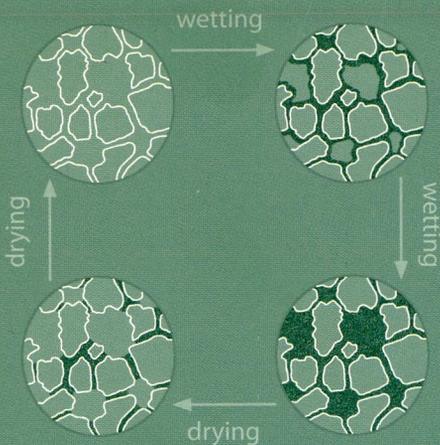


POROUS BUILDING MATERIALS

Materials Science for Architectural
Conservation



Giorgio Torraca



ICCROM

Porous building materials
materials science for
architectural conservation

Porous building materials: materials science for architectural
conservation
by Giorgio Torraca

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INTRODUCTION

Brick, mortar and porous stone undergo deterioration processes when exposed to the aggressive action of the environment. The rate and symptoms of such processes are influenced by a number of variables, partly depending upon the properties of the material itself and partly upon several environmental factors, acting separately or in various combinations.

As a consequence, the rate and symptoms of deterioration can vary within a wide range and direct relations of cause to effect are not easy to define. If, however, dispersed data, available from various fields of science and technology, are arranged in a general framework, the model thus obtained can play a useful role, allowing a tentative interpretation of deterioration processes and conservative action based on such an interpretation. During practical application, the theory can reveal its shortcomings and allow a progressive refinement of the model.

The present booklet is an attempt to collect relevant concepts from several domains and expose them in a descriptive way, avoiding formulas and in-depth treatment of single topics.

This is done with a double aim: on the one hand, to stimulate the specialists in the various fields involved to provide criticism or more accurate information and, on the other hand, to allow conservators to recognize the practical implications of the theory and attempt an application in conservation practice.

The immediate purpose of the booklet is to provide a basis for a short course on technology of building materials to be included in a general course on architectural conservation, such as the one presently organized by ICCROM and the Faculty of Architecture of Rome University.

In the model presented here, deterioration is shown as resulting from chemical processes (*corrosion*) acting in conjunction with

mechanical stresses. For porous materials, however, one must consider not only stresses imposed on the material by the external environment (*external stress*), but also stresses arising within the material in special situations (*internal stress*).

The whole deterioration process of porous building materials can therefore be defined as a peculiar type of stress-corrosion in which both internal and external stresses combine with chemical processes.

Besides the fact that chemical action is possible only in the presence of water, water is also an essential factor in the generation of internal stress. We decided, therefore, to begin the discussion of deterioration processes with a description of water movement inside porous bodies (Chapter I) before passing to mechanical stress, external and internal (Chapter II) and chemical corrosion processes (Chapter III). Biological factors of deterioration are described in Chapter IV, while the action of mechanical vibration as an additional cause of deterioration of structures is discussed in Chapter V. Problems concerning some classes of building materials, like adobe or mud-brick (Chapter VI), mortars (Chapter VII), stone (Chapter VIII) and masonry in general (Chapter IX) are introduced in the second part of the booklet, followed by a short discussion of some materials used in conservation, such as synthetic resins (Chapter X) or silicates and silicones (Chapter XI).

Chapter I

WATER MOVEMENT IN POROUS SOLIDS

1.1 HYDROPHILIC SURFACES

Bricks, stones and mortars are composed of crystals of carbonate, silicates, aluminates or oxides. Vitreous (i.e. glassy, non-crystalline) silicates are also occasionally present.

The surfaces of these crystals, or glasses, are rich in oxygen atoms which carry negative electrical charges. The reason for this is that oxygen is the most electro-negative (i.e. electron-attracting element, so when it forms bonds with other atoms (e.g. carbon silicon, aluminum, etc.) it tends to attract negative electrons away from them.

It is believed that frequently the surface oxygen is bound, on one side, to a hydrogen atom forming a -O-H group which is called *hydroxyl* group. This group carries both negative (on the oxygen) and positive (on the hydrogen) electric charges (or electric poles) because the oxygen is more electro-negative than the hydrogen and tends to pull closer to itself the two electrons that the two atoms share to make up the bond between them.

Surfaces that show electric poles due to oxygen atoms or to hydroxyl groups are called *polar*. They are also called *hydrophilic* (from ancient Greek, water-loving) because they attract water molecules.

The strong electrical attraction (or electric field) created by the hydrogen atom, in the direction opposite to its bond with the oxygen, causes the attraction of water molecules by hydroxyl groups, or of water molecules by other water molecules. This particular attraction is called a bond, because it is so directional, namely the

hydrogen bond. The formation of the hydrogen bond and the attraction of water molecules are shown in the sketches of Figures 1 and 2. Normally, every oxygen atom forms two hydrogen bonds, besides the two chemical bonds it always forms. The four bonds form a tetrahedral arrangement around the oxygen. Every hydrogen atom can form only one hydrogen bond, in the opposite direction from its chemical bond.

FIGURE 1 . THE HYDROGEN BOND

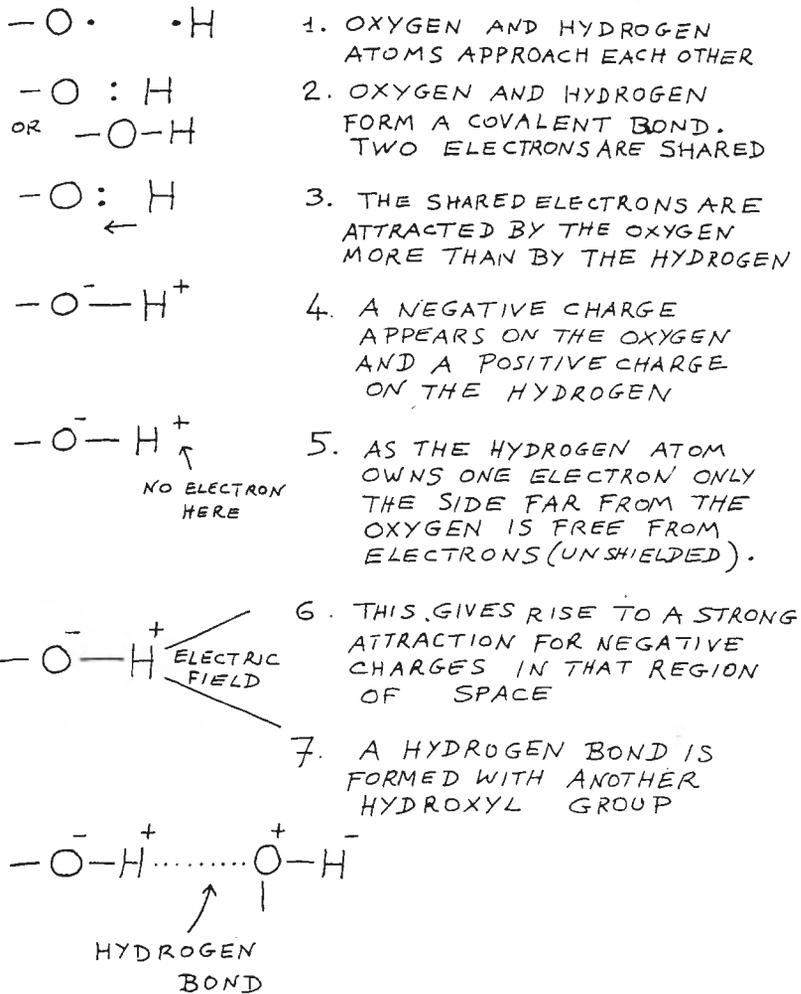
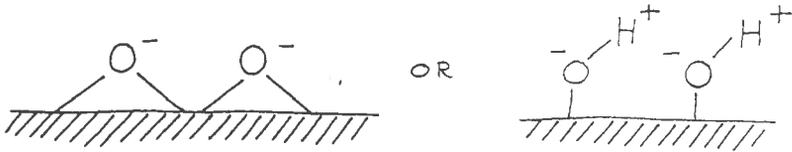
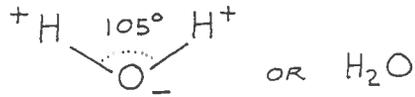


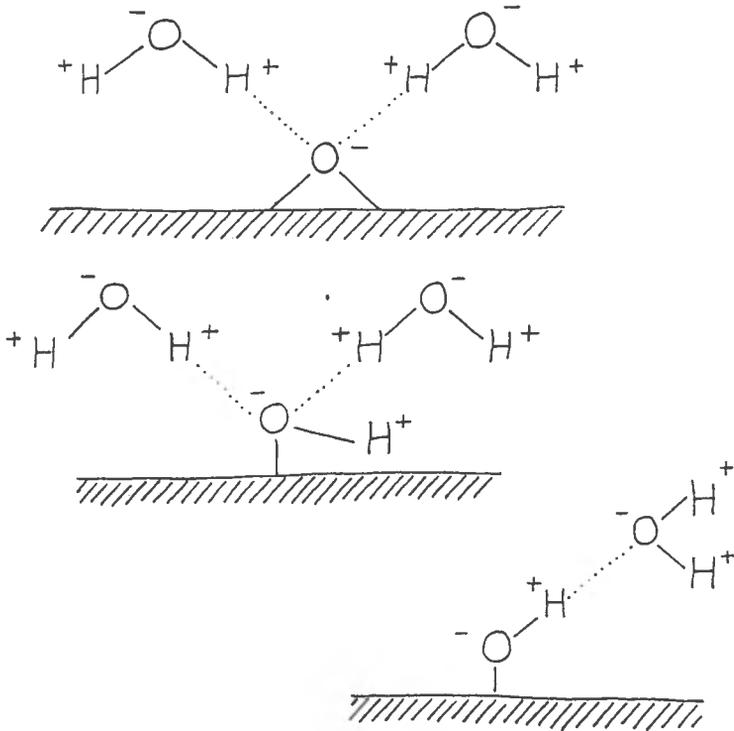
FIGURE 2. THE HYDROPHILIC SURFACE



THE WATER MOLECULE



WATER ATTRACTION BY A HYDROPHILIC SURFACE



The hydrogen bond is ten times (or more) weaker than a normal chemical bond; still, it is strong enough to require a sizeable amount of energy in order to break it. This energy is about 60,000 joules per 18 grams of water, each water molecule forming two hydrogen bonds. This figure corresponds to one watt-hour per gram of water.

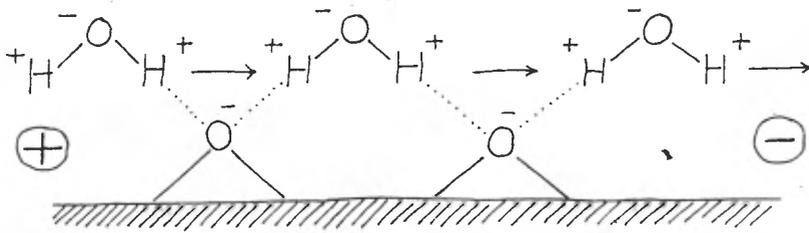
Water molecules attracted to (or adsorbed on) the surface by an oxygen atom would turn their positive side towards the surface itself, as shown in Figure 2. In the case of surface hydroxyl groups, attraction to both the positive hydrogen and the negative oxygen is possible, but the attachment from the positive side of the water molecule would prevail even in this case because the oxygen can form two hydrogen bonds while the hydrogen can form only one.

In such conditions a kind of electrical double layer is formed, with a positive layer in the adsorbed water and a negative layer on the solid surface.

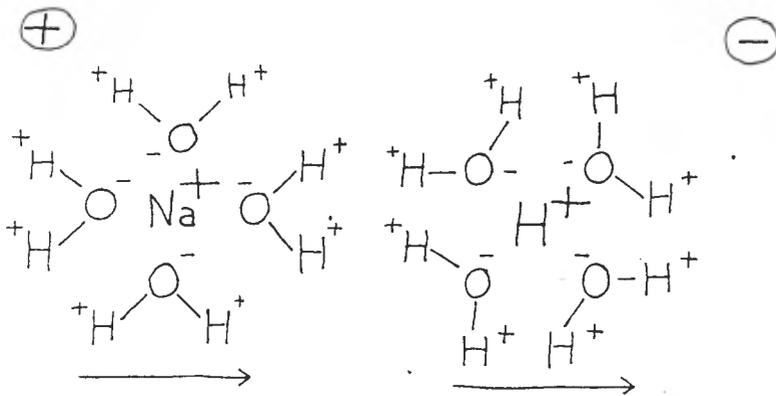
If an electric potential is applied to a porous hydrophilic material when it is wet, the water tends to move towards the negative electrode, and sizeable amounts of liquid may be displaced in that way. It is not clear whether the double layer itself, that is the adsorbed water molecules, could move towards the negative electrode, as these molecules show a layer of positive charges turned towards the solid surface, while their negative side is attached to other water molecules.

The electrical movement of water (electrokinetic) is also frequently explained, however, by the presence of positive and negative ions (i.e. electrically charged atoms or groups of atoms) formed by dissolved salts or by the water itself, dissociating into hydrogen and hydroxyl ions. Positive ions are smaller than negative ones and therefore possess a more concentrated electrical charge which is capable of attracting more water molecules. Positive ions, therefore, are more efficient carriers of water molecules when the electric field starts pushing the ions towards the electrode of the

FIGURE 3. HYPOTHETIC MOVEMENT OF WATER DOUBLE LAYER IN AN ELECTRIC FIELD



MOVEMENT OF POSITIVE IONS IN AN ELECTRIC FIELD



HYDRATION WATER IS CARRIED ALONG

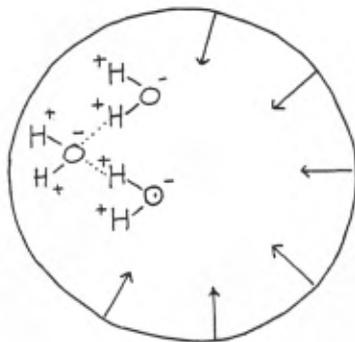
NEGATIVE IONS ARE LARGER AND CARRY LESS WATER MOLECULES

opposite sign. The water appearing to migrate towards the negative electrode would then be the excess water carried by the positive ions over that carried by the negative ones.

Whatever the mechanism, the amount of energy required to shift water inside the pores of hydrophilic material should not be exceedingly large, so long as the water molecules that are shifted are replaced by new ones. In such a case, two new hydrogen bonds are formed immediately and give back the energy required to break the first two bonds. The movement requires only some activation energy to surpass the barrier of potential that probably exists between any two stable positions of water molecules near the surface. Such energy should be far less than the 1 watt-hour per gram figure mentioned above. If, however, new water molecules do not replace the shifted ones, the entire energy necessary to break the hydrogen bonds is actually required for the movement.

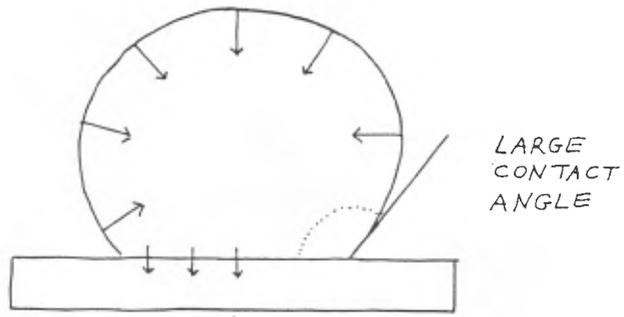
1.2 WATER DISTRIBUTION IN HYDROPHILIC PORES

Water Drop. All molecules on the surface are attracted inward by hydrogen bonds formed with other water molecules, inside the drop. The result is a tendency to reduce the surface to the most economical form, in this case a sphere (*surface tension*).

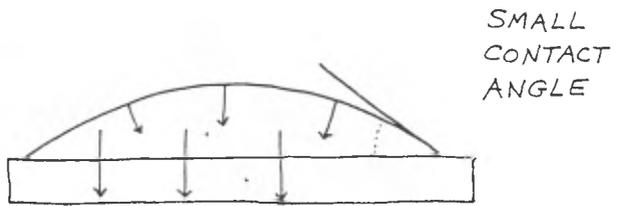


WATER
DROP

Water Drop on the Surface of a Hydrophilic Solid. The shape of the drop is determined by the force of attraction of water molecules to the solid surface. The measurement of the contact angle allows such forces to be evaluated. In polar liquids like water, a large contact angle (that is, a high drop) shows that the force of attraction water-to-solid is weak. Conversely, a small contact angle (a low drop) indicates that the attraction force is strong.



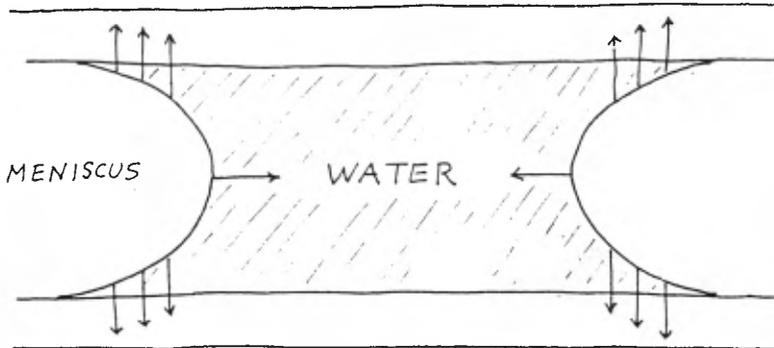
LOW ATTRACTION BETWEEN SOLID AND LIQUID



STRONG ATTRACTION BETWEEN SOLID AND LIQUID

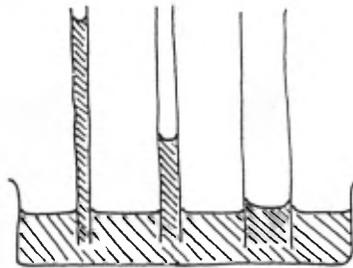
Non-polar liquids always show small contact angles (low drops) not because of high attraction to the solid surface but because of low internal attraction between molecules in the liquid (low surface tension).

Water Inside a Hydrophilic Porous Solid. The typical *meniscus* shape of the water surface inside small pores is determined by the attraction towards the pore walls. The centre of the water surface is drawn inward (in the liquid) by the attraction to the other water molecules.



Capillary Suction. Very small pores are called capillary pores or capillaries (from Latin, hairlike). Water is drawn into them if the attraction to the surfaces of the pores is stronger than the water-water attraction. The size of the suction force thus depends upon the nature of the surface and the diameter of the pore. The smaller the diameter of the pore, the stronger the suction force. The capillary force is frequently large enough to offset the force of gravity and make water rise inside pores that are sufficiently small (*capillary rise*).

CAPILLARY
RISE



If the water suction is not counterbalanced by other mechanisms, such as water evaporation, the rise against the gravity pull inside porous masonry might reach a height of many metres.

Capillary rise is therefore a spontaneous phenomenon due to hydrogen bond attraction of water towards some surfaces. It is not necessary to resort to electrical potentials to explain it, although application of an electrical potential could modify it, causing other movements of water molecules.

It has been reported that a difference of potential, with respect to earth, can be measured in porous masonry after water has risen into it from the soil. Apart from the fact that such measurements are rather unreliable, such a difference of potential is more likely to oppose the capillary rise than to favour it, on the basis of Le Chatelier's principle.

Water Distribution in a Porous Hydrophilic Solid. If the amount of water present in the pores of the solid is not sufficient to fill them up completely, water is distributed in such a way that the lowest possible energy state is reached. This would be the state in which the best possible exploitation of the attraction forces takes place, except for the disruptive effect caused by heat which can favour more disorderly arrangements.

For the sake of clearness, the progressive occupation of pore space by water can be schematized as passing through four levels of increasing water content.

Level I The material is completely dry. All pores are empty.

Level II Only the smallest pores (capillaries) are filled, surfaces of large pores are dry. The possibility of such a distribution is based on the assumption that, below a given pore diameter, it would be convenient to fill the pores even at the cost of leaving dry the nearby surfaces of larger pores.

