

INTERNATIONAL CENTRE FOR THE STUDY OF THE
PRESERVATION AND THE RESTORATION OF CULTURAL PROPERTY

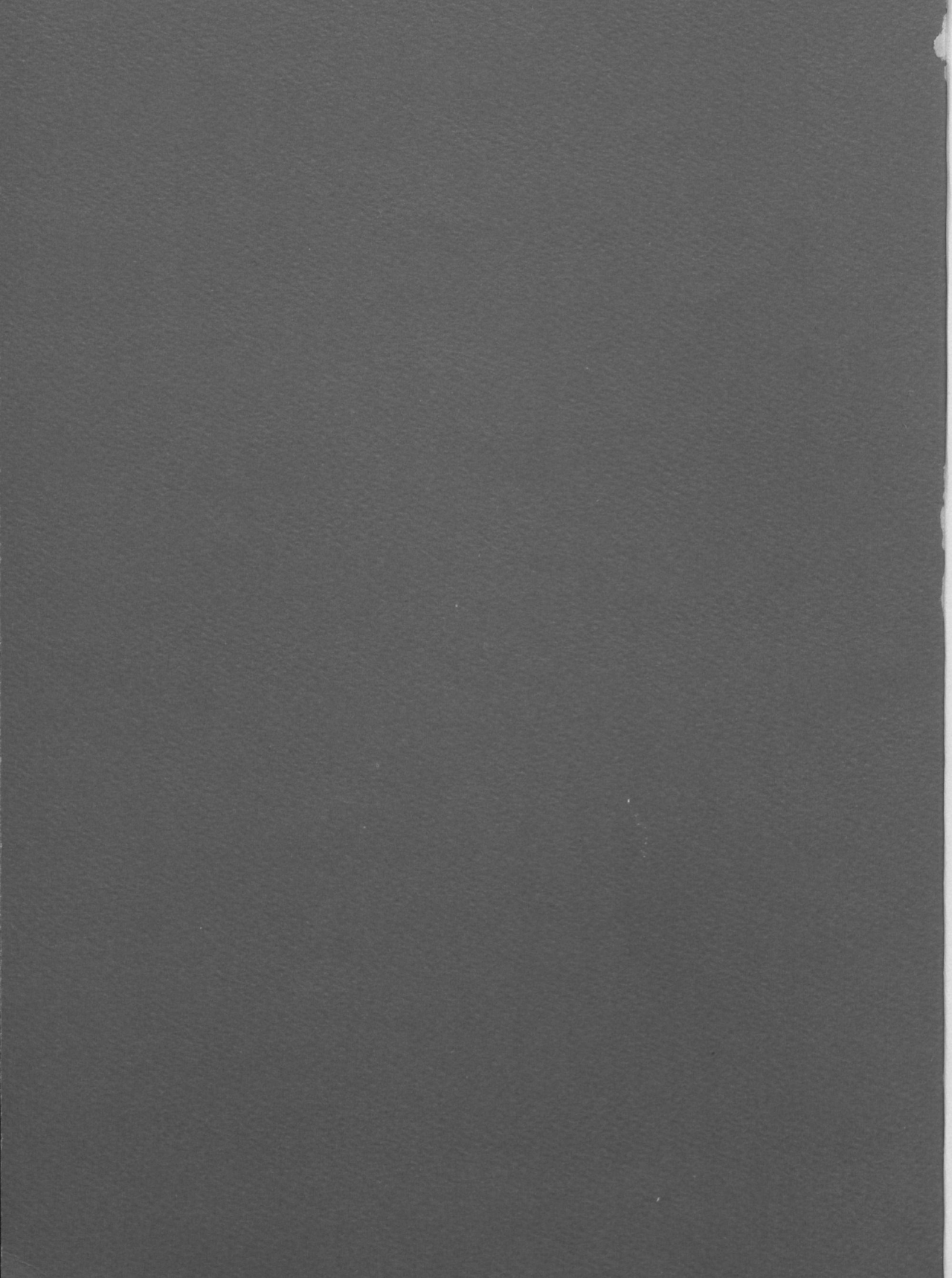
The Deterioration and Conservation of Porous Building Materials in Monuments

A Review of the Literature

T. Stambolov

J. R. J. van Asperen de Boer





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1. INTRODUCTION

This literature review is a survey of deterioration phenomena and conservation methods in relation to ancient monuments. Although only a small percentage of the technical literature used is directly concerned with monuments, much information contained in such publications may be applied to monument preservation directly or with modifications. A selection from the vast literature on building research is necessary, because the major interest in that field is modern materials, such as concrete, which still hold little interest in connection with the preservation of monuments.

Progress in building research may be followed in the Building Science Abstracts published by the Building Research Station (50). Technical aspects of monuments preservation are abstracted in IIC-Abstracts (133). Periodicals reporting on the restoration of monuments in various countries (1) publish little which may be concerned as technical information in the restricted sense of this review, but are mainly concerned with historical and architectural problems. General books on the restoration of monuments have also been published (e.g. 20, 180). General aesthetical questions in relation to the restoration of monuments have occasionally been discussed in the literature (39, 145, 241). Problems related to civil engineering have not been treated in this review. The reader is referred to such general publications as Johnson (138) for repair and strengthening of structures, and Kollbrunner (169) in relation to foundations and consolidation of buildings. Some applications in monument preservation have been reported in the literature (6, 106, 332, 333).

Wood and other organic materials have been excluded from the present survey, and for preservation of building timbers the reader is referred to the literature (63, 125, 184). Although some Eastern European literature has been mentioned the authors feel that contributions and problems from Asia, Africa and South-America have been poorly covered.

It should be emphasized that this survey as a literature review is non-critical in the sense that methods and recipes given have not been tested by the authors. In no respect the various procedures for treatment are to be considered as recommendations by the authors.

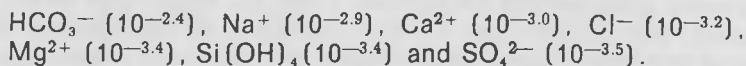
Photographs, tables or other illustrations have not been included. The reader is referred to the original literature for such additional material. This book is the result of a combination of two preliminary reviews presented to the ICOM Committee for Museum Laboratories at its meeting in Brussels September 1967 and to the ICOM Committee for Conservation at its meeting in Amsterdam 1969. These reports however have not been published in the open literature and have therefore remained inaccessible to the general public.

2. WEATHERING BY MOISTURE AND SALTS

2.1 General

Building stones, bricks, mortars and plasters are porous materials permeable by water and water vapour to a degree depending on their capillary structure. Water vapour, which is almost always present in the air, penetrates in a complex manner (92, 288) into the pores and a specific quantity is held in the porous material at equilibrium with the relative humidity of the air. A sufficient decrease in temperature or an increase in water vapour concentration may condense the water vapour. Moisture in building materials is the subject of section 3.

Owing to respiration of organisms, water percolating in the ground contains a few hundred times more carbon dioxide than moist air and therefore reacts as a dilute solution of carbonic acid (285). A consequence of this is the gradual dissolution of the following minerals: Na-feldspar, Ca-feldspar, Ca-montmorillonite, kaolinite and calcite. With calcite in particular the dissolution is carried out rapidly until an equilibrium between calcium carbonate, carbonic acid and calcium bicarbonate is reached. Any further dissolution of calcite is then determined by more carbon dioxide entering this equilibrium system (14). The other minerals, however, undergo incongruent dissolution, that is, their dissolution is accompanied by a phase change. The constituents decompose after being converted to carbonate, and through hydrolysis, form less soluble hydroxides. Stamm and Leckie (285) reported the following major constituents and their median molar concentration in terrestrial waters:



Rainwater also reacts acid on account of the air-polluting gases dissolved in it. In the air of large towns, the concentration of sulphur dioxide varies between 0.1 and 10 mg/m³ while the content of carbon dioxide does not exceed 10 g/m³ (143). A considerable amount of sulphur dioxide is oxidized by sunlight (143) or by pollutants as vanadium pentoxide (116) or iron (III) oxide (235) to sulphur trioxide, so that the sulphuric acid resulting from its dissolution may greatly increase the acidity of rain water.

Water in building materials is transported through the capillaries. In the course of this movement, soluble salts are extracted from the building materials and then subjected to diffusion, hydrolysis or precipitation. In the presence of a thermal gradient these dissolved salt ions migrate towards the warmer parts while the water moves towards the cooler parts (298). Some of the dissolved salts may then hydrolyze or react with other dissolved compounds and thus give rise to insoluble, voluminous deposits (147).

Evaporation of water from porous materials takes place at the surface and depends on the moisture supply from the interior (92, 288). When water enriched in soluble salts flows towards the surface, evaporation increases the salt concentration. Depending on the solubility of the salts

and the rate of water evaporation, precipitation and crystallization are observed at different points in the pores (298). This occurs at the surface when the water is regularly supplied to the surface (efflorescence) and below the surface as the liquid front retreats inwards, which happens when the larger surface pores are emptied (subflorescence) (112, 147, 165, 166, 197, 198, 298, 315). Both kinds of salt deposition can exist next to each other and are often interconnected (165). The origin of precipitated salts may be in the building material itself (73, 198). Kaiser (144), and later Weber (317), explained the high concentration of sulphur ions in sedimentary rocks (e.g. sandstone, limestone, clay) and metamorphic rocks (e.g. quartzite, marble, slates) by the slow disintegration of pyrite (FeS_2) and marcasite, present in those rocks, into iron (III) hydroxide and sulphuric acid. Atmospheric pollution, however is the most important source of soluble salts (40, 57, 144, 256, 257).

Grün (116) stated that lead tetraethyl, an anti-knock additive for motor fuels, tar, bitumen, carbon dioxide, sulphur dioxide and sulphur trioxide were the major air-pollutants that penetrate into building materials. However, common salt, cement and humus must also be added to this list (218).

2.2 Crust formation

The movement of water in porous materials tends to impoverish their cementing media. Sedimentary stones, mortars and plasters lose some of their adhesives, which, being dissolved, are transported to the surface. During evaporation of the water they are precipitated in the order: calcium carbonate, magnesium carbonate, calcium sulphate and various chlorides. Accordingly, close to the surface the pores are filled gradually at the expense of internal weakening so that the crusts containing calcareous matter, gypsum, chlorides, etc. that are developed in this manner are only the top-layer of a corrosion structure subdivided into the following zones from the surface inwards:

1. crust, 2. adhesive-impoverished stratum which may consist of several substrata, and 3. sound core of the material (16, 166, 244, 249, 265, 277, 297). If the salts, responsible for the crust, are poorly soluble, the material acquires a protective coating (stone patina). This is particularly the case with crusts that consist of hydroxides of iron, aluminium and magnesium, or of phosphates (166). On the other hand, gypsum, chlorides, nitrates (29, 82, 112, 117, 123), and salts of organic acids (198, 305) deposited at or under the evaporation front are the cause of severe deterioration (71). Chlorides are very hygroscopic and during condensation of water from the surrounding air are the first salts to be redissolved. Once in solution, they are very active in three respects: they are extremely movable and thus penetrate and break many crystalline structures; they peptize, i.e. suspend in water, large conglomerates of molecules; and finally, they augment the non-stoichiometry of the crystals. These properties of the chlorides explain the harmful leaching out of the cementing media observed in stones containing these salts. Hence such

building materials tend to pulverize. Similarly harmful are the nitrates and the salts of organic acids.

Quite different is the action of soluble sulphates on building materials (222).

These salts (Na_2SO_4 , MgSO_4 , CaSO_4) are precipitated in the pores from their oversaturated solutions as hydrates ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and as the evaporation of water proceeds, the deposit of these hydrates dries out. The anhydrous salts formed thus are micro-crystalline aggregates and owing to their fine porous structure, they promote the flow of more solutions from the interior of the pore to the surface (212, 215), which may lead to the gradual filling of the porous space behind the evaporation zone. Increase in relative humidity of the air (during cooling, mist, fog or rain) will hydrate the dried-out anhydrous salt which will lead to volume expansion and therefore to pressure on the walls of the pores (pressure of hydration) (212). The formation of anhydrous and hydrated salts, as well as the conversion from one form to the other, depend on their vapour pressure and temperature. Accordingly, a hydrated salt loses its water if its vapour pressure is higher than the partial water vapour pressure in the air. On the contrary, a partial water vapour pressure in the air, prevailing over the vapour pressure of an anhydrous salt will hydrate it. In the case of a sodium sulphate solution, for instance, at temperatures below 32.4°C sodium sulphate precipitates as the hydrated compound $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, but at temperatures above 32.4°C it is converted to the anhydrous Na_2SO_4 . Increase in relative humidity will again convert it to the hydrate, but whether this conversion will be complete or partial is determined by the degree of difference between partial water-vapour pressure and vapour pressure of the salt in question at a defined temperature. Hence the amount of damage resulting from the rhythmic contraction and pressure on the walls of the pores is not determined by the maximum volume increase a particular salt is capable of, but the pressure of hydration which may develop in given circumstances. In other words, not the total pressure of hydration but the one proportional to the ratio of the vapour pressure of the hydrate to that of pure water at a fixed temperature is of significance to the deterioration of the pores through volume expansion of salts (212). When the pressure of hydration surpasses the resistance of the walls of the pores, the latter are broken up, and as a consequence more space for precipitation of salts becomes available (242). Materials thus altered are very permeable to air and with it more vulnerable to volume expansion.

In the parallel direction (with respect to the pore-wall) such an increase in volume on the surface can be consumed by the atmosphere, but in the direction perpendicular to the wall it can not. The surface must then corrugate and will most probably appear as a dirty, darkened, crumpled crust (265). If chlorides are also present (they pulverize a corroding surface due to activities already mentioned) the exfoliation becomes quite intensive because the scaling off is assisted by the ability of these salts to destroy crystalline structures. Corrosion crusts may

display various colours (199, 270), but in practice such discolourations are dominated by the greyish-black colour of the soot.

Very diluted solutions of soluble sulphates, e.g. sodium and magnesium sulphates, are capable of producing grave deterioration. According to Butterworth (55), this is due to the fact that most pores have elliptical cross-sections. Evaporation of solution from a capillary glass tube (circular cross-section) leads to regular withdrawal of the meniscus in the interior of the capillary and the concentration of the solution created under the meniscus is removed by diffusion inwards. In the case of a pore of elliptical cross-section (or any irregular cross-section in which an elliptical curvature is included) the meniscus is not displaced inwards at the locations where the major axis ends and the loss of solution through evaporation there is compensated by lateral supply. Local oversaturation is the result and this produces efflorescence at points where the pore is narrow, and then hydration expansion leads to deterioration, even though the pore is not filled with salt. Solutions containing more than 0.1% of sulphate are considered dangerous for porous materials (56, 85).

2.3 Weathering of various building materials

The main agents of weathering have been discussed at length by Winkler (328). Carbon dioxide (from disintegration of organic materials, photo-synthesis and from industrial sources), sulphur dioxide, sulphur trioxide, chlorides, nitrates, smog, rain-water, groundwater, plants and animals etc., influence the disintegration of stone (19) in buildings and monuments (87) in a number of ways. Among these, the sulphur compounds and especially the sulphates have been considered as the most corrosive (282).

2.3.1 *Sedimentary rocks*

The sedimentary rocks are severely attacked by water because they are porous enough to allow frequent movement of salt solutions (148, 196). In various sorts of limestone, crusts consisting of a number of lamellae occur. The crust is at first soft and porous, grey, white or yellow in colour but after some time it becomes hard (cementation) by the continuous flow of dissolved calcium carbonate towards the surface, and its colour changes to yellow-reddish-brown (249). The uniformity of the crust is destroyed by outbreaks appearing at pyrite inclusions in the stone structure (151, 317), or by conversion into gypsum (124, 244, 265). Air pollution (244), as well as sulphates in the ground water (56, 85, 114, 151), may be responsible for the gypsum crust. Areas on limestone which remain wet for a long time are the first to develop gypsum crusts (82) and are rapidly blackened by dust and dirt (168).

Eventually such crusts flake off (265). Blocks of limestone containing iron salts become reddish-brown after exposure to wet air and, due to the increase in volume accompanying the hydrolysis of iron com-

pounds, tend to disintegrate (17). The same holds, to an even larger degree, for marble (151, 317).

In an article dealing with the crystalline structure of limestone De Henau (77) has suggested that the degree and distribution of crystallization of calcite are important in understanding weathering. After studying microscopically forty types of limestone De Henau concluded that in cases of oolites being embedded in a microcrystalline matrix, contact with sulphates led to a considerable disintegration as the pressure of expansion, characteristic of the conversion of calcium carbonate to gypsum could not be absorbed by the compact crystalline mass. On the other hand, types of limestone consisting of oolites that were connected to each other by a porous, loose cementing matter could absorb such pressure and could therefore withstand the action of sulphate solutions.

