability of the stone was described as a function of where it was quarried and not of its composition. As long as the stone was supplied from familiar quarries, inherent vice could be avoided. However, in the absence of a durability index based on mineralogy, it would be difficult to predict the performance of stone from a newly opened quarry. Even in this century, the durability of stone has still been specified largely by its place of origin (Merrill 1908) rather than in terms of a quantitative relationship using mineralogical and petrological parameters. This lack of a general theory of stone decay has been identified as a major problem in the field of architectural conservation (Torraca 1982).

This is not to say that mineralogy was totally ignored. To the extent that different rock-types could be identified by macroscopic properties like color, texture and hardness, crude estimates of durability could be made. Vitruvius observed that certain types of rocks such as travertine were generally more dura-

ble than others found in Italy. A century ago, Julien (1883) published a listing of the lifetimes of different building stones in New York City, which indicated that gneiss was the most durable and brownstone the least (Table 1).

A drawback to this method of specifying durability is that visual appearance could be deceptive. Thus building stones of widely differing mineralogy were sometimes mistaken with each other, creating confusion about true performance as building materials. For instance, a building stone used widely in Flanders during the Middle Ages was known as "petit granit" or little granite from its resemblance to granite, although it is in fact a compact grey limestone (Nijs 1985). Similarly, the term alabaster was applied interchangeably with onyx marble and with gypsum until this century (Merrill 1908, p. 243). Since the solubility of the latter is an order of magnitude greater than the former, an architectural element made of gypsum where marble was actually intended would show unexpectedly rapid deterioration when exposed to weather. Thus the first step for the architectural conservator in diagnosing the causes of deterioration is to verify that the mineralogy of the building stone is actually what the property owner thinks it is.

Nevertheless, certain types of inherent vice could be attributed to easily distinguishable heterogeneous minerals occurring as veins or inclusions (Lewin & Charola 1979). For example, the prominent silicate stylolites in Tennessee marble will weather out preferentially (Winkler 1975, p. 144). In a somewhat similar case, the marble from Lee, Massachusetts, used on some of the exterior of the U.S. Capitol contains small flakes of tremolite, which weather to talc upon exposure. The associated changes in dimension, plus the presence of moisture that encourages frost damage, create localized centres of deterioration (Winkler 1982). The result is a pockmarked appearance on the stone surface (Fig. 1). Another type of differential weathering has been observed on sculpture in India made of "khondalite", a quartzofeldspathic gneiss. This contains prominent crystals of garnet, which tend to weather out preferentially, leaving noticeable voids and pockmarks (Lal 1985).

The existence of troublesome heterogeneously distributed minerals is not always so apparent to the naked eye. For example, the limestone that was used in the Kansas State House contains varying amounts of silicates (Grisafe 1982). The deterioration of the stone appears to correlate with higher clay and silt contents (Fig. 2). This was only established through a detailed mineralogical examination. Similarly, certain Egyptian limestone artifacts have been known to disintegrate rapidly when washed. An analysis of the stone showed that the most sensitive contained relatively high amounts of chlorides as well as silicates (Barton & Blackshaw 1976). These findings were used to establish an index of washability, in

TABLE 1. LIFETIME OF BUILDING STONES IN NEW YORK CITY*

Coarse-grained brownstone	5-15
Fine-grained brownstone	20-50
Compact brownstone	100-200
Nova Scotia sandstone	50-200
Ohio sandstone	Centuries
Coarse fossiliferous limestone	20-40
Fine oolitic limestone	30-40
Coarse-grained marble	30-40
Fine-grained marble	50-100
Fine-grained dolomitic marble	60-80
Granite	75-200
Gneiss	Centuries

* Julien (1883).

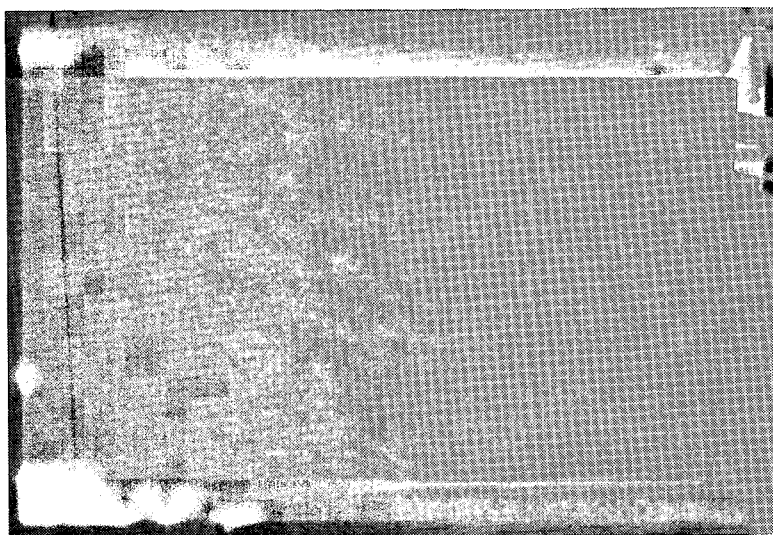


FIG. 1. Pockmarks on the U.S. Capitol as a result of the selective weathering of tremolite.

terms of these two variables, that could be used to determine whether it is safe to wash a given artifact (Fig. 3).

A more benign form of inherent vice concerns the esthetic problems that arise when a stone discolours after installation on a building. This is particularly a problem with stones containing iron hydroxides and oxyhydroxides, which may not be stable when exposed to the atmosphere. Also, many of these stones contain a certain amount of porewater. After the stone has been quarried and put into place, the evaporation of the porewater can cause significant changes in the mineralogy, leading to color changes. The sandstone used in the Smithsonian Castle in Washington, D.C., for example, was intended to be a lilac grey, but over time the color of the sandstone has deepened to a dark red (Witherington 1975). Another example is the white Pentelic marble used on the Parthenon, which turns to a golden color when exposed to the atmosphere, owing to trace quantities of Fe-bearing pigment deposited on the surface upon drying out of the stone (Winkler 1975, p. 78). A third example involves white Bethel granite from Maine. This is particularly susceptible to staining in the presence of water due to the rapid kaolinitization of the feldspars (Gale *et al.* 1985).