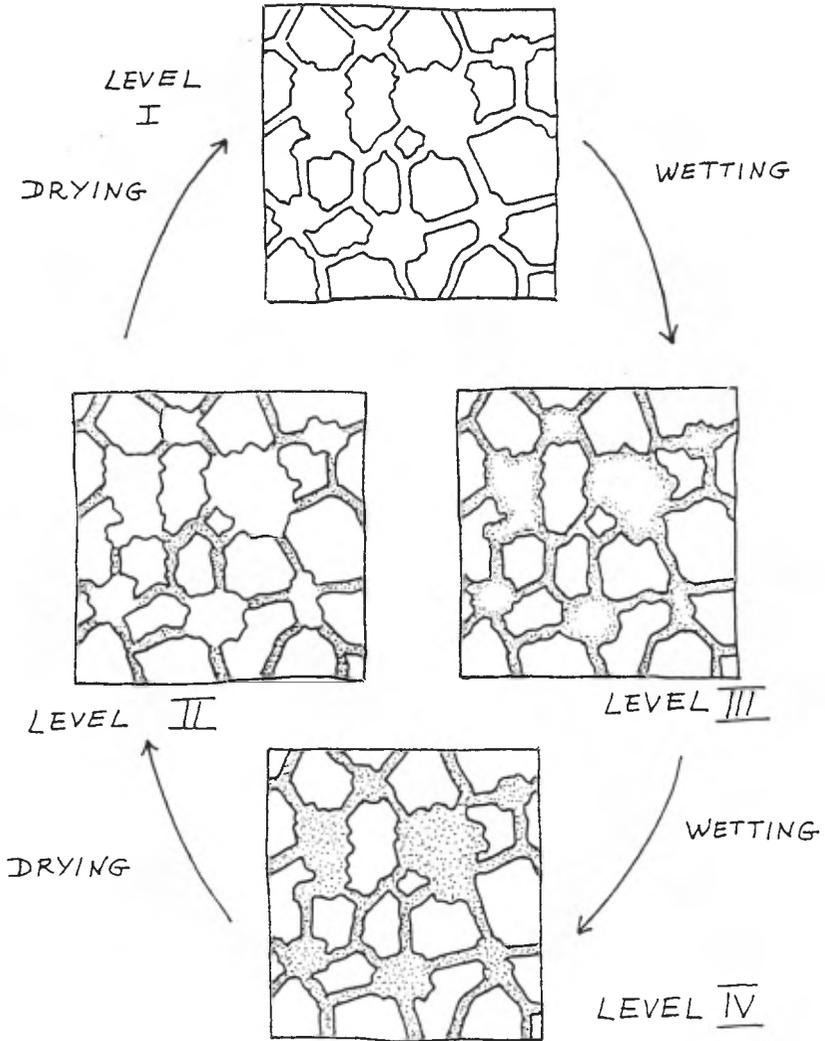


FIGURE 4. WATER DISTRIBUTION IN A POROUS HYDROPHILIC BODY

Level III Capillaries are full and the surfaces of the large pores are provided with a film of water.

Level IV Both capillaries and large pores are full.

Intermediate steps are obviously possible between all levels.

The four levels are schematized in Figure 4.

Level III is mainly encountered upon wetting and level II upon drying.

Any water content above that corresponding to level III should allow transfer of water in the liquid phase. Level III might thus be equivalent to the *critical water content* introduced by Vos and others.

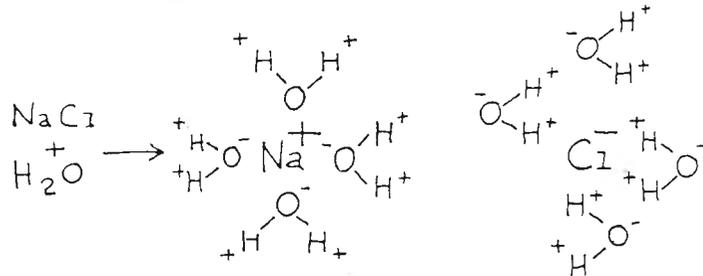
The critical water content should be determined by the nature of the material and the geometry of its porous system (in particular by the number of small pores). However, the presence of soluble salts would considerably increase the critical water content because of the hydration and hygroscopicity of the salt ions (see below).

1.3 MOVEMENT OF WATER IN THE LIQUID PHASE

Several types of forces can cause the movement of liquid water inside a porous solid.

- a. Suction. Movement from a region in which the water content is above level III (i.e. capillaries full and surface of large pores wet) to a region in which it is below level III. An example is the wetting of a dry solid when water is fed into one section by contact with wet materials and then transferred to the dryer ones.
- b. Diffusion. This would take place with water content above level III. Water moves from a region with higher water content to one with lower water content.

- c. Osmosis. Soluble salts dissolved in water are dissociated into ions, i.e. electrically-charged atoms. All ions attract water molecules by electrical forces (*hydration of ions*).



HYDRATION OF IONS

As a consequence, water moves from regions in which there are few ions (low salt concentration) to regions where there are many ions (high salt concentration).

- d. Electrokinesis. As shown earlier, water migrates towards the negative pole inside a porous body subject to an electrical field. If ions formed by soluble salts are present, they migrate to the pole with the opposite electrical charge carrying along the hydration water (electro-osmosis).
- e. Heat. In a wet, porous solid, water moves from a warmer region to a colder one.

While the suction mechanism (a) requires the existence of wet and dry areas, all the other mechanisms of transfer of liquid water are based on the existence of a continuous water film through which water molecules are transmitted. Therefore the mechanisms of diffusion (b), osmosis (c), electrokinesis or electro-osmosis (d) and heat (e) are applicable only when the water content is above the amount required to fill the capillary pores and to coat the surfaces of the larger ones (level III or critical water content).

1.4 MOVEMENT OF WATER IN THE VAPOUR PHASE

a. Condensation and Adsorption

Water molecules can be transported in the gas phase to the surface of a porous solid, or inside it.

Condensation. When the temperature of a surface is below the dew point of the nearby air, free water molecules present in the air (water vapour) join together to form a film of liquid water on the surface itself. The liquid water can then move inside the pores by one of the mechanisms outlined above.

Interstitial Condensation. The temperature of a surface of a porous body might be above the dew point of the nearby air but the temperature inside the body could be lower than that. In such a condition, condensation of water molecules takes place *inside* the pores of the material.

Vapour Diffusion. In a partially-dry, porous solid (water content below level III), water can be transferred from regions where there are many water molecules in the air (i.e. high vapour pressure) to regions where there are fewer water molecules in the air (i.e. lower vapour pressure). This can result in evaporation from one pore and condensation in another one. Such a transfer of water can take place when liquid transfer is not possible, but it is less efficient.

Hygroscopicity. Hydrophilic surfaces of pores can attract water molecules which become adsorbed on the surface, even if the temperature of the latter is above the dew-point temperature of the air.

Hygroscopic adsorption is possible when the relative humidity of the air is above a limiting value, which depends upon the nature of the material but also upon the diameter of the pores. Smaller pores favour hygroscopic adsorption

and can fill up with water at relative humidities below 100%. Soluble salts are particularly hygroscopic and can adsorb considerable amounts of water at relative humidities well below 100%; for instance sodium chloride adsorbs water from the air at a relative humidity above 75%.

The water content of a hydrophilic porous material can therefore increase by condensation or adsorption from the vapour phase even if the material does not come in contact with liquid water.

b. Evaporation and Desorption

In view of the electrical attraction existing between the hydrophilic surfaces and the water molecules, it is far easier to make water enter hydrophilic pores than to remove it.

Evaporation. Evaporation from liquid water films on the surface of porous bodies takes place, in principle, whenever the air in contact with the surface has a relative humidity below 100%; in practice, however, reasonable efficiency is achieved at much lower relative humidities or when the air moves continuously, carrying away the water molecules as soon as they pass into the vapour phase. Inside the pores, lack of air circulation causes rapid saturation (100% relative humidity) and so the only surface on which evaporation can be really efficient is the external one.

Water must be continuously fed to the surface in order to allow evaporation to proceed at a good rate. When, however, the liquid water content of the porous solid decreases below the critical water content (or level III distribution) transport of liquid water to the surface is no longer possible and only the less efficient vapour diffusion mechanism remains available. The drying rate drops at this stage when considerable amounts of water may still be present.

Complete drying of the material is quite difficult.

Desorption. Desorption of adsorbed water is also possible when materials are in contact with air of low relative humidity; air circulation also favours removal of water in this case. Hysteresis phenomena, however, make desorption more difficult than one could estimate from adsorption data. This means that desorption will always take place at a relative humidity lower than the lowest one at which adsorption is possible; for instance, sodium chloride can adsorb water from 75% humidity upwards but starts releasing it only below 70%.

The fact that suction and adsorption are easy, while drying and desorption are difficult, makes one guess that the natural conditions towards which a hydrophilic porous material tends, in a temperate climate, is a rather wet one, perhaps close to level III of our classification. In other words, once such a material has picked up water from the environment it can be quite difficult to dry it below level III, as this would require a lot of energy and time. Furthermore, unless adequate measures are taken, the dried material, left to itself, would more or less rapidly return to the moisture content that is in equilibrium with its average environment.

1.5 CAPILLARY RISE IN POROUS MASONRY

If foundations in buildings are not insulated from damp ground, water is drawn into the structure by the suction mechanism. The height that water can actually reach in a structure is influenced mainly by the balance between the water intake and the evaporation from the wall surfaces. When intake and evaporation are equal the rise should stop.

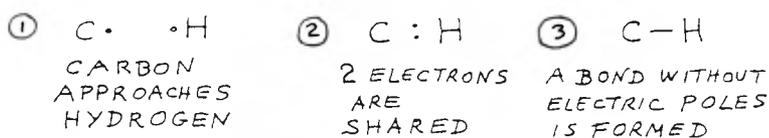
As the water intake also depends on the thickness of the wall, the height of rise is greater for thicker walls. The influence of

gravity, opposing the rise, appears to be negligible with respect to the effect of evaporation. Air circulation near the surface accelerates evaporation and causes a reduction of the moisture level.

In the long run, soluble salts also play a role in the capillary rise because they are accumulated in the masonry on the evaporation surfaces. Besides causing damage when they crystallize, salts attract water by osmosis and can determine a further rise of the water level. As accumulation of salt never stops, it is likely that a stable equilibrium is never reached; other conditions being equal, the height of the rise should increase with the age of the wall.

1.6 HYDROPHOBIC SURFACES

Several organic substances, including mineral oils, bitumen, fats and many synthetic and natural resins, are principally composed of carbon and hydrogen atoms. As carbon and hydrogen have almost the same electronegativity, the electrons shared to make up a carbon-hydrogen bond are symmetrically distributed between the two atoms and no electric pole is formed. The same holds for carbon-carbon bonds.

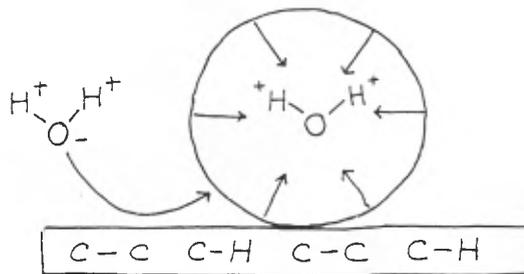


NON-POLAR BONDS

Such substances are called *non-polar* and are unable to attract water molecules because they cannot form hydrogen bonds with them. Water molecules on such non-polar surfaces attract each other, forming drops of water and do not spread on the surface. No

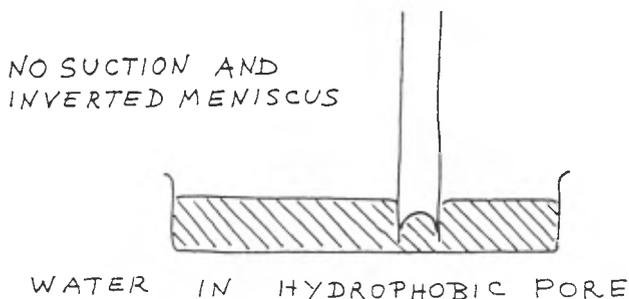
water film is formed; the water does not wet the surface and the contact angle of the drops is quite large.

WATER ON NON-POLAR SOLID SURFACE



As water appears to be repelled rather than attracted by these surfaces, they are also called *hydrophobic* (water-hating in Greek).

No capillary suction can be exerted by a hydrophobic pore on water, as there is no force of attraction between water and the pore walls. Actually, water appears to be pushed out from the pore; in an experiment of capillary rise the water level would be lower inside a capillary tube than on a free water surface and an inverted meniscus surface would be formed.



Chapter II

DETERIORATION OF POROUS MATERIALS

MECHANICAL STRESS

2.1 STRESS-STRAIN BEHAVIOUR OF BRITTLE MATERIALS

The mechanical behaviour of brick, mortar and stone can be defined as brittle or, in more detail, as hard, rigid and fragile.

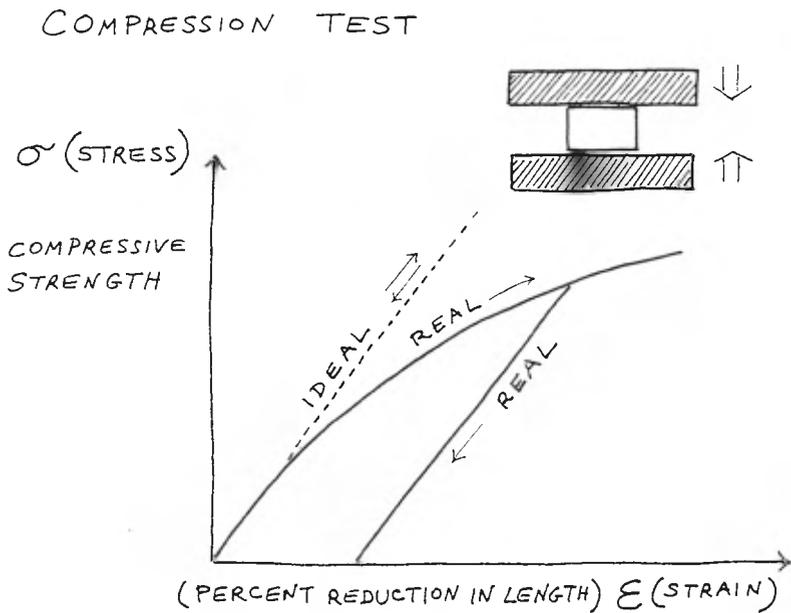
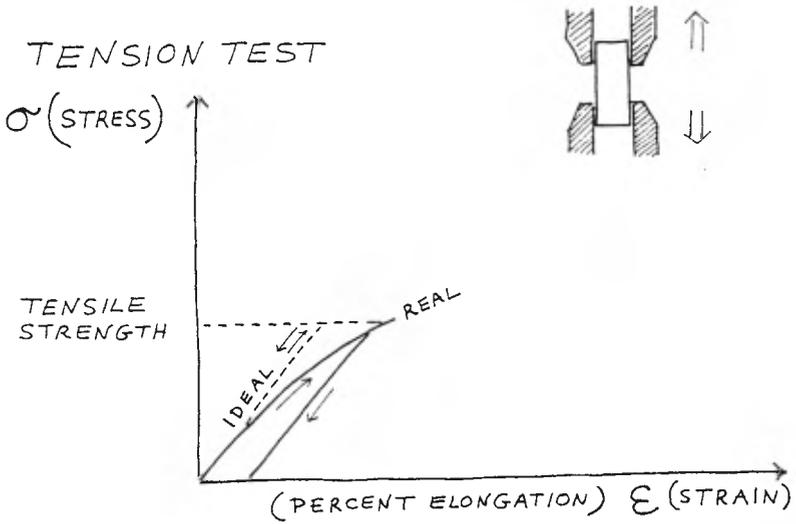
Mechanical behaviour is frequently studied by means of tension and compression tests in which a measured sample is submitted to increasing stresses (or loads) and undergoes a strain (or change of dimension) which is recorded continuously or intermittently. The stress under which the sample breaks is called the tensile (or compressive) strength of the material.

The results of the tests are normally presented in diagrams in which stresses are recorded on the ordinate (y or vertical) axis and the corresponding strains on the abscissa (x or horizontal).

Examples of typical diagrams for brittle materials are shown in Figure 5. For brittle materials, in an ideal case, the diagram would be a straight line, indicating that the strain is proportional to the stress inflicted on the sample. The stress-to-strain ratio, that is the slope of the straight line, would then be a constant which gives an idea of the material's ability to oppose any change in its dimension. This constant, which does not depend upon the shape of the sample but only upon the nature of the material involved, is called the *modulus* (or elasticity modulus or Young's modulus). The value of the modulus depends upon the strength of the bonds that connect the atoms and crystals together inside the material.

In the ideal case, also, when the stress is removed the strain should return to zero, i.e. the material should recover its initial shape.

FIGURE 5 STRESS-STRAIN DIAGRAMS OF BRITTLE MATERIALS



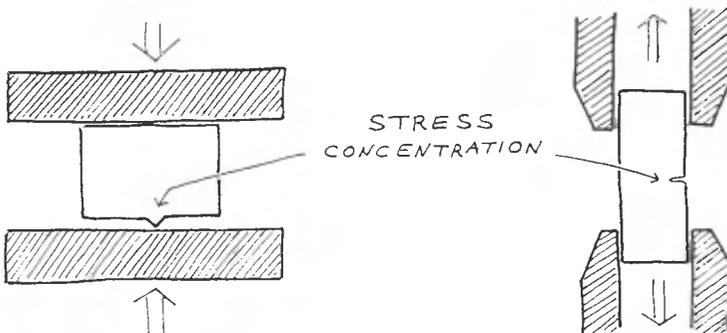
Such behaviour is called *elastic*.

A perfectly elastic material, which goes back to the initial dimensions when the stress is removed, does not exist. An irreversible deformation, remaining after removal of all stress, is called *plastic*. The diagrams show that in a test on a real building material the line is not straight, as the slope keeps changing; therefore, the *modulus* is no longer constant. Also some plastic, irreversible deformation occurs. This can be in part explained by the fact that real building materials are heterogeneous. They are composed of many different crystals, or glasses, held together by joints with variable strength. Some elements, or joints, start breaking before the others, causing irreversible deformations.

Another important cause of deviation from ideal behaviour is the fact that stress is not homogeneously distributed throughout the sample being tested. As a consequence of the fact that stress is frequently concentrated in some areas (*stress concentration*), some parts are subject to a larger-than-average stress while others are stressed less than one would expect. The overstressed sections start breaking before the others, even if the material is perfectly homogeneous.

Typical situations of stress concentration are the following:

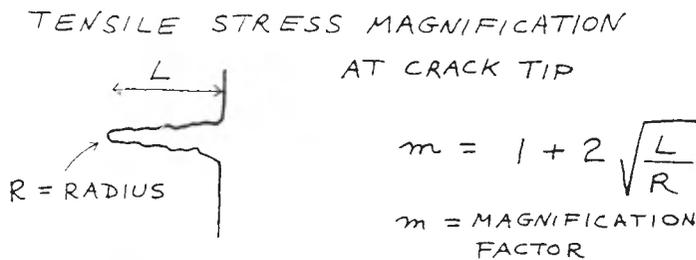
- irregular surfaces in compressive tests,
- surface cracks in tensile tests.



Irreversible deformation in brittle materials is probably not really plastic, at least not in the sense this word is used for metals, which are the typical plastic materials. In metals, plastic deformation occurs because of slip inside crystals, and the planes of regularly disposed atoms join perfectly again after slip. The result of the slip is that the material becomes stronger in the deformed areas than in the unaffected ones.

In brittle materials, irreversible deformation occurs mainly because of localized fractures (cleavage in crystals, fracture in glass, detachment of crystals) which do not close again after the stress is removed. The deformed area is weaker than the undisturbed material and contains many microscopic cracks.

The effect of stress concentration is particularly deadly in the tensile test. Formulas for tensile stress concentration show that the magnification factor at the tip of a surface crack is proportional to the square root of the ratio between the depth and the width of the crack. A hairline crack on the surface can thus produce at its tip a stress 10 to 100 times larger than the average tensile stress applied.



In such conditions a crack propagates easily in the material and fracture occurs at a stress value much inferior to that shown by the same material in a compressive test.

Brittle materials resist compressive stresses far better than tensile stresses. Tensile strength is strongly dependent upon the condition of the surface (i.e. presence or absence of cracks).