The appearance of a scanty whitish or yellowish efflorescence which has been called *mond-milch*, on rocks, seems to be the result of a complex process involving the action of ammonifying and iron-reducing microfloras on calcareous, dolomitic or calcium phosphate inclusions. A cryptocrystalline form of calcite, lublinite, has been suggested as representative of the *mond-milch* but presence of clay and quartz can markedly modify its constitution (137). *Mond-milch* is generally not deleterious to rocks, but it may obscure sculptured reliefs cut in them as at the Borobodur (313) or blur the outlines of murals as in the cave of Lascaux (137).

In sandstones where the adhesive consists of calcareous matter the corrosion pattern does not diverge from that of limestone (13, 40, 199). A notable phenomenon of sandstone deterioration is the dissolving of the siliceous constituent of the adhesive as colloidal silicic acid (73, 124).

Sandstone as a building material weathers on a large scale in an unfavourable environment. An extensive study of erosion and crust formation on sandstone monuments in Cambodia has been published by Delvert (79).

Examination of natural building stones in Germany showed that corrosion due to carbonic acid (carbon dioxide in water) appeared on walls exposed to rainfall, while sulphate disintegration (gypsum crust, efflorescence) was confined to areas protected against direct effects of rain-water (115).

2.3.2 *Igneous rocks*

The igneous rocks, being products of the cooling of lava, are non-porous, coherent and firm and therefore stable in contact with water. Their stability is, however, diminished by temperature changes. Erosion, resulting from alternating irregular expansion and contraction, renders the igneous rocks porous from the surface inwards, so that they become accessible to water. Granite and basalt are markedly vulnerable to this kind of deterioration (22, 40, 283), because after the mechanical loosening of their surface, water penetrates and dissolves the feldspar in them (198).

Although igneous rocks do not contain pyrite, they may be contaminated by it in a number of ways and then attacked by the products of its oxidation and hydrolysis (317). Igneous rocks made porous by erosion are also attacked by aqueous solutions. Weathering of this kind has been observed in London (54), and on the andesite blocks of the Borobudur in Java (313).

2.3.3 Bricks

Porous baked clay bricks are greatly deteriorated by efflorescence and subflorescence (25, 55, 56, 58, 85, 233, 270). The mechanism of efflorescence on brickwork is still not clear (37) but has been considered as due to soluble salts in the mortar joints (119, 260). The origin of the deposited salts in bricks may be the clay itself (56, 251), or the fuel used during firing (126), but quite often these harmful salts enter the bricks from outside (groundwater, mortar joints, air-pollution) (110, 114). In particular, the mortar joints are, according to Schmidt (260), the main source of harmful soluble salts, and the damage in the bricks resulting from their activity is believed to correspond to the easy transfer of these salts from the mortar to the bricks. Hence two possibilities for the formation of efflorescence have been suggested:

- 1) dissolved alkali-hydroxides from the mortar, together with carbonic acid from the humid air convert gypsum enclosed in the bricks to easily soluble salts, e.g. magnesium sulphate,
- 2) by exchange reactions calcium hydroxide from the mortar transforms otherwise insoluble alkali- and magnesium compounds in the bricks into soluble salts (260).

It has been observed, however (51), that in certain cases percolating water transports soluble sulphates from the bricks to the mortar joints where they lead to efflorescence. If the mortar contains Portland cement such sulphate solutions bring about the formation of calcium sulphoaluminate. This is accompanied by expansion that causes a progressive disintegration of the mortar joints. More on the damage of efflorescence on various buildings is to be found in the work of Moritz (210).

Stains on bricks may also be due to efflorescence (156, 289). Deterioration of brick masonry caused by thermal fluctuations are similar to those observed on stone masonry, and have been discussed in detail by Kieslinger (154).

2.3.4 Mortar and plaster

Mortar and plaster consist of admixtures such as sand, crushed stone, or pulverized bricks, cemented in a compact mass by lime or cement. The durability of mortars and plasters depends on the grain-size distribution of their admixtures (123, 225, 226). Suitable admixture compositions for mortars and plasters are presented in the following table (84).

	Admixture grain-size (mm)				
	3-7	1-3	0.2-1	0-0.2	total
good for all mortars and plasters	40%	36%	12%	12%	100%
good for lime mortars and plasters	25%	35%	22%	18%	100%
good for cement mortars and plasters	0	30%	45%	25%	100%
not to be used	0	0	65%	35%	100%

An admixture of equally sized, small grains possesses a large surface which cannot be covered by the amount of adhesive prescribed in common recipes and this weakens the mechanical properties of the mortar (141). In addition, excess of fine grains in the admixture composition may lead to partial solidification of the adhesive, that is, a thin, dense layer is formed on areas of exposure to the air under which the mortar remains as a soft paste. Such a barrier obstructs the absorption of carbon dioxide by the mortar, as well as the evaporation of water. Accordingly, the requirement for efficient deposition of calcium carbonate from slaked lime [moisture content of the mortar 0.6 to 1.2% (122)] is not fulfilled and the mortar does not harden (123). The usual ratio admixture/adhesive is 3:1. But larger amounts of adhesive are also used in the case of fine plastering, lime washing, murals, etc. (99, 123, 134).

Dry walls should be wetted before plastering as otherwise they extract water from the plaster applied on them. This usually impairs the bond wall-plaster (321) and is believed to be responsible for many phenomena of plaster-deterioration (123, 176). Efflorescence is particularly harmful to plasters (176) because, on account of the migration of salt solutions extracted from the walls behind them, their pores are preferentially filled with sulphates and chlorides. Consequently, after a number of evaporation-hydration cycles, the efflorescence cannot be tolerated any more and a collapse of the plaster is observed (110, 300). Soluble sulphates in plasters react with the calcareous adhesive in the plaster and form gypsum which by slow dissolution and expansion tends to destroy the entire plaster (21). Addition of casein to the plaster does not prevent the formation of gypsum (146). Soluble salts other than sulphates, while not causing any mechanical damage, often produce yellowish, greenish or brownish discoloration (21).

In addition, when iron or magnesium compounds find access to the pores of the plaster, various discoloration patterns are likely to appear (189).

Efflorescence on cement, concrete or mortars containing cement is due to uncombined calcium oxide in the cement (15). Uncombined magnesia in amounts exceeding 5% may also be responsible for efflorescence (16). Particularly serious deterioration can occur when sulphates from sulphate-bearing soils and ground-water come in contact with such cements (52). Since efflorescence and the formation of gypsum gradually destroy plasters, recommendations were made in the earlier literature

on the subject to add organic adhesives such as eggs, milk, ox blood, etc., to the plaster prior to application (34). However, these materials interfere with the hardening of the plaster and are therefore no longer in use.

3. MOISTURE IN POROUS BUILDING MATERIALS

3.1 Introduction

Hygrometric aspects of moisture in monuments were discussed during a symposium organized by ICOMOS in 1967 (204, 310). Vos (311) has given a survey of hygric properties and their measurement and has suggested that for building materials used in monuments data should be collected on the hygroscopic moisture content, the water-absorption coefficient, the critical water content, the maximum water content and the vapour conductivity. Mamillan (193) has suggested methods to measure physical and mechanical parameters of stones used in monuments and Pochon and Jaton (229) have surveyed techniques for the study of biological deterioration in such stones.

The advantages of such a systematic approach to the preservation of monuments have been discussed (10).

Methods for the measurement of humidity in monuments have been reviewed by Pacquet (219). The influence of moisture on the deterioration of monuments has been considered by a number of authors. Plenderleith (228) considered moisture in an outline of problems encountered in the preservation of monuments and data collected by Coremans (72) on a number of monuments in or near the tropics includes information on climatic conditions. In many cases heavy tropical rainfall and large temperature variations are found to be important causes for the degradation of stone. Effective drainage systems to prevent accumulation of rain water are an important element in the preservation of monuments in the tropics (102, 103, 313). The effects of moisture on monuments in desert regions have been discussed by Kidder (150). However, more research is needed into the effects of impregnation and consolidation (295) in desert and tropical regions considering the extreme fluctuations in relative humidity and surface temperatures. It would seem that progress in the preservation of monuments can only be made by the effective collaboration of specialists from many different disciplines working together in a team (313).

The majority of publications on moisture in building materials do not deal with monument preservation. In the following therefore a brief outline of some theoretical aspects will be given as a background for problems related to monuments.

3.2 Hygric aspects

Moisture is of paramount importance in the deterioration of siliceous building materials.

Frost damage (cf. section 4.2) is obviously improbable without moisture. Biological deterioration depends on the presence of moisture (132). Air pollutants react with water to form acidic solutions which attack stone and related materials (cf. section 2). The majority of deterioration phenomena can be explained by cyclic humidity changes in the presence of soluble salts (cf. section 2.2). In such cases, the damage is proportional to the number of cycles and not to the concentration of hydrated salts (55, 212).

Moisture occurs as vapour, liquid and ice. The absolute humidity or water-vapour concentration (c) is the mass of water-vapour per unit volume of dry air. This is dependent on the temperature; for each temperature there is a corresponding maximum water-vapour concentration. In decreasing the temperature of air which contains water-vapour, the saturation point is reached and water starts to form. The temperature at which this occurs is called the dew-point. The relative humidity φ is the ratio between the water-vapour concentration (c) in the air and the maximum concentration (c') possible at the same temperature. It is expressed in %. Tables of temperature measured against c' have been published (185, 288, 322).

The moisture content of a porous material is normally defined as

$$\psi = \frac{100 m_{\text{H}_2\text{O}}}{m_{\text{dry}} + m_{\text{H}_2\text{O}}} \quad [\%] \quad (\text{F1})$$

with m_{dry} the mass of the dry material (185, 322).

This definition includes ice and hydrated water (cf. section 2.2). The moisture content of a porous material may change with the transport of both water-vapour and water.

Porosity is defined as the ratio of the volume of the pores (V_p) to the total volume of the porous material (V).

If ρ_s is the density of the solid part of the porous material and ρ the total density, the porosity is (94).

$$\varepsilon = 1 - \frac{\rho}{\rho_s} = \frac{V_p}{V} \quad (\text{F2})$$

Building materials with a high porosity have considerable space for water and, provided their pores are interconnected, they will have a high moisture content when saturated. Porosity, however, is not a straightforward measure of permeability to liquids or suction (cf. section 3.2.2).

3.2.1 Diffusion of water-vapour

If a dry material is placed in an atmosphere containing water-vapour, the moist air will diffuse into the material. For each material a relation exists between the relative humidity of the surrounding air and the amount of water-vapour taken up by the material.

This amount is called hygroscopic moisture content (ψ_H).

The curves of ψ_H plotted against relative humidity depend on the temperature. They are frequently called sorption-isotherms and have been measured for many porous materials (92, 185).

They show a slight hysteresis and can be explained for low relative humidities by the absorption of water molecules on the walls of the capillaries, and at higher relative humidities by capillary condensation (92, 288). Capillary condensation occurs only in very narrow capillaries [$r < 5 \cdot 10^{-8}$ metre (288)] because the maximum water-vapour concentration is lowered in such micro-capillaries.

Materials such as brick with a very low hygroscopic moisture content at 95% relative humidity are called non-hygroscopic. Wood on the other hand is very hygroscopic ($\psi = 22\%$ at $\varphi = 95\%$) (288).

The amount g of water-vapour diffusing unidirectionally through a layer of thickness d may be described as (61, 288)

$$g = \frac{\delta}{d} (c_1 - c_2) = \frac{c_1 - c_2}{Z} \quad [\text{kg/m}^2 \cdot \text{s}] \quad (\text{F3})$$

where c_1 and c_2 are the water-vapour concentrations [kg/m^3] at the surfaces. δ is the water-vapour conductivity. This quantity depends on the temperature and moisture content of the porous material. Values for δ have been published by a number of authors (175, 184, 288). Z is the diffusion resistance [s/m].

Vapour barriers have a high diffusion resistance and thus low δ -values. The amount of water-vapour diffusing through a particular wall may be calculated from formula F3.

3.2.2 Transport of liquid water

3.2.2.1 Horizontal transport of water

The transport of water through porous materials depends on the capillary structure. Horizontal transport of a liquid by capillary forces can be written as (92, 118, 288)

$$x = A\sqrt{t} \quad (\text{F4})$$

where x is the displacement of the liquid front after a time t . The constant A is indicative of the permeability of the porous material to the liquid. Hisschemöller (127) found for water transport in brick:

$A = 0.3 \cdot 10^{-3} - 3 \cdot 10^{-3} \text{ m/s}^{0.5}$, and in mortar (1 cement : 3 sand : 1/8 lime)
 $A = 10^{-3} \text{ m/s}^{0.5}$.

For sandstone, $A = 3 \cdot 10^{-3} \text{ m/s}^{0.5}$ has been measured (213). From experiments on rain penetration by Mamillan (191) on limestone test-walls the following approximate values may be calculated:

$3 \cdot 10^{-3} \text{ m/s}^{0.5}$ (Gerberie), $2 \cdot 10^{-3} \text{ m/s}^{0.5}$ (Fontvieille) and $0.8 \cdot 10^{-3} \text{ m/s}^{0.5}$ (Tervoux).

The factor A is related to the pore-size distribution. Such distributions have been measured e.g. for limestone (191) and bricks (129, 316).

Using a simplified model of straight, uniform horizontal capillaries, the factor A may be written as (119, 288)

$$A = \sqrt{\frac{\sigma r}{2\gamma_i}} \quad (\text{F5})$$

where σ is the surface tension [N/m], γ_i the dynamic viscosity [Ns/m²] and r the radius of the capillaries.

Thus measurement of the factor A permits an estimation of the average pore-size and a calculation of the time needed for water penetration of a wall.

It may also be used to calculate the time needed for a satisfactory impregnation of deteriorated building materials with various fixatives (cf. section 5.3) (213). Water will have penetrated through a wall with thickness d after a time

$$t = \frac{d^2}{A^2} \text{ [s]} \quad (\text{F6})$$

Vos and Tammes (88) showed that $t=8$ hours for brick-walls of 33 cm thickness and considered such walls not water-tight.

Mamillan (191) tested three different limestones for water penetration in walls of 35 cm. He found $t=3.15$ hours (Gerberie), $t=8$ hours (Fontvieille) and $t=50$ hours (Tervoux), but concluded that a wall not penetrated after one hour could be considered satisfactory. Such judgments obviously depend on the expected driving-rain intensity (cf. section 3.2.2.2). Mamillan (191) also showed that water penetration through limestone walls is primarily governed by the permeability of the stone, but in brick-walls the joints are about four to ten times more permeable than the bricks.

3.2.2.2 Rain penetration

The mechanism of rain penetration in buildings has been reviewed by Ritchie and Plewes (239) and Birkeland (238, section 3-0). It depends on the construction and condition of the exposed surface. Generally, a film of water is formed over the surface and is forced into the wall by wind pressure and capillary suction.

To study rain penetration, experiments have been carried out both outdoors and with artificial rain (62, 100, 191, 238 section 3-2, 240).

Wind causes differential air pressures around a building, depending on the wind velocity, and the height and shape of the structure (32, 263). Wind causes the rain to strike the wall, and this may lead to air pressure differences across the wall. Both factors may increase rain penetration.

Although the influence of wind pressure on the horizontal transport of water through stone and mortar is negligible (288), it may be important

In the case of cracks, crevices and other openings (32). This stresses the importance of regular maintenance of joints in monuments, especially when murals are to be preserved on the inside. Rain penetration further depends on the prevailing direction of the wind. This is not only because of the pressure involved, but also because those parts of a building which are in the lee receive less rain.

Kieslinger (151) introduced a plot of the driving rain intensity against the wind direction for a particular building. Such plots are useful because orientation and exposure conditions of a monument may influence deterioration phenomena.

Driving-rain maps also exist for larger geographical areas. Lacy (238, section 3-4) reviewed the methods used in plotting these maps.

Measured moisture distributions in walls show marked differences according to the orientation of their exposed surfaces (268, 269, 270).

The influence of gravitational forces on horizontal water transport in a wall is small but cannot be neglected for thick walls (288). Thus rain penetration will occur first in the lower parts of the wall. This should be kept in mind when judging the effects of rising ground water (cf. section 5.1.1).

3.2.2.3 Vertical transport of water

The transport of water in the vertical direction occurs when water rises in walls from the ground or enters the wall from above through leaking gutters, etc. (cf. section 5.1).

When no external forces are present, the velocity of water transport in the vertical direction may be approximated using a model of straight vertical capillaries with radius r (173, 288):

$$v = \frac{dx}{dt} = \frac{r^2}{8\gamma x} \left(\rho g x \cos \alpha + \frac{2\sigma}{r} \right) \quad (\text{F7})$$

Here γ is the viscosity of the liquid, ρ the density of the liquid, σ the surface tension, g the gravitational acceleration and α the angle between the capillary and a vertical.