These instances of inherent vice can be explained in terms of clearly identifiable mineralogical characteristics. However, there are other situations where the causes are not so apparent. There is a great variation in durability among limestones and marbles that does not appear to be attributable to the

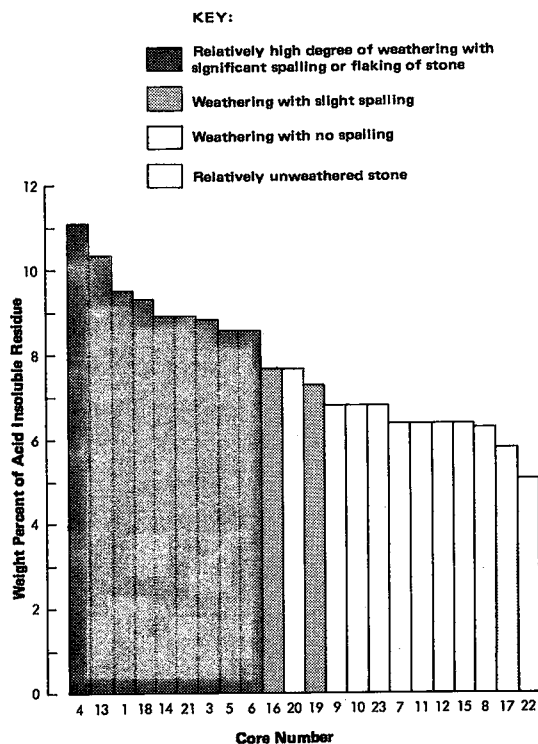


FIG. 2. Durability of Kansas City Courthouse limestone as a function of mineral composition (Grisafe 1982).

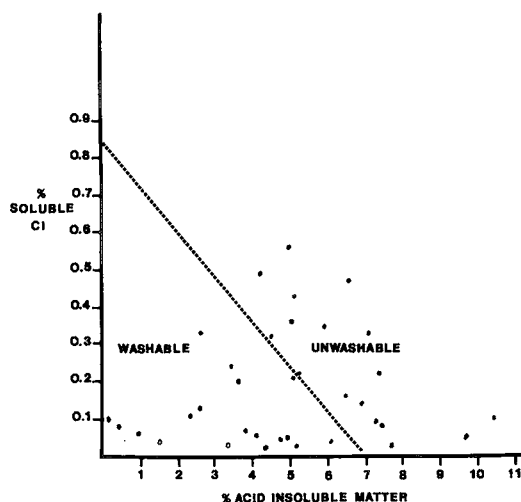


FIG. 3. Criteria for hazards of washing Egyptian limestone as a function of insoluble and chloride content (Bar-ton & Blackshaw 1976).

presence of prominent heterogeneous minerals such as silicates or salts. One school of thought holds that the differences are associated largely with physical characteristics related to the petrographic texture, such as pore-size distribution (Robertson 1982) or internal surface-area (Hudec 1977). Another school leans toward a mineralogical explanation, including degree of dolomitization (Caner & Seeley 1981, Pellerin 1976). Presumably, both the petrographic and mineralogical effects could be related aspects of a more fundamental phenomenon associated with diagenetic or metamorphic processes.

Finally, it should be noted that inherent vice is a relative concept, since a stone that is unsuitable for exterior use can still be utilized under shelter. Consequently, whether or not a material is said to suffer from inherent vice depends to a certain extent on how wisely it is used. Even alabaster can be used for architectural purposes if sheltered from rain, as in the case of the windows of Galla Placidia's tomb in Ravenna (Winkler 1975, p.45).

Inherent vice is also relative to the desired lifetime of the material in service. If the material falls significantly short of surviving for the specified lifetime, then it can be said to suffer from inherent vice. Some materials like galvanized fences may be expected to last for 20 years, whereas most structural materials are expected to last the lifetime of the building. The building's life is itself relative. For economic purposes such as amortizing construction costs, a building's life can be set at fifty years (AIA 1977). However, this may not reflect the real lifetime. In some cities like New York, many buildings have lasted for

less than 35 years before being replaced by larger ones. On the other hand, historic monuments are expected to last indefinitely. The longest finite time period that has been specified for the durability of building materials is 10,000 years. This has been proposed for markers at disposal sites for nuclear waste (Berry 1983).

Mankind is also inadvertently shortening the life-time of many buildings by changing the environment, so building materials once appropriate are no longer as durable. The effect of increasing levels of air pollution on stone deterioration has been well documented (Amoroso & Fassina 1983). Another example of the deleterious effect of human activities on stone durability concerns the Temple of Karnak in Egypt. After surviving for thousands of years, the temple is being threatened by deterioration caused by the recrystallization of soluble salts within the stone. This is associated with changes in the movement of groundwater that occurred after the construction of the Aswan Dam (Hartline 1980).

SURFACE LAYERS

A building material, upon exposure to the atmosphere, will commonly react with various environmental agents to produce a surface layer. This is especially true with metals, but may also occur with certain types of stones. The presence of this layer can modify the mechanisms and the rates at which degradation occurs. Furthermore, depending upon the specific system of materials and environment factors involved, the effect of the surface layer can be either detrimental or beneficial.

The simplest case is probably that of oxidation of metals. Upon exposure to the atmosphere, a bare surface will begin to react with oxygen. As more and more of the surface becomes covered with a layer of oxide, the rate of reaction slows down. Eventually, the surface becomes coated with a layer of oxides, which introduces a barrier to further reaction. The oxygen must diffuse through this layer in order to react with metal; the rate of reaction will tend over the long term to be proportional to the square root of time, rather than a linear function, which would be the usual case for the bare metal (Uhlig 1964). The slowing down of the rate of reaction in effect is the slowing down of the corrosion rate, and, under these conditions, the metal is said to be passivated (Pourbaix 1973). In fact, this is an oversimplification, and the actual mathematical forms of the corrosion rate are still not completely resolved (Evans 1968). Nevertheless, the concept remains useful in understanding the importance of the mineralogy of the surface layer in protecting against further deterioration.