In brittle building material the modulus is not a constant and is not frequently measured. Knowledge of the modulus would be useful,

however, for masonry mortars in order to evaluate the amount of deformation that a joint can sustain. In order to make a consistent use of the modulus, as it is not a constant, it should be specified at what stress it must be measured, in order to obtain comparable results. Lime mortars, for instance, show a modulus that is inferior to that of cement mortars by an entire order of magnitude; they are deformed far more easily (although they also break far more easily).

When a brittle material has been subjected to a rather high stress without breaking but undergoing some permanent deformation, it is likely that some microscopic cracks have been formed in the overstressed sections. These cracks behave like pores, especially with respect to water suction and to the occurrence of internal stress (see below). The lack of true plasticity in brittle building materials therefore establishes a connection between mechanical stress and deterioration processes caused by the access of water in the pores.

The importance of mechanical stress in the deterioration processes of brittle materials can help explain the discrepancies often met between accelerated weathering tests and actual field behaviour when the performance of preservative materials is tested. In accelerated testing, samples are cycled between temperature extremes that correspond to field conditions but, as the samples are small and free from constraints, the resulting stresses are much lower than those that act on a piece of material in an exposed section of a real building.

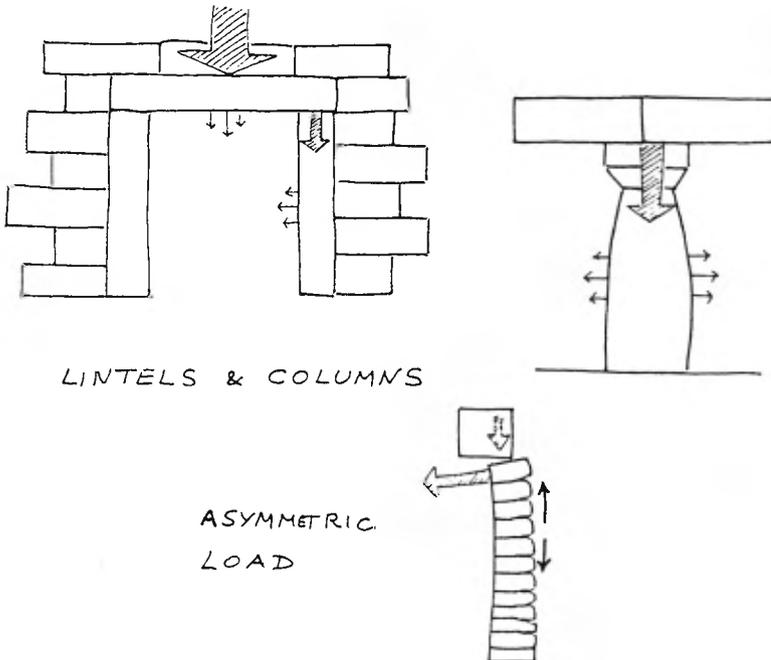
The tensile strength of porous building materials is also influenced by materials present inside the pores. According to theory, water should cause a reduction of the tensile strength as its very polar molecule can form bonds with the surfaces of newly-opened cracks, making their formation easier. Non-polar materials should, by the same argument, influence tensile strength in a favourable way. It has been shown by experiment that paraffin wax, which has no tensile strength to speak of, can cause an increase of up to 400% in the tensile strength of limestone.

2.2 EXTERNAL STRESS

Mechanical stresses induced in a building material by its environment can lead to damage, particularly in the case of tensile stresses towards which the resistance of brittle materials is low. Even if actual macroscopic breaking does not occur, stress can be the cause of permanent deformation and microscopic cracks, resulting in an overall acceleration of the weathering rate.

There are several mechanisms that can generate localized high stresses in building materials.

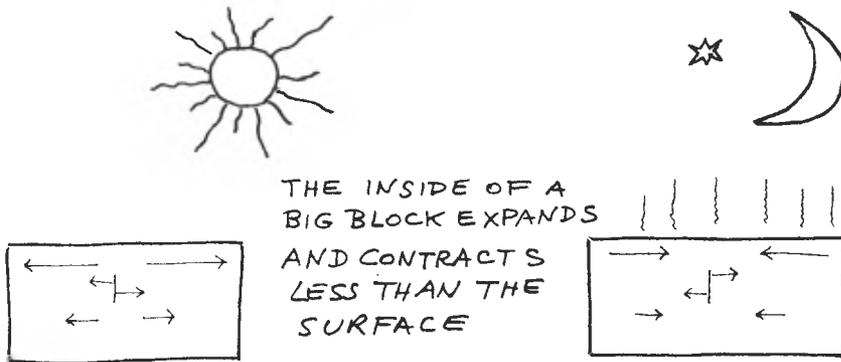
Load. In every structure some parts receive higher stresses than others: columns, lintels, pillars, for instance. The design of buildings, in general, aims to minimize tensile stresses and allow materials to work mainly under compression. Nevertheless, roofing systems, asymmetrical loads, side thrusts, and so on, inevitably cause some tensile stress. It is frequently noted in buildings that parts under particular stress deteriorate more quickly.



Thermal Expansion. Materials in buildings are subjected to daily and seasonal temperature cycles. Such cycles are important sources of stress because materials expand on heating and contract on cooling.

Dimensional changes are proportional to the length of the elements involved; therefore long pieces are liable to generate larger stresses than small ones.

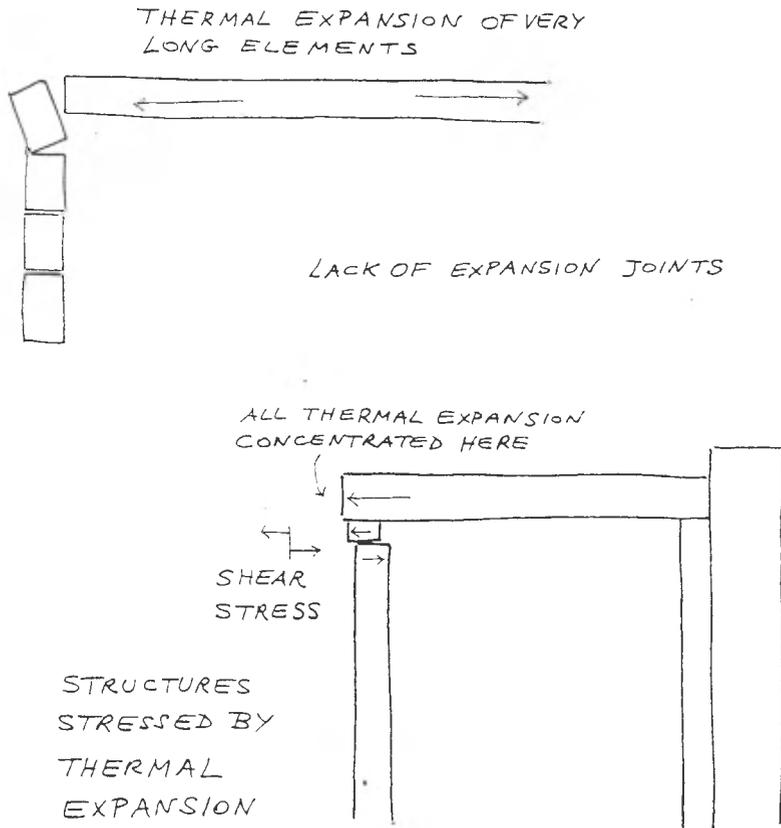
Stresses arise even inside a homogeneous piece of material, between the surface, which is directly exposed to the environment and undergoes a greater temperature change, and the inner part, where the temperature variation is smaller.



A SHEAR STRESS RESULTS

The change of temperature between day and night is very high when the weather is clear (e.g. desert areas). At night the earth cools by radiation towards the black sky.

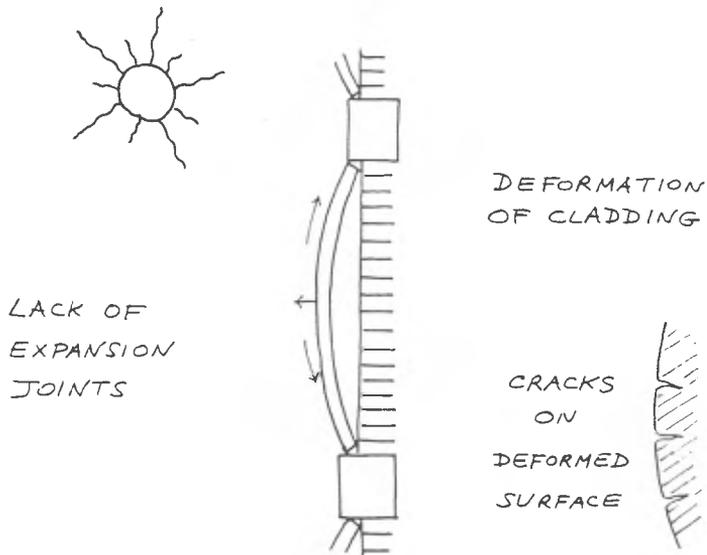
In building structures, thermal expansion movements are frequently important. If they are restricted, they cause stresses resulting in deformation or cracks.



When joints open, they often do not close again completely on contraction, because debris can get into the crack. So the crack opens progressively more and more.

Cladding materials are subject to important stresses if design does not make allowance for thermal expansion.

Restricted expansion of stone cladding causes bulging, stress and micro-cracks on the surface which is easily deteriorated. If several slabs are blocked together they behave as one single piece.



It has been calculated that a 6 m slab would bulge by 25 mm for a length variation of 0.25 mm (about 10°C increase in temperature).

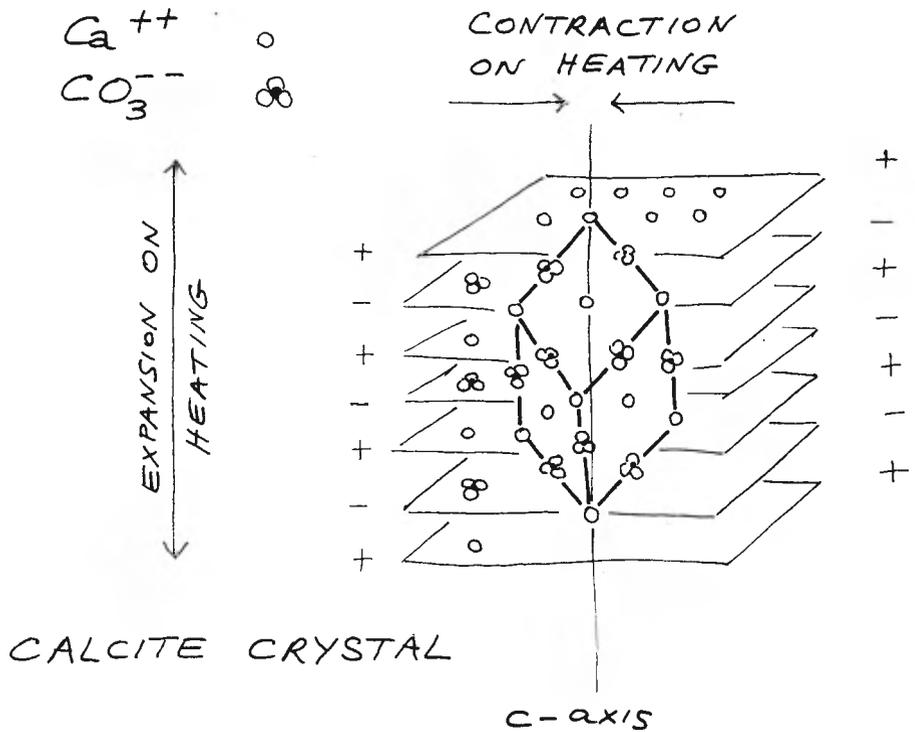
Deterioration of Marble. Marble is composed of large crystals of calcite (calcium carbonate). The thermal expansion coefficient of calcite changes according to the direction in the crystal.

The thermal expansion coefficients of the calcite crystal are:

$25 \cdot 10^{-6}$ m/m°C along the C-axis

$-5 \cdot 10^{-6}$ m/m°C across the C-axis

Following an increase in temperature, the crystal actually expands in the C-direction and contracts (!) in the transverse directions.



Such movement causes either a stress between two crystals (both expanding) or detachment of one crystal from another. Thermal stresses result in internal cleavage of crystals and detachment of crystals.

A system of cracks is thus created into which water can gain access, causing the onset of deterioration processes that can involve the inner part of the material.

Porosity of marble increases progressively with exposure to the environment.

Differential Thermal Expansion. Some building materials differ strongly from others as to the thermal expansion coefficient.

Approximate unrestrained movements for a 30°C change in temperature for pieces of one metre in length are as follows:

Marble	0.15 mm
Cement concrete	0.3 - 0.4 mm
Limestone	0.15 mm
Granite	0.25 mm
Lime-sand mortar	0.3 - 0.4 mm
Brick and terracotta	0.15 - 0.20 mm
Iron	0.3 mm
Glass	0.3 mm
Aluminium	0.7 mm
Thermoplastic resins	1.5 - 3.0 mm
Reinforced plastics	0.7 mm

It must be underlined that steel and concrete have coefficients approximately twice as large as those of brick, limestone, sandstone and lime mortar. Such considerations are very important when planning structural reinforcement of old structures with materials such as steel or concrete. When two elements are rigidly connected and tend to expand (or contract) in a different way, a stress develops in both but it is the weaker one that must give, by breaking or being deformed (i.e. undergoing microscopic cracking).

Frequently old masonry elements near modern reinforcing structures undergo an accelerated deterioration, and micro-cracks are a possible explanation.

A list of thermal expansion coefficients of materials commonly used in buildings is provided in Table I (see page 37).

Expansion Due to Moisture. Most porous building materials expand when they absorb water and contract when they release it.

Frequently the expansion coefficients are small, and the stresses involved are therefore negligible with respect to those caused by temperature variations.

In materials that contain clay, however, moisture expansion is important; in this group belong some sandstones, widely used for buildings (e.g. the Swiss "molasse"), which expand on wetting about as much as for a 50°C temperature increase.

In such cases moisture expansion can cause important stresses, particularly between the surface of the stone and its internal part when the surface is wet.

Stress Caused by Working Techniques. Mechanical abuse of the surface of building materials can take place in the course of preparation for use or of mechanical cleaning. This has particular importance in the case of stone which might be fissured when it is quarried (e.g. by the use of dynamite) or when its surface is carved (bush hammer or chisel work); cleaning methods like grit blasting or scratch brushing can also cause mechanical damage on the surfaces. An increase in the number of microscopic cracks always produces acceleration of weathering rates.

Conversely, it is also well known that stone surfaces finished (polished) in such a way as to eliminate all the material damaged by the work offer a smooth front to the environment and are more resistant to deterioration.

In all masonry materials, deterioration rates depend strongly upon the condition of their surface.

2.3 INTERNAL STRESS

Large stresses can arise inside a porous material when crystals of ice are formed in the pores (frost) or when water evaporates leaving behind crystals of dissolved materials (salt crystallization). In both cases the growing crystals exert a stress which is balanced by the resistance to compression of the material around them. Near the

surface, however, a thin section of material will be subject to a thrust from inside which is equivalent to a tensile stress pulling from outside, a situation in which a brittle material can easily break.

The mechanisms by which internal stresses originate have been the object of considerable debate; sufficient data are, however, available now for a reasonable explanation, even if basic research is still needed.

Frost. Two mechanisms are mainly indicated in the recent literature. The first is *frost heave* which was introduced to explain the swelling of frozen soil. This model is based upon the notion that ice crystals, or ice lenses, grow in relatively large voids (fractures or large pores) but are unable to develop in the small pores, unless under pressure.

Water present in the small pores is fed to the growing crystals by diffusion instead of freezing on the spot. If water is still available in the small pores when all the larger spaces are occupied, a pressure is developed which would allow ice crystals to grow also in the small pores.

It is interesting to note that the frost heave pressure does not depend upon the fact that water increases in volume when it freezes. Damage by frost heave is more likely to occur in materials that show a prevalence of small pores in the pore-size distribution. Experience seems to indicate that pore sizes in the range of 0.1 to 1 micron could be the ones that give rise to the largest stresses.

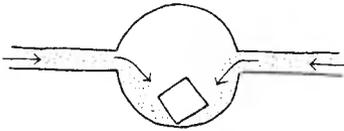
The second mechanism is *water entrapment* which depends upon the volume increase associated with freezing. In this model liquid water, still not frozen, remains trapped in the pores between already frozen areas and no space is left to allow for its expansion when it freezes.

Therefore a stress is originated when the residual water does actually freeze.

Salt Crystallization. Also in this case, two mechanisms have been proposed. A *heave* model, analogous to frost heave, depends upon the growth of salt crystals in large pores or cracks while liquid solution is fed from the small pores to the growing crystals.

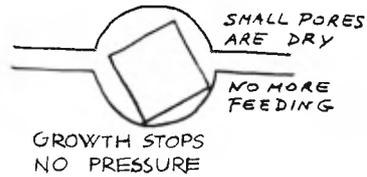
Stresses will develop when the large pores are full of crystals, if feeding solution is still available in the small pores. Also in this case the ratio of the volume of small pores to the volume of large pores determines the magnitude of the stress. The largest stresses are always developed in materials with a large proportion of small pores.

A CRYSTAL GROWS IN A LARGE PORE. THE SMALL PORES FEED THE GROWTH

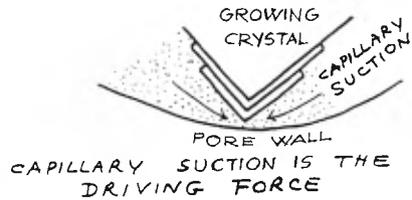
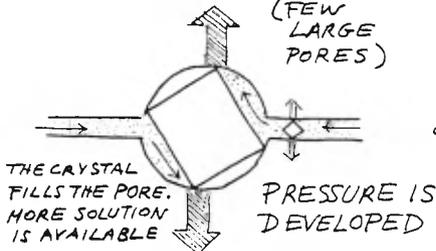


CASE 1.

MANY LARGE PORES
(FEW SMALL PORES)



CASE 2. MANY SMALL PORES
(FEW LARGE PORES)

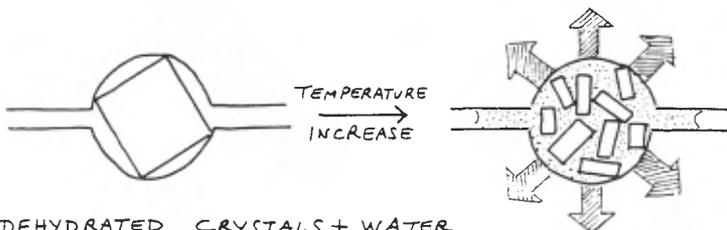


The second model concerns salts that form *hydrated salt crystals*.

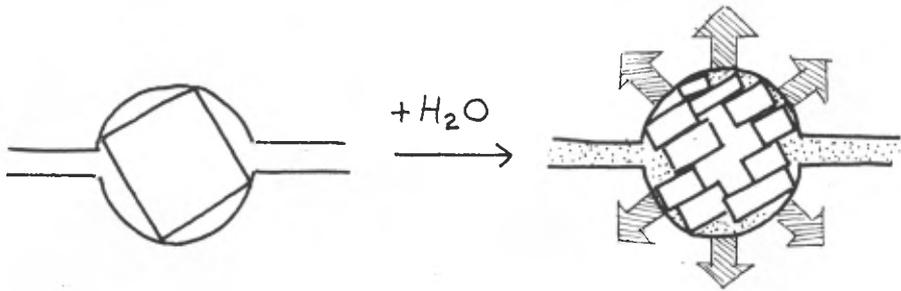
These are crystals in which some water molecules occupy well-defined positions in the crystal structure. Examples are sodium sulphate, sodium carbonate, calcium sulphate, but there are many more; actually it is less common to find a salt that does not form hydrated crystals (such as sodium chloride) than a salt that does.

Hydrated salts can also exist in crystal forms without water (anhydrous) which occupy a smaller volume. As the hydrated salts are quite bulky, they more easily fill the space available in the large pores and originate a more efficient heave mechanism. However, their particular ability in creating disruptive stresses is also explained by their transformation into anhydrous, or less hydrated, forms under the influence of a change of environmental conditions (higher temperature and lower relative humidity favour the less hydrated forms). In such cases a stress can arise when a hydrated crystal, trapped in a pore, is transformed into a less hydrated one, setting some water molecules free, the total volume of the final products being larger than that of the original crystal. On the other hand, an anhydrous (or low hydration) salt crystal which fills a large pore can be transformed into a more voluminous hydrated form by picking up water from surrounding capillaries, thus generating an additional stress.