For rising water $\cos \alpha = -1$ and (F7) becomes

$$v = \frac{r^2}{8\gamma x} \left(\frac{2\sigma}{r} - \rho g x \right) \quad (\text{F8})$$

When equilibrium is reached $v=0$ and the maximum height above the liquid table is

$$x_{\text{max}} = \frac{2\sigma}{\rho g r} \quad (\text{F9})$$

For water, (F9) becomes (290, 295)

$$x_{\max} = \frac{15 \cdot 10^{-6}}{r} \text{ [m]} \quad (\text{F10})$$

Measured pore size distributions for bricks (129, 316) have averages from 1-10 microns yielding values for x_{\max} between 15 and 1.5 metres. In deriving formula (F9) it is supposed that no evaporation takes place. It has indeed been observed (151, 153) that water can rise very high in walls where evaporation is hindered. Normally, however, equilibrium is reached by evaporation from the wall and x_{\max} is not attained.

Walls are generally constructed with mortar and this material should be taken into account in evaluating the capillary rise (200, 288). Columns and walls of monuments are often made of different materials and filled with rubble. Such non-homogeneous structures make calculations difficult. It should be remembered that the model of straight capillaries with uniform radius is too simplified. In practice the flow of moisture requires a more complicated description. The concept of maximum capillary rise may still be used, however, with the restriction that the moisture content may decrease with increasing height (288).

Schofield (198) wrote (F9) as

$$pF = \log_{10} x_{\max} = \log \frac{2\sigma}{\rho g r} \quad (\text{F11})$$

which is called 'pressure deficiency' or 'suction'. Suction/water-content relationships have been used as a measure of the durability of stone (129). Water-suction may also be used to classify various building materials according to their capillary structure (59, 60, 92).

Walls may become wet not only if they are in actual contact with the water table, but also by suction from the ground. The maximum capillary rise from the water table in soils is given by (288, 290).

$$x'_{\max} = \frac{60 \cdot 10^{-6}}{D} \text{ [m]} \quad (\text{F12})$$

where D is the grain diameter of the smallest particles which are still abundant in the soil.

Values for D range from $0.1 \cdot 10^{-3}$ - $2 \cdot 10^{-3}$ [m] for sand to $1 \cdot 10^{-6}$ - $10 \cdot 10^{-6}$ [m] for clay corresponding with a maximum capillary rise of 0.06 to 60 metres (288).

Thus, without taking into account possible lateral flow of water (cf. section 5.1.1.4), the distance from the water table to the foundation of the wall should exceed x'_{\max} to prevent the access of rising water in the structure. Lowering of the ground-water table is therefore a means to prevent the access of rising water in walls (cf. section 5.1.1.4).

The movement of water through the ground is described by Darcy's law:

$$v = -kJ \quad (\text{F13})$$

where v is the flow velocity and J the hydraulic gradient. k is called the permeability coefficient and in ground-water hydrology has the dimension of a velocity (288). Water may thus seep from various sources to the vicinity of the wall where suction may commence.

3.3 Drying phenomena in porous materials

In the drying process of a homogeneous structure, water is transported through the capillary system to the surface where evaporation takes place. The drying velocity is nearly constant to a point where the moisture content near the surface has decreased so much that the water-network is no longer complete. The greater capillaries at the surface are no longer filled with water, the waterfront retreats into the wall, and the drying velocity decreases rapidly (173, 174, 309). The moisture content corresponding to this discontinuity is called critical moisture content (ψ_k).

The drying rate may be written as (288)

$$G = \beta (c_s - c) \quad (F14)$$

where β is the surface coefficient of water-vapour transfer (m/s), c_s the water-vapour concentration at the surface, and c the concentration of water-vapour at a distance from the wall.

The drying rate depends on the ventilation. If unsaturated air passes along the wall it prevents local saturation and thus stimulates evaporation. From plots of the drying rate against the average residual water content (vol %) in the structure, the critical moisture content may be deduced. Such graphs have been published for a number of building materials (92, 173, 174, 288). The crystallisation of dissolved salts (efflorescence) at the surface of a wall will start when the critical moisture content is reached and the water-front retreats. Frequent cycles of drying and wetting thus cause an oscillating front accompanied by periodic crystallisation and dissolution of salts. This process is responsible for most weathering phenomena.

In stagnant air, the humidity near an evaporating wall may be very high (149). Thus without ventilation walls and murals with a moisture content $\varphi > \varphi_k$ will not deteriorate to a great extent although attack by micro-organisms is likely. When air-circulation starts, e.g. when tombs are opened, deterioration by efflorescence may rapidly occur.

Measurements of changes in the moisture content of drying walls have been published by a number of authors (92, 267, 268, 269, 308).

3.4 Thermal aspects

Heat transfer in porous materials takes place by conduction, radiation and convection. Unidirectional heat transfer in a homogeneous wall of thickness d may be written as (288, 307)

$$q = \frac{\lambda}{d} (T_1 - T_2) = \frac{T_1 - T_2}{R} \quad (F15)$$

where λ is the thermal conductivity and T_1 and T_2 are the boundary surface temperatures. R is the heat resistance. Thermal conductivities have been measured for many building materials (7, 318). Thermal conductivity increases with increasing moisture content and the thermal insulation of the structure is thus influenced by moisture. Heat transfer from the surfaces of the wall to the surrounding air is given by (288)

$$q = \frac{T_1 - T_2}{R_i} \quad (\text{F16})$$

$$q = \frac{T_2 - T_e}{R_e} \quad (\text{F17})$$

where R_i and R_e are heat transfer resistances and T_1 and T_e the air temperatures inside and outside. The heat transfer resistance depends on the air velocity. Approximate values are $R_i = 0.15$ ($\text{m}^2\text{h}^\circ\text{C}/\text{kcal}$) and $R_e = 0.05$. R_e is lower than R_i because wind promotes convection (170, 288, 318).

When the wall consists of n layers, the heat resistance is found by addition of the individual values:

$$R = R_1 + R_2 + \dots + R_n \quad (\text{F18})$$

to which the heat transfer resistances should be added.

The temperature T_s of the wall at the inner surface is given by (170, 288)

$$T_s = T_1 - \frac{R_i}{R_i + R + R_e} (T_1 - T_e) = T_1 - \frac{R_i}{R_t} (T_1 - T_e) \quad (\text{F19})$$

This formula may be used to calculate the risk of surface condensation (cf. section 3.5.1).

Walls should have a sufficient heat capacity to prevent quick temperature changes (170), otherwise condensation may occur when the heating is shut off or reduced at night.

Insufficient thermal insulation may cause surface condensation which may also occur locally in colder areas such as corners (234). Dirt and dust more readily accumulate in cold places than on warm surfaces, and dirt patterns may appear showing the structure behind the wall (67, 176).

3.5 Condensation (41, 92, 288, 309)

Condensation occurs when the water-vapour concentration reaches the maximum concentration possible at a given temperature. Thus water-vapour condenses when it arrives in areas where the temperature is lower than the dew-point of the water-vapour containing air. Condensation may occur on the surface of the wall or inside the construction.

3.5.1 Surface condensation

Surface condensation is stimulated by high relative humidities and low surface temperatures. The latter may be caused by insufficient thermal insulation of walls and roofs (178), and low temperatures or excessive ventilation outside. High relative humidities result from the introduction or production of moisture, and low temperatures or insufficient ventilation inside the building (216). A human being produces between 50 and 100 litres of water-vapour per hour (92, 98). Visitors may thus raise the relative humidity in a building considerably. Gas heating, which is sometimes used in monuments, also produces much water-vapour (92) (1 m³ gas gives approximately 1200 litres per hour). The surface temperatures of the wall may be estimated with formula (F19) section 3.4.

Condensation will occur when the surface temperature is below the dew-point of the water-vapour in the air close to the surface.

The quantity of condensing moisture is given by (288)

$$g = (c_i - c_s) \quad [\text{kg/m}^2\text{h}] \quad (\text{F20})$$

where c_i is the water-vapour concentration close to the wall and c_s the maximum concentration possible at the surface, with temperature T_s .

3.5.2. Interstitial condensation

Water-vapour may condense interstitially if the temperature reaches the dew-point somewhere in the interior of the wall.

Different temperatures inside and outside cause temperature gradients across the wall.

Thus, for example, warmer air from the inside diffuses into the wall and the water-vapour in the air may condense there. To calculate the condensation-risk at a point x in the interior of the wall, the temperature T_x and water-vapour concentration c_x should be compared (170):

$$T_x = T_i - \frac{R_{ix}}{R} (T_i - T_e) \quad (\text{F21})$$

$$c_x = c_i - \frac{Z_{ix}}{Z} (c_i - c_e) \quad (\text{F22})$$

where R_{ix} and Z_{ix} are the heat resistance and the water-vapour diffusion resistance of the layer from the inside surface to x .

Condensation occurs when $c_x \geq c_{\text{max}}$ at the temperature T_x . Usually, graphical solutions are used for a particular wall (28, 92, 170). The physical significance of such graphical solutions has been criticized and discussed by Vos and Tamme (288) and Vos (309). Generally, interstitial condensation requires high relative humidities and stops after some time.

Water-vapour barriers should not be placed at the outside, because they increase the condensation risks when temperatures inside are higher than outside.

Interstitial condensation may involve the transport of soluble salts to areas nearer to the surface, because water will be transported to areas with a lower moisture content. Moreover, condensed water may cause frost damage in the interior of the wall.

In practical situations measurements will be indispensable for a proper diagnosis of moisture occurrence, because in the non-homogeneous walls so frequently encountered in monuments, rising, penetrating and condensing water should be carefully separated. Approximate calculations, however, may help in estimating the contribution of condensation.

3.6 Determination of moisture

A distinction should be made between the measurement of moisture in the air and the determination of the moisture content of porous materials. Both types of measurements have been treated comprehensively by Lück (185). Newer developments are to be found in Wexler (322) and in the Proceedings of the RILEM Helsinki Symposium 1965 (238).

In practice, it is often important to know whether deterioration is due to rising ground-water, infiltration or condensation. A few measurements in a representative area of the wall can yield much useful information (200, 201). Methods for the determination of the moisture content of the surface and the surrounding air are non-destructive. Measurements of the moisture content in the interior of the wall require a small sample. Thus, if repeated measurements are to be carried out in monuments where a large amount of sampling is not possible, for instance on murals, continuous methods should be used (44, 308). Continuous or repeated determination of moisture distributions is indicated in connection with condensation phenomena (cf. section 3.5.2). Hygric aspects of museum buildings should not be confined to the relative humidity of the air. The risk of atmospheric moisture condensation on paintings hanging on cold walls has been considered (27) and it has been pointed out that the thermic and hygric behaviour of walls on which paintings or tapestries are to be exhibited should be investigated (301).

In the preservation of monuments, surprisingly little attention has been paid to the importance of temperature and moisture distributions although they often contain vital clues for the diagnosis of the deteriorating phenomena. The literature is accordingly very sparse (200, 201).

4. OTHER DETERIORATION PHENOMENA

Disintegration of stone caused by changes in temperature, including frost, has been briefly discussed in a comprehensive article on decay and conservation of stone by Sneyers and De Henau (278).

4.1 Insolation and fire damage

Due to its inhomogeneous character, a building structure undergoes *erosion* as a consequence of different volume expansion of the materials involved. Besides, after expansion a stone does not contract to the same amount. This so-called permanent "set" also contributes to erosion (315). In a similar way, an increase in temperature due to *fire* does damage to stone, bricks and mortar (114, 151, 152, 154, 251). Examples of damage by fire observed on various building stones have been given by Kieslinger (159, 160, 161) in a number of publications in German. The same material has also been published in French (157, 158).

4.2 Frost damage

Frost is harmful to porous materials because freezing increases the volume of the water in the pores (the volume of ice is one tenth greater than water; ice floats on it). Damage, however, is also observed when a liquid, e.g. nitrobenzene, freezes in the pores without volume increase (129). In a capillary pore filled with water, at temperatures below the freezing point, laminated ice deposits start to form from the meniscus inwards. Thus, water molecules are immobilized in the ice lens which leads to a decrease in molecular motion below this lens and consequently to a pressure difference between the freezing front and the rest of the water in the capillary. In order to restore equilibrium, water moves towards the ice lens and thus contributes to the immobilization of more molecules. In such a manner, the ice lens thickens by water pulled towards it through the capillary. In stones, bricks and mortars the capillaries are distributed between particles, and the accumulation of ice, as described, starts from the surface inwards as the atmospheric temperature falls below the freezing point of water. After ice-formation, the surface tension tends to extend the remaining water to cover the particle over the dried area occupied by the ice. Normally, the surface tension overcomes the weight of the ice and the latter is lifted. Then the water layer separating the ice lens from the particle freezes again and adds a new lamina to the ice lens. The water consumed by freezing causes drainage of the surrounding capillaries and the ice lens may grow to exert a large pressure in all directions. Above the ice lens this will cause destruction; under the ice lens it will depress the freezing point of the water (251). Consequently, water will be able to flow and become available at the ice lens where it freezes, its flow and velocity depending on viscosity and capillary size (95, 109, 140, 195, 299, 322). Porous materials having a *saturation coefficient** smaller than 0.8 are not affected by freezing (129), because this implies a structure containing many large pores in which the ice-lens building can proceed without the development of

(*) The ratio of the volume absorbed by immersing a porous sample in water for 24 hours to the total volume of the accessible pores in the material.

a destructive pressure. Such large pores are rare in plasters and mortars and therefore in a wall these materials are the first to be attacked by frost. According to Moritz (51) 90% of the damage observed on roofing tiles during the first three years after placement is due to frost. Earthenware tiles also undergo frost damage (91). One type of frost damage occurs when outside water comes in contact with a glazed ceramic tile and freezes there. The damage appears characteristically as chips of glaze broken out with particles from the body of the tile adhering to them. Mamillan (192) has carried out an experimental study of frost damage on lime-stone and concrete in relation to recent theories on the mechanism of the expansion of freezing water in pores. The influence of soluble salts on the resistance of concrete to frost has been studied by Schäfer (255).

4.3 Wind erosion

Wind loading on buildings also contributes to the corrosion processes (88, 110, 166). The wind pressure on an area of a building is proportional to the square of the wind speed. At the point of contact with the front-side of a cubic building the wind creates overpressure (loading), whereas at the back, in the main, but also on the other sides, an underpressure (suction) is created. Moreover the wind loading increases with the height of the building. Wind loading depends on the angle at which a plane of the building is struck (263). Strong winds (64, 273) are very harmful, but moderate winds (air speed less than 10 m/sec) are also destructive, especially when polluted with coarse particles (71, 83, 166, 188, 212, 318). Kieslinger (151) discussed the effects of wind erosion on some Greek and Austrian monuments.

4.4 Dust pollution

The atmosphere of industrial cities is heavily polluted by gases as well as solid particles (soot, sand, salts, etc.). Because of their minute size such particles are easily air-borne and produce dust (particle size between 150 and 1 μ^*) or smoke (containing particles below 0.5 μ in diameter) (113). Systems of dust or smoke are thermodynamically instable and their solid particles tend both to settle and to cling to each other in large clusters. Since the fine dust has a large external surface, water vapour from the air is absorbed on individual particles and carried along to the area of deposition. Thus dust may contribute to moisture accumulation. In moist layers of dust the dissolved constituents react either alkaline or acid and, depending on the character of the porous material, a chemical attack of the porous substratum may result (112). In addition, dust particles penetrate to various degrees into the pores and thus permanently blacken the building exterior. Bricks which have

(*) $1\mu = \frac{1}{1000}$ mm

been fired at a temperature of about 900°C readily acquire a dark-coloured surface in contact with polluted moist air. Refractory bricks, on the contrary, retain their original colour for a long time. Stenestad (281) supposed that a submicroscopic capillary system in the ordinary fired bricks kept the surface damp and therefore dust was attracted, while refractories dried soon after wetting and lacked the moisture needed to bind dust particles. A similar difference in discoloration by dust is seen in sedimentary stones, plasters and mortars and, on the other hand, igneous stones (82, 151).

The combined action of all air pollutants blackens the buildings and covers them with blisters and scales, which are subsequently removed by erosive agents or by intentional cleaning. In both cases deeper layers of the building material (already impoverished in adhesives) are exposed to the same attack that made their disclosure possible. However, after intentional cleaning, measures are usually taken to prevent further exfoliation (190, 265).

4.5 Deterioration by biological agents

4.5.1 *Trees and plants*

Trees and plants may have some importance in the deterioration of monuments if they grow on or close to the building. Trees and bushes in the vicinity of monuments may hinder evaporation of moisture from the walls (200, 267).

Trees and plants growing on monuments generally indicate a high local moisture content in the building materials. They are rather harmless, but in some cases their roots may increase the deterioration of the masonry (151).

There is evidence (328, 330) that marble and lime-stone in contact with roots may develop root marks which are due to the etching effect of the slightly acid sap of the root cells. Rotting roots, because they produce humic substances, can also stain calcareous stones. Plants on monuments, however, often indicate poor maintenance and are the result rather than the cause of deterioration.