If the surface layer is to be protective, it must form a continuous, tightly adherent layer. Since metal

oxides are usually brittle, and thus not able to resist tensile stresses, it is important for the surface layer to be in compression to avoid cracking. This led Pilling and Bedworth (Uhlig 1964) to propose a criterion of protection based on the ratio of the molar volume of the metal oxide in the surface layer (V_s) to the molar volume of the original metal (V_m). If the ratio is greater than one, the surface layer would be in compression rather than tension:

$$\frac{V_s}{nV_m} > 1 \quad (1)$$

where n is the number of metal atoms in the chemical formula of the surface layer. Therefore, the mineralogy of the surface layer, which determines the molar volume, is important in determining the metal's resistance to corrosion.

Values of the Pilling–Bedworth ratio for a number of metal oxides are presented in Table 2. It can be seen that the ratio is less than one for lithium, calcium and sodium. Consequently, these metals will all tend to oxidize completely upon exposure to the atmosphere, and thus are not usable for structural purposes. The metals aluminum, lead, zinc and tin have a ratio in the range between 1 and 1.3, and thus are suitable for construction. Copper has a fairly high ratio, and the ratio for iron exceeds 2. This amount of expansion can cause significant compressive stresses in the surface layer, causing it to spall off. In fact, these two metals tend to form thick layers known as scale, which do not adhere as well to the surfaces.

Although it was originally developed for oxidation in dry atmospheres, as in the case of mill scale formed on heated iron slabs, the Pilling–Bedworth ratio is useful as a conceptual tool to understand the behavior of a surface layer in other circumstances. For metals used in architecture, outdoor exposure usually means exposure to moisture. A wet metal surface can develop a variety of alteration products besides oxides. The most obvious would be the hydroxides, but it is possible also to form carbonates through reactions with atmospheric carbon dioxide (Feitknecht 1959). In coastal areas where marine salt is present in the atmosphere, metal chlorides are also

TABLE 2. VOLUME RATIO OF METAL TO METAL OXIDE*

METAL	OXIDE	RATIO
Lithium	Li ₂ O	0.58
Titanium	TiO	1.20
Aluminum	Al ₂ O ₃	1.28
Tin	SnO ₂	1.32
Lead	PbO ₂	1.37
Zinc	ZnO	1.55
Copper	Cu ₂ O	1.72
Iron	Fe ₂ O ₃	2.10

*Derived from CRC Handbook (1972).

TABLE 3. MOLAR VOLUME RATIOS, TYPICAL SURFACE-LAYERS ON METALS*

		MINERAL/METAL MOLAR VOLUME RATIO
Lead		
Cerussite	PbCO ₃	2.2
Hydrocerussite	2PbCO ₃ ·Pb(OH) ₂	2.3
Zinc		
Smithsonite	ZnCO ₃	3.0
Goslarite	ZnSO ₄ ·7H ₂ O	15.6
Copper		
Malachite	CuCO ₃ ·Cu(OH) ₂	3.8
Brochantite	CuSO ₄ ·3Cu(OH) ₂	4.0
Atacamite	CuCl ₂ ·3Cu(OH) ₂	1.9
Iron		
Goethite	FeOOH	3.0
Melanterite	FeSO ₄ ·7H ₂ O	10.0

*Derived from CRC Handbook (1972)

found. Finally, in areas with significant air pollution, sulfates formed by reaction with sulfur dioxide gas or sulfate particulates may be found on the surface.

The most common of these surface-layer minerals and their molar-volume ratio are listed in Table 3. The molar-volume values all easily satisfy the Pilling–Bedworth criterion. Many of the typical minerals in corrosion layers are not neutral salts, but rather the basic compounds that incorporate additional hydroxide molecules. Thus, on copper surfaces, brochantite CuSO₄·3Cu(OH)₂ is found rather than chalcantite CuSO₄·7H₂O.

This prevalence of basic compounds can be explained by two factors. One is the low concentrations of SO₂ and chlorides relative to oxygen in the

TABLE 4. SOLUBILITIES OF SIMPLE AND BASIC SALTS OF METAL-CORROSION PRODUCTS*

METAL	OXIDE	SIMPLE SALTS				BASIC SALTS		
		HYDROXIDE	CARBONATE	SULFATE	CHLORIDE	CARBONATE	SULFATE	CHLORIDE
Al	-	1.0§	-	26.7 10 ⁺⁴ §	70.0 10 ⁺⁴ §	-	-	-
Pb	64.0†	-	1.8†	26.0 10 ⁺⁴ †	70.0 10 ⁺⁴ †	1.3†	22.0†	79.0†
Zn	1.6†	2.6 10 ⁻³ †	10.0†	36.0 10 ⁺⁴ †	78.0 10 ⁺⁴ †	-	-	-
Cu	-	2.9 §	30.0§	18.0 10 ⁺⁴ §	1.5 10 ⁺⁴ §	59.0†	143.0†	169.0†
Fe	-	0.07§	67.0†	42.0 10 ⁺⁴ §	39.0 10 ⁺⁴ §	-	-	-
Sn	-	2.0§	-	16.0 10 ⁺⁴ §	73.0 10 ⁺⁴ §	-	-	-

* Earth-surface atmosphere and 25°C; values in mg/L.
Sources: † = Linke(1965), § = Stephen & Stephen (1963).