DEHYDRATION OF A HYDRATED CRYSTAL
(FORMED AT LOW TEMPERATURE)



DEHYDRATED CRYSTALS + WATER
OCCUPY MORE VOLUME THAN
THE HYDRATED CRYSTAL



HYDRATION OF AN ANHYDROUS CRYSTAL
(FORMED AT HIGH TEMPERATURE)

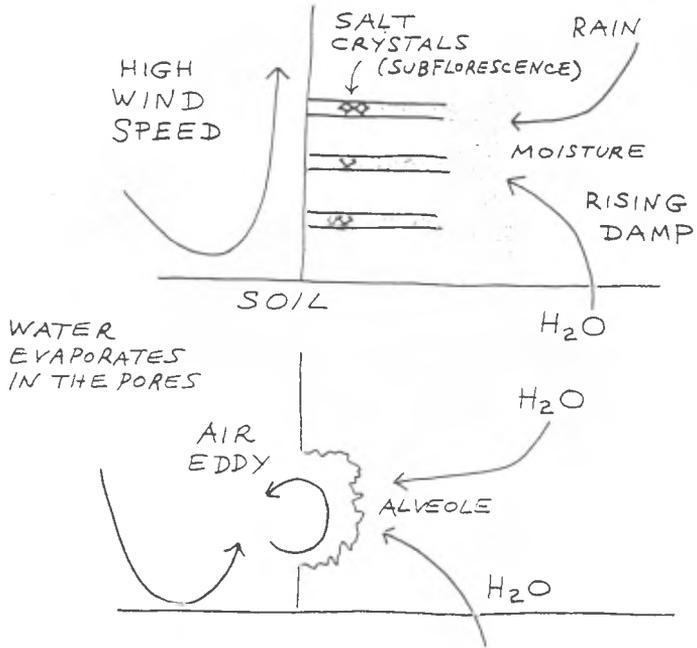
Alveolar Erosion. Alveolar erosion is a type of deterioration of porous materials in which salt crystallization plays an important role. It is characterized by the fact that disgregation proceeds preferentially in some areas, forming deep cavities (or alveoles), while nearby surfaces remain unaffected. This process of water circulating in the pores is accelerated in such a way that a liquid film cannot form on the external surface because evaporation is so rapid that water does not reach the surface at a sufficient rate. The material appears to be dry but evaporation is actually taking place immediately below the surface, in the pores.

As the disruptive effect of crystallization is greatest in such a situation, the evaporation surface is disgregated quite rapidly. Furthermore, the process undergoes progressive acceleration when a cavity is formed, due to wind speed increases inside it because of air eddies, so evaporation is further enhanced in that specific area.

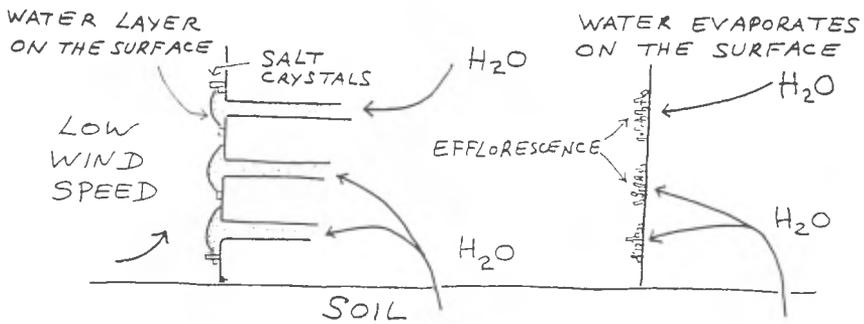
The process is summarized in Figure 6.

It was believed in the past that sand blasting caused by the wind was the essential cause of alveole formation; for this reason this type of deterioration used to be called "aeolic erosion". The indispensable intervention of salt crystallization was recognized more recently.

FIGURE 6 a) ALVEOLAR EROSION



b) EFFLORESCENCE



If the role of evaporation in the process is overlooked and conservation is attempted by filling cavities with hard materials impervious to water, evaporation is shifted to the surrounding surfaces of original material which start deteriorating in turn.

Efflorescences. Efflorescences are salt crystals formed on the surface of porous materials when water evaporates there, because the water feed is large or the wind speed is low. In this case the salt crystals are formed mainly outside the pores and the disruptive effect is smaller. This case is also shown in Figure 6.

Corrosion of Iron Cramps. Corrosion of iron results in an increase of volume of the metal because the more or less hydrated oxides (rust) occupy more space than the original material.

If iron elements are embedded in building materials, for assemblage or reinforcement, corrosion can be delayed for decades because the access of water and oxygen to the metal surface is extremely slow.

When, however, some corrosion starts, the increase in volume of the iron causes internal stress and the formation of minute cracks in the surrounding material; the result is the easy access of water and air to the metal surface. Therefore the destructive process, after a very slow start, suddenly accelerates, leading to catastrophic results in a short time.

Examples of damage produced by reinforcing iron elements in historic structures are widespread; among them one can cite the temples on the Acropolis of Athens, the Pantheon in Paris and St. Paul's Within the Walls in Rome.

TABLE I - THERMAL EXPANSION COEFFICIENTS OF
MATERIALS USED IN BUILDINGS (Unit $m/m^{\circ}C$)

(From E.B. Grunau, B. Diergarten: *Rev. Technique du Bâtiment et des Constr. Ind.* N° 51, p. 75, 1975)

Concrete	$10 \cdot 10^{-6}$
Concrete with gravel	$9 - 12 \cdot 10^{-6}$
Concrete with expanded clay	$7 - 9 \cdot 10^{-6}$
Cement mortar	$10 - 11 \cdot 10^{-6}$
Lime mortar	$8 - 10 \cdot 10^{-6}$
Limestone	$7 \cdot 10^{-6}$
Brick	$5 \cdot 10^{-6}$
Granite	$8 \cdot 10^{-6}$
Glass (10% alkali)	$4.8 \cdot 10^{-6}$
Iron	$11.5 \cdot 10^{-6}$
Steel	$10 - 14 \cdot 10^{-6}$
Copper	$16.8 \cdot 10^{-6}$
Aluminium	$23.8 \cdot 10^{-6}$
Lead	$29.4 \cdot 10^{-6}$
Pine, along fibres	$5.4 \cdot 10^{-6}$
Pine, across fibres	$34.1 \cdot 10^{-6}$
Oak, along fibres	$3.4 \cdot 10^{-6}$
Oak, across fibres	$28.4 \cdot 10^{-6}$
Fir, across fibres	$58.4 \cdot 10^{-6}$
Wood laminates	$10 - 40 \cdot 10^{-6}$
Polyester resins	$100 - 150 \cdot 10^{-6}$
Glass-polyester laminates	$35 - 45 \cdot 10^{-6}$
Epoxy resins	$60 \cdot 10^{-6}$
Epoxy with silica fibres (1:5)	$20 \cdot 10^{-6}$
Acrylic resins	$70 - 80 \cdot 10^{-6}$
PVC	$70 - 80 \cdot 10^{-6}$
Nylon 66	$70 - 100 \cdot 10^{-6}$

Chapter III

CHEMICAL PROCESSES

CORROSION

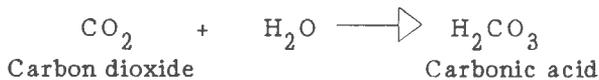
Chemical reactions always require the presence of water, therefore chemical corrosion is possible only when building materials are wet.

In discussing chemical action it is useful to make a distinction between water provided by direct action of rain and water films deposited on the surface by condensation.

All the water that reaches building materials by passing through other materials (rising damp, percolating rainwater) is not active from a chemical point of view because it has already been in contact with solid materials of the same type, and its chemical activity or solvent power has been exhausted. This kind of water is dangerous as a possible source of internal stresses but not in general as a chemical agent.

3.1 ATTACK BY RAINWATER

Rainwater is always slightly acidic because air contains carbon dioxide, which forms carbonic acid (a very weak acid) when dissolved in water.



Under such conditions, carbonates of calcium and magnesium (e.g. lime mortars and plasters, limestone, dolomitic limestone, marble) can be transformed into bicarbonates and slowly dissolved.

Insofar as ceramic products are concerned (bricks and tiles in particular), their main components are silicates of calcium and aluminum which are mostly water insoluble. They should be quite resistant to rainwater, but it must be added that their slow reactions with slightly acidic water are not so well known. On the other hand, glazes used on decorative tiles can be rich in alkaline oxides and so somewhat soluble in acid water, or even in neutral water.

Sandstones contain some silicate minerals (micas, chlorites, feldspars) which can be attacked by water in the long run. When such a reaction takes place, some metallic ions (calcium, aluminum, potassium, sodium) are leached out; most of the sandstone remains insoluble but is transformed into clay minerals which are much softer and bulkier than the original minerals.

As sandstones are normally very porous, rainwater penetration can be deep and water can remain in contact with the minerals for rather long periods each time they become wet for any reason (actually condensation water would also be effective for this process). As a consequence, surface layers of several millimetres thickness can become softened and swollen, causing extensive decay of the exposed surfaces.

In general, the rate of the corrosion process is strongly dependent upon the porosity and the type of minerals that are present. Also, higher temperatures cause an acceleration of corrosion (wet tropical climates).

3.2 ATTACK IN POLLUTED ATMOSPHERE

Polluted atmospheres inside or near urban centres contain variable amounts of sulphur dioxide produced by the burning of sulphur-containing fuels.



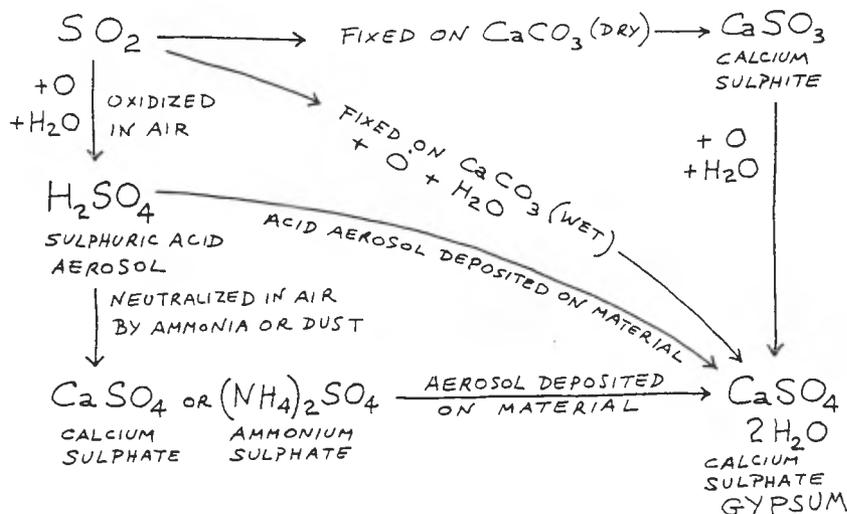
Oxidation of sulphur dioxide leads to sulphuric acid, a strong acid that can cause the deterioration of several minerals (carbonates, silicates) at higher rates than water containing carbonic acid only.

Winkler calculated 1 mm erosion on marble in 25 years by the observation of quartz veins in marble monuments.

The action of air pollution is, however, rather complex and not completely known. In the first place, other pollutants besides sulphur dioxide are always present, and some of these can cause the formation of other acids (hydrochloric acid, nitric acid, hydrofluoric acid) which also exert a corrosive action.

Second, the sulphur dioxide attack on materials can follow different paths as shown by the diagram.

POSSIBLE PATHS
OF SULPHUR FIXATION ON CALCAREOUS MATERIALS



3.3 WETTING-DRYING PROCESSES (CONDENSATION or SPRAY)

Frequently the exposed surfaces of building materials are covered by a film of water which is too thin to allow the water to run

down, over the surface. As a consequence, impurities deposited from the atmosphere or the products of the reaction of acids with the material are not washed away.

Films of water can be formed by condensation or by deposition of droplets of water suspended in air, as a fine mist, during rain or fog.

Water in this form can cause more damage than the direct action of rain impinging on exposed surfaces because it is normally acid and transports all particulate pollutants present in the atmosphere (soot, dust, etc.).

Deposited water can penetrate to some depth in the materials, exploiting pores or cracks formed by previous deterioration processes, but it returns to the surface to be evaporated when drying conditions prevail.

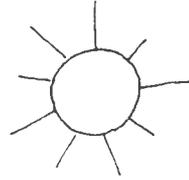
The wetting-drying can thus cause damage both in the wetting phase (because of acid attack) and in the drying phase (because of crystallization of pollutants and reaction products).

Surfaces affected by wetting-drying processes are easily recognizable in buildings because hard crusts, soiled by soot or dust, are formed on them. The crusts are seldom continuous and impervious to water because cracks frequently traverse them; they do not constitute a protective layer.

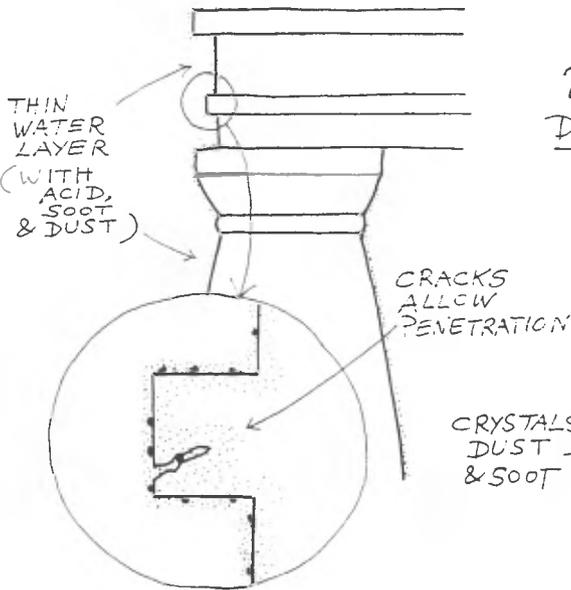
Deterioration can continue behind the crust that is often found lying over incoherent, disgregated material. Damage induced by wetting-drying can thus proceed rapidly under the deceptive appearance of a well-preserved surface covered by a dark patina. Only close-range inspection (tapping, sampling) enables the real condition of a weathered surface affected by condensation to be assessed.

Resistance to the wetting-drying process depends more on the pore structure and the mechanical strength of the material than on its chemical properties. Materials with low porosity and good tensile strength are the most resistant to this type of deterioration.

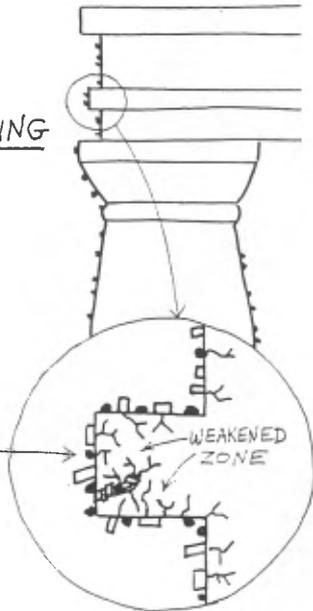
FIGURE 7



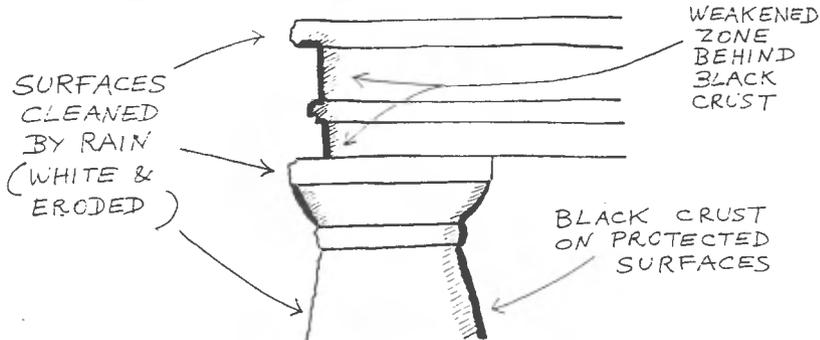
1. WETTING



2. DRYING



3. WEATHERING (MANY CYCLES)



Well-fired bricks or tiles are substantially resistant; they can get soiled but they do not disgregate. Instead, low-quality ceramic material can be damaged.

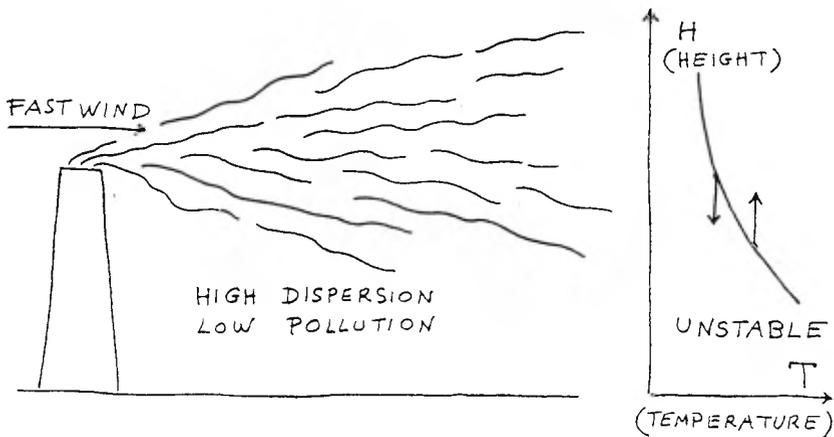
Most limestones and sandstones are deeply attacked as well as lime mortars. However, low porosity materials belonging to these groups might well show good resistance, an example being Istrian stone, a microcrystalline, low-porosity limestone.

In all types of stone, more resistant beds can alternate with less resistant ones in the same quarry, a matter of porosity and internal cohesion rather than of chemical composition.

White marble is affected by weathering up to surprising depths because it becomes progressively more porous with ageing due to the internal cracking brought about by thermal cycles.

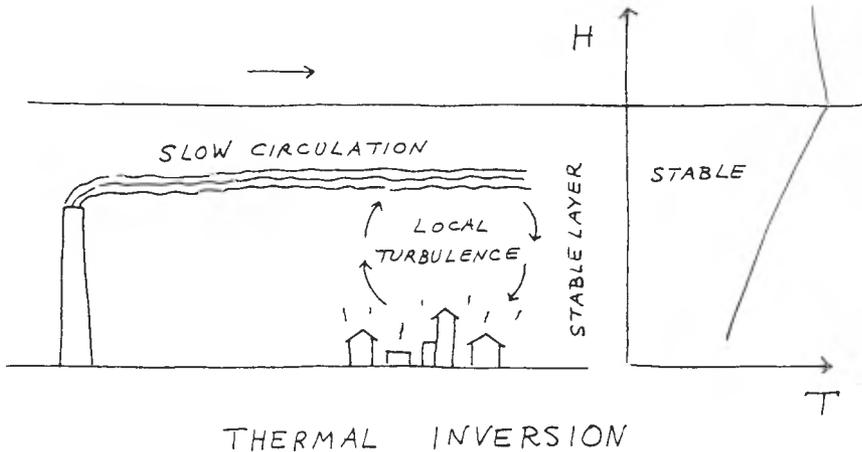
3.4 AIR POLLUTION CLIMATOLOGY

The extent of air pollution is determined by the amounts of pollutants produced and also by meteorological factors. If the pollutants are dispersed in a large volume of air, the resultant pollution is low:



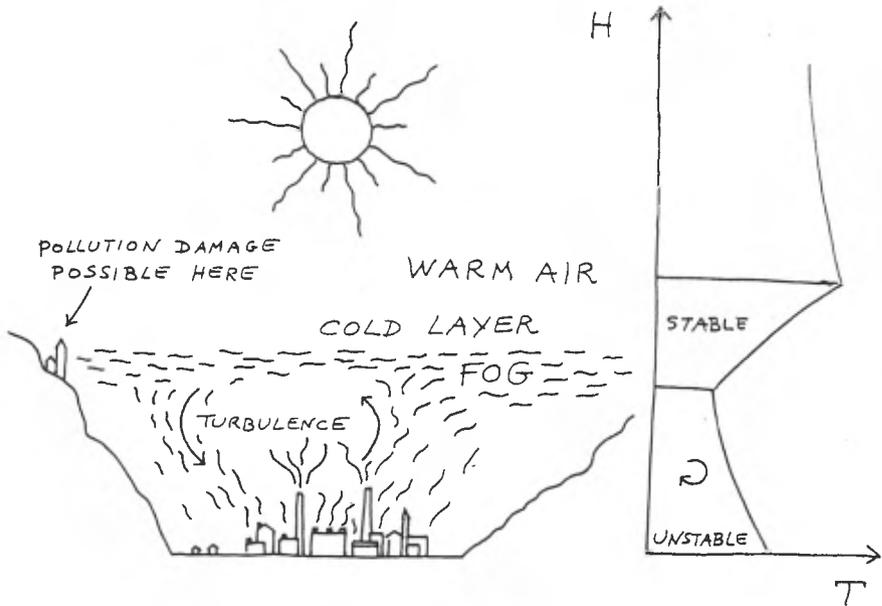
In the atmosphere, the temperature normally decreases as the height increases. In such conditions the air is unstable because the warmer air tends to rise above the colder air.