4.5.2. *Algae and lichen* (42)

Monuments are often locally covered by algae and related organisms. This invariably indicates a high moisture content in the substratum and is in fact frequently encountered near rain-pipes and in the lower parts of the building wetted by capillary rise of water from the ground. The presence of algae may thus serve as a rapid estimate of the moisture distribution in the building.

It has been pointed out in section 2.2 that deterioration occurs mainly as a result of frequent wetting and drying of the stone. Where algae cover the walls the moisture content will often be found to be continuously above the critical level ($\psi > \psi_k$ cf. section 3.3). Thus the

outer part of the wall in such areas will be well preserved because the number of drying/wetting cycles is small. However, in the adjacent areas and at the corresponding surface inside the building deterioration will be accelerated.

Apart from mechanical damage, algae and lichen may contribute to the chemical deterioration of limestones. This matter has been reviewed by Degelius (76) and Hueck (132). Lichens (a symbiotic association of algae and fungi) cannot tolerate soot or sulphate and are therefore unlikely to attack buildings and monuments in urban and industrial areas. But in other locations, they may have a destructive effect on calcareous rocks, sandstone and igneous rocks. The processes involved are complex (328). In tropical climates the effect of lichens on monuments is so alarming that their removal becomes an indispensable element of any preservation programme (103).

4.5.3 *Fungi and micro-organisms*

Fungi, when present on porous building materials, disfigure these substratas and may cause damage to paint films in murals (294). Their role in decaying porous materials is less clear (132), but fungi-tests have been used to indicate high humidities on walls (167, 234).

The role of micro-organisms in the deterioration of building materials has been reviewed by Hueck (132). Plenderleith (228) has also drawn attention to biological processes contributing to the decay of stone. Further, it has been suggested (229, 230, 328) that the activity of various bacteria may also lead to the weathering of rocks.

Silicate rocks which bear bacterial pollutions, have in particular a tendency to disintegrate very slowly at first. This process is, however, accelerated after a certain time. For this reason silicate rocks affected by bacteria are not to be recommended for exterior use as the decay is expected to progress very rapidly once it has started (328). Although some contribution to the decay of stone may certainly be attributed to micro-organisms, their influence seems rather doubtful from a quantitative point of view (256, 257).

Various fungicides may be used against fungi (42). A survey is given by Hueck (132).

4.5.4 *Animals*

The damage caused by insects is generally confined to organic materials such as wood, which are outside the scope of this review (cf. 63, 184).

Birds have some influence as their excrement contains nitrates which contribute to the deterioration of stone (151, 252). Excrement also disfigures the surface of the buildings concerned. Weathering of a soapstone temple monument in India has been reported by Sharma (272). A thick deposit of soot, white efflorescence and bat's droppings were responsible in this particular case for the decay. The droppings in particular have initiated bacterial action by providing the organic matter.

Since such action produces organic acids, rain-water falling on the monument became more acid and therefore more aggressive, and this contributed to the disintegration of the soapstone (talc) to clay.

4.6 Quality of building stone

Stone building materials should comply with certain requirements if their coherence during use is to be lasting. Stones of igneous origin, with the exception of granite because the feldspar it contains hydrolizes easily, are very resistant to corrosion. Sedimentary stones and metamorphically formed marble, however, easily decompose. Limestone and marble containing iron compounds show yellow-brown discolorations after some time and eventually disintegrate as the iron compounds in contact with moisture hydrolize and increase in volume (17).

The same effect is observed if these stones are contaminated with pyrite (151, 317). Rupp (248) has warned against the use of limestone that "swarms" with black points (pyrite) as well as against stone blocks with veins; the less a stone is intersected by coloured veins the longer it will remain a sound building unit.

Sedimentary stones cut in a way which does not permit parallel positioning of their strata with respect to the ground level, decay rapidly due to penetration of water (usually from the ground, but also on account of gravitation during rainfall) (75, 155). Sedimentary stones with considerable amounts of soluble sulphates and chlorides or with a saturation coefficient less than 0.8 are also considered to be of bad quality (40, 129).

4.7 Metal corrosion

Iron in contact with building materials will corrode depending on the pH value of the immediate environment. Normally, severe corrosion takes place in acid conditions (143) but substantial corrosion has also been observed in alkaline milieu, and especially when sodium chloride (142) or magnesium chloride (53) are present. As the volume of rust is 6 to 8 times larger than the metal iron used to produce it (151), the appearance of crevices and other flaws (217) in the material surrounding iron parts are understandable. In order to avoid such damage iron is often wrapped in lead foil, but in contact with limestone, mortar (329) or wood (69), lead itself is attacked so that in such cases no protection of iron against corrosion is to be expected.

Copper and its alloys also corrode (136, 304, 324) but generally only a greenish-blue discoloration of the building materials is observed.

4.8 Cracking (48)

Cracks in buildings may result from expansion and contraction due to temperature changes, over-loading, great changes in moisture content, soil movements, vibration by traffic (182), aeroplanes or church bells (172) and damage to foundations such as rotting of piles. In addition, metals in contact with stone and masonry may cause cracks (cf. sec-

tion 4.7). Roots of trees and plants may promote the formation of crevices and cracks.

4.9 Sonic boom

The effects of sonic boom on buildings have received increased attention (187, 326). Damage caused by such shock waves to monuments in France has been reported by Parent (220). A survey of the literature on various aspects of the sonic boom, including damage to buildings, has been compiled by Coene and Stigter (68).

5. CONSERVATION OF BUILDING MATERIALS

5.1 Remedial measures against moisture

In this section various remedies to prevent or decrease moisture in constructions are reviewed. In many countries, commercial firms execute various methods in connection with normal building practice. Occasionally, these methods have been used in the preservation of monuments.

It would seem that more frequent and systematic applications of remedies against moisture would increase the effectiveness of monuments' restoration (36). References to representative applications in the conservation of monuments and related works of art such as murals have been included under the appropriate headings. Most examples are given by Massari (200). Philippot and Mora (223) included a chapter dealing with the preservation of murals in humid conditions. It may be recalled that mural paintings behave essentially as plaster with regard to moisture and soluble salts. The practice of detaching murals is often indicated when the supporting wall is mechanically unstable and cracks. However, too little attention is generally paid to a proper diagnosis of the deterioration. In such cases it would be important to investigate first moisture distributions as a function of climatic conditions inside and outside the monument over a certain period. It may well be that in many cases proper remedies against moisture and regular maintenance could suffice to preserve the murals (139).

Experiments to measure the moisture content of building materials containing various salts have been announced (312). Preliminary results indicate that bricks containing 20 mg NaCl per cm^3 may have a moisture content of 10-15 vol % at 90% RH, although brick without salts absorbs almost no hygroscopic moisture. It is thus by no means certain that deterioration by efflorescence will cease when walls containing salts are made "dry". Hydration of salts in cycles may be expected to continue. It is important to investigate the number and magnitude of variations in relative humidity as a function at the amount of damage caused by hydrating salts in plasters and stones.

A historical survey of the prevention of moisture access in antiquity is to be found in Varlan (302).

5.1.1 *Remedies against rising groundwater and seepage*

5.1.1.1 *Damp-proof courses*

Damp-proof courses are used to prevent the movement of water in the vertical direction. They may be applied in walls and floors to prevent rising water and can also be used against downward movement e.g. in chimneys, window-sills and parapets and have been applied in monuments (74, 200). Methods to apply damp-proof courses may be divided into two classes: those requiring horizontal sectioning of the wall with subsequent insertion of the impermeable material, and methods where liquids are injected into the wall. Materials used in the first group include metals (5), bituminous mixtures, plastic sheets (3), mixtures of epoxy resins with sand or marble powder, semi-rigid mastic-asphalt mixtures, concrete, dense bricks and slates. Many of these methods are standardized. They have been reviewed e.g. for Great Britain (4, 43, 46, 49) and Germany (211, 236, 318).

The incorporation of damp-proof courses in buildings has been compulsory in Great Britain since 1875.

Several methods are being commercially applied in which liquids are injected into holes drilled in the wall. Substances used are e.g. silicone solutions, silicate/latex mixtures, silicates, hot wax and thermo-setting resins. Experience with such methods is still limited, but the silicate/latex mixtures seem most satisfactory (46).

The execution of such methods has been explained by Moritz (211). In selecting a method the cost-factor may well be the most important criterium.

5.1.1.2 *Reduction of the cross-section of the wall*

A decrease in rising water may be obtained by reducing the cross-section of the wall, because less capillaries are then available for vertical transport. Massari (200) has discussed this method and reported a successful application in connection with a mural by Domenichino in the church of San Luigi de' Francesi in Rome.

5.1.1.3 *Methods using vertical moisture barriers*

The amount of ground water reaching the wall by seepage may be reduced by providing moisture barriers around the lower exterior parts of the wall or by making a pathway. Such methods have been discussed by Massari (200). Pathways also increase the evaporation from the wall. Porous tubes are sometimes inserted in the wall to encourage evaporation. It is claimed that such devices increase the drying rate of a wall but this is difficult to prove (46, 200, 211).

Vertical moisture barriers applied to a damp wall at the inner surface only conceal the effects of moisture and salts. They impede

evaporation and may cause the water to rise higher (cf. section 3.2.2.3). Their use against condensation is thus only indicated in walls where the moisture content is otherwise below the critical value (cf. section 3.3). This should be remembered when large areas of a wall are to be covered with detached murals on supports involving glass-fibre/polyester linings (223). Sufficient ventilation between support and wall should be available if such walls are still wetted by rising groundwater.

5.1.1.4 *Drainage*

Drainage may be used to decrease lateral seepage or to lower the water-table to such a level that ground water can not reach the wall by capillary rise (cf. section 3.2.2.3). A survey of the methods used in drainage is outside the scope of this review but may be found in handbooks on soil mechanics and related specialisms (290, 293). Lowering of the ground water-table has been proposed to preserve the Philae monuments in Egypt (297) and the ruins of Mohenjo-Daro, Pakistan (298) and has occasionally been applied in connection with the preservation of monuments (152, 182). A consequence of drainage is the increased density of the soil. It is therefore applied in soil consolidation and foundation techniques (8, 47, 169, 290). However, changes in the soil structure may cause damage to buildings. Serious damage to monuments in West-Germany has been reported (186) in connection with the lowering of the water-table for mining purposes.

In countries with a high ground water-level wooden piles have been frequently used as foundations. The lower water-table may cause the piles to rot. This often causes damage to the foundations and structures.

5.1.1.5 *Electro-osmosis*

Electro-osmosis is frequently used in drainage and soil consolidation (169, 290, 303). In using electro-osmosis for drying walls and as a moisture barrier, electrodes are placed in the wall and the ground. A voltage is maintained between them.

Although successful application of this method has been reported from Russia (334), Rumania (208), Austria (323) and by various authors (9, 78, 128, 207), the use of electro-osmosis remains a controversial subject. Some authors are indeed sceptical (46, 70, 200). In view of this controversy, the principles involved will be briefly discussed (101, 253, 290).

The walls of capillaries in inorganic porous materials carry a negative charge. Neighbouring water molecules are charged positively and positive ions concentrate near the walls. When a voltage is applied, the positive charges are attracted to the cathode and, if the capillaries are small enough, the enclosed column of neutral water in the centre may follow this movement as a result of its viscosity. Unidirectional liquid flow in a porous medium is described by Darcy's law (cf. section 3.2.2.3).

$$v = - kJ$$

When an electrical field is applied, a voltage may be chosen so that the liquid flow is exactly compensated. In equilibrium, the total flow velocity is then zero:

$$v_T = -kJ + k_E E = -k \frac{H}{L} + k_E \frac{U}{L} = 0 \quad (\text{F23})$$

where E is the electric field strength and k_E the electro-osmotic permeability coefficient ($\text{cm}^2/\text{Volt}\cdot\text{sec}$). H is the hydraulic pressure and U the potential difference per length L .

Thus

$$H = \frac{k_E}{k} U \quad (\text{F24})$$

A criterion for the applicability of electro-osmosis, which requires sufficiently narrow pores in the material to be treated is given by (101)

$$\frac{k_E}{k} \geq 10 \quad [\text{cm/Volt}] \quad (\text{F25})$$

Schaad and Haefeli (253) found for silt-sand

$$\frac{k_E}{k} = \frac{8.7 \cdot 10^{-6} \text{ cm}^2/\text{Volt}\cdot\text{sec}}{10^{-7} \text{ cm/sec}} = 87 \text{ cm/sec}$$

Values of k for some building materials are given by Scheidegger (258)

sandstone	$5 : 10^{-7} - 3 : 10^{-3} \text{ cm/sec}$
limestone	$2 : 10^{-6} - 4 : 10^{-5} \text{ „}$
brick	$4.8 \cdot 10^{-6} - 2.2 \cdot 10^{-4} \text{ „}$

The latter value agrees with $4.8 \cdot 10^{-6}$ quoted by Moraru (207), who gives for sandstone $3 \cdot 10^{-7} - 1 \cdot 10^{-5}$. Unfortunately, no corresponding k_E values could be found in the literature. Moraru (207) quotes $k_E = 2.8 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ for red brick which would give if intended per Volt

$$\frac{k_E}{k} = 0.6 - 4.9 \ll 10$$

For sandstone, using Moraru's figure of $1.3 \cdot 10^{-6} - 4.5 \cdot 10^{-6}$ the value is at best

$$\frac{k_E}{k} = 2 - 9$$

Thus the pores in brick and sandstone would be too large to use successfully electro-osmotic drying.

Methods for the measurement of k and k_E have been discussed by Schaad and Haefeli (253) and with quantitative figures for various building materials used in monuments more precise results might be obtained. However, it would seem that in many cases electro-osmosis is not feasible.

Reported successful applications might to some extent also be due to the reduction in the cross-section of the walls obtained by inserting metallic electrodes.

In addition, for effective drying of a wall the moisture content should be below the critical value. Thus bricks should be dried from a saturation value of 25 Vol % to below 6 Vol %, a requirement which is much more severe than in ground consolidation where moisture contents of 50% are tolerable (200).

Wieden (323), using electrodes to ground the wall (passive electro-osmosis) has preferred such methods for drying walls in monuments.

His experiments and data, however, are not convincing and positive results could well be explained by the removal of plaster from the walls before installing the electrodes.

Electro-osmosis seems to have been used successfully in removing salts from mural paintings (224).

Systematic and comparative investigations into the merits of electro-osmotic drying of walls are now being carried out (334) or planned (312).

Depoorter (81) has compared the effect of electro-osmosis and the injection of silicone products based on polymethyl siloxanes and silicone resins as damp-proof courses against rising water. He reported better results with the injection methods.

Similar investigations using continuous moisture content measurements have been announced, aimed also at examining the effect of methods for the prevention of rain penetration (312). Systematic research on moisture distributions in churches in Venice has been reported (202, 203) and announced (312).

5.1.2 Remedies against condensation

High relative humidities inside the building which may cause condensation on cold surfaces can be reduced by ventilation, especially when heating is undesirable. The required ventilation can be calculated from (288)

$$nV = \frac{G}{c_i - c_e} \quad (\text{F26})$$

where G is the total moisture production (kg/hour) in a building of volume V which is completely ventilated n times per hour and where c_i and c_e are the water-vapour concentrations inside and outside the building. It is clear that ventilation is only useful when $c_i > c_e$, otherwise moisture would be introduced from the outside. Condensation is frequently observed in countries where humid warm air enters poorly heated buildings with

thick walls in springtime (155). Surface condensation may be prevented if the walls and roofs have sufficient thermal resistance and heat capacity. Remedies include readily warmed linings (41, 98) and anti-condensation plasters (254). The latter only accumulate condensed moisture and do not prevent condensation. The walls themselves may also be heated to prevent condensation, and ventilation channels are sometimes used (200).

In modern building practice vapour barriers on the inner side of the building, such as aluminium foils and bitumen papers, are used to prevent interstitial condensation (92, 131).

In monuments, where such remedies are only possible when the walls are not covered with murals (38), when rising and infiltrating water have been eliminated and when the temperatures inside the building are higher than outside throughout the year. Frequently all four conditions are not fulfilled. In such cases, only measurements over a longer period of time can provide clues for the best remedies.

5.1.3 *Drying by means of heating*

The implications of installing heating systems in monuments have recently received some attention. Damage caused by various heating systems to organs has been discussed by Supper (287). In an important article Schlieder (259) has published measurements of temperature and relative humidity in German churches before and during the operation of heating systems. Schlieder has suggested the sole use of heating systems which can be well controlled and which heat continuously with a maximum room temperature of 16°C. He has also criticized the drying of walls in churches which are later to be heated. In such cases the walls, whose moisture content has become less than the critical moisture content, are unable to release humidity when the relative humidity in the building decreases. Schlieder has found that in churches with dry walls, the relative humidity inside rapidly followed changes outside and that heating to 20°C caused a drop in relative humidity to 40%.