FIG. 4. Streaks of color on bronze statue due to differences in contact with rainwater. Also, stains on marble pedestal due to runoff of soluble copper salts. Corcoran Gallery of Art, Washington, D.C.

atmosphere. This results in a low ratio of these anions on the surface compared to the hydroxides. The other reason is that the solubilities of most of the neutral salts are much higher than those of their basic counterparts, as can be seen in Table 4. Consequently, in the presence of flowing water, the simpler minerals would be dissolved rapidly, whereas the basic compounds would tend to remain, forming a protective layer. The inability of zinc to form sparingly soluble basic sulfates may explain why its corrosion rate remains linear with time in polluted areas, whereas other metals show a more typical slowing down with time as the surface layer builds up (Haagenrud *et al.* 1983).

The effect of wetting can be seen most dramatically on copper or bronze objects that are partly sheltered from rain. The dry areas will retain their blackish brown character associated with the oxides cuprite and tenorite. However, the areas frequently washed by water will display a variety of bluish green colors characteristic of chloride or sulfate compounds (Fig. 4). In most urban situations, the copper patina will be predominantly sulfates, except near marine areas where chlorides may dominate. This

is a reflection of relative concentrations of chlorides *versus* sulfur species at the site. However, in the case of the Statue of Liberty, surrounded by the sea, the patina contains mostly brochantite with very little atacamite (Walker 1980). This indicates the relatively high prevailing levels of sulfur dioxide in the vicinity, as well as the fact that for thermodynamic reasons, the sulfate will displace the chloride anion (Evans 1968).

The prediction of which minerals will appear on a given metal surface under a particular set of environmental conditions is extremely complex. Generally, electrochemical processes on the surface must be taken into account. Since the exposure usually involves intermittent wetting by rain rather than continuous immersion in water, steady-state equilibrium conditions are not maintained, and chemical thermodynamics must be modified by kinetic aspects (Pourbaix 1973). Finally, the composition of the metal must be taken into account in the case of alloys.

Observant readers will have noticed that the ratios in Table 3 are usually much larger than unity. According to the discussion of scaling given above,

this suggests that the corrosion layers would continually spall off. This does occur in some cases; for example, if the basic carbonate layer on zinc becomes thick enough it will break off (Waite 1980).

However, the buildup of compressive stresses can be avoided in a number of ways. Often the corrosion product incorporates enough water to make it gel-like and, thus, more flexible. In other cases, several different corrosion-layers are stacked up, so that even though the total change in volume is large, the differential change going from one layer to the next is not drastic. For instance, the stable greenish blue patina found on outdoor copper or bronze consists of malachite. Table 3 indicates that the malachite/copper ratio is 3.8, which suggests that the layer would be under considerable compressive stress. However, the patina actually consists of two layers, with an inner layer of cuprite Cu_2O separating the malachite from the native copper (Walker 1980). The volume ratio for the pairs copper/cuprite and cuprite/malachite equals 1.7 and 2.3, respectively. Thus the effective compressive stresses are not as severe.

Another example of the importance of the stacking of corrosion layers is the performance of weathering steel. This, unlike ordinary carbon steels, forms rust layers that are stable, so that the rate of rusting slows down with time. This effect appears to be due to the presence of specific trace elements, notably copper, in concentrations around 0.3%. These elements affect the crystal structure of the rust products, which, in the case of the ordinary non-weathering steel, are composed mainly of alpha ferric oxyhydroxide, goethite and hematite. However, on weathering steel, a distinct inner layer develops, consisting of cubic phases, including magnetite and lepidocrocite FeOOH as well as cryptocrystalline ferrous hydroxide $\text{Fe}(\text{OH})_2$ (Keiser *et al.* 1982). This inner layer seems to be more compact and less permeable to diffusion of oxygen and moisture. The electrical resistance of the cubic phase is also higher, thereby reducing the rate of electrochemical reaction (Suzuki *et al.* 1980).

Regarding the role of copper in this phenomenon, Inouye (1968) found that small amounts of it stabilized the ferrous hydroxide crystallites. A definite peak in the size of the crystallites ($3.5 \mu\text{m}$) was reached at a copper content of 2%. This is consistent with field experience that weathering steel initially rusts rapidly, but in the process, the copper remains behind, becoming enriched in the surface layer. When a copper content of about 2% is reached in the surface layer, the rust layers become stabilized. The supply of ferrous iron may account for the formation of magnetite, which gives the resulting layer of rust its characteristic dark brown color, in contrast to the normal reddish color of rust due to hematite.

SURFACE LAYERS ON POROUS MATERIALS

One important difference between metallic and nonmetallic surfaces is that the latter generally have a significant pore-structure; thus the material is no longer two-dimensional, and quite different results occur. The most typical problem is the formation of crusts of gypsum on carbonate stone. This is due to the deposition of sulfur compounds from the atmosphere in various forms *via* acid rain or sulfur dioxide gas (Amoroso & Fassina 1983). As Table 5 indicates, there is a significant increase in molar volume in going from calcite to gypsum. Over time, this means that the gypsum layer becomes so thick that it spalls off, exposing fresh calcite to the surface for further reaction. Moreover, gypsum will also crystallize within the pore spaces. As the pores become completely filled, the gypsum will begin to exert stresses on the pore walls, eventually leading to brittle failure of the calcite. Also, the gypsum tends to entrap dust particles, which give it a characteristic black color (Camuffo *et al.* 1983). These features are shown in Figure 5.

As Table 5 also shows, the solubility of gypsum exceeds that of calcite by a factor of forty. This means that on those areas of the stone surface that are exposed to frequent washing by rain, the gypsum and dust will generally be entirely removed, leaving behind an apparently clean white calcite surface. In the process, however, the erosion rate of the stone has been increased dramatically over that for natural rainwater, and fresh calcite has also been exposed for further reaction.

SOLUBLE SALTS

The previous section indicated that the crystallization of gypsum within the porous material can give rise to severe expansive stresses. This problem is not limited solely to gypsum created by reaction with air pollution. There are a variety of soluble salts that can be transported into the material by water movement, there to crystallize, expand and cause destruction. Vitruvius pointed this out as a major factor in stone deterioration (Morgan 1914).