On winter nights, however, near the ground, a layer is frequently formed in which temperature *increases* with height. In such conditions the air is stable because the cold air tends to remain at the bottom. This condition is called *thermal inversion*.



Circulation of air is normally slow in such a situation and pollutants are not dispersed. They tend to propagate at constant height but can be brought to the ground by local turbulence caused by warm surfaces (e.g. heated houses).

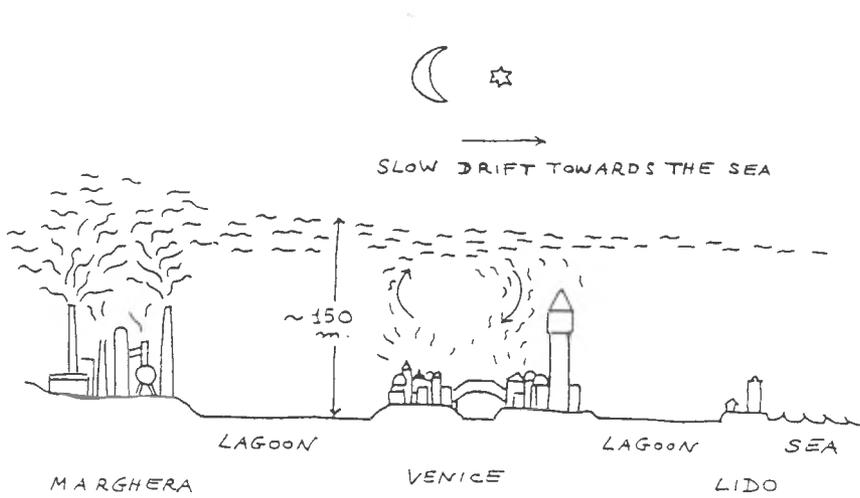
High pollution cases occur, for instance, in valleys in winter when a thermal inversion is formed in a situation of high pressure, low wind speed and fine weather.



THERMAL INVERSION IN A VALLEY
IN A WINTER MORNING

A special case is that of Venice where pollution is caused both by local sources (heating systems) and transport from the industrial zone of Marghera when a thermal inversion is formed, as is often the case in autumn and winter.

Local turbulence over the city is caused by the fact that, in winter, it is warmer than the lagoon.



VENICE ON A CLEAR WINTER NIGHT

Chapter IV

DETERIORATION OF POROUS MATERIALS

4.1 BACTERIA AND FUNGI

Several strains of bacteria draw the energy necessary for their vital activities from inorganic chemical reactions of reduction or oxidation which they have the ability to produce.

Such reactions can result in the formation of acids, both strong and weak, and can corrode building materials that are sensitive to acids.

A well-known example is constituted by the bacteria of the sulphur cycle (thiobacilli) which can synthesize sulphuric acid from sulphur, sulphides or even sulphur dioxide.

When large numbers of thiobacilli are found (over 10,000 per gram) and when simpler explanations are not available, the microbiological hypothesis appears as a possible explanation of corrosion accompanied by formation of calcium sulphate (e.g. Angkor Wat in Cambodia and some buildings in country towns in France).

An analogous hypothesis for bacteria of the nitrogen cycle producing nitric acid is not substantiated by positive results of analyses in the actual study of deterioration cases.

Other types of bacteria and fungi draw their energy from the oxidation of organic materials and yield organic acids as the final product of the reaction. One of such acids is oxalic acid, and this fact can be invoked to explain several findings of calcium oxalate among the materials present in surface crusts on ancient stones.

It is not easy in general to assess the importance of such microbiological processes with respect to chemical and physical

deterioration. It is quite probable that a continuous interplay takes place between the two types of processes, physico-chemical deterioration frequently opening the way to biological colonization but frequently receiving an added impulse by its output of reactive acids.

4.2 ALGAE

Algae attack on masonry material is frequent in very damp atmospheres, such as tropical climates (e.g. Borobudur, Java) or caves (Lascaux, Domus Aurea in Rome).

Deep disgregation of materials is rare, although the case of algae boring into andesitic stone and causing swelling and bursting of the rock was demonstrated in Borobudur.

More frequent is the superficial damage caused by the algae vegetation which is particularly noxious in the case of painted or carved surfaces.

Most algae need the energy of light to carry out their vital functions, so in caves they frequently develop only on illuminated surfaces.

Control of algal infections is possible by means of cleaning and disinfecting agents but the activity of disinfectants lasts only a limited time and continuous attention is required in damp climates. Also, it must be kept in mind that some proprietary products for treatment are alkaline and can form soluble salts or cause colour changes on the surface.

4.3 LICHENS

Lichens are formed by the association (symbiosis) of fungi and algae.

Development of lichens over masonry materials is widespread on external surfaces; several species, however, cannot live in polluted atmospheres.

White "crustaceous" lichens extend their growth several millimetres inside the material and decompose it to some extent by means of the production of organic acids (for instance oxalic acid).

Other lichens show a lesser penetration power. In general the damage caused by lichens progresses slowly but the disfiguring effect on decorative surfaces (paintings or architectural decoration) can be quite serious.

Cleaning of lichen-infested surfaces is not easy, and prevention of attack demands continuous care. Some success was obtained recently in the removal of "crustaceous" accretions with basic jellies (see the cleaning of stone in Chapter VIII).

4.4 MOSS

Moss can exert a definite disruptive action on the surface of building materials and up to a depth of a centimetre or more.

It appears that its development is favoured on alkaline surfaces, such as cement concrete or lime mortars, and occasionally it has been noted to take place on stone surfaces located near areas where cement concrete was used for consolidation.

4.5 HIGHER PLANTS

Roots of weeds, bushes or trees can cause disruption of masonry materials even at some distance from the plant. Control of such processes falls, however, within the normal routine of maintenance of buildings so they become important only in the case of semi-abandoned structures.

Chapter V

VIBRATION

5.1 INTRODUCTION

Vibration caused by traffic, trains, machinery or sonic boom induces rapidly alternating tensile and compressive stresses in buildings. The effect of such stresses on complex structures is not easily analyzed.

In technical literature several cases are mentioned in which vibration caused serious damage or even collapse of buildings.

Experiments conducted in the past 70 years have allowed the calculation of stresses induced by vibration and the evaluation of safety limits for buildings. In most cases the stresses caused by the most frequent types of vibration (e.g. traffic) are not sufficient to cause damage to a building if considered alone.

However, if vibration stress is considered as superimposed on the other types of stresses acting on structures and materials (load and environmental stresses) it must be accepted that vibrations may cause an increase in the deterioration rate.

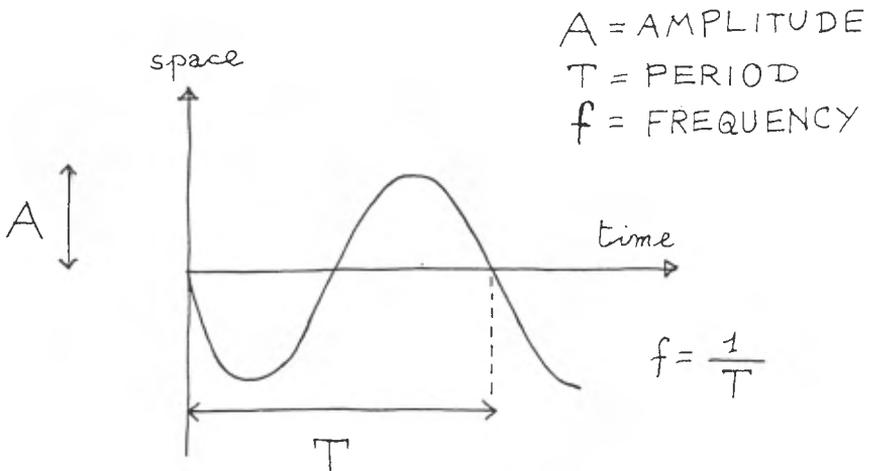
As acceleration of deterioration processes is quite difficult to measure, the problem of evaluating allowable limits for vibration is not easily solved, particularly for old buildings of great value.

The maximum allowable limit of vibration should be such that vibration superimposed on the other stresses acting on the building still results in a tolerable deterioration rate (a tolerable deterioration rate being that which can be controlled by the maintenance service foreseen for the building in question).

Such an assumption connects the maximum allowable limit of vibration to the conditions of the building and to the maintenance system that might be envisaged for it in the future.

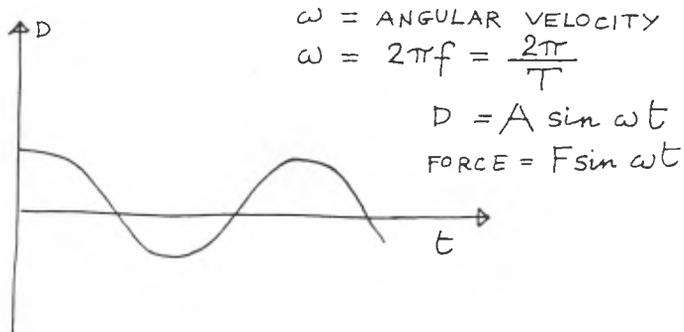
5.2 DEFINITIONS AND MEASUREMENTS

Vibration is the alternative movement of a body on both sides of an equilibrium position.

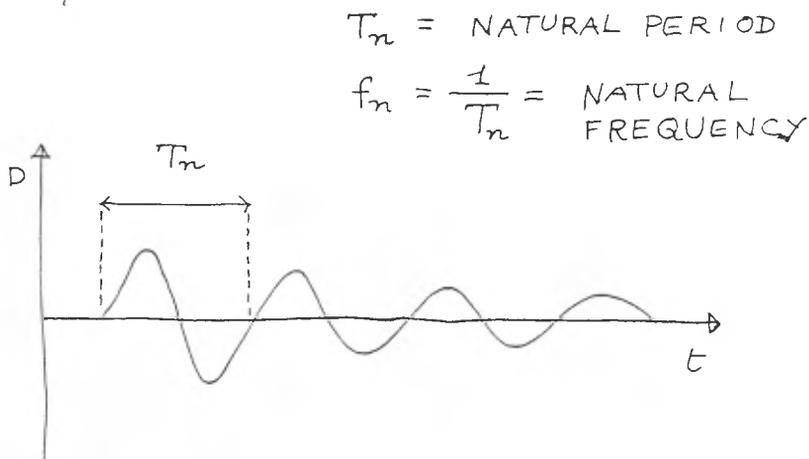


Most vibration can be described by approximation as a sinusoidal curve or as a combination of several sinusoidal curves.

The position of the body and the force acting on it can then be described by equations.



Vibrations can be caused by individual impulses (blasting, pile driving, etc.), that cause objects to vibrate with their natural frequency (i.e. the reverse of their natural period).



All vibrations dissipate energy and are dampened more or less rapidly.

Continuous vibration is caused for instance by machines at work. They force objects to vibrate at the frequency of the exciting vibration.

If the natural frequency of the object is close to the frequency of the exciting vibration, the object's response to the excitation is much stronger (resonance).

Vibrations are measured by means of accelerometers which transform mechanical impulses into electrical ones which are recorded and analyzed to yield data of frequency, amplitude and velocity (or acceleration) of the vibration.

5.3 NATURAL FREQUENCY OF BUILDINGS - RESONANCE

A single blow excites the natural frequency of a building. If T_N is the natural period of oscillation of a building and f_N its natural frequency:

$$f_N = \frac{1}{T_N}$$

Empirical rules allow the calculation of the natural period of a building. For instance:

$$T_N = \frac{\text{NUMBER OF STOREYS}}{11}$$

Some examples of data on natural frequencies and periods of buildings are reported in the literature.

- Low buildings $f_N \sim 10 \text{ Hz}$
- Towers 30-40 m $f_N \text{ (BENDING)} = 1.64 \div 2.86 \text{ Hz}$
- Skyscrapers $f_N = 0.2 \div 0.5 \text{ Hz}$ $T_N = 5 \div 2 \text{ sec}$
- Empire State Building $T_N = 8.25 \text{ sec}$
- New Severn Bridge (vert. flex.) $T_N = 7 \text{ sec}$ $f_N = 0.14 \text{ Hz}$
- Long Creek Bridge (Canada) $f_N = 0.6 \text{ Hz}$ $A = 200 \text{ mm}$

The natural frequency of many floors and slabs is between 10 and 30 Hz.

Continuous vibration induces its own frequency in a building. When the frequency of the exciting vibration (f) is near the natural frequency of the building (f_N) the amplitude of the induced vibration is increased. This phenomenon is called resonance.

Amplification due to resonance depends upon the "damping factor" (D) of the building; for most types of structures and building materials amplification can be assumed to be equal to $1/2 D$.

Amplification at resonance can be measured by artificial stimulation of the structure and by calculation of the number of cycles required for amplitude to diminish to half a given initial value. If N is such a number:

$$\text{AMPLIFICATION} = 4.35 N$$

A more accurate method is to calculate the number of cycles (N_1) required to reduce the amplitude to $1/10$ of the initial value. In this case:

$$\text{AMPLIFICATION} = 1.365 N_1$$

5.4 AMPLITUDE

The effect of the amplitude of vibration on buildings or man depends upon the frequency.

Amplitude is normally measured in microns μ (10^{-3} mm). The threshold of perceptibility is 10 microns at 5 Hz. At 50Hz the same amplitude is decidedly annoying.

At 5 Hz a 400 microns amplitude "generates discomfort" while at 50 Hz a 15 microns amplitude is classified as "painful".

Road traffic causes vibration of 5-25 microns amplitude at 10-30 Hz.

Experiments carried out in the past with explosive charges allowed the establishment of inferior limits of damage for new (400 microns) and old buildings (200 microns). In more recent papers (Teichmann and Westwater - 1957) a limit of 100 microns is advocated for "structures of great value and frailty or properties in poor condition".

5.5 PEAK VELOCITY

Velocity, or, more correctly, "peak particle velocity" of the vibrating object can be calculated from the accelerometer data and is the best guide for assessing the risk of damage to buildings.

The formula:
$$v = 2\pi Af$$

is valid for sinusoidal vibration but is used as an approximation in most cases.

The threshold of perception by man is around 0.2 mm/sec. A velocity of 2.5 mm/sec is qualified as "annoying".

From blasting experiments on buildings (1949-1965), several threshold values for minor damage have been established by different authors. They range from 50-120 mm/sec.

More recent studies, however, appear to shift these limits towards considerably lower values.

DIN specification 4150 (draft 1970) gives the values indicated below as maximum allowable velocities for transient vibrations (sudden shocks). For sustained vibrations the specified values must be reduced by 1/3.

DIN 4150 (1970 Draft) Valid 8-80 Hz

<u>Class</u>	<u>Description</u>	<u>Maximum allowable velocity</u>
1	Ruins and buildings of great historic value	2 mm/sec
2	Buildings with existing defects	5 mm/sec
3	Buildings undamaged (minor defects such as cracks in plaster)	10 mm/sec
4	"Strong" buildings	10-40 mm/sec

DIN 4150 requires measurement of vibrations on the external foundation at ground level. Combined vectorial components of vibration must be measured in the vertical and in the horizontal directions.

For vibration velocities measured on floors and ceilings the maximum allowable value is 20 mm/sec. Data from more recent specifications are shown in Table II.

5.6 ACCELERATION

Results of vibration measurements are often expressed as acceleration which is related to amplitude and frequency by the equation:

$$a = 4\pi^2 A f^2$$

valid for sinusoidal vibration but used as an approximation in most cases.

Acceleration is measured normally in g-units (g = gravity acceleration, i.e. about 10 m/sec²).

TABLE II - VIBRATION DAMAGE IN BUILDINGS

PEAK VELOCITY

$$v_{r \text{ MAX}} = \sqrt{v_{x \text{ MAX}}^2 + v_{y \text{ MAX}}^2 + v_{z \text{ MAX}}^2}$$

DIN 4150 (DRAFT 1978)

<u>$v_{r \text{ MAX}}$</u>	<u>DAMAGE</u>
< 2.5	NO DAMAGE
2.5 to 6	VERY UNLIKELY
6 to 10	UNLIKELY
> 10	POSSIBLE

ISO/TC 108/SC-2

<u>$v_{r \text{ MAX}}$</u>	<u>DAMAGE</u>
3 to 5	VISIBLE CRACKS (> 0.02 mm) IN SECONDARY ELEMENTS: PARTITIONS, RENDERINGS
5 to 30	VISIBLE CRACKS IN PRINCIPAL ELEMENTS: MASONRY WALLS, BEAMS, PILLARS, FLOORS
> 100	LARGE PERMANENT CRACKS REDUCTION OF LOAD BEARING CAPACITY

The minimum acceleration that causes a noticeable effect on people is 0.01 g. An unpleasant effect is caused by 0.04 - 0.05 g and a painful effect over 0.1 g.

Data on blasting experiments (Thoenen and Windes 1942) show damage to buildings for 1 g. The authors assumed that a safety limit for buildings is 0.1 g.

It is likely that such a value should be drastically reduced for ancient buildings if sustained vibration and the effect of other stresses applied to the building are considered.

5.7 TRAFFIC VIBRATION AND ITS EFFECT ON BUILDINGS

Road traffic causes vibration of the ground and of buildings. Amplitudes of 2-25 microns at frequencies of 10-30 Hz are reported in the literature. Larger amplitudes and lower frequencies can be generated by bigger vehicles; amplitudes of 5-50 microns at 7-8 Hz are reported for loaded buses, tractors and trailers.

Irregularities of the road surface are the main cause of vibration. In an example reported in the literature, an irregularity of 20 mm amplitude caused vibration with velocity up to 5 mm/sec, well above the DIN 4150 limit for ancient buildings.

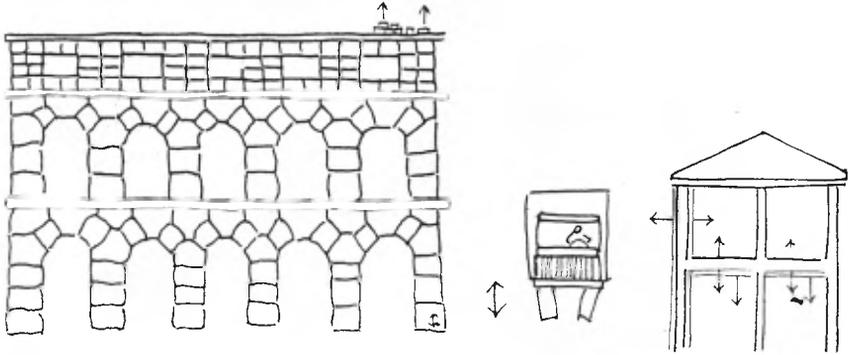
Experiments carried out with prepared obstacles 4-38 mm thick allowed amplitudes up to 76 microns at 8 Hz to be measured (about 4 mm/sec).

The distance between the building and the road surface irregularity is obviously an important factor. It has been stated that, in general, doubling the distance causes a reduction of amplitude by a factor of 2, or slightly more.

Traffic vibration can seldom be considered the sole cause of structural failure in buildings. Its effect must be considered in relation to other deterioration processes as it can result in their acceleration. It is not easy to assess it in quantitative terms.

Some general rules, however, can be stated.

- a. The effect of traffic vibration is more important on small elements than on large ones.



As the natural frequency of buildings is normally much lower than the frequency of traffic vibrations, resonance of building structures due to traffic is unlikely to take place. However, single lightweight elements such as floors, ceilings and windows are more prone to resonance amplification, as smaller elements have higher resonance frequencies.