Powerful humidifying equipment is required to protect organs, wooden sculpture, panel paintings, etc. in such cases. Schlieder has suggested that in many cases an efficient system of gutters and pipes may decrease the presence of efflorescence in the lower parts of the walls. Clearly more systematic investigations are needed into the climatology of monuments.

Drying of walls by increased evaporation (heating) should be applied at the outer surface when murals or plasters are to be preserved at the inner surface, because otherwise soluble salts will be transported to the inside, promoting subsequent deterioration by hydration of crystallized salts (cf. section 2). Although drying from the front at least two metres below the mural by propane/butane gas jets has been considered safe enough (202), the application of infrared heat from the rear has proved to be more effective in preserving Florentine frescoes (330).

When heating from the rear was impossible, it was found that projecting heat from the front through plastic sheeting, sealed onto the mural at the edges, prevented the formation of efflorescence (330).

5.1.4 Remedies against various other sources of moisture

Infiltration of water from above may be prevented by regular maintenance of roofs, gutters, windows, etc.

Water penetration through the wall may be prevented by careful maintenance of the mortar joints (134, 276). Mechanical removal of mortar in joints before rejoining often produces damage to the brick or stone. This may lead to increased water penetration through the stone.

Rejoining of masonry in the preservation of monuments is frequently executed with lime mortars. The proper sand/lime mixtures should then be used, taking into account the optimal grain size distributions (cf. section 2.3.4). Various additives are reported to improve the qualities of such mortar (117). Plasters require similar precautions. The application of water-repellents (cf. section 5.3.5) may contribute to the prevention of rain penetration. In cavity walls mortar may form moisture-bridges (288). A careful execution of the masonry is thus important.

5.2 Cleaning

The removal of dirt is a surface chemical process. In the contact between a soiled body and the cleansing liquid, the surface tension of the latter will determine whether or not cleaning is possible. If the surface tension of the liquid is high with regard to the solid, the liquid forms spherical drops and a minimum contact between the two phases is observed, e.g. water on a fatty surface. On the other hand, a low surface tension of a liquid relative to a solid causes maximum wetting of the latter, e.g. water on clean metal (18, 218). The rule then is to apply to a soiled body a cleansing liquid that has a lower surface tension than the dirt it must remove. Water or water-solutions clean dirt which contains debris of metals, glass, ceramics, metal oxides, silicates and most minerals. Oils, fats and other organic deposits are cleaned with organic solvents (292).

5.2.1. Pure water

Pure water has been used to clean buildings (190, 232) in applications that involve spraying from a series of fine nozzles moved up and down against the walls (from 1 to 3 days), water jets with a pressure from 4 kg/cm² to 14 kg/cm² (from 4 hours to 3 days) or running water along the walls (for about a week). During all these treatments the water-soluble constituents of the dirt were removed, while the remainder swelled and afterwards was removed by brushing. Mechanical removal of insoluble dirt is, however, rarely satisfactory and an increase in the wetting of the soiled surface is sometimes attempted through addition of surfactants.

5.2.2 *Surfactants*

These chemicals are long-chain hydrocarbons with polar groups and are soluble in oil as well as in water. Accordingly, they are adsorbed at the oil-water interface; the hydrocarbon chain being projected into the oil phase and the polar group attached to the water phase. They thus decrease the interfacial tension. As a result, one of the phases spreads over the other one. On account of their polar groups the surfactants are classified as: anionic, non-ionic and cationic. The cationic surfactants are readily adsorbed on stone and ceramics (moist inorganic building materials are usually negatively charged) so that they do not contribute to the removal of dirt from these materials. The anionic surfactants are more suitable, but they may react with limestone or dolomite and form insoluble calcium- and magnesium-soaps which would rather solidify the dirt than help in removing it. The non-ionic detergents do not have the above disadvantages and in addition have a greater wetting capacity than the other surfactants (218).

Surfactants having a long hydrocarbon chain are good emulsifiers for oil and grease. Surfactants with a comparatively short chain (8 carbon-atoms) are good wetting agents (279). The composition of the dirt deposit therefore determines the choice of surfactant. Experiments have shown (286) that hexametaphosphate is effective in swelling the carbon deposits, that alkylbenzenesulfonate is good for cleaning stone in general and that dimethylamylbenzylammonium was effective in removing dirt on limestone.

5.2.3 *Sand blasting*

Jets of a water-sand mixture are very efficient in removing scale and dirt from limestone (190, 222), but are also used on other building materials (sandstone, mortar, bricks, metals). The pressure of the water-sand jet usually varies from 1 to 3 kg/cm², and at a distance of 30 cm from the wall, a surface layer of 0.2-0.6 mm thick is removed after 15 sec. However, non-homogeneous walls are eroded in accordance with the different hardnesses of the materials of which they consist (the mortar pattern will stick out from a brick wall; igneous stones will show a protruding profile next to sedimentary stones, bricks, etc.). Sculptures submitted to a water-sand jet lose the sharpness of their contour (190). Sand blast cleaning of marble plates stained by rust or copper compounds is sometimes recommended but it requires careful application. Iron-free sea sand or other unpolluted abrasives should be used for this purpose and the pressure should not exceed 2.7 kg, the nozzle of the hose being kept at least 7 cm from the stone (2). However, this procedure may be rather dangerous even when carried out with utmost precaution. Rubbing off rust stains from a marble surface with water and abrasives is recommended by Weber (317). Rust spots caused by the oxidation of pyrite in marble are often very deep and therefore impossible to remove entirely. Carrara marble is particularly vulnerable to pyrite discoloration of this kind (317).

5.2.4 *Steam cleaning*

Steam cleaning is another variety of dirt removal from stone by means of pure water. The steam is generated in a boiler and is directed to the stone surface via a pipe and a nozzle with a diameter of 1 to 1.6 cm. The steam pressure is 68 kg (for old stone) and about 56 kg (for new stone) (89). Condensation of steam on the pipe interior, friction and expansion after emerging from the jet reduces the pressure of the steam so that it is not more than 0.5 kg/cm² at the point of contact with the stone (315). Steam cleaning is considered to be the only method so far available which allows the removal of dirt from very irregular surfaces without any mechanical damage. Polluted stone surfaces other than limestone require, for effective steam-cleaning, previous treatment with certain chemicals in order to soften the grime (89, 315). Caustic soda should be avoided as a medium for dirt-softening because it usually causes efflorescence, but a mixture containing complex phosphates (Na₆P₆O₁₈; Na₄P₂O₇; Na₅P₃O₁₀), potassium-silicate and some anionic soap can be a good substitute (218). Diluted phosphoric acid (5% in water) may also be employed. Steam cleaned brickwork does not develop whitish or greyish bloom, nor is there any disturbance of the mortar joints (315). For effective steam cleaning, marble is first covered with a slurry of an alkaline cleaner for about 15 minutes and then subjected to the steam-jet. Afterwards a thorough rinsing of the cleaner or loosened dirt is indispensable (2). Steam cleaning, however, imparts to some marbles an unnatural appearance and afterwards they may be more easily polluted (130). According to Przedpetski (231), for an efficient steam cleaning the pressure of the steam when emerging from the nozzle should be 1.5-2 atm and the duration of the treatment should be from 6 to 10 minutes per m².

5.2.5 *Criticism of cleaning with water*

Cleaning methods employing water may be deleterious to various building materials. The amount of water absorbed by these materials and the time needed for each of them to become wetted thoroughly vary greatly. Bricks, for instance, absorb about 3 times as much as lime-sand stone. Water penetrates into them rapidly and soon the core and the surface of a brick are equally wet. But once the contact with water is ended the absorbed water evaporates with equal rapidity. With the sedimentary stones, however, this is quite different as in them the water permeates slowly (on account of the random distribution of large and narrow pores, while the rate of penetration is determined by the narrow ones) and the water also evaporates slowly (92). Walls of buildings constructed with materials other than bricks will therefore retain, after water-cleaning and particularly steam cleaning, most of the water they have absorbed during treatment and dampness on the inside walls of the building, with efflorescence, discolorations and plaster exfoliation, may appear.

5.2.6 *Chemical cleaning*

The drawbacks of cleaning with water are reduced by using water-soluble chemicals which decompose the layers of dirt. To diminish the penetration of water into the cleaned material still more, the chemicals are mixed with water and an absorbent powder into a paste which absorbs the dirt after application. Absorbent powders should have a very large specific surface and a fine porous structure (113, 319). Starch, chalk, talc (talcum), corn meal, flour (205), magnesia (319) or magnesium silicate are common absorbent powders. The water solution of the chemicals used for cleaning are either acid or alkaline and the pastes made with them are normally applied as a 3 mm thick layer on the surface to be cleaned (319). The concentration of the chemicals should be mild rather than strong and cleaning should be done gradually (130). Cleaning must always be carried out from below upwards (26). A recommended practice in removing stains and spots is first to wet them with water, thus preventing a contact with too high a concentration of a cleaning chemical and to obstruct as far as possible the spreading of the stain during cleaning (205). Areas treated with chemicals must afterwards be patiently rinsed with water (130).

5.2.6.1 *Alkaline cleaners*

The most common alkaline cleaners contain caustic soda and these are of no use as far as inorganic building materials are concerned because after cleaning they produce efflorescence and surface deterioration (190, 315). Ammonia, however, with whiting makes a good poultice for the removal of oil or grease stains on marble (107).

Stains or efflorescence of iron compounds on stone have been removed by applying to them cotton-wool pads soaked in a 15% solution of sodium hydrogen citrate ($\text{NaC}_6\text{O}_7\text{H}_7$) in water. The pads are pressed down with glass plates (to hinder a rapid evaporation) and upon these plates are placed weights to promote better contact between stains and cotton-wool fibres. Addition of some glycerine to the solution of $\text{NaC}_6\text{O}_7\text{H}_7$ is helpful as it keeps the pads damp for a longer time. Every 3-4 days, the pads are soaked again and the treatment is repeated until a satisfactory removal of the stains is achieved. This procedure is suitable for stains without a defined periphery. Stains with a sharp outline are cleaned as follows:

After rinsing the stain with water, a cotton-wool pad soaked in a 15% solution of $\text{NaC}_6\text{O}_7\text{H}_7$ is placed upon it and the latter is covered with a paste (ground chalk and water). On this paste a thin layer of crystalline sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) is powdered and left thus for one hour. Surfaces treated accordingly may appear slightly etched and may need some polishing (231). A paste containing 1 part sodium citrate, 6 parts water, 7 parts glycerine and chalk has been recommended as a formula especially suitable for marble stained with iron salts. Applied thickly and left on the stain for a couple of days it also will remove rust from marble. Very dark iron stains should according to

Edel be wetted with sodium citrate solution (1:6) prior to this treatment (90). Another method of cleaning rust stains is to cover them with a 10 mm thick layer of a paste containing 15% potassium sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), 35% water and 50% glycerine, mixed with chalk in the ratio 1:4. The treatment lasts for 3 to 4 days and may be repeated. Best results have been attained if a 2% solution of potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) is added to the mixture (231).

Discolorations caused by copper compounds have also been removed by alkaline pastes containing potassium cyanide (90). Because potassium cyanide is poisonous, such stains may also be removed by repeated applications of a poultice made of the following chemicals: 9 parts Komplexon III solution (sodium salt of ethylenediaminetetra-acetic acid, 37.2 g per litre of water), 1 part buffer solution of pH=10 (70 g ammonium chloride dissolved in 570 ml concentrated ammonia and then water added to make the volume 1 litre) (93) and sufficient absorbent powder to form a paste.

Stains of copper compounds have likewise been cleaned with the following paste: ammonium chloride and talcum in the ratio 1:4 are mixed and then stirred into a paste with ammonia. Instead of ammonium chloride, aluminium hydroxide would also be effective (231).

5.2.6.2 Acid cleaners

The use of acid in stone cleaning is not to be recommended because acid cleaners dissolve limestone and penetrate deeply into sandstone, where they are retained for many years (97, 315). Cleaning with hydrofluoric acid is occasionally carried out and Sneyers (277) reported cleaning of stones darkened by soot, silica and gypsum with a 3-10% solution of hydrofluoric acid which was continued for 20-30 min. However, cleaning with hydrofluoric acid causes discoloration on stones as this acid reacts with iron compounds which are usually brown and forms with them colourless complex iron fluorides (315). After having investigated several commercial acid cleaners containing ammonium hydrogen fluoride (NH_4HF_2), Mamillan (190), however, reported with regard to limestone that:

1. no change in surface hardness before or after cleaning, was observed;
2. the treated surface remained permeable;
3. the rain permeability was equal for a chemically cleaned and a water-cleaned surface;
4. the evaporation after chemical cleaning was not obstructed;
5. limestone cleaned with a NH_4HF_2 containing mixture remained vulnerable to sulfuric acid aerosols from the industrial atmosphere;
6. some efflorescence was observed, and
7. the chemical cleaning did not discolour limestone more than cleaning with water.

While cleaners based on NH_4HF_2 may be considered reliable for limestone, sandstones and igneous stones may develop a whitish discolora-

tion due to a partial dissolution of certain silicates and the subsequent precipitation of colloidal silicic acid (235).

Hydrofluoric acid has been proposed for the cleaning of iron stains (205) but sodium fluoride seems to be more effective (31). Rust stains from marble can be satisfactorily cleaned by phosphoric acid followed by rinsing with ammonia for neutralization (317).

5.2.6.3 *Organic cleaners*

In removing oil and grease from a soiled surface, the surface tension of the liquid-displacing agent must be lower than the surface tension of the 'oil' to be displaced (the larger the difference in surface tension the better the cleaning). The displacing agent must, in addition, be sufficiently soluble in the oil or grease. Perfluorocarbons (1-chloroperfluorononane) and dimethyl-silicone derivatives vigorously replace oil, but aliphatic hydrocarbons such as n-hexane and n-decane are also strong replacing agents (18).

It has been reported that dirt consisting of grease and water-soluble matter is best cleaned with organic solvent/water emulsions. Two parts of an aliphatic hydrocarbon (Stoddard solvent, flash point 104°F) and one part of a chlorinated solvent (methyl chloroform) when emulsified with a non-ionic surfactant (1%) with water (65%) will form an emulsion which is capable of cleaning very obstinate greasy residues (18). The emulsion may be applied as a spray or with an adsorbent powder. Oil stains on marble are cleaned by covering them with cotton-wool pads soaked before use in a liquid of the following composition: 6 parts alcohol, 3 parts butyl acetate and 1 part amyl acetate (26). Cotton-wool pads soaked in a mixture of equal parts acetone and amyl acetate ($\text{CH}_3\text{COO.C}_5\text{H}_{11}$) also clean oily stains well. To reduce evaporation of these solvents, the pads should be pressed with glass-plates, and the treatment should be repeated at least 3 to 4 times. If after that a stain is not entirely removed, its cleaning is carried further with a poultice made of: (in equal parts) chalk, chloride of lime and marble powder, all stirred into a paste with benzene. However, this treatment may etch the cleaned surface (231). Old greasy residues have been removed by applying on them a 10 mm thick layer of asbestos fibres soaked in amyloctane. The asbestos pad is then covered with a marble plate upon which a hot steel plate is placed (increase in temperature promotes the dissolving of grease) (231).

Stains of organic origin have been bleached either with a 3% hydrogen peroxide solution (107, 205) or (for obstinate stains) with the same solution to which sodium perborate—1 teaspoon in 1 l 3% hydrogen peroxide—has been added (205). Marbles have also been bleached by 0.5% potassium permanganate. This solution is painted on the contaminated area, and just before complete drying, the area is wetted with ammonia. Directly after that follows a treatment with sodium hydro-sulphite (90).

5.2.7 *Cleaning of various building materials, statues and murals*

Efflorescence on buildings or statues is best brushed off when it is dry (37). Metal brushes should be avoided because of a risk of discoloration due to residual metal particles. Wetting of the surface in order to facilitate cleaning is not to be recommended as the presence of water will simply regenerate the chemical and physical processes responsible for efflorescence (210).

Cleaning dirt from murals has been attempted with breadcrumbs. Wetting the mural with wine spirit prior to rubbing has been reported as making the cleaning easier (65). An erasing rubber is found to be a better cleaner than breadcrumbs, because the elasticity and porosity of the eraser are superior in removing or absorbing dirt. Lightly wetted surfaces are easier to clean with an eraser as a film of water between mural and eraser serves as a lubricant as well as a dirt-mobilizer. Dark rings developed on murals during previous cleaning with organic solvents may also be removed with an eraser (306). Various other techniques and the corresponding materials needed for the cleaning of murals have been reviewed by Philippot and Mora (224).

Some remarks on cleaning of murals in India are to be found in publications by Bhardwaj (39).

Granite polluted by urban atmosphere has been cleaned in London by energetically scrubbing it with bristle brushes whilst applying at the same time water containing a non-ionic detergent, e.g. an ethylene oxide condensate. Tarry deposits were softened with an emulsion of 9 parts of carbon tetra-chloride, 1 part of benzine and 1% aqueous solution of the detergent. Scrubbing with this emulsion was carried out until the granite became reasonably clean (54).