One of the salts most commonly found in such cases is sodium chloride (halite), which is ubiquitous in marine coastal areas. In Venice, for example, this

TABLE 5. PHYSICAL PROPERTIES OF PORTLANDITE, CALCITE AND GYPSUM AT 25°C

NAME	FORMULA	MOL. VOLUME (cm^3/mol)	SOLUBILITY (mg/L)	SOURCE
Portlandite	$\text{Ca}(\text{OH})_2$	31.6	1,650	a
Calcite	CaCO_3	37.7	50	b
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	60.0	2,080	c

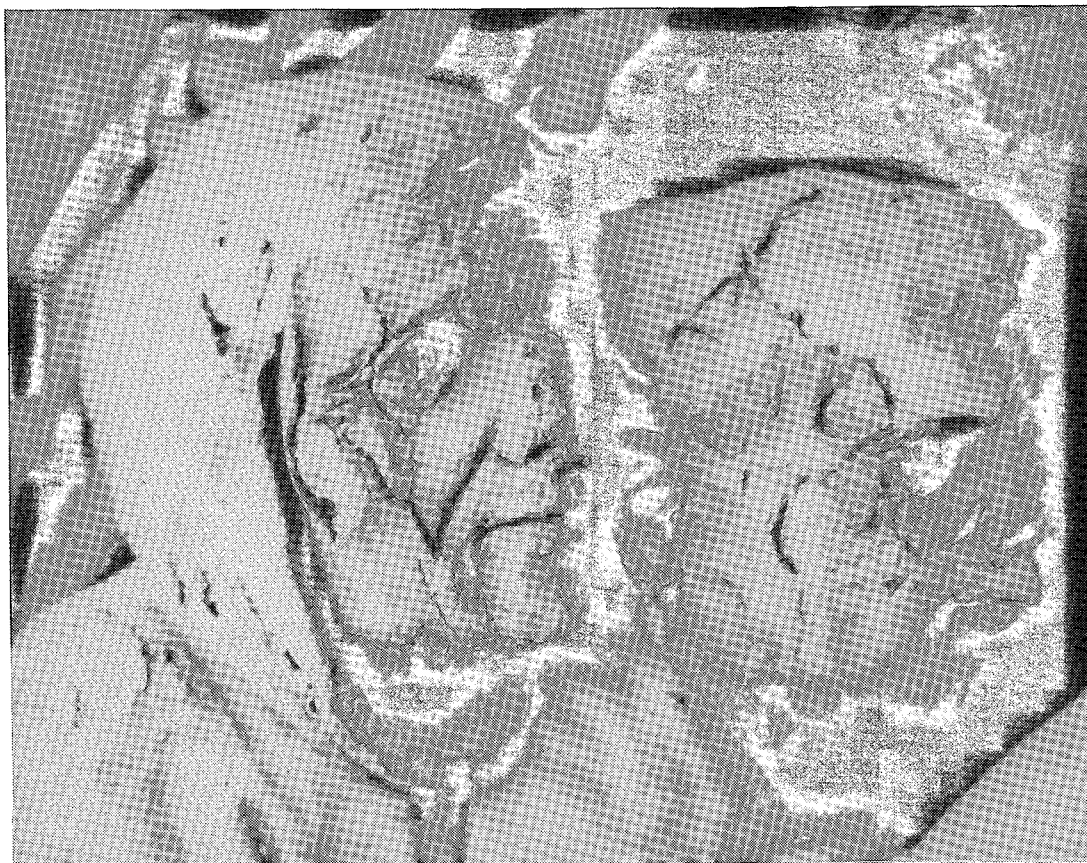


FIG. 5. Deterioration of marble figures due to gypsum crusts. Also, spalling of stone due to use of consolidants. Church of S. Giovanni e S. Paolo, Venice, Italy (courtesy G. Helms).

creates serious deterioration of buildings. The damage does not occur simply at the waterline. Owing to capillary forces in the porous building-material, the water can rise as high as several metres. Although rising brackish groundwater is a major source of halite deposited in porous materials, there are other ways in which the salt can appear. One is the use of salt-contaminated building materials. For instance, the lime used for mortar to construct the Taj Mahal apparently contained significant amounts of salt. This now appears to be a graver threat to the building than prevailing air pollution (Lal 1984). In some cases, the building itself may have been used to store salt, with the result that salt deposits can be found wherever the merchandise came in contact with the wall. The *Magazina di Sala* in Venice is a clear example of this kind of problem.

Away from marine areas, other types of soluble salts become important. Arnold (1984) has identified, among others, Epsom salts, sylvite and sodium

nitrate and potassium nitrate as causing damage in Switzerland. These appear to originate from groundwater containing Mg^{2+} , Ca^{2+} , Na^+ and K^+ in solution with CO_3^{2-} , Cl^- and NO_3^- . The nitrate and, to some extent, the carbonate ions arise from biological activity. As the groundwater rises through walls it can come into contact with gypsum, either in the form of wall plaster or as the result of the reaction of air pollution with carbonate materials. Consequently, the more exotic sulfate species can form. Beyond all these, one of the most prevalent sources of damaging salts in North America is antarcticite $CaCl_2 \cdot 6H_2O$ used for de-icing roads. The greatest damage with all these salts occurs when they periodically dissolve and then recrystallize. The recurring cycle creates a wedging action that can be very destructive.

In addition to dissolution-recrystallization cycles, certain salts can also undergo significant changes in volume by changing their state of hydration.