- b. Structural members show maximum amplitudes of vibration where they are farther removed from restraining connections to other members (e.g. centres of floors).

As a general conclusion it can be stated that elements more susceptible to vibration damage in buildings are as follows:

- Plasters, particularly if not well attached
- Cracked masonry
- Small masonry elements not well connected to the structure (e.g. rubble infill, isolated bricks). Their vibration can grind off the mortar.

Sior (1961) notes that when vibration is near the damage threshold value it can act as the trigger mechanism, producing damage that is basically attributable to other causes (e.g. weak foundations).

Vibration stress can also interfere with physico-chemical processes of deterioration and cause an increase of deterioration rates.

Cracks can widen during the vibration cycles and admit dust which does not allow the re-establishment of the original condition. Also access of water in micro-cracks, formed or expanded by vibration stress, can cause other destructive processes such as crystallization of salts, frost or chemical attack to propagate towards the interior of materials.

In buildings of historic or artistic value the acceptable level of vibration is particularly low because, even if the structure might not be affected, damage to minor elements such as plasters is usually not tolerable.

The problem is particularly acute when the plaster bears mural paintings. A good example is the Villa Farnesina in Rome where mural paintings by Raffaello and his school were damaged by traffic vibration and threatened by total destruction.

In an attempt to solve the problem, the road nearby (Lungotevere della Farnesina) was completely rebuilt in 1970 and suspended over rubber blocks for a length of 60 metres.

Other, less drastic preventive measures are smoothing the street surface and banning heavy traffic. In exceptional cases, entire buildings have been mounted on springs.

5.8 SONIC BOOM

Sonic waves created by jet planes when they break the sound barrier result in an overpressure applied to buildings and can cause damage.

The largest overpressure recorded is 2000 N/m^2 (New Mexico 1962). Studies carried out for the Concorde showed that overpressure caused by this supersonic plane should always be below 100 N/m^2 .

The highest probability of damage concerns objects with large surface and small mass, not pre-loaded and having rather low tensile strength. It applies, therefore, in the first place to plaster, particularly if not well attached, then to glass and finally to roofs.

Damage should be rare at overpressures below 500 N/m^2 , but the effect of "tuning" of the structure with the sonic wave can introduce some amplification of the vibration.

The period of the sonic waves, frequently called the "signature interval", depends upon the type of plane; for the Concorde it is 0.35 seconds. Structures with natural frequencies close to 3 Hz can, therefore, undergo increased vibration because of resonance.

As in other vibration cases, the type of building and its condition have great importance in determining the effect of the sonic waves.

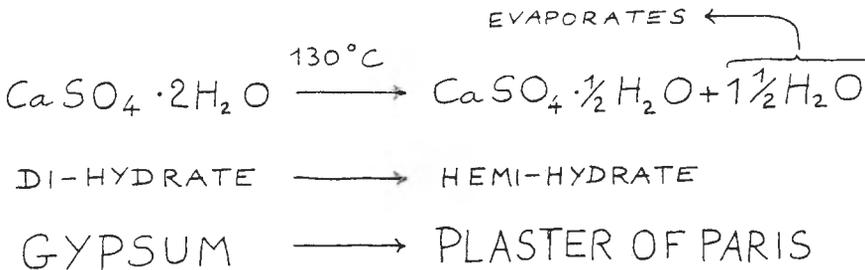
Chapter VI

BINDERS

6.1 GYPSUM

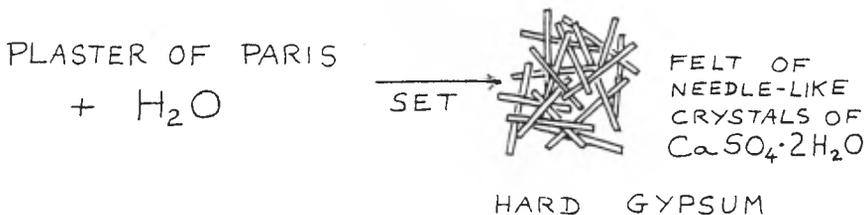
Gypsum was used in Egypt both as a mortar between blocks of stone (pyramids) and as a plaster already at the beginning of the third millennium B.C. In Mesopotamia its use also dates from very early times.

Gypsum plasters or mortars are prepared by heating gypsum minerals or selenite rocks (both are composed of hydrated calcium sulphate) at moderate temperatures.



The hemi-hydrate is the main component of *plaster of paris* which is prepared by heating the hydrate at $150^\circ\text{--}160^\circ\text{C}$.

Plaster of paris sets (= hardens) rapidly when mixed with water.



The speed of setting is influenced by the conditions under which the previous heating took place. Actually two kinds of hemi-hydrate, having different crystal shapes and different rates of reaction with water, are known.

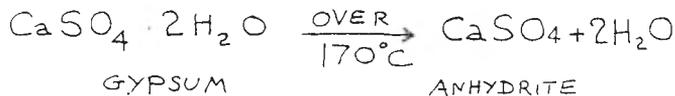
α - Hemi-hydrate is called the crystalline hemi-hydrate. It is formed by heating at high pressure in the presence of water vapour, in an autoclave. It is well crystallized and not very porous. It reacts more slowly with water.

β - Hemi-hydrate is called the microporous hemi-hydrate. It is formed in a dry atmosphere; its crystals are smaller and contain pores of relatively large dimensions. It reacts more rapidly with water.

In the course of the setting reaction the material warms up and loses a little water by evaporation; this volume change is, however, offset by the expansion of the crystals caused by hydration, therefore the setting of gypsum takes place with a slight expansion (useful in making moulds). No fillers are required to avoid contraction and cracking.

Setting is accelerated by adding gypsum dust or salt and is retarded when organic materials such as glue or starch are present.

If the hydrate (or the hemi-hydrate) is heated above 165°-170°C the remaining water is also eliminated and anhydrous calcium sulphate (anhydrite) is formed.



Anhydrite may re-hydrate, but rather slowly.

Transformation of hydrated gypsum into anhydrite can take place spontaneously in dry, hot climates (e.g. in the Egyptian desert). As a result the mechanical strength of gypsum plaster can be sharply reduced.

As calcium sulphate is slightly soluble in water, gypsum is not used normally on exposed surfaces in damp climates.

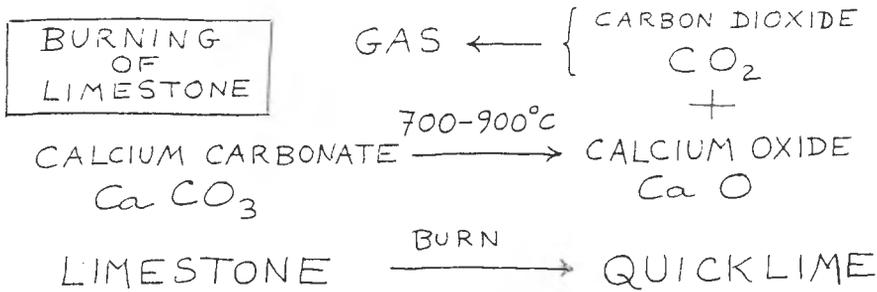
6.2 LIME

The use of lime in the neolithic period is demonstrated by occasional finds of lime washes.

In the historic period, lime plasters appear in the Mycenaean and Minoan civilization (Knossos palace 1700 B.C.).

Use of lime in Egypt starts quite late (Ptolemaic period, 300 B.C.). Some earlier mortars contained both calcium carbonate and gypsum and were made starting from mixed minerals that could yield either lime or gypsum mortars. Lime, however, must be prepared at much higher temperatures than plaster of paris, therefore use of lime technology is unlikely in such cases.

Lime is made by heating limestone, which is composed essentially of calcium carbonate.



Marble is not a suitable source of calcium carbonate, because its large grains form lumps of quicklime that are not easily slaked.

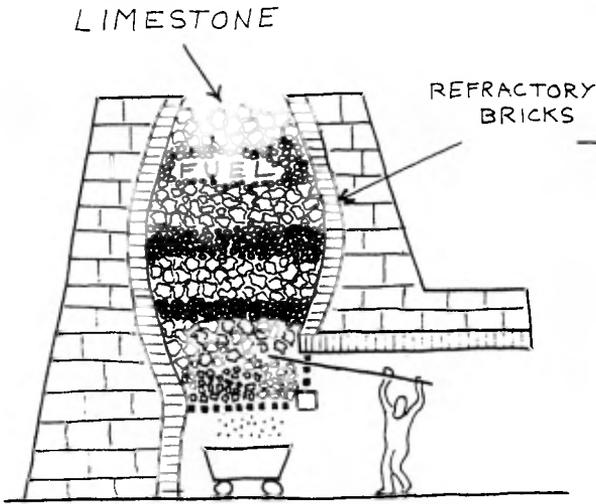
If limestone is overheated the lime that is obtained does not react well with water (formation of lumps).

Heating of limestone was carried out in kilns that became progressively more and more refined (see Figure 8).

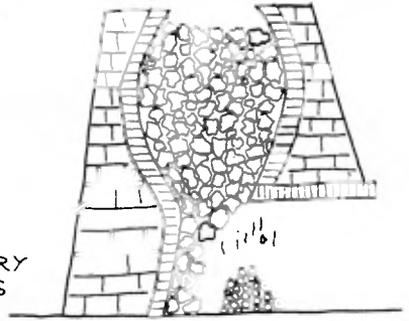
FIGURE 8. LIME KILNS

1. FLARE KILN

DISCONTINUOUS
HEATING TIME
~ 1 MONTH



LIMESTONE

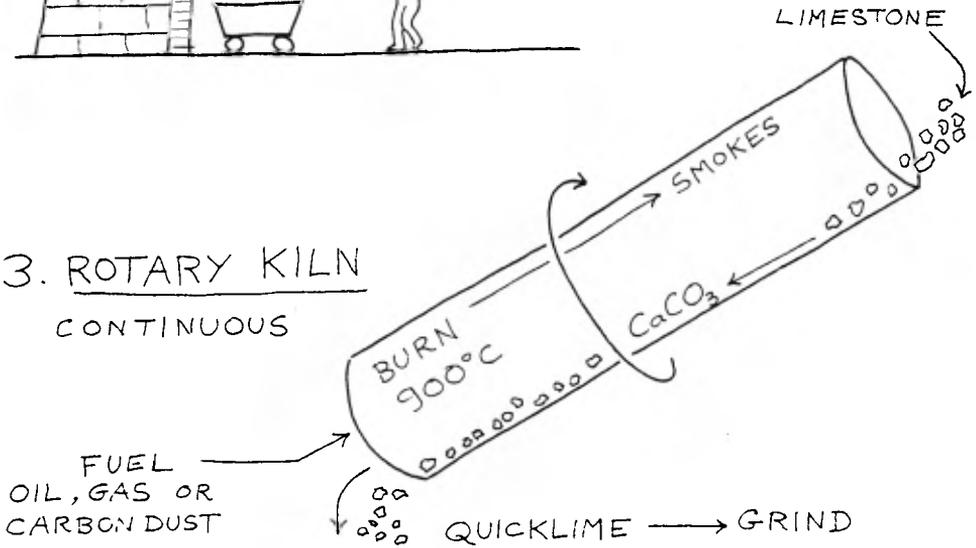


2. DRAW KILN.

CONTINUOUS

3. ROTARY KILN

CONTINUOUS



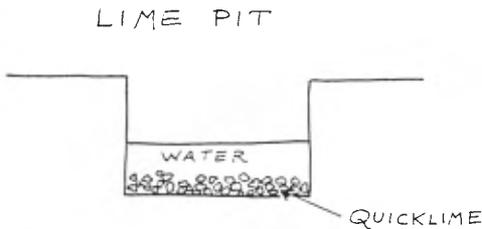
SLAKING is the reaction of quicklime with water.

CALCIUM OXIDE \longrightarrow CALCIUM HYDROXIDE



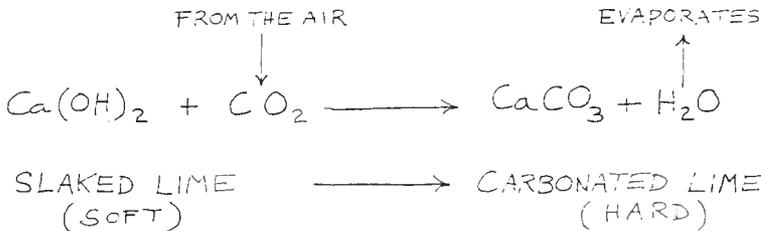
QUICKLIME \longrightarrow SLAKED LIME

The reaction develops heat and must be carried out with great attention to obtain a good product. If the right amount of water is used, a powder of calcium hydroxide is obtained (hydrated lime powder). If some excess of water is used a soft, greasy mass is obtained (lime paste).



Lime was once slaked in lime pits, where it was kept for several months or even years. Prolonged slaking favours the growth of platelike hydrated lime crystals (Portlandite) and improves plasticity of the lime putty.

HARDENING of slaked lime takes place by reaction with carbon dioxide (from the air) and evaporation of water.



Hardening therefore requires contact with air and progressive drying. The loss of water causes a contraction in volume. Slaked lime is never used alone, but always with a filler in order to avoid cracks.

LIME MORTARS - Sand is the typical filler for lime. Sand must be washed clean to remove salts (which cause efflorescences), clay or organic materials (which slow the hardening process).

Some typical formulations are the following:

	Parts by volume	Parts by weight
Slaked lime	1	15
Sand	2 - 3	100
Water	As required to make a paste	

Accurate mixing is necessary.

Lime mortars show good workability if water is rather generously added. Conversely, the mechanical properties of the hardened mortars are improved if the amount of water is reduced.

Workability can be achieved, however, without excessive loss of strength, through the use of fluidizers (also called water reducers because they allow the use of less water without affecting workability).

Energetic mixing, resulting in air entraining, also allows improvement of workability without excessive addition of water.

A mason needs a lot of experience in order to achieve a proper balance between workability and strength.

A further difficulty in the use of lime mortars is due to the fact that they set very slowly and might not even set at all in a very damp atmosphere (drying is required for hardening).

These difficulties limit the use of pure lime mortars nowadays, and encourage the addition of hydraulic components that can produce rapid setting even under wet conditions (lime-pozzolana, lime-cement mixtures).

It must be remembered, however, that lime mortars present physical and mechanical properties close to those of mortars used in ancient masonry and, therefore, their use in conservation of old buildings is highly desirable, if the inherent technological difficulties can be satisfactorily solved.

6.3 HYDRAULIC MORTARS

Hydraulic mortars set by chemical reaction with water. No air is needed. Mortars made with hydraulic compounds set even under water and, when hard, they resist the destructive action of water and even of sea water. Their use is, therefore, required for works (bridges, dams, piers) to be executed in the sea or in waters of any type or with the concrete technique, when large blocks are cast and contact with air is unlikely in the core.

Lime forms hydraulic mortars only if it can react with silica (SiO_2) or alumina (Al_2O_3). This reaction is only possible at high temperatures (modern cement) or, at room temperature, if some very reactive forms of silica and alumina are used (ancient Roman cement).

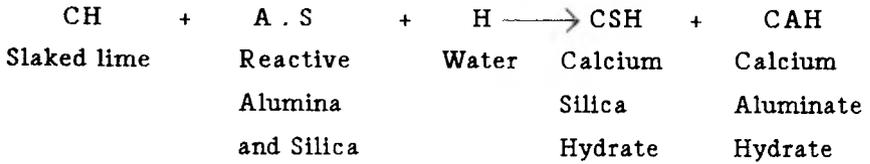
In the Hellenistic period (around the fourth century B.C.) it was discovered that some earths, of volcanic origin, when mixed with slaked lime formed mortars that could harden even under extremely wet conditions.

From the name of the most renowned of these earths (Pozzolana, which derives from the city of Pozzuoli, near Naples), all materials that can produce a hydraulic reaction with slaked lime are designated as pozzolanic materials.

Natural pozzolanic materials used in the classical age were: pozzolana, tuff of Santorin (Aegean islands), pumice, trass (from the Rhine region).

These materials contain silica and alumina in a reactive form because they were melted in the volcanoes and then ejected into the air where they were rapidly cooled. As a result they have a glassy (vitreous) structure, blown up by bubbles of gas, which is amorphous and unstable and exhibits a large specific surface.

The reaction between slaked lime and pozzolanic materials can be summarized as follows, using abbreviated formulas as is normally done in cement chemistry (a list of abbreviations is given in Table III).



The calcium silicate hydrates form a network of fibrous crystals or gelatinous amorphous material (gel) which can be considered as the main cause of hardening of the mortar (see also the illustration of the setting of modern cement in paragraph 6.4).

Artificial pozzolanic materials were also used in the classical age, in particular iron slag and crushed terracotta bricks or pots (which are less reactive, however). It must be noted that these materials have also been subjected to very high temperatures and are partly vitrified.

Pozzolanic materials are still used in modern technology, a recent addition to the list of traditional ones being fly ash. Occasionally pozzolanic materials are added to modern cement to improve its resistance to attack by sulphate-containing water by reacting with the lime formed in the setting reaction.

The use of hydraulic compounds permitted the execution of water works in the Roman period and the adoption of concrete casting in wooden moulds.

R O M A N C O N C R E T E (accurate mixing and ramming in the moulds)	}	Lime Pozzolana Broken bricks or tiles
---	---	---

Lightweight concrete could be produced by using a pumice aggregate instead of the terracotta fragments; a very good example is the dome of the Pantheon in Rome.

A very accurate technology produced a strong and durable material.

In the Middle Ages the technology of concrete and hydraulic mortars appears to have been scarcely employed (or not at all), although the filling with rubble of cores of large, masonry-lined walls might involve the use of hydraulic materials.

However, technical information on hydraulic mortars had been transmitted through the works of Vitruvius and is reported in the treatises of the early Renaissance (fifteenth century). At the beginning of the Industrial Revolution, when development of harbours, roads and aqueducts required the large scale use of hydraulic concrete casting techniques, the know-how was still available, but the materials were scarce.

In the construction, by an English architect, of a new pier in the harbour of Tangiers (1669), material (pozzolana) and consultants were imported from Italy.

In the north, trass (tarras) or iron slag was employed instead.

The second road to hydraulic materials is by the reaction of lime (or limestone) with silica or alumina at high temperature. It had been known, probably since the Middle Ages, that impure limestone from some quarries would produce, after burning, a quicklime that had to be mixed with water at the moment of use and would harden quite rapidly, even under water. Palladio (sixteenth century) explicitly mentions this as limestone (from the Colli Euganei) of gray-to-black colour.

The study of hydraulic limes progressed dramatically in the second half of the eighteenth century.

In 1796 PARKER patented ROMAN CEMENT, which was produced by firing a special argillaceous (clay-rich) limestone called "septaria" at a temperature around 800°C.

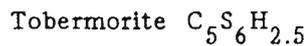
FROST (1811) and VICAT (1818) produced hydraulic materials by firing ground marly (silicate-containing limestone) or mixtures of clay and chalk. The product was called HYDRAULIC LIME.

TABLE III - ABBREVIATIONS USED IN CEMENT CHEMISTRY

<u>Name of compound</u>	<u>Chemical formula</u>	<u>Abbreviation</u>
Alumina	Al_2O_3	A
Iron oxide	Fe_2O_3	F
Lime	CaO	C
Slaked lime	$Ca(OH)_2$	CH
Silica	SiO_2	S
Water	H_2O	H
Carbon dioxide	CO_2	\bar{C}
Sulphur trioxide	SO_3	\bar{S}
Tri-calcium silicate	$3CaO \cdot SiO_2$	C_3S
Di-calcium silicate	$2CaO \cdot SiO_2$	C_2S
Tri-calcium aluminate	$3CaO \cdot Al_2O_3$	C_3A
Calcium iron aluminate	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF
Calcium silicate hydrate*	$CaO \cdot SiO_2 \cdot nH_2O$	CSH
Calcium aluminate hydrate**	$CaO \cdot Al_2O_3 \cdot nH_2O$	CAH

* A family of compounds with varying C/S ratios and water content.