Marble monuments and statues are cleaned more safely with hard water than with distilled water as the latter can dissolve some of the marble due to absorption of carbon dioxide from the air. But, if distilled water must be used for cleaning, a small amount of waterglass or soap should be added (177).

Plant stains on marble have been removed from marble statues with methylene chloride and ethyl alcohol, while ordinary dirt soiling the statue has been covered with a paste of magnesium silicate and de-ionized water. The dirt was thus drawn out into the paste and subsequently the latter was brushed off (121). Removal of soot and smoke from carved areas has also been carried out with alcoholic ammonia (272).

Marble busts have been cleaned with a weak decoction of soap-nut to which a few drops of ammonia are added prior to use. The bust is then washed with water and dried with a soft piece of leather. The white colour of soiled marble may be recovered by applying to it a coating containing waterglass, zinc oxide and kaolin. After drying, this coating flakes off and the dirt absorbed by it is removed from the marble.

Oil-stains on marble are first impregnated with petroleum and then covered with a layer of pipe-clay. After oil and petroleum have been extracted from the stone and transferred to the clay, the latter is re-

moved. Obstinate stains may require several impregnations and extractions before appearing satisfactorily clean. Soft, porous marble showing signs of fading can be renewed by dabbing its surface with a cotton-wool pad previously soaked in a mixture of alcohol and gasoline. This is followed by the application of a thin coating of a paste containing hydrogen peroxide and fine kaolin. After drying, the coating is brushed off (177). Marble discoloured by tar or other similar products can be cleaned with a mixture of butter and whiting diluted with a suitable solvent, e.g., alcohol, acetone, toluene, etc. The mixture is rubbed in the stone, allowed to mobilized the tarry matter and then extracted by a layer of pipe clay (as already described). This treatment reportedly yields good results if repeated several times. The dark discoloration left after such cleaning may be removed by bleaching with pastes consisting of kaolin and either hydrogen peroxide or hot potassium permanganate (60°C) or chloride of lime (261).

Soiled or weathered surfaces of natural stones have been cleaned with diluted fluorosilicate solutions, e.g., zinc fluorosilicate. After the mechanical removal of the loosely held dirt and exfoliations the surface is scrubbed with a bristle brush that is dipped regularly into the fluorosilicate solution. Washing with pure water must follow. To prevent the appearance of stains from fluorosilicates that have not penetrated into the stone, the excess water should be taken away with a piece of cloth or a sponge (243).

Algae, lichens and moss on buildings or statues have been removed by scrubbing with a 2% aqueous solution of zinc fluorosilicate (228). Mould growths have been treated in a similar way and fungicidal solutions other than fluorosilicates, i.e. a hot 1% aqueous solution of soda, a 1% aqueous solution of chloride of lime or a 0.5% aqueous solution of a chlorinated K-Na-waterglass (Trosilinflüssig/BAYER) may be used with similar effects (210). Moreover, copper naphthenate in an organic solvent is also a good fungicide (272). However, as biological growth is closely related with the presence of moisture, a successful cleaning by no means implies a permanent result. The reappearance of algae, lichens and moss depend on moisture supply and only the control or elimination of this supply determines whether or for how long the building or statue will remain disinfected. The same holds for efflorescence.

5.3 Consolidation and protection

Disintegrating building materials have been treated with both inorganic and organic preservatives but without much success (183, 236). The difficulty is the insufficient penetration of the consolidating fluids into the porous materials. In most cases, these fluids are either real or colloidal solutions, and having entered the stone they must react with some other agent introduced later or lose their solvents through evaporation in order to produce a deposit that will cement together the loose particles of the stone. However, real solutions tend to precipitate at the evaporation front, whereas colloidal dispersions are broken down soon

after the contact of their solid phase with the walls of a pore or with electrolytic contaminants (flocculation) (235). In addition, due to their comparatively large particles, colloids have no access to micropores, a real drawback wherever the consolidation of crumbling stone is concerned. On the other hand, polar solvents used to dissolve organic preservatives are preferentially adsorbed at the stone boundary and this leads to premature precipitation of the dissolved adhesive. As a result, only a superficial consolidation is achieved in either case. Such external hardening of a porous body is useless as it hinders the evaporation of moisture from the interior and also attracts dust and dirt. At the few places at which water can still evaporate, efflorescence of salts may lead to the development of blisters and exfoliation. Oil, wax and natural or synthetic resin coatings on stone are particularly dangerous in this respect (151). This, however, does not hold for sculptures or decorations kept indoors as they are usually dry. Hence waxing after previous polishing with putty powder (3 parts tin oxide, 1 part oxalic acid) has been recommended for marble kept indoors (107).

Since the penetration of a fluid into a porous body is inversely proportional to its viscosity, preservative solutions must be very dilute and applied many times before a satisfactory result is attained. In general however such treatments appear, after some years, to be either complete failures or to have been unable to decrease the deterioration (66, 236, 284, 315). For these reasons various attempts to consolidate stones with lime-water, lime-mixtures (291), barium hydrate (181, 315), metallic salts of the fatty acids, shellac solutions, vegetable oils, oil (metallic soaps, waxes, gum resins)-in-water suspensions etc. (315) are only briefly discussed here.

Weathering of stone is often restricted by treatment with organic consolidants. Although the depth of penetration of such chemicals in the stone is quite limited and the preservation doubtful, a number of waxes and resins are constantly employed in the practice of protecting decayed stone. The granite of Cleopatra's Needle in London, e.g., was impregnated with a paraffin wax of low melting point, (about 50°C). A 10% solution of this wax in white spirit was applied twice on the structure; the solvent was allowed to evaporate and the surface was heated with a blowlamp to melt the wax into the fissures (54). Sculptural elements, showing advanced deterioration caused by the presence of salts, were consolidated by a mixture of 2 parts of beeswax and 8 parts of paraffin wax. The molten wax mixture was poured drop by drop over the stone which was kept hot by being constantly heated with an infrared lamp (278). For the consolidation of murals on dry walls Church (65) has recommended paraffin wax (or ceresin) solution in white spirit. For murals on a damp or saline background however, a hot spray of about 5% of pure gelatin, dissolved in very weak spirit, should be used according to the same author and good results would also be attained if murals, on which damp and saline matters are present, are treated with a 7% solution of casein in very dilute ammonia, containing 1% of glycerine.

Fissures in masonry can be filled by injecting into them liquid cement. Portland-blast-furnace-slag cement is preferred to other cements as it is capable of retaining more water and moreover injecting liquids made from it are less viscous. Its poor frost resistance is improved by the addition of powdered bricks or chalk. Fissures in the masonry are well wetted and then depending on their width are treated in one of the following ways:

1. Fissures 1.5 to 2 mm wide can be injected with a liquid cement to which 0.02 to 0.25% of a retardant, e.g. a hydrophilic alkali sulphite and 10% of a plasticizer e.g. polyvinyl acetate emulsion (59%) are added.
2. Fissures 3 to 10 mm wide can be injected with a liquid cement containing sodium abietate surfactant and a filler, e.g. powdered bricks or chalk.
3. Deep fissures can be injected with a liquid cement containing 20% powdered brick and 0.02 to 0.03% of sodium abietate or 10% polyvinyl acetate emulsion.
4. Liquid cement containing 0.2 to 0.3% of sodium abietate is suitable for the consolidation of building elements (columns, parapets, etc.) that must withstand rapid freezing. With respect to the type of fissure the ratio water to cement varies from 1:6 to 1:0.7.

In practice the point of injection is marked with a lump of gypsum into which an opening is perforated for the muzzle of the injecting device. The liquid cement is injected via this aperture into the fissure under pressure of 0.5 to 1.0 atm. But in some cases the pressure employed may reach 4 atm. Repeating injecting is carried out at intervals of 20 to 30 min. (335).

Water-repellent mortar may be prepared by adding 0.3-0.5% by weight of calcium stearate to the dry mix prior to mixing. An amount greater than 0.5% lowers the strength of the rendering (171).

5.3.1 *Sodium and potassium silicates*

These chemicals are commercially available as liquids ($\text{Na}_2\text{O}\cdot\text{SiO}_2$, sp gr 1.34-1.38; $\text{K}_2\text{O}\cdot\text{SiO}_2$, sp gr 1.26-1.30) (314) and are considered to be silicic acid sols stabilized with alkali hydroxides. Exposed to air, these colloidal dispersions absorb carbon dioxide, which turns the alkali-stabilizers into carbonates and, consequently, silicic acid precipitates as a transparent, soft gel. Stones impregnated with alkali silicates, therefore, would acquire a surface layer of silica gel, and develop efflorescence due to the alkali carbonates. However, if applied from diluted solutions (1 part of commercial silicate, 3 parts of water) on much deteriorated stone fragments, they have been reported to produce a good consolidation (83).

One disadvantage in the deposition of silicic acid under the action of carbon dioxide is that it occurs from the periphery of the treated material inwards, and, owing to the limited access of the gas through the already formed silicic acid gel, remains incomplete. Acidic additives (15-20 wt-% of sodium or potassium fluorosilicates) bring about simulta-

neous bulk deposition of silicic acid, and also immobilize the alkali ions as slightly soluble fluorides (17). The chances for efflorescence are thus reduced but such compositions harden rapidly (after 40 min.) and therefore are more suitable as adhesives than for impregnation. An effective deposition of silicic acid can also be generated by an after-treatment with solutions of alkali chromate, alkali pyrophosphate, or salt solutions of phosphoric, tungstic or pyro-antimonic acid. The latter three acids precipitate the alkali ions as well (314). Pure alkali silicate solutions do not wet stone materials well and after drying produce layers of low elasticity. This can be corrected by the addition of glycerine, alkali soaps, sulphonated oils, fatty alcohol sulphonates or the sulphates of naphthalinic acid (314). Nevertheless the merits of the alkali silicates as stone preservatives are doubtful (236, 256, 257, 315).

5.3.2 Hydrofluoric acid (HF)

Deteriorating limestone can be consolidated with hydrofluoric acid. Reaction between this acid and calcium carbonate produces insoluble calcium fluoride and carbon dioxide. The treatment is best carried out if some surfactant is added to the acid, as in that case the interfacial tension HF/stone is reduced and a better penetration to the core of the stone is claimed (265). Since hydrofluoric acid dissolves quartz, the silicates thus formed serve as adhesives and make this treatment equally suitable for sand-lime stone. After reacting on a stone for about 20 sec., the hydrofluoric acid is supposed to have penetrated deep enough so that by means of a water jet it is possible to remove scales, blisters or other remnants of the corrosion crust (265).

Hydrofluoric acid is however poisonous and dangerous in contact with the skin (247).

5.3.3 Fluorosilicic acid and the fluorosilicates

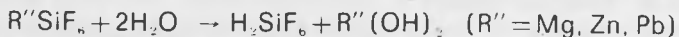
Limestone is converted to calcium fluoride in contact with fluorosilicic acid (H_2SiF_6), but as this acid is about as strong as sulphuric acid (235), the reaction is vigorous and the reaction products tend to crystallize, hence their possible function as adhesives is lost (315). Moreover, the commercially available fluorosilicic acid undergoes partial disintegration to silicon fluoride and hydrofluoric acid, any time the ratio F/Si is larger than 6 (314). The liberated hydrofluoric acid then induces discolorations (the iron compounds are rendered colourless) whereas the remaining products after fluorosilicic acid treatment are reported (315) to produce patches of efflorescence. Applied on sandstone fluorosilicic acid slowly dissolves the sand grains and the silica of the binding material, which leads to the development of a hard, dense crust that will eventually scale off (315).

Better results in stone consolidation have been attained with fluorosilicates (80). Many of these salts of fluorosilicic acid are commercially available as solutions. For stone preservation, magnesium fluorosilicate ($MgSiF_6$, pH=2), zinc fluorosilicate ($ZnSiF_6$, pH=2.5), aluminium fluoro-

silicate ($\text{Al}_2(\text{SiF}_6)_3$, $\text{pH}=1$) and lead fluorosilicate (PbSiF_6 , $\text{pH}=1$) are important. The latter two, due to their considerable acidity, cause effervescence on limestone (314). Each of these chemicals may be used for a specific purpose, e.g. aluminium fluorosilicate neutralizes well fresh plaster; magnesium fluorosilicates hardens old plaster and limestone; lead fluorosilicate protects a treated surface against atmospheric pollutants, sea-water and humus; while zinc fluorosilicate is most effective in the hardening of concrete (123). Limestone, treated with either aluminium-, magnesium- or zinc fluorosilicate, has shown a remarkable resistance to frost damage (177). Solutions with especially adjusted properties containing various fluorosilicates are also available (314). Because they react with calcium carbonate:



($\text{Me}=\text{Mg, Zn, Pb}$) the fluorosilicates are effective only if applied to limestone or other calcareous materials (314). However, the carbon dioxide effervescence renders the deposited products spongy and the tendency of calcium fluoride to take on a crystalline form weakens the coherence of the stone instead of strengthening it (315). The initial hardening of a fluorosilicated limestone should therefore be evaluated with some reserve, as in many cases deterioration of the stone under the hard crust has been observed to continue (315). In discussing the effect of fluorosilicates on calcareous building materials, Rodt (243) has suggested that in aqueous solutions they hydrolyze according to the equation:



The fluorosilicic acid formed, reacts with the insoluble carbonates of the stone and as a result there is either evolution of carbon dioxide or formation of a new insoluble carbonate with the heavy metal of the fluorosilicate. As the reaction products besides carbonates also include the formation of fluorides and silicates with various degrees of hydration, it is important, according to Rodt, to select a fluorosilicate which, on reacting upon calcareous stone, will produce insoluble compounds. This is the case with magnesium fluorosilicate and in a lesser degree with zinc fluorosilicate, as the hydrated zinc fluoride is soluble in water. This warrants the use of magnesium fluorosilicate for the hardening of mortar, concrete and old plaster.

Sandstone must be impregnated with a dilute alkali silicate solution (with all risks of efflorescence) prior to fluorosilicate treatment (284, 314, 315).

For a good consolidation, the stone surface must be soaked (e.g. by brushing) several times with a fluorosilicate solution of increasing concentration (from 10% to 30%), allowing sufficient time after each application for the above reactions to take place (315). A mixture of fluorosilicates ('FLURALSIL-M' Firma Desowag Chemie-GmbH, Düsseldorf) brushed on stone statues two times as a 10% solution followed by three

brushings as a 20% solution (with 8 days interval after each application) has been reported to produce a satisfactory consolidation (80). Lead fluorosilicate is recommended for use on limestone or on sandstone which has previously been treated with a dilute solution of potassium silicate and the trade mark TROPLEXIN (Firma Willi Schmalstieg KG, Adolfstrasse 10, Hannover), a fluorosilicate solution of unknown composition, has been used for this purpose (284). This fluorosilicate produces a hardened zone on the stone but does not consolidate its interior (284). Good results in deep penetration of magnesium fluorosilicate into limestone statues or architectural decorations have been reported by Sanpaolesi (261). This author used a reservoir in front of the part to be treated (so that one side of the reservoir is the treated part itself), filled it with the fluorosilicate solution and applied, on the opposite side of the reservoir, suction with a vacuum pump. Another procedure for impregnation of natural building stones uses repeated brushing with 5, 10 or 15% solutions of magnesium fluorosilicate, aluminium fluorosilicate and sodium fluorosilicate allowing 24 hours to pass after each brushing. It is recommended that this treatment be repeated every 8 years (246).

The use of fluorosilicic acid and the fluorosilicates in stone consolidation is at present not very popular on account of the failure of these liquids to achieve a deep penetration. On fresh plasters, where neutralization of the residual alkalinity and superficial hardening is important, they may be applied (123, 314).

5.3.4 *Silicone esters*

The most common silicone ester used in preservation of building materials is ethyl silicate $(C_2H_5)_2SiO_2$, which has some importance as an impregnating and hardening chemical. In contact with water, it decomposes to alcohol and silicic acid gel. For the purpose of rapid precipitation of this gel, some commercial brands of silicon ester are partially hydrolyzed with cyclohexanone, glycol or tetralin so that moisture will deposit from such a solution silicic acid which adheres well on rough surfaces (314). Used as a surface preservative, silicone esters have shown but little influence on the weathering velocity. Poor quality stone treated was damaged by exfoliation but a satisfactory preservation was attained after immersion of the stone fragments in silicone ester (45). Silicone ester and methylethoxysiloxane in the ratio 1:1 dissolved in ethanol have been used to consolidate decaying sandstone. Methylethoxysiloxane also hydrolyzes in stone and produces methylsilicic acid which, apart from its contribution to the stabilization, also renders the stone waterproof. The following compositions have been proposed in the literature (33):

1. For impregnation: 160 ml mixture (1:1) of ethyl silicate and methylethoxysiloxane, 61 ml ethanol to which a few drops of hydrochloric acid have been added.
2. Cement for the substitution of missing stone parts: 250 ml ground sandstone, 112.5 ml liquid of formulation nr 1, and 7 g magnesium oxide.