TABLE 6. HYDRATION RELATIVE HUMIDITY OF TYPICAL SOLUBLE SALTS, 25°C*

TRANSITION	RH
$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	48%
$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	79%
$\text{NaSO}_4 - \text{NaSO}_4 \cdot 10\text{H}_2\text{O}$	72%

*Puehringer et al. (1985)

TABLE 7. HYGROSCOPIC POINTS OF SOLUBLE SALTS (25°C)*

SALT	RH, %	ZONE
K_2SO_4	97.0	A
KNO_3	92.5	A
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	92.0 (18.5°C)	A
$\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$	87.0	A
KCl	84.3	B
NaSO_4	81.0	B
NaCl	75.3	B
NaNO_3	73.9	B
NH_4NO_3	61.8	B
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	52.9	C
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	50.0	C
$\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	42.8	C
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	33.0	C
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	29.0	C

A salt rarely deliquescent, B salt fluctuates from solid to deliquescent, C salt usually deliquescent
 * Arnold (1982).

Table 6 lists several that may be important under surface conditions. The sodium carbonates are notable in this respect as well as the mirabilite-thenardite pair. Arnold & Kueng (1985) reported seeing natron and mirabilite dehydrate and rehydrate on a daily cycle on a building in Switzerland.

A third aspect of the soluble salts is their hygroscopicity. As Table 7 shows, many of the important soluble salts have hygroscopic points at relative humidities considerably below 100%. Thus they can become deliquescent when their critical relative humidity is exceeded; when the relative humidity drops below the critical point, they will recrystallize. Therefore, this makes it possible to have many more dissolution-recrystallization cycles than would be predicted simply from the number of rain events per year.

Arnold (1982) has pointed out an interesting corollary. The prevailing relative humidity is a predictable function of the local climate. In many temperate climates, the relative humidity rarely drops below 55% and also rarely exceeds 85%. Therefore, salts such as antarcticite practically never dry out. On the other hand, salts with a high critical relative humidity rarely become deliquescent. However, those with intermediate values can cycle between deliquescence and crystallinity in response to day-to-day variations in the relative humidity.

The results can be seen in the form of distinct zones on walls. The least soluble salts will precipitate first from rising groundwater and thus will not rise very high. Consequently, the lower parts of the wall will show crystals of such minerals as magnesite and gypsum. The most soluble and hygroscopic

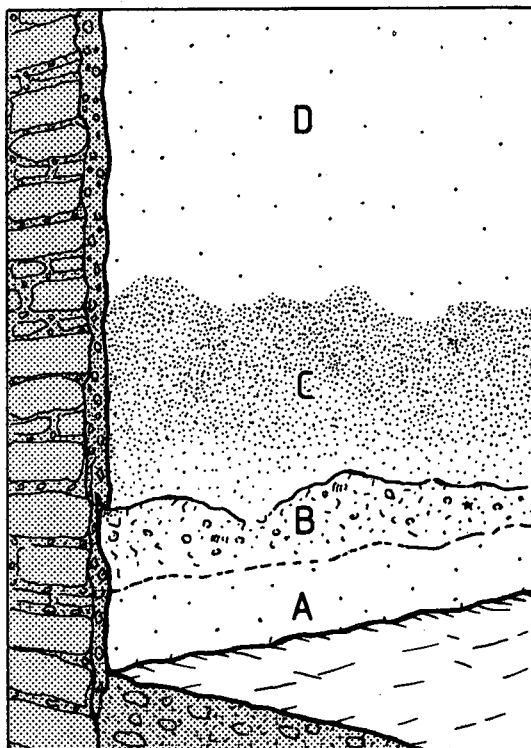


FIG. 6. Arnold's zones of salt deposition as a function of hygroscopicity. A. Salts are seldom deliquescent, relatively little damage. B. Deliquescence varies, region of greatest damage. C. Salts are usually deliquescent, darker colored, moderate damage. D. No soluble salts present, undamaged. See Table 7 for data on individual salts (Arnold 1982).

salts, such as antarcticite or nitrocalcite, will be transported to the higher zone of the wall, which may appear darker owing to the continuous presence of moisture. In between will be the zone of greatest damage, where salts of intermediate hygroscopicity are found. These zones are illustrated in Figure 6.

Thus a critical part of diagnosing the condition of a building is taking surface samples and analyzing the saline minerals present. Arnold (1984) has shown that this can be done readily using the traditional methods of optical mineralogy and microchemistry.

MATERIAL INTERACTIONS

An evaluation of the damage to buildings must also take into account the possible interaction between the materials. Galvanic corrosion between two dissimilar metals in contact in the presence of an aqueous solution is the classic example. The corrosion due to the galvanic cell created between the copper skin and the wrought iron armature of the

Statue of Liberty is the major reason for the restoration work now in progress (Neilsen 1984).

Galvanic corrosion does not occur between non-metallic materials, but they can still interact in other ways. As noted above, many of the alteration products are soluble and can be washed from one part of the building to another, causing further problems. For example, gypsum is produced by the reaction between calcite and sulfur dioxide in the atmosphere. The gypsum can then be transported from the limestone or marble to another material, where it can recrystallize. This has been observed in the case of a limestone wall on top of a sandstone course, where the latter is deteriorating from air-pollution attack on the former (Melville & Gordon 1979).

Another problem often encountered is the use of iron bars as clamps or reinforcements in masonry and concrete. As shown in Table 3, creation of rust leads to a major increase in volume. When this occurs within the wall, the result can be expansive forces that can break off the masonry. A well-known example of this effect involves the buildings on the Acropolis in Athens. As originally built in the 4th century B.C., the marble blocks were fastened with iron clamps, but the Greek architects were aware of the problem of rusting. Consequently, the bars were all wrapped with lead, which served to exclude air. However, during the restorations at the start of this century, the stones were put back together with bare iron rods. These have rusted and caused cracking of the stone. As a result, it has been necessary to dis-

mantle the buildings and remove the iron (Skoulikides 1976). The buildings are being reconstructed using titanium fittings (Angelides 1976).

A related problem occurs in reinforced concrete where the iron reinforcements eventually begin to rust and expand (Gonzalez *et al.* 1983). In this case the situation is more complicated because the mineralogy of the cement paste itself changes over time. After it has initially hardened, the cement still contains some residual calcium hydroxide. However, over time this hydroxide reacts with CO_2 to form calcium carbonate, resulting in a volume decrease (Neville 1981). Thus the alteration product does not move outward to form a crust. Instead, a carbonation front is produced within the material that moves progressively inward from the surface.