Example:



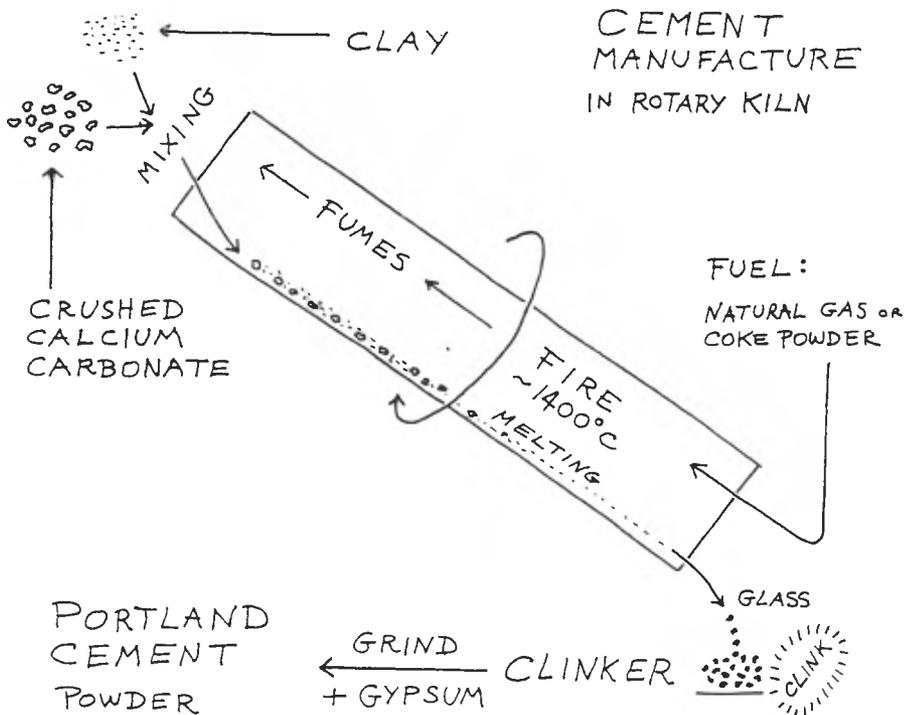
** A family by compounds with varying C/A ratios and water content.

6.4 PORTLAND CEMENT

ASPDIR (1824, England) patented PORTLAND CEMENT, manufactured by firing limestone and crushing the lime so produced with clay and re-firing the mixture at temperatures that probably ranged between 1000°C and 1200°C. The product was named portland cement because its colour was similar to that of portland stone. It was, however, still of inferior quality in comparison with modern standards.

The technological breakthrough that led to high strength cement came through the work of JOHNSON, a former assistant of Aspdin's, who discovered in 1838 that firing at much higher temperatures (1400°-1500°C) caused partial melting of the silicates and vitrification upon cooling.

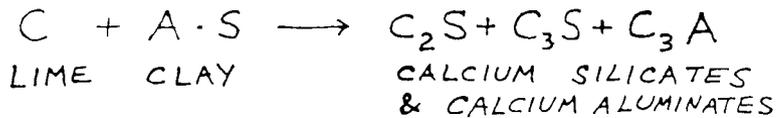
The modern manufacture of cement is carried out in rotary kilns.



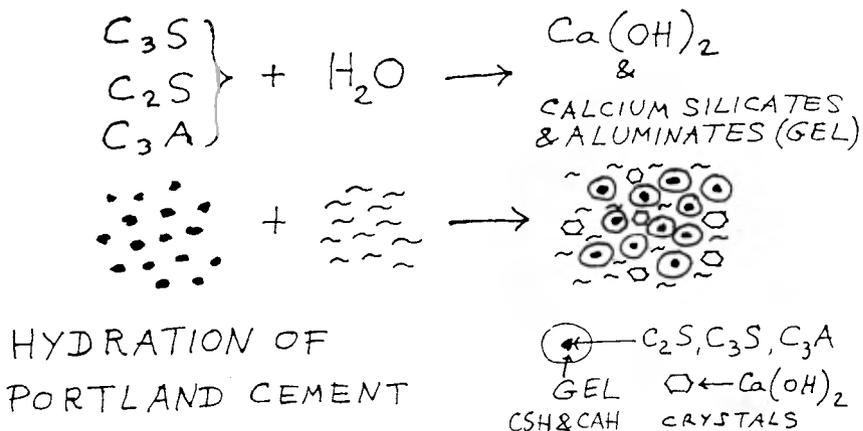
The output of the rotary kiln is a vitrified mass called a "clinker", from the sharp sound it yields on falling; when finely ground, it reacts rapidly with water, forming a plastic mass that sets into a hard, brittle material in a short time.

Although after a few days the material is already quite hard, setting reactions continue inside and mechanical properties keep improving; testing is normally done after about a month (although a six-day term can be applied, with a calculated correction factor).

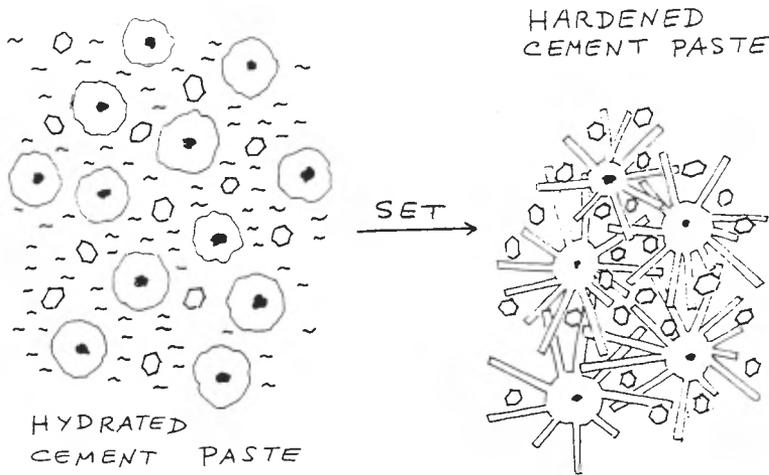
According to the theory presently accepted, the setting of cement is explained by the formation in the kiln of silicates and aluminates of calcium as a result of the reaction of lime, formed by the decomposition of limestone, with silica and alumina contained in the clay. In the abbreviated form:



The calcium silicates and aluminates react with water and form hydrated lime and a gelatinous substance (gel) composed of hydrated calcium silicates and aluminates which contain less calcium than the initial compounds.



During the hardening of portland cement, the water becomes very basic (pH 12 to 13) because of the presence of free lime. In a second stage, water is able to penetrate through the coat of gel formed on the solid particles, and the reaction continues inside it, leading to the formation of fibrous shoots (mainly of CSH).



SETTING OF PORTLAND CEMENT

A network is then formed throughout the entire material, causing the solidification.

After drying, the lime formed in the reaction is converted slowly into calcium carbonate and the full strength of the material is developed.

Gypsum is added to control the rate of the setting reaction which can be too unpredictable for current use. Present specifications allow the addition of hydrated gypsum up to 6-7%.

6.5 MODERN CONCRETE

Modern concrete is made by adding sand and gravel (or crushed rocks) to cement and mixing the mass quite accurately.

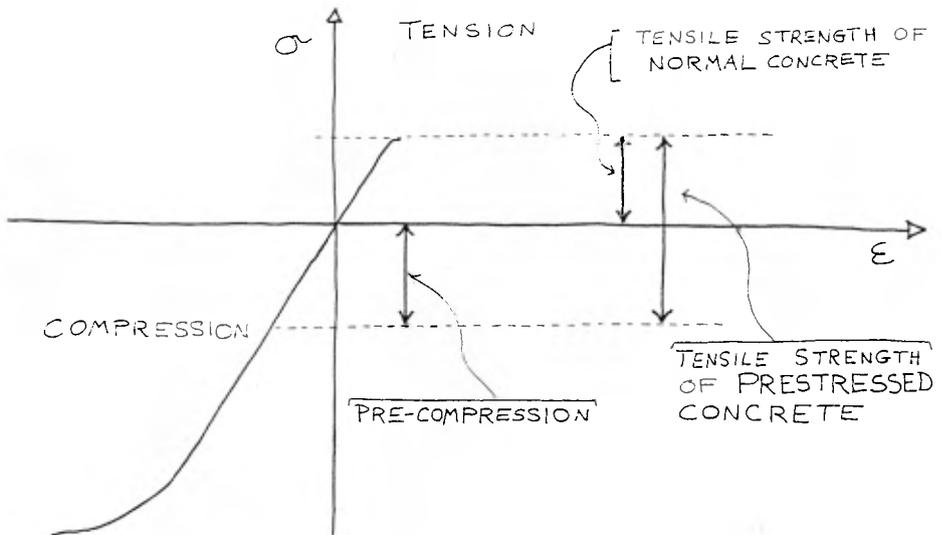
A hard and brittle material, concrete can withstand compressive stresses quite well, but is very weak against tensile stresses.

This weakness is overcome by coupling concrete with steel (a high tensile strength material).

Reinforced concrete (the concrete-steel composite) was introduced in the second half of the nineteenth century in France.

Steel has almost the same expansion coefficient as concrete (12×10^{-6} per $^{\circ}\text{C}$) and cement also adheres very well to its surface; cement, on the other hand, provides a basic environment (high pH) in which the corrosion rate of steel is very low.

A hundred years later another improvement in resistance to tensile stress was brought about by the use of pre-stressed concrete. Steel cables passing through the concrete are subjected to a tensile stress which, in turn, produces a compressive stress in the concrete. The compression of concrete results in an increased tensile resistance.



6.6 DEFECTS OF PORTLAND CEMENT

Portland cement does not contain only calcium and aluminium silicates, but also calcium sulphate (as we have seen) and some alkaline salts formed when clays or fuels containing sodium or potassium are used in the firing process (the alkali content of normal cement can be as high as 2%).

As a consequence, several soluble (or partially soluble) materials are formed during the setting reaction:

Ca (OH)_2	CALCIUM HYDROXIDE
Na (OH)	SODIUM HYDROXIDE
$\text{Na}_2 \text{SiO}_3$ (and other formulas)	SODIUM SILICATES
$\text{Na}_2 \text{SO}_4$	SODIUM SULPHATE
CaSO_4	CALCIUM SULPHATE

If the liquid in which the reaction takes place is allowed to migrate into neighbouring porous materials (as might happen in the structural repair of old masonry) these can be damaged for the following reasons:

- (i) Dark spots can appear because of the action of alkali on some sandstones and limestones.
- (ii) Semi-insoluble efflorescences of silica and calcium carbonate can be formed (cases of Karnak and Borobudur).
- (iii) Stronger crystallization stresses can be caused by sodium sulphate, a very soluble salt.

Low alkali, low sulphate cements should be specified for concrete to be used in contact with ancient materials, but they are not always easily found on the market. Water barriers should also be used to protect old materials from cement water.

Cement plasters and mortars are dangerous if applied on old masonry for the following reasons:

- (i) They can feed soluble salts to the old masonry.
- (ii) They have a very low porosity and do not allow easy evaporation of water. Therefore, as rainwater sooner or later penetrates behind the plaster through cracks, a tension can be created behind the cement plaster at both low temperature (freezing) and high temperature (evaporation). As a result the plaster is easily detached from the wall or the dampness of the masonry is increased.
- (iii) Cement concrete, a high density and high thermal conductivity material, also tends to favour condensation. Use of low density concrete should be considered in the restoration of old, damp buildings.

The use of cement concrete for structural reinforcement of old buildings is also subject to cautions.

In the first place it must be remembered that the expansion coefficient of cement concrete can be twice as great as that of some types of stone (marble, limestone) and of bricks. Stresses can easily arise under thermal cycles unless due attention is given to the problem in the design of the concrete elements inserted in the old structure.

Another important consideration is that cement concrete is a strong material of very high elasticity modulus. When old buildings undergo deformation (because of subsidence, thermal cycles, etc.), concrete discharges all strains on adjoining weaker materials (brick, mortar, stone) which receive more than their usual share of stress. As a consequence, their decay rates can be increased.

6.7 LIME-CEMENT MORTARS AND OTHER MIXTURES

Mortars showing a definite hydraulic behaviour and sufficient strength can be obtained by adding a relatively small amount of cement to hydrated lime (e.g. 1:4 in volume).

Mixed lime-cement mortars avoid some defects of cement mortars while being easier and more reliable to use than pure lime mortars.

In order to keep the formation of soluble salts at a minimum, low alkali cement should be used in such mixtures, if possible.

Another way to produce mortars more compatible with ancient materials, insofar as mechanical strength is concerned, is to dilute cement with calcium carbonate. Actually some of the modern "hydraulic limes" are in fact composed of cement diluted with inert fillers.

6.8 DETERIORATION OF CONCRETE AND REINFORCED CONCRETE

Concrete's imperviousness to water and high mechanical strength gave its first users the illusion that they were dealing with an indestructible material. Artificial stones were made out of crushed stone aggregated with portland cement and were used extensively in the nineteenth and twentieth centuries in the restoration of monuments.

Nevertheless, the cross on the roof of St. Paul's Within the Walls in Rome and the capitals in the bell tower (around 1875) show extensive deterioration due either to direct corrosion by acid rain or to crust formation and disgregation as a result of condensation in a polluted atmosphere.

Similar cases are reported elsewhere.

Portland cement concrete is attacked in general by sulphate-containing water (e.g. sea water), because the lime formed in the setting reaction forms a compound with alumina and sulphates (calcium aluminium sulphate called Ettringite) whose crystallization causes strong internal stress.

Reinforced concrete can deteriorate rapidly if cracks allow water to reach the steel reinforcement. Around the cracks, free lime

is completely carbonated and the pH drops to neutral or acid values after some time. The steel structure, which is no longer protected by a basic environment, is then corroded and undergoes an expansion in volume; the internal stress that is produced can in turn cause further cracking of the concrete and acceleration of the corrosive process.

Cracked concrete is frequently repaired by injection of synthetic resins that can be very fluid, but set to a hard material within some time under the action of a hardening agent added before injection. Even hairlike cracks can thus be completely closed, causing restoration of strength and arrest of corrosion of the metal.

Chapter VII

CONSERVATION OF STONE

7.1 DIAGNOSIS

A study of the deterioration process is required before any treatment of stone. Such a study always includes the determination of the chemical and mineralogical type of stone (in both its sound and deteriorated parts).

Knowledge of the amount and distribution of cracks and pores within stone is essential because they provide opportunities for the access of water and the onset of internal stresses (see Chapter D).

As water is a determinant factor in several deterioration processes, its distribution in the deteriorating stone (and in the adjoining structure) should be determined and conclusions should be drawn as to the reasons for its presence (condensation, capillary rise, rain infiltration, etc.).

A survey of environmental conditions (temperature variations, air pollution level, salinity of soil, wind, etc.) can provide additional clues for the identification of the deterioration process. (Examples are salt crystallization, frost, condensation in a polluted atmosphere, algae attack, etc.) Where a decisive influence of biological factors (algae, bacteria, etc.) is suspected, these should also be analyzed.

In general, conservation provisions should be taken only after identification of the deterioration process, at least on a tentative basis, in order to reduce the risk that the action taken might prove useless or even damaging in the long run.

As shown in Chapter I, the combination of deterioration factors pertaining to the stone itself or to the environment can result in a number of different deterioration processes and by no means the same provisions apply to all cases.

7.2 CLEANING

A stone surface should be as clean as possible when a consolidant or a protective agent is applied.

It is also well known that stone that is kept clean (e.g. by rain) never undergoes deep deterioration processes (although it can be slowly eroded).

Unfortunately, several cleaning processes that are widely applied today cause some damage to the surface and introduce potential dangers for the future. Furthermore, considerable losses of material can occur if cleaning is not done with the required sensitivity; this is not acceptable when surfaces of artistic value are involved.

Examples of cleaning methods that can cause damage are listed below.

Acids irregularly erode the surface of stone and cause the formation of soluble salts which can be absorbed in the pores and cause internal stresses. Hydrochloric, sulphuric and nitric acid are the most dangerous.

Hydrofluoric acid and ammonium bifluoride are less dangerous for stone (as the salts they form are less soluble), but far more dangerous for the operators.

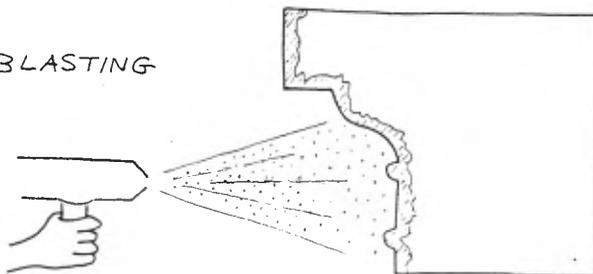
Alkalis (caustic soda or potash) cause the formation of soluble salts.

Grit blasting (dry or wet) can cause losses of material and produces new surfaces that, being very uneven and full of cracks, are frequently prone to further deterioration at an accelerated rate.

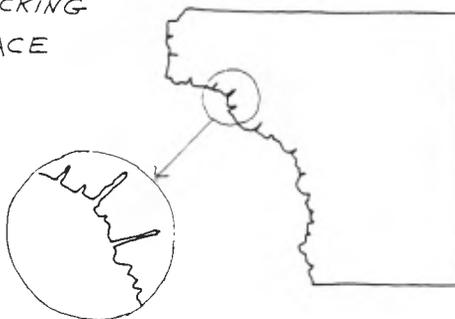
Chiselling or scraping with metal tools or brushes has the same drawbacks as grit blasting, on an even larger scale.

Water jets can cause deep penetration of water inside porous stone if large amounts of water are used. This results in increased dampness of the masonry and can introduce or accelerate some deterioration process.

GRIT BLASTING



MAY CAUSE LOSS OF
DETAIL AND CRACKING
OF STONE SURFACE

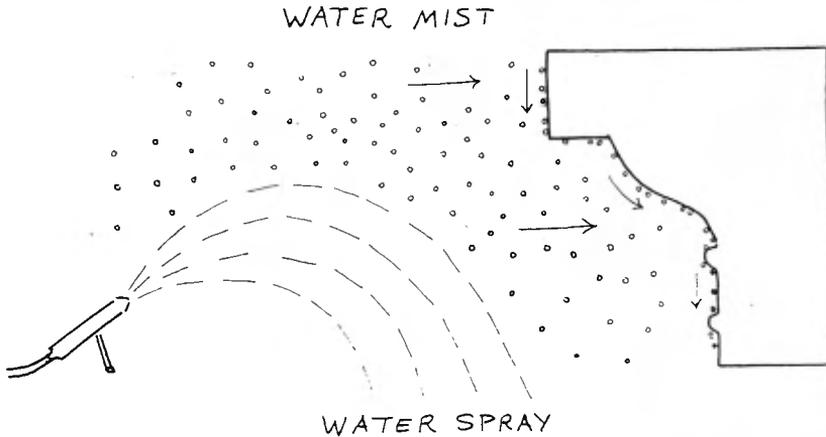


Cleaning of stone of artistic or historic importance must be done with great care, employing methods that have been developed expressly for such cases.

Examples of methods suitable for application on the stone of monuments are listed below.

Water mists are highly efficient in dissolving soot crusts on stone because the tiny droplets suspended in the air have a large specific surface and create a large interface when they are deposited on the stone.

Micro-blasting is performed by a special apparatus that ejects a very narrow beam of grit with a force that can be adjusted according to the effect desired. If well employed it can eliminate hard encrustations that resist other cleaning methods, without causing loss of detail or mechanical damage on sculpted surfaces.



Clay packs formed of highly absorbent clay, such as Attapulgite or Sepiolite (often reinforced by short cellulose fibres and mixed with water) have a slow but safe action on soot crusts and are particularly useful when soluble salts must be extracted from porous stone.

Basic jellies containing bicarbonates and chemical agents that are capable of removing calcium ions and of keeping them dissolved in water (chelating or sequestering agents) are more active than the clay packs on very hard crusts. The jelly is formed by a water-soluble adhesive (such as methyl cellulose) or by silica gel in micron-size particles (micronized silica). This makes it possible to apply the process on vertical or overhanging surfaces without allowing the liquid to run off the treated area (thixotropic effect).

A drawback of all delicate cleaning methods suitable for use on monuments is that they are relatively slow and require the use of specially trained personnel; they are therefore more expensive than the commercial cleaning methods normally applied in building maintenance.

Some deteriorated stone surfaces are so weak that application of any cleaning process would result in the loss of large amounts of

material. When this is not tolerable, special methods are devised by which the surface is first temporarily consolidated (e.g. with a thermoplastic synthetic resin) and then cleaned (by the use of micro-blasting or basic jellies). Sometimes several partial consolidation and cleaning operations are alternated until a satisfactory result is obtained.