3. For siringe application: 80 ml mixture (1:1) of ethyl silicate and methylethoxysiloxane, 31 ml ethanol in water acidified with hydrochloric acid in the ratio 15:4:1.3 and 10 ml pure ethanol.

Sculptures and sandstone cleaned with hot water and then dried, have been treated three months later by coating them with ethyl silicate (275). A promising recent material for the consolidation of sandstone is a modified silicone ester which polymerizes after the addition of a catalyst to produce a continuous film of inorganic silica. So far, all varieties of silicone ester deposited silica in the form of an amorphous mass with little or no binding power. The material is delivered as a two-component sandstone consolidator (Sandsteinverfestiger, Th. Goldschmidt A.-G., 43 Essen, W-Germany) of specific gravity 0.96 and viscosity 1.1 cP at 20°C. A mixture of 3 parts of silicone ester and 1 part of catalyst is applied on sandstone, by brushing or immersion, and due to its low viscosity penetrates well. Such a mixture has a 5 day pot-life, after which it solidifies. A mixture suitable for casting in forms, for the sealing of crevices or as an adhesive consists of 1000 cm³ ground sandstone, 28 g magnesium oxide and 450 cm³ sandstone consolidator (3:1). It hardens after 6 to 8 hours at 20°C.

Stabilization of weathered sandstone with ethyl silicate has recently been carried out according to a procedure which instead of ethyl silicate only, combines this chemical with silicones, i.e. methyltriethoxysilane (262). The advantage of the method is that besides stabilization the treated stone becomes water-repellent, a property which is expected to retard weathering considerably. In practice the stone object (relief, statue, ornament, etc.) is first cleaned from efflorescence, dirt or old protective coatings and then either immersed in a bath or imbibed by spraying or brushing. In any of these applications a liquid mixture of the following composition is used: 100 parts of ethyl silicate, 100 parts of methyltriethoxysilane, 70 parts of 80% ethyl alcohol and 1 part of hydrochloric acid (catalyst).

During treatment the stone should not be exposed to direct sunlight as this will increase the evaporation of alcohol and therefore interfere with the curing of the consolidating liquid. Shiny layers appearing on the stone directly after impregnation can be removed by rubbing with pads soaked in alcohol; after polymerization of the preservative mixture, however, such layers have to be taken away mechanically.

5.3.5 Silicones

Two kinds of silicones are used on masonry. The most common is a silicone resin with reactive hydroxyl and alkoxy groups which is applied on building stones from solutions with organic solvents by brushing or spraying. The resin cures by atmospheric hydrolysis of the reactive group and condensation of some of the intermediate reaction products (24). The cured resin then reacts either with hydroxyl groups or adsorbed water on the mineral surface and leads to a primary valence bond between resin

and material. Thus, thin, highly water-repellent resin films on masonry are produced (206).

The silicone resins (85, 266, 274, 280, 327) possess good resistance to heat, oxidation, and weathering. They are formed by cross-linking one of a number of available silicone fluids. The polymeric molecules of the silicone fluid normally have free hydroxyl groups, which interact in the course of polymerization to produce cross-linking by oxygen bridges. Such reactions may be induced by raising the temperature and possibly by the use of catalysts, e.g. zinc naphthenate or triethanolamine. The ratio of methyl groups to silicon is a measure of the amount of cross-linkage and $\text{CH}_3\text{:Si}$ ratios 1:2, 1:3, 1:4 and 1:5 give colourless solids with densities decreasing from 1.20 to 1.06. The time required for hardening at 100°C increases from 2 to 24 hr. The ethyl-group attached to silicon in place of the methyl-group in a siloxane-chain produces a softer, more soluble and slower-curing product. Substitution of a phenyl-group for a methyl-group leads to brittle and weak resins. By attaching both alkyl and phenyl-groups to the same silicon atom, or by co-condensing alkyl and phenyl-silicons to make a co-polymer, resins have been produced with advantageous intermediate properties. Small additions of silicons to other polymers promote de-aeration of these products, and increase their to weathering resistance.

The second type of silicones is a sodium silicate solution in water. Hydrolysis of this salt brings about a reaction, and consequently binding, between silicate and the mineral surface. Upon evaporation of the water, a water-repellent film is formed (206). Sodium silicate renders limestone and marble effectively water-repellent, while the silicone resins give poor results with these materials (24). However, if previously treated with a 40% solution of fluorosilicate, alkali silicate or silicone ester, silicone resins may render limestone water-repellent (35). The introduction of silicium containing materials in limestone is necessary, because according to Gregg (113) the silicones react chemically with silicon atoms in the surface, while with materials lacking silicates only a physical adsorption occurs. Limestone treated with sodium methylsilicate solution (4% in water) caused an effective water-repellency (179), while a 3% solution of sodium methylsilicate was found efficient in making sandstone hydrophobic (23). In addition, brick masonry is occasionally made water-repellent with sodium methylsilicate because only one treatment is needed for satisfactory results (134). Silicone resins must be applied several times on such masonry. As silicones are very sensitive to moisture and alkaline reactions, fresh masonry work should be allowed at least to dry and decrease its alkalinity from three weeks (134) to one year (35) before silicone treatment. Building bricks of great refractoriness are unsuitable for silicone treatment because penetration into them is minimal and the silicone layer remaining on the surface attracts dust and causes discolorations.

Masonry heated by the sun should be cooled before siliconating because otherwise the vapour of the quickly evaporating solvent fills the pores and creates a pressure which hinders a deep penetration of

the silicones. In cool walls, however, the silicones can penetrate as deep as 5 to 10 mm. Any crevice on masonry must be sealed before water-repellent treatment as otherwise the extremely thin silicone film on the walls of the pores will break at such openings and thus diminish the value of the treatment (134). Silicone layers are not sufficiently repellent to water striking them with a certain pressure (35). A wall treated with silicones, for instance, when exposed to rain carried by a wind of 50 km/h, will allow water penetration through all pores with a diameter larger than 0.05 mm (91).

Considering the chemically inert character of the silicone films once absorbed by a material, the water-repellency induced by them may last well (8 to 10 years) (35). However, the permanence of water-repellency due to a silicone treatment depends on the local air pollution. Walls of siliconated buildings on the sea coast exposed to the sea have been reported to lose their water-repellency in two years, while the rest of the walls of the same building that were not directly exposed to the sea retained their water-repellency for about 10 years (35). The permeability of silicone films to water vapour is believed to be an additional advantage (24) as this diminishes the moisture content of the treated materials by both reducing access of water and allowing evaporation of water already present in their interior. However, discoloration due to crystallization of salts behind the water-repellent zone (35, 111), and scaling caused by their hydration (45) have been reported. In addition protection against frost and pollution, thought to be the consequence of silicone treatment, has not been observed in practice (35, 45, 163). An exception to this is limestone which, when treated with sodium silicate, remains clean for longer compared with untreated limestone, probably because the water-repellency in such cases makes the contaminated rain drops roll down, while a film of silicone resin remains somewhat sticky. This is, however, of little importance as the alkaline content of the silicate produces an increased erosion through efflorescence (45). The superior resistance to weathering of the silicone resins was used by Marchesini (194) for consolidating decayed marble statues from Venice. A statue was placed in an autoclave, which was procured with openings and outlets for de-ionized water, hot air, silicone resin considerably diluted with organic solvents, nitrogen and a connection to a vacuum pump. After the statue was deposited in the autoclave, de-ionized water was run through it until all soluble salts in the marble were dissolved and removed. The water was replaced by hot air, in order to dry the object, and when this was achieved the air was evacuated by a vacuum pump; the pressure in the autoclave being reduced to 0.01 Torr. Using the suction created by the vacuum, silicone resin was drawn in the autoclave, and to ensure deep penetration of the resin into the marble, nitrogen gas was also pumped into the autoclave, to create an overpressure. This was followed by the removal of excess resin and solvent, and heating with hot air, in order to initiate polymerization of the silicone resin. Finally the object was taken out of the autoclave and its surface retouched. Marchesini claims that penetra-

tion of the polymerized resin in the marble statue was about 5 cm deep. An additional advantage is that all stages of the treatment take place in the autoclave, making accidents unlikely. Marchesini's method for impregnating marble sculptures with silicone resins has received encouraging publicity (10, 11).

Silicone resins were also used to render the gypsum containing ground, on which mural paintings in the Ghur-Emir (Soviet Central Asia) had been executed, water-repellent. For this purpose the murals were sprayed with 6% of polymethylphenylsiloxane in xylene. As the silicone resins are poor adhesives, stabilization of the exfoliating areas was done with an aqueous dispersion of 1% of 2-ethyl hexylacrylate. This was carried out on already siliconized and therefore water-repellent murals, but the adherence of the flaking painting to the background was satisfactory. Casein glue rests, used in previous restoration of the same murals, were softened and together with the background of the mural were simultaneously stabilized with water solutions of the co-polymer of polyvinyl alcohol and polyacrylamide (135).

Stones, limestone in particular, are optically darkened by the silicone resins. Sodium silicate also darkens limestone but to a lesser degree (35).

5.3.6 *Synthetic monomers*

Objects made of unbaked clay or other deteriorating porous materials (stone, wood) can be stabilized by impregnation with synthetic monomers, which are subsequently polymerized. In the Soviet Union, for instance, this has been done with methyl methacrylate. Inhibitor was removed from the commercially available monomer by repeated washing with 1% sodium hydroxide, and drying with dehydrated sodium sulphate. Then 9 parts of the cleaned monomer were mixed with 1 part of xylene. To 983 ml of this mixture, 20 g of a catalyst (benzoyl peroxide) was added and the solution was poured in drops over the object which had been placed in a vacuum exsiccator from which the air had been previously evacuated. Complete impregnation was accomplished in 5-10 min. The object was then taken out of the exsiccator, the excess monomer was removed, the object was wrapped in polyethylene foil to prevent evaporation of the monomer and placed in an oven. During the first 2-3 hours the temperature of heating was gradually increased from 70-100°C and after that raised to 110-120°C. This temperature was maintained for 2-3 hours. The object was then removed from the oven and cooled to room temperature. The treatment was reported to impart to porous objects remarkable stability and resistance to changes in environmental humidity (96). However, this method has limitations (relatively small space in the exsiccator, the required evacuation of air, and thermal manipulations etc.) that confine its use to small objects. These drawbacks have, to a certain degree, been eliminated by the selection of more appropriate polymerization initiators. For example, 5 g of technical methyl methacrylate (Röhm and Haas, Darmstadt, Germany), without removing the inhibitor, was cured in about 1 hour at 25°C upon the addition of 2% benzoyl peroxide and 0.6% dimethyl paratoluidine

by Munnikendam (213). Samples of sandstone, impregnated by immersion in this mixture for 10 min. showed that for good retention of polymerized methyl methacrylate in the treated sample, prevention of evaporation of monomer was essential. Packing the samples in aluminium foil delivered a percentage retention (ratio of the polymer weight to the amount of monomer originally introduced) that varied from 50 to 75%. After the spraying of monomer on murals, evaporation was greatly reduced by a surface coating of polymethyl methacrylate in acetone, carried out with a spray-gun. After polymerization the excess polymethyl methacrylate was cleaned with acetone or chloroform (213). However, covering the impregnated object with a film of a liquid immiscible with methyl methacrylate, such as water or glycol, was found to be a better barrier against evaporation than any solid coating. To facilitate practical application these liquids were thickened respectively with starch or kaolin and, after impregnation of the porous material, one of them was used on it as a coating. After polymerisation of the monomer, i.e. in about a few hours, this coating was removed with lukewarm running water (214).

5.3.7 *Synthetic polymers*

Because of their large molecules, the synthetic polymers must always be applied from very dilute solutions. But even then a real impregnation with polymers is only possible for a few mm into the surface of a porous material as the polymeric deposit is controlled by the evaporation of the solvent and takes place from the evaporation-front inwards. Polymeric surface coatings are, however, not very useful in stone preservation as they obstruct the evaporation of moisture and thus provoke intensive blistering at points of film flaw (151, 315). This is especially obvious in outdoor conditions.

Samples of limestone and sandstone have been treated with polymethyl methacrylate 1% in trichloroethylene, rubber 0.5% in benzene, polystyrene 0.5% in benzene and polyvinyl chloride 2% in white spirit (221). Sandstone specimens have also been treated with a copolymer of styrene and butadiene 5% in xylene, and silicone resin 5% in xylene (245). As later investigation showed, all these treatments procured to the samples a coating which reduced to various degrees the porosity of the surface layer and therefore increased their stability and resistance to external agents of corrosion. However, as the deterioration of stone is primarily due to internal migration of moisture, exfoliation of these coatings must eventually take place (151, 315).

Consolidation of decaying plaster and murals could be accomplished by spraying with 5% solution of one of the following polymers: polyvinyl acetate, polyvinyl acetal, or butyl methacrylate (105). Gettens (105) recommended to use 50 g of the selected polymer dissolved in the solvent mixture: 700 ml toluene, 200 ml ethylene dichloride, 40 ml cellosolve acetate and 20 ml dibutyl phtalate (105).

Philippot and Mora (223) considered a solution of 1% of polybutyl methacrylate in toluene very suitable as a fixative for murals, while the

same concentration of that synthetic resin in xylene was reported to have been used successfully to consolidate deteriorating murals, limestone, sandstone, marble, ceramics, plaster, etc. Philippot and Mora (223) proposed as a good fixative for murals a 1 to 5% solution of PARALOID B 72 * (a methyl acrylate ethyl methacrylate copolymer) in toluene. A somewhat concentrated solution of polybutyl methacrylate (15 to 20% in a mixture of acetone and carbon tetrachloride) was also used for consolidation of plaster and murals recovered by excavation (271).

Stabilization of crumbling sandstone has been attempted by impregnation with a 2.5 to 5% solution of BEDACRIL-122-X ** (a polymethacrylic ester) in toluene (104). For sealing of crevices in plaster, it has been recommended (117) to stir the slaked lime-sand mixture with an acrylic dispersion (25 wt-% of solid acrylic resin suspended in water) instead of with pure water. The acrylic resins are preferred because they do not swell or hydrolyze in the normal atmosphere conditions.

Consolidation of corroded stone and plaster with epoxy resins, polyester in cross-linking with maleic acid, and wax-paraffin mixtures has been applied with varying success (277). Mud layers on walls, known as a particularly difficult matter to conserve, have been stabilized, according to Sakurai and Iwasaki (250), with urea resin.

Philippe (222) reported the consolidation of disintegrating sculptures with a mixture of paraffin and polyethylene applied with a spray gun. Epoxy resins, as stone consolidants, have been extensively studied (86). Experimenting with a variety of epoxy resins, dissolved in organic solvents, Domasłowski (86) has impregnated limestone and sandstone either through immersion in a tank or by attaching specially made pockets filled with epoxy solution to vertical stone surfaces. He obtained the following results:

1. The epoxy resins were best dissolved in a solvent mixture containing 1 part of a hydrocarbon and 2.5 parts of an alcohol. The most suitable selection of solvents for the mixture consisted of toluene and methanol. A 10% solution of epoxy resin (a Polish product Epidian 4, epoxy number 0.42-0.45, 'Sarżyna' Sarżynie, Poland) in this solvent mixture penetrated the stone sample to a depth of 15 cm; a sample with a cross section of 26.92 cm², in contact with this mixture, was penetrated 15 cm in 19 min.
2. The impregnated stone must be covered with cotton wool pads, soaked in a solvent of low vapour pressure, and then wrapped in polyethylene sheeting. This must be maintained for at least 10 days, in order to prevent evaporation of the solvent mixture and secure a complete hardening of the resin.
3. No discolorations due to the introduction of resin appeared on the stone.

* Röhm and Haas, Chemische Fabrik GmbH, Darmstadt, W-Germany.

** Manufactured by I.C.I., London, Great Britain.

4. Impregnated stone became water-proof.
5. Impregnation imparted to the stone resistance to decay by micro-organisms, soluble salts and atmospheric pollution.

Epoxy resins are also used as adhesives. Broken ceramic statues in the park of Wilanów (Warsaw) were mended with the following mixture: 18 parts of powdered porcelain sherds, 1 part of zinc oxide, 5 parts of epoxy resin (Epidian 5, epoxy number 0.48-0.52 'Sarżyna' Sarżynie, Poland), 6 parts of xylene and 0.6 parts of catalyst triethylene tetra amine ('Ver-samidem 125' General Mills) (162).

The Sigiriya frescoes in Ceylon have been stabilized by impregnation with a 5% polyvinyl acetate in toluene, while cracks and fissures in the same frescoes were injected with a viscous cement of 20% of polyvinyl acetate and 1% of dibutyl phtalate (plasticizer) in toluene (298). A 2.5% solution of polyvinyl acetate with a small addition of a silicone in xylene was also used to impregnate the crumbling surface of some Coptic frescoes in Nubia prior to detachment (227).