When the carbonation front reaches the reinforcement, rusting begins and the concrete is broken open, as shown in Figure 7. The rusting is often attributed to the carbonation process itself, which reduces the pH in the vicinity of the rod from about 13 to 8. However, Gonzalez *et al.* (1983) have shown that even when the carbonation front is at the reinforcement, significant corrosion does not take place unless the relative humidity is above 50% or chlorides are present. This suggests that the main role played by carbonation is to open the pores in the concrete, allowing the usual agents of rusting, oxygen and moisture to reach the iron. Consequently, by measuring the progress of the carbonation front after several years, it is possible to estimate the remaining lifetime of the concrete (Sentler 1984).

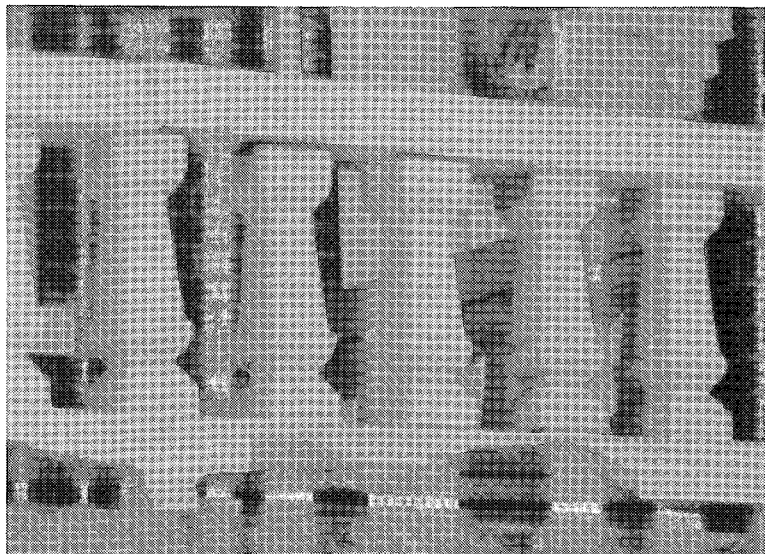


FIG. 7. Bursting of concrete balustrade rail due to rusting of iron reinforcements. Washington, D.C.

A third type of material interaction can be observed where a bronze statue is placed on a marble pedestal. The result is frequently a greenish blue staining of the marble due to soluble copper compounds being dissolved from the statue (Fig. 4). As the runoff washes over the marble, the copper is deposited on the stone. Although this effect has been known and studied for many years (Kessler & Anderson 1953), very little has been published on the mineral species involved. In some cases, marble deterioration has been observed, but in other cases, it has not. Consequently, it is not possible to say

whether the deposition of copper causes the deterioration or is merely a symptom of an underlying effect associated with the flow of the water over the stone.

Another type of staining problem occurs with weathering steel. As noted above, its durability derives from the stability of the rust layer, which develops as copper is concentrated in the surface layer. During the initial period, while the layer is being built up, there is a significant amount of iron that washes off and can stain concrete foundations (Fig. 8). These wash stains are typical of weathering



FIG. 8. Staining of concrete by runoff from weathering steel. College Park, Maryland.

steel construction and, in some cases, may be objectionable on esthetic grounds (Evans 1968).

BIOLOGICAL ATTACK

Building materials are subjected to attack from a variety of organisms ranging from algae and bacteria to birds and rodents. Generally, the cause of the attack can be identified by visual inspection or appropriate biological analytical methods. Mineralogy can be applied in a few instances, however. For example, unknown surface deposits can be classified as to their origin, either as inorganic or organic, *e.g.*, pigeon droppings, by the presence of phosphates or nitrates. If present in significant quantities, these anions are unlikely to have been derived from air pollution. Instead, an organic source would be probable. In some cases, a mineral form of uric acid, uric acid, can also be found (Del Monte & Sabbioni 1986).

Many forms of plant life attack stone surfaces by secreting oxalic acids in order to extract nutrients. In a particular case on the island of Torcello near Venice, calcium oxalate crystals were found on limestone columns in the form of whewellite and weddellite. These minerals are found in a variety of plant and animal tissues, but rarely in an inorganic setting. In the case of Torcello, it was confirmed that the minerals are due to the activity of specific bacteria (Del Monte & Sabbioni 1983).

TREATMENTS

Given all the problems discussed in this article, it is not surprising that man has attempted to find ways to mitigate damage to buildings. This most commonly takes the form of a protective coating that is intended to isolate the material from the aggressive environment. This approach has worked reasonably for metal surfaces and for wood, but has not been very successful for stone (Price 1982).

This has not been for lack of trying. Ever since stone deterioration was observed on the Houses of Parliament in the 1850s, treatments have been proposed, sometimes with a very questionable scientific basis. The proposals have ranged from esthetically impossible approaches such as applying tar, to the mysterious method put forward by Szerelmey, who claimed the ancient Egyptians used it on the Pyramids (Lewin 1966). In most cases, the proposers were well meaning, but ignorant about the long-term effects, which sometimes could be more detrimental than the problem they were meant to cure.

Generally, the treatments involved applying organic compounds to the stone, either to serve as a water repellent or as a binder to consolidate crumbling stone. However, there have been some methods that imitated petrological processes. The oldest is lime washing, which has been used on limestone since

the Middle Ages. This consists simply of washing the stone periodically with water that is saturated with calcium carbonate (Ashurst 1984). As the solution dries, some calcite is left behind in the pores and cracks. However, the deposited calcite can be readily washed out again by rainwater. Consequently, rather than being a permanent treatment, the lime wash serves in effect as a sacrificial coating (Price & Ross 1984). As long as more calcite is being deposited on the stone by this method than is being washed off by rainwater, the original stone should be to a large extent protected. This is really only feasible on unpolished surfaces where changes in the finish due to the limewash layer are not noticeable.