Some critical observations, concerning the application of synthetic resins to building materials and murals, have been made by Hedvall (120).

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SUPPLEMENT 1975.

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1. INTRODUCTION

This supplement is related to two previous contributions by the authors to the ICOM Committee for Conservation (45, 46). A combination of these two reviews was published by the International Centre for Conservation in 1972 as the first edition of the present booklet (47). Since 1969 a number of articles and books have been published relevant to the subject matter. Many of these, however, compile or review certain aspects without bringing much new material (17, 53, 59). Several international meetings have, in recent years, been partially or completely (21) devoted to the deterioration and conservation of porous building materials in monuments. The International Institute for Conservation of Historic and Artistic Works (IIC) organized a conference in 1970 in which stone was one of the two subjects (23).

The Centro per la Conservazione delle Sculture all'Aperto in Bologna, Italy, has organized meetings of the Joint Committee for the Conservation of Stone of ICOM, ICOMOS and the International Centre for Conservation (37, 38, 43). The Joint Committee also publishes a newsletter (20). A symposium was organized in 1972 in La Rochelle, France, of which the proceedings have been published (7). Unesco has continued to stimulate work on the actual preservation of important monuments and although most of the Unesco reports on these projects have a limited distribution some have found their way into the open literature (53).

A special issue of *Studies in Conservation* stressed the importance of preliminary investigations in conservation by reporting about the work in relation to the Indonesian Borobudur temple complex (5). The problems of tropical and arid zones have received increasing attention (18, 24). Weathering of monuments and archaeological sites of mud-bricks has been the subject of some special studies (6, 52) but much remains to be done. The investigation of erosion and driving rain, requiring long term studies including the collection of data on the microclimatological conditions is usually neglected — frequently through lack of adequate funds. The much needed collaboration between

those engaged in the conservation of monuments and decorative sculpture and stone and those specialized in Building Research Science could still be much improved. While a number of common research projects have been formulated (26), very little results have been reported due to lack of financial support for such investigations. It would seem that in each country a percentage of the budget allocated to monument preservation should be reserved for research aiming at better diagnosis and improved treatment. The need for experimenting on a semi-industrial scale with promising methods developed in the laboratory is clearly felt. In the absence of such facilities, progress will be slow and applications to actual monuments incidental.

The supplementary data below is arranged according to the sections of the authors' previous 1972 publication (47) — the numbering and headings are identical to those in the first part of the present booklet.

2. WEATHERING BY MOISTURE AND SALTS

The weathering of igneous and sedimentary rocks generally and as building materials remains the subject of continuing studies. Some new data relevant to the conservation of monuments is compiled by Winkler (59); more about the weathering of stone, ceramics, plaster and murals is to be found in Urbani's *Problemi di Conservazione* (54). Both works treat the subject matter meticulously and explain the processes responsible for the decay, clearly.

3. MOISTURE IN POROUS BUILDING MATERIALS

Investigations into the thermal and hygric behaviour of certain individual monuments over a longer period have been reported. Lacy analysed the moisture balance of King's College Chapel, Cambridge, and concluded that there was little chance of the relative humidity inside falling below 50% in winter because of the absorbance by the structure of moisture exhaled by summer visitors (28).

Boekwijt reported about continuous automated moisture distribution measurements in the S. Sebastiano church in Venice (3), Boekwijt and Vos about such measurements in the S. Bavo Cathedral in Haarlem, The Netherlands (4). A most interesting collection of papers has only recently become available in English translation of a Russian conference on moisture control in the masonry of historic buildings (56).

3.2.2.2. Rain penetration

Some papers read during the 1974 2nd CIB/RILEM Symposium on Moisture Problems in Buildings (10), although concerned with modern buildings, could have useful implications for monuments. Couper, e.g., discussed the conversion of wind-driven rain to surface runoff and studied

the discharge patterns of rain falling onto projections and their shedding ability (12).

3.2.2.3. *Vertical transport of water*

Vos (57) discussed the rising of ground-water and derived a theoretical formula for the height of rise. Applying this formula to practical examples he shows that water rising from the ground into a wall cannot be expected to reach a height of more than a few meters, unless the relative humidity is very high. This would indicate that if water is found at a height of many metres it is improbable that it originated from the ground. Aspects of rising ground-water in monuments have been discussed by Vos and Tammes (58).

3.4. **Thermal aspects**

The measurement of surface temperatures — important, e.g., for investigating the heat transfer characteristics of walls in monuments and related condensation risks — has been facilitated by the use of infrared-to-visible image translation systems. Thermograms of frescos, painted canvases and walls in two churches in Lodi, Italy, have been published (55).

3.6. **Determination of moisture**

There has been little reported progress in methods of determination of both relative humidity and moisture content of building materials likely to have useful applications in monument preservation. An interesting procedure to predict distributions of relative humidity, air and surface temperatures in air conditioned rooms was published by Nielsen (34). Apart from obvious applications in museum climatology this approach could be useful to predict effects when measures of conditioning monuments are considered.

4.4. **Dust pollution**

Observations for which — seemingly — enough evidence had been provided in the past, are now being questioned or challenged on the ground of new data. A case in point is the controversy about the role the air-pollutant sulphur dioxide plays in the crust formation on stone.

Riederer (35) believes that the conversion of sulphur dioxide to sulphur trioxide — a reaction essential for the production of sulphuric acid — is only possible at temperatures between 400 and 600°C and in the presence of catalysts. In view of this requirement the development of gypsum crusts on limestone and marble cannot be accounted for by the action of sulphuric acid, and even less so the sulphuric acid could be held responsible for the deterioration of sandstone free from calcareous inclusions. Riederer

assumes then that the observed decay of stone must be due to dust (containing calcareous particles) settled on the surface of the stone and there gradually transformed to gypsum. Considering the very fine size of the calcareous grains and the presence of catalysts in the dust, the formation of gypsum is then, at least partially, related to the presence of sulphur dioxide gas. However, sulphate building bacteria are also mentioned as possible initiators of the gypsum accumulation.

Similar assumptions have been advanced by Italian geologists (30) who state that gypsum found on decaying stone is not of inorganic origin. The presence of gypsum is again ascribed to metabolism of sulphur bacteria, although the authors admit that no linear correlation had been noted between these bacteria and the amount of gypsum found in their samples.

As far as the conversion of sulphur dioxide to sulphur trioxide is concerned, in both papers literature discussing the oxidation of sulphur dioxide at room temperature, and even patents which recommend this process for the continuous production of sulphuric acid are overlooked (44). According to several investigators — in the presence of iron either as metal or as iron oxide or as iron hydroxide — sulphur dioxide is spontaneously oxidized to sulphur trioxide (42). In fact, even without any catalyst the oxidation of sulphur dioxide will occur in the atmosphere as sunlight alone is capable of generating it through photochemical reaction (44). The sulphur trioxide gas resulting thus, influences the humidity balance of the ambient air in such a way, that the temperature of the dewpoint of the system sulphuric acid-water assumes values that are above the normal temperature of the surrounding air. Which is to say that industrial air inevitably leads to the origination of sulphuric acid aerosols (25). The damage done by the sulphuric acid aerosols through gypsum formation as well as by the pressure of hydration inherent in the behaviour of the soluble salts: sodium sulphate and magnesium sulphate whenever exposed to air of fluctuating humidity, have been exhaustively covered at the IIC London Conference on Museum Climatology 1967 (49) but is also discussed by Winkler (59). Moreover Thomson and White (50) have shown that urban rain dissolves limestone at least fifty times faster than unpolluted rain, which actually means that seepage of water and change of temperature (30) alone, are not capable of explaining the decay of alkaline stone. The action of acidity content of the air pollution must, therefore, be added to these physical factors in order to make the deterioration of stone comprehensible.

4.5. Deterioration by biological agents

The origin of calcium oxalates and the action of micro-organisms in their creation at the surface of monuments and their role in the deterioration of stone has been investigated (36). The important role of biological agents in the deterioration of monuments in tropical zones has been stressed by the work of G. Hyvert. She described in her thesis in detail

the influence on the alteration of the monuments in Cambodia (18). Later systematic research was carried out by her into the biological factors affecting the deterioration of the Indonesian Borobudur temple complex (19).

5.1.1. *Remedial measures against rising ground-water*

A useful review in German was published by Schelling (40). Mamillan and Boineau (31) reported a comparative investigation of various methods of combating rising damp. These authors also produced a colour film comparatively illustrating the effect of various methods commercially available in France and installed by various proprietary firms. The data point to insatisfactory results for electro-osmotic methods and devices based on the Knapen-siphons approach. Experience with methods using injection fluids aiming at impermeabilisation, is encouraging but not conclusive.

5.1.1.5. *Electro-osmotic drying*

Electro-osmotic methods have received a great deal of attention (33). It would seem that statistically more positive results are reported from countries in Middle and Eastern Europe than elsewhere. This may be related to the preponderance of certain types of building stone, possibly containing mainly narrow pores. Some investigations in the USSR, however, strongly point to the limited feasibility of electro-osmotic drying. Kurdenkov (27) measured the electro-osmotic permeability coefficient k_e for a number of stone materials in historic buildings. He judged building materials electro-osmotically active when the index $k_e/k > 2.5$ cm/V. This criterium is less severe than that of Schaad and Haefeli (39). However, Kurdenkov's data show only one limestone with $k_e/k = 2.93$ cm/V all other values being < 2.5 cm/V. For bricks the values are between 0.09 and 0.75 cm/V. Kurdenkov's conclusions are well worth attention: '... in most cases the use of electro-osmosis for material drying is not effective. Only in exceptional cases when there are materials with $h_e (= k_e/k) > 2.5$ cm/V and in rather rare cases of materials of incomplete activity, can electro-osmosis be effective, and then only with the use of high voltages (above 100 V)'. He also concludes that passive electro-osmosis 'where galvanic electricity is used with a difference of potentials of not more than 3-5 V does not dry buildings.' Kurdenkov supposes that in cases of reported positive results, the main drying 'must be the result of some other phenomena'.

5.1.2. *Remedies against condensation*

Torraca (51) has proposed to protect temporarily monuments — in spring under Italian conditions — with protective plastic covering. This would allow to keep out the moist air and associated aerosols. Mild heating

of the air inside the space between the plastic and the building would further diminish risks of condensation.

5.1.3. *Drying by means of heating*

Some attention has been paid in the literature to the adverse effects of heating monuments. The conflicting requirements of providing conditions agreeable to church-goers and suitable to the conservation of works of art have been discussed (41). It should be realized that while short periodic heating is better for panel paintings, sculpture, furniture and organs than continuous heating (48), cycles in temperature and the related relative humidity are detrimental to mural paintings, plaster and stone inside the monument. No heating at all is the only course to be recommended, the exception being the occasional heating of the structure itself to prevent condensation (32).

5.2.6. *Chemical cleaning*

The already known method for the treatment of stains, caused by metallic salts with chelate complexes is reported to be cheap enough for the cleaning of building exteriors (8). Characteristic for these complexes is that the chemical groups involved, catch the metal ion of the corresponding salt and keep it sequestered. The chelate complexes composed thus, are soluble in water, provided the complexes satisfy a number of requirements of which the most important is that the milieu should be either slightly acidic or alkaline. To stress the significance of this, it should be mentioned here that chelating as a chemical reaction implies the displacement of hydrogen ions from a neutral organic molecule and that, therefore, the efficiency of the chelating agents — which are very weakly acidic — would depend on both their dissociation constants and the pH-value of the solutions concerned. Strong acid milieu would block the dissociation of the organic reagent and consequently, no chelating would occur.

The formulation of an effective stone cleaner based on chelating agents (in practice, the sodium salt of ethylenediaminetetra-acetic acid is most commonly employed) demands that the pH-value should be kept above 7 and that the chelate solution is thickened with suitable fillers to produce a paste. Materials capable of colloidal swelling mixed with finely powdered asbest, chelating agent and water, deliver one type of a cleaner known as colloidal paste. This is applied on a stone surface, left there for about two days and then peeled off. Contaminants from the stone accumulated in the colloidal film during drying are thus removed. In this manner horizontal stone surfaces can be cleaned. However, for vertical surfaces, and especially carvings, another filler in the cleaning mixture is preferred. In this case the chelating agent is blended with bentonite to form a paste which is then applied on the stone surface and again left

for about two days to dry. Afterwards, the paste-layer together with the dirt that has entered it, are brushed off.

Several publications discussing systematically and critically all cleaning techniques have been issued (1, 11, 14, 15) and could be of great service if consulted prior to cleaning treatment. The problem of stone cleaning has also been discussed in international meetings of experts and their proceedings, containing directives how to handle these problems, have been published (23, 38).

5.3 Consolidation and protection

Papers dealing in detail with all techniques of consolidation and protection involving inorganic and organic preservatives have been repeatedly published (2, 13, 23, 29, 38, 54, 59). These papers, useful as reference sources, present no new approaches and for this reason, their content is left out of account here.

5.3.4. *Silicone esters*

In a series of articles Chvatal (8, 9) clarifies the mechanism of solidification of silicone ester-based stone preservatives and makes some recommendations about their use. The silicone esters undergo hydrolysis and polymerization which lead to the formation of silicagel. The hydrolysis liberates alcohol, whereas for the initiation of polymerization catalysts are needed. Among these catalysts phosphoric acid precipitates silicagel quickly; hydrochloric-, sulphuric- and nitric acid precipitate it slowly; the alkali catalysts as sodium-, potassium- and ammonium hydroxide precipitate it immediately; the organic bases such as triethanolamine and morpholine precipitate silicagel with a moderate speed. Accordingly if the precipitation of the silicagel is completed while the liberated alcohol is still present, the precipitate is about to shrink and, after evaporation of the alcohol, will become brittle. On the other hand, if the liberated alcohol evaporates before the hydrolyzed silicon ester, i.e., silanol, has been cured through polymerization, a certain amount of the silanol will be carried to the evaporation front and deposited there as a crust with no merit whatsoever as stone consolidator. Moreover, an objectionable feature pertaining to the selection of catalyst would appear if for that purpose mineral acids are chosen. By reacting with carbonaceous matter omnipresent in stone, they would liberate carbon dioxide gas and thus thwart deep penetration of the consolidating fluid. This reaction would also neutralize some of the acid, i.e., exhaust to a certain degree the catalyst, and in this way protract unnecessarily the polymerization of the silanol.

Bearing all this in mind, and drawing conclusions from his own experimental work, Chvatal proposes a number of two-component stone consolidators; the one component consisting of the silicone ester, and the other

one containing solvent and catalyst. The formulations that seem to be most promising are listed below.

60 parts by volume of tetramethoxysilane
 25 parts by volume of ethyl alcohol
 15 parts by volume of water
 0.1 per cent of triethanolamine

50 parts by volume of methylpolysilicate
 40 parts by volume of acetone
 11 parts by volume of 5 per cent formic acid

50 parts by volume of methylpolysilicate
 40 parts by volume of acetone
 11 parts by volume of water
 0.2 per cent of morpholine

After the two components are blended the mixture is at once applied on the stone, preferably in the evening, in order to retard the evaporation of solvent and water.

More significant slowing down of the evaporation is achieved by covering the treated surface with a plastic foil.

5.3.5. *Silicones*

The conventional procedures used to render stone materials water-repellent by employing silicones, are the subject of an article (16) which describes coherently the various aspects of these remarkable hydrophobic agents. However, the weak point of the usage of silicones, namely the failure to produce a continuous film, remains yet unchanged, i.e., it is easy using silicones to make a piece of stone water-repellent, but quite difficult to attain the same strong water-repellency on masonry that contains these very stone pieces.

This deficiency of the silicones may be avoided if instead of alkali silicone or polyhydrosiloxane, as the practice now is, an alkyl silicone ester, for example methyltriethoxysilane, is employed to provide the water-repellency. Through the use of an alkaline catalyst (potassium hydroxide) this type of silicone ester polymerizes, and solidifies in the pores of the stone. And because it possesses only 3 or 2 hydrolysable groups, the silicagel deposited after polymerization, is highly hydrophobic, whereas the film formed by it in and over the stone surface, exceeds greatly the thickness of the silicone film, and therefore, makes the water-repellency continuous, better distributed and more lasting (8). The practical

formulation for the hydrophobic treatment of stone is a mixture containing: (in parts by volume) 100 methyltriethoxysilane, 70 ethyl alcohol, 15-20 water and 0.05-1.0 per cent by weight (as calculated with reference to the content of silicone ester) potassium hydroxide. At room temperature the quantity of the catalyst determines the velocity of precipitation and deposition of silicagel:

Addition of KOH in % by weight (with reference to silicone ester)	2	1	0.5	0.25	0.1	0.05
Precipitation of silicagel at 20°C in hours	20'	40'	1	1½	6	15

As with silicones, the hydrophobic treatment with silicone ester renders the stone equally permeable to gases.

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