Church, in 1862, was one of the first to try the barium hydroxide approach (Lewin 1966). This was based on the concept that if the weathering of calcite is due to its dissolution, perhaps it could be slowed by replacing the surface with a more insoluble carbonate such as witherite. This would be done by applying a barium hydroxide solution to the stone, which would react with the calcium carbonate to form insoluble barium carbonate. This approach has been demonstrated in the laboratory; witherite has been found to define a solid solution with calcite, binding the grains together (Lewin & Baer 1974). However, it has not worked very well in the field. The chief drawback lies in the rapid rate of the reaction, which occurs very near the surface. Consequently, the barium hydroxide solution does not penetrate very far into the stone. The result is a hard surface-layer overlying a soft and friable interior, possessing different coefficients of thermal expansion. Over a certain number of thermal cycles, the harder surface layer will tend to spall off (Hosek & Panek 1985).

A large number of researchers have attempted to get around this difficulty by modifying the solution to slow down the reaction and thus increase the depth of penetration. The best known is the barium hydroxide-urea method (Lewin & Baer 1974). Even with this refinement there are problems if sulfates are present, which is usually the case where stone is deteriorating owing to air pollution. The resulting reaction-product will tend to be barium sulfate rather than barium carbonate, which does not act to bind the grains together (Padfield 1984).

An applied mineralogy approach has also been attempted for silicate rocks, particularly sandstones. This uses various compounds built around the SiO_4 tetrahedron, linked by any of a number of organic groups to form polymers. After injection into the stone, the organic groups volatilize, leaving behind the SiO_4 tetrahedra, which then bind to the available silicate surfaces to consolidate the stone. This approach also dates back to the 1860s (Lewin 1966). One of the simplest formulations uses ethyl groups to link the tetrahedra, giving the formula:

$\text{Si}(\text{OC}_2\text{H}_5)_4$. Upon hydrolysis, this yields hydrous silica $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ as the cement and ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, which evaporates (Amoroso & Fassina 1983).

However, as with the barium hydroxide approach for carbonate stone, there is a trade-off between penetration and volatility. A compound that volatilizes easily, and thus does not leave behind an organic residue, is also one that tends to react rapidly, limiting its penetration. A large number of organic formulations have been tried. The most promising appear to be the alkylsilanes. However, the cost of the material as well as the special precautions required because of the potential hazards to the health of workers limit their use to the more valuable sandstone carvings and sculptures. The possibility of applying them to large wall-areas thus seems remote (Lewin & Wheeler 1985). In view of the ingenious application of mineralogy in this method, it is discouraging to learn that some manufacturers of these compounds are now recommending their use on limestones, which cannot be justified from mineralogical principles.

Finally, mineralogical analysis has also been used to identify past treatments on particular monuments. For instance, Zehnder & Arnold (1984) discovered that efflorescences of soluble salt that cause damage to the sandstone of the Erlacherhof in Berne, Switzerland, are composed of calcium and magnesium formates. These compounds were presumably created in the process of cleaning the building with a formic acid solution.

In another case, peculiar oxalate and silicate layers were discovered on the surface of the marble of Trajan's Column in Rome (Guidobaldi *et al.* 1982). These were ultimately recognized as the residue from restoration work around the turn of the century. The oxalates are apparently due to oxalic acid used in cleaning and polishing the marble. The silicates may be traces of water glass remaining from a protective coating applied after the stone was cleaned.

These findings are a reminder of the fact that many of the most prominent monuments may have undergone some type of treatment in the past. The percentage of monuments that have been treated in some way remains unknown because no centralized databank has been established. In any event, this type of activity was often regarded largely as maintenance work, and detailed records were not kept. What makes the situation worse is that in many cases, the treatments were experimental. That is, the inventor of the treatment had not tested it extensively before applying it to a major monument. The resulting trial-and-error process of treatment testing has unfortunately revealed many failures, to the detriment of the monuments used as test beds. Thus some of the deterioration now being attributed to other causes may in fact be due to some undocumented treatment

applied some time in the last 150 years. As a result, the U.S. National Academy of Sciences Committee on the Conservation of Historic Stone Buildings and Monuments has recommended against the application of experimental treatments to registered historic landmarks. It has also recommended the creation of a census of treated monuments (Baer 1982).

In situations where it is not possible to conserve the original material, particularly where inherent vice is involved, it may be necessary to substitute some other material. An example of the drastic measures that may be taken is Cologne Cathedral, where an entire section of the original sandstone was replaced by basalt. Another example is the Renwick Gallery in Washington D.C., where artificial stone is being used to replace deteriorated sandstone (Stevens & Lewin 1983).

CONCLUSION

Mineralogical methods are applied extensively in the field of architectural conservation to diagnose causes of damage to buildings and other structures. Optical and electron microscopy are used as well as X-ray diffraction. Some of the ways in which mineralogy is applied include characterization of the original material for its suitability for a particular building. Alteration layers can also be studied to determine whether they protect the building or cause damage. Agents of deterioration such as air pollution or soluble salts can be identified. The efficacy of protective treatments can also be investigated.

There are certain aspects of the field that distinguish it from the more conventional sectors of geology. One is that obtaining samples can be extremely difficult, since most curators are extremely reluctant to permit even the most minute disruption of the surface of such monuments. Another is that when samples are obtained, the phases of most interest are often thin surface-layers that may be amorphous or cryptocrystalline, making mineralogical analysis difficult. Also, the practitioner in this field, in addition to knowing mineralogy, must also have some familiarity with the building trades, architectural history and art conservation. Finally, as can be seen from the list of references, research in this field is generally not published in mainstream geological or mineralogical journals. Most of the work has been published in journals for the architect or the art conservator, or in the proceedings of specialized conferences on stone. Recognition of this field as a branch of applied mineralogy would have the benefit of bringing it to the attention of a wider audience of geologists and mineralogists.

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