7.3 CONSOLIDATION

7.3.1 Definition of aims

As a consequence of deterioration, stone can lose cohesion and disgregate up to a certain depth. In other cases the stone can be cracked, allowing easy separation of splinters or even relatively large pieces.

The aim of stone conservation in monuments being to avoid any loss of material, consolidation (i.e. reinstatement of cohesion) is an essential part of the conservation process if the stone has lost cohesion and its survival is imperilled.

Some consolidation processes also provide a certain degree of protection, that is they improve the stone's resistance to the environment. However, this not always true and it is more convenient in general to consider that all stone that has been consolidated still requires protective treatment.

Stone exposed to an aggressive environment should be protected by a sacrificial protective layer which should be periodically removed, making sure that no attack can be made on the bulk of the original (or consolidated) material.

7.3.2 Impregnation

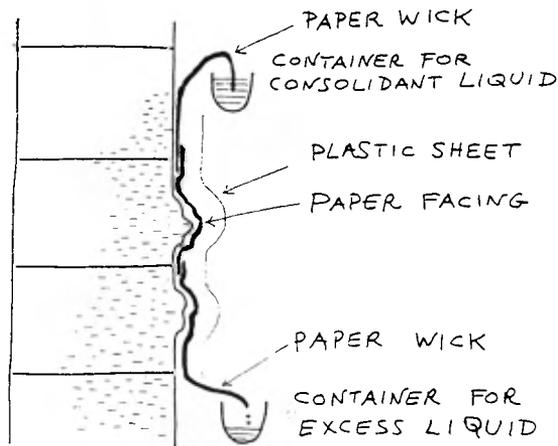
The consolidant material (usually a liquid) should penetrate deeply enough to reach the sound core of the stone and connect it to all deteriorated parts that could be easily detached.

If the loss of cohesion affects even the core, penetration must be total.

It is relatively easy to achieve sufficient penetration in isolated objects that can be brought into a laboratory and immersed in a suitable solution. Penetration is also improved by carrying out the immersion in a vacuum, as the removal of air from the internal pores allows easy access of the liquid.

When stone is connected to the structure of a building in such a way that detachment and transport to a laboratory is impractical, there are still methods that allow deep impregnation with consolidant liquids. An example is the paper facing technique in which paper sheets are attached to the surface of the stone with a light adhesive.

The paper facing is then kept continuously wet with the impregnating liquid, as shown in the figure.



The principle on which such impregnation systems are based is to keep the surface continuously wet for several hours (up to a few days in some cases) and to avoid evaporation of the liquid until deep penetration is achieved.

A vacuum can be applied even on very large objects or on sections of masonry by wrapping a plastic (or rubber) sheet over the surface and introducing suction by means of a valve passing through the sheet. The consolidating liquid is then sucked into the stone through a suitable section of the surface that is left free.

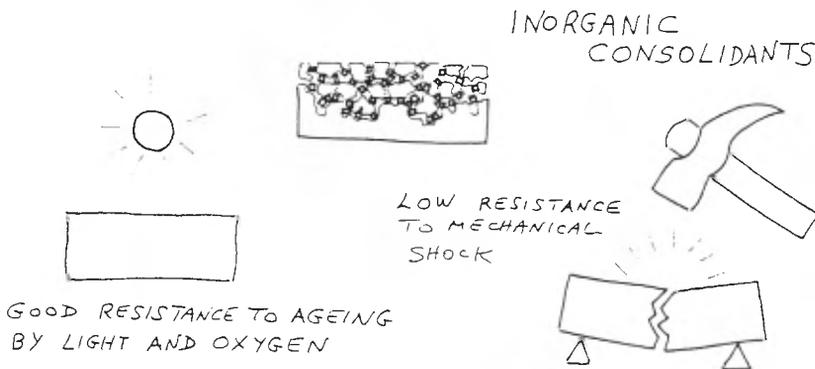
7.3.3 Stone consolidants

Stone consolidants can be divided into two groups: inorganic and organic.

Inorganic consolidants include liquids which, under suitable conditions, form an insoluble substance, inorganic in nature, which is capable of binding together separated crystals of deteriorated stone.

Inorganic consolidants owe their consolidation action to the formation of hydrated silica (this is the case of silicates, see Chapter VI, and fluosilicates) or of calcium or barium carbonates (lime and baryta processes) or of alumina (potassium aluminate process).

Some inorganic consolidants form soluble salts as a by-product of the consolidation reaction. Such is the case with sodium silicate and potassium silicate. Such consolidants should be used only when the greatest care is taken to remove all soluble salts from the stone after consolidation.

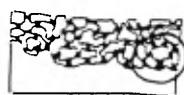


Organic consolidants are mainly based on thermosetting synthetic plastics (see Chapter V) which are introduced into the stone as a liquid mixed with a hardener that will cause the setting reaction to take place inside the pores and cracks of the stone. Epoxy and polyester resins are used for this purpose; frequently they are mixed with solvents that reduce viscosity, delay the setting reaction and avoid completely filling the pores of the stone with resin (which is generally considered undesirable).

Organic consolidants improve the mechanical properties of stone but the resins themselves slowly deteriorate under the effect of oxygen and light.

ORGANIC CONSOLIDANTS

IMPREGNATION WITH THERMOSETTING RESINS



WITH SOLVENT



WITHOUT SOLVENT
FILLING OF PORES
AND CRACKS

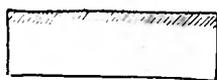
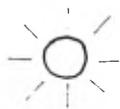


RESIN COAT

RESIN BRIDGE

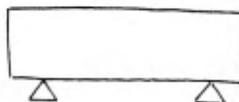
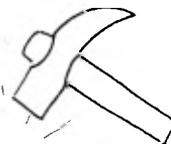
EMPTY SPACE

IDEAL CASE



SURFACE DETERIORATION
ON AGEING BY
OXYGEN AND LIGHT

GOOD
MECHANICAL
PROPERTIES



Organic materials inside pores can, however, survive a very long time as they are protected from the main weathering agents.

Silicones are partly organic and partly inorganic in nature (see Chapter VI) and so represent a possible compromise between the properties of the two groups of consolidants.

Their most useful property is the water repellency conferred on the materials to which they are applied.

As water is an essential part of most deterioration processes, water repellency is an important factor in reducing deterioration rates.

Silicones, however, are also oxidized by oxygen and light, even if more slowly than the thermosetting resins.

Temporary consolidants are used when some consolidation must be immediately achieved but a final decision on the type of conservation process still cannot be taken. Mainly thermoplastic resins (see Chapter V) are used in this case.

Thermoplastic resins do not penetrate easily in small pores because their molecules are very large; also their mechanical properties are inferior to those of the thermosetting resins. However they are reversible, i.e. they remain soluble in suitable solvents, while thermosetting resins, silicones and inorganic consolidants are irreversible materials (i.e. insoluble). Furthermore, some thermoplastic resins, acrylic resins in particular, are far more resistant to oxidation than the thermosetting resins.

The problem of selecting the most suitable consolidant for a given case of stone deterioration is not easy to solve.

Selection is frequently done on the basis of comparative weathering tests carried out on the stone in question. In such tests untreated samples and samples treated according to several processes are submitted simultaneously to the same weathering cycle and results are compared.

The choice of the process sometimes depends upon the type of stone: sandstones are frequently treated with silica-forming

consolidants while for limestones calcium (or barium) carbonate-forming consolidants are preferred.

Silicones and thermosetting resins are applied on any type of stone.

7.3.4 Adhesives and stuccoes

Consolidation processes normally do not bridge gaps larger than a few tenths of a millimetre; therefore, they neither reinstate adhesion among large fragments nor inhibit water access to a crack.

It is a basic conservation requirement, however, that the stone present a compact surface to the environment and that penetration of aggressive liquids be avoided.

Therefore all cracks and other discontinuities must be filled up with a suitable adhesive substance in such a way that mechanical resistance is improved and all possible access routes of water to the inner parts of stone are closed.

Thermosetting resins in the fluid state, or moderately charged with a filler to make a paste, are used as adhesives for fine cracks (epoxy resins are the most used material so far).

To fill large gaps, stuccoes are employed which are composed of a filler (frequently the stone itself, crushed) and a binder, either organic (synthetic resin) or inorganic (pure lime or ethyl silicate should be preferred).

FILLING OF CRACKS



CRACKED &
DETERIORATED



CONSOLIDATED



FILLED WITH
STUCCO

7.4 PROTECTION

7.4.1 Surface films

The application of protective surface films on the surface of stone was quite usual in the past. Materials used for this purpose included drying oils (such as linseed oil), animal fat, waxes and paraffin wax.

A protective film must be applied over clean and strong stone; actually the treatment is best applied on unweathered stone. Weathered stone must first be cleaned, if dirty, and consolidated, if it has lost cohesion.

Surface films afford the best protection on stones of low porosity. In the case of soft porous stone, the surface film can be bypassed by water gaining access to the masonry through other routes. In such a case internal stresses would develop at the interface between the film and stone.

In recent times paraffin wax is still used as a protective material together with microcrystalline wax (a tough wax obtained from high boiling fractions of mineral oil) and acrylic resins.

Silicones (see Chapter VI) are also occasionally used for surface protection, although their performance is rather variable as commercial types show strong differences in performance.

In view of the variability of performance among products that belong to the same chemical family, testing of protective agents is essential before a choice is made for any specific application. Also in this case comparative weathering tests are most useful.

It should be well understood that a surface film is a sacrificial protective material which has a limited useful life. Therefore provisions should be taken to repeat the treatment before its life span is due to expire.

7.4.2 Environmental protection

Control of the aggressive properties of the environment is obviously the best protection for stone.

The easiest way to do this is to remove the stone to a controlled environment, which, in the simplest case, is an internal area heated in winter. Unfortunately, this is not always feasible.

Temporary protection can be afforded by the application of an opaque thermal insulation layer on the surfaces to be protected. As this obviously obscures the surfaces, one could periodically remove the insulation in the good season when air pollution and condensation are less frequent and freezing does not occur. This would allow the stone to be seen by visitors and be inspected periodically by those responsible for its preservation.

Transparent showcases, instead, are potentially dangerous because the temperature can rise to very high levels when they are hit by solar radiation (greenhouse effect). Thermal expansion would then originate serious stresses in the stone. On the other hand, air conditioning inside the showcase is expensive and unreliable.

External roofs provide protection against rain but not against condensation. If such a solution is adopted, a surface protective film should be applied to the stone.

Complete revision of water disposal systems in buildings, control of rising damp in masonry, climatic provisions tending to eliminate condensation from the surface to be protected are the basic points of the environmental protection of stone. However, it is frequently not easy to apply such provisions to stone of artistic value which is directly exposed to weathering on the external structures of monuments.

7.4.3 Maintenance

All conservation provisions have a limited useful life which is not exactly foreseeable.

Conservation of stone monuments therefore requires periodic inspection and maintenance of all protective systems used.

Failures of the protective systems (rainwater disposal, protective films, roofs, etc.), if detected in time, can be repaired before an aggressive process develops in the stone to be protected.

A protection policy, such as the one outlined above, requires a profound change in the structures and practices of the conservation services, including the development of equipment for inspection or remote monitoring of the objects that are entrusted to their care.

The aim of such a policy is to avoid the onset of deterioration processes rather than to repair their consequences with spectacular restoration operations.

Ancient stones should be viewed as hospital patients, or better still, as patients being cared for in their own homes. A clinical file should be prepared on each of them with extreme care because the patient should survive the doctor (or at least we hope so) and the next doctor should know all the facts. Routine visits and immediate intervention, when required, constitute the medical practice to be carried out by the conservation service.

Chapter VIII

CLAY, ADOBE, BRICK

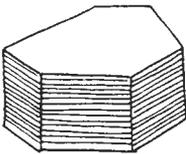
8.1 CLAY MINERALS

Clays are minerals formed by atmospheric weathering of several types of rock.

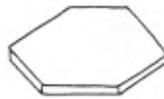
The main components are silicon oxide (also called silica, SiO_2) and aluminium oxide (also called alumina, Al_2O_3).

Clay crystals are very small in size (below 2 microns) and often have an approximately hexagonal shape.

Each crystal is composed of a series of wafers (several hundred of them).



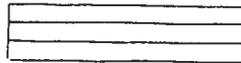
CLAY
CRYSTAL



WAFER

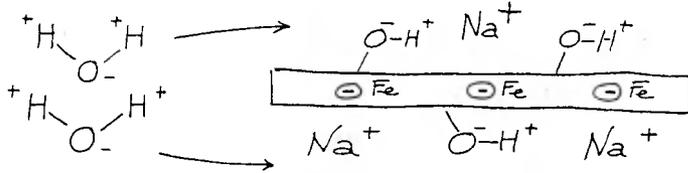
In the most common clays (e.g. Montmorillonite or Illite) the wafer is composed of two layers of silica and one layer of alumina interposed between them.

MONTMORILLONITE
AND ILLITE
WAFER

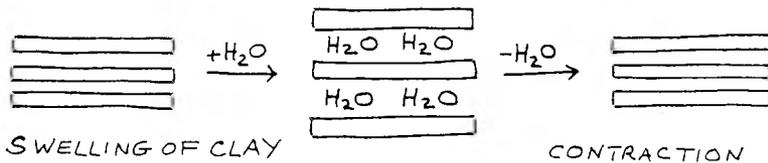


SILICA
ALUMINA
SILICA

The wafers carry hydroxy (-OH) groups and negative charges, due to the presence of impurities (e.g. iron) which are able to take the place of silicon and aluminium even if they have fewer positive charges. (Iron causes the yellow or red colour of fired clay, and the green colour of molten clay.)



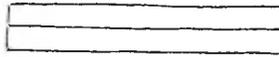
As a consequence, positive ions, like sodium in montmorillonite, are frequently trapped between wafers and water is able to penetrate the crystal as it is attracted by the hydroxy groups.



The access of water results in the increase of the distance between wafers and so in the swelling of the clay. In a dry atmosphere the water is lost and the clay contracts.

Illite contains calcium between wafers and this ensures a stronger attraction between them. The swelling of illite is, therefore, smaller.

Kaolin is a very pure clay which contains no iron and has a two-layer wafer (one of silica and one of alumina).



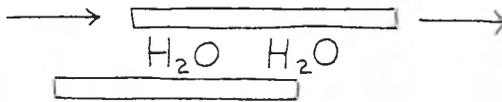
ALUMINA
SILICA

KAOLIN WAFER

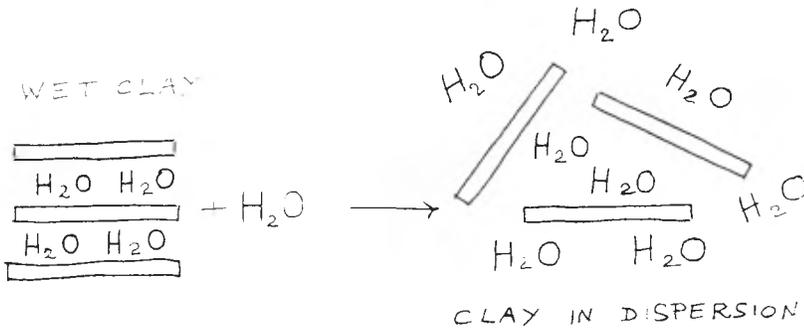
As a result, the wafers have no negative charge and there are no ions trapped between them. The wafers are kept together by relatively strong hydrogen bonds and water is unable to separate them.

A little swelling also takes place in kaolin, however, as water is attracted to the surface of the thin, flat crystals and is able to separate them.

All clays are plastic when wet because the thin crystals slide easily over one another under a slight pressure.



If more water is added to wet clay it is completely dispersed.



8.2 SOIL

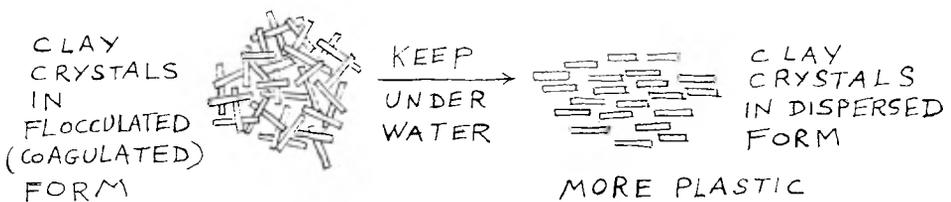
Soil contains clay minerals and other minerals (feldspar, calcium carbonate, quartz, etc.), which normally have particle sizes larger than clay. Soil constituents are normally classified by size only, according to the following scheme:

Clay	: particle size below 2 microns
Silt	: 2 microns 20 microns
Sand	: 20 microns 2 millimetres (i.e. 2000 microns)
Gravel	: above 2 millimetres

A clay-rich soil is plastic and greasy to the touch; it contracts strongly upon drying and cracks. A sand-rich soil is not plastic, and is dry to the touch.

8.3 SOIL AS BUILDING MATERIAL

Clay is the binding material in soil. Frequently its crystals are arranged in a flocculated form that is not very plastic, but if it is left under water for some time the arrangement is changed into a dispersed form that is more plastic.



The preparation of building materials from the soil always involves a period of storage of the clay-rich soil under water in order to improve plasticity.

Non-clay minerals are useful as inert filler in order to reduce contraction upon drying and so avoid cracking. If necessary (i.e. if the soil is too rich in clay, or too greasy), sand is added.

Other possible additions are:

- a. fibrous organic materials
 - straw or rice husks
 - animal hair
- b. low cost, slightly adhesive, organic materials
 - dung

Fibrous materials improve the tensile strength of the final product, which is very low. In contrast, the compressive strength is reasonably high (10-45 kg/cm²).

Organic additives can improve the resistance to water, introducing a stronger connection between clay wafers and hindering dispersion.

Mud bricks are made in square, open-bottom moulds in sizes often around one foot with 6-10 cm thickness. A mortar of similar composition is often used to make up the masonry.

In another type of technology the material is prepared roughly in the shape of spheres that are preserved damp for some time and then placed in position and rammed together to build up the desired structure.

When soil is used to make up a concrete, additions of gravel, stones or potsherds are possible.

In building up structures, mud-bricks are often coupled with other materials in order to overcome some obvious weaknesses of mud-brick masonry.

- Wood : where tensile or flexural strength is required.
- Palm-leaf mats : to distribute compressive stress in heavy structures.

- Rush ropes : for internal binding of heavy structures.
- Fired bricks : for weather protection.
- Stone : in foundations or water resistant bases of walls.

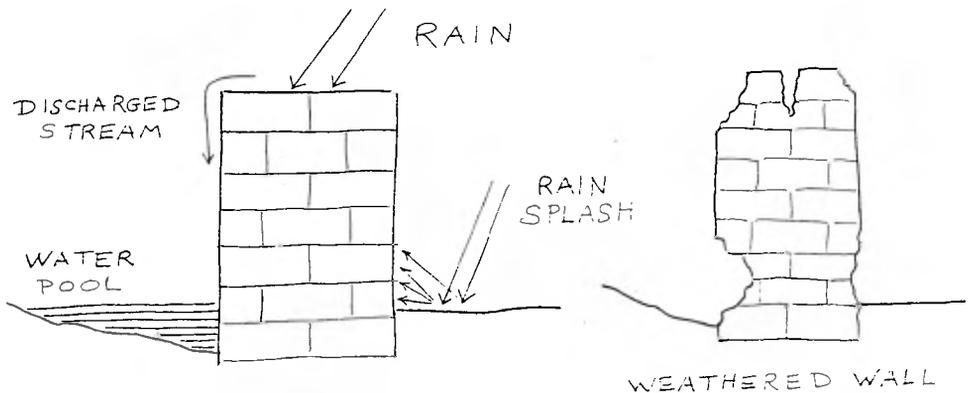
Normally the surface of mud-brick masonry is covered with a mud plaster sometimes reinforced by fibrous materials (e.g. hay, straw, rice husks).

Such a plaster weathers out easily and must be frequently repaired (sacrificial protection).

Harder, weather-resistant plasters such as lime or gypsum are also employed. The danger in such cases is that the core material of a wall can be attacked while the surface material resists and so conceals the damage until it is beyond repair. Inspection and maintenance are not easy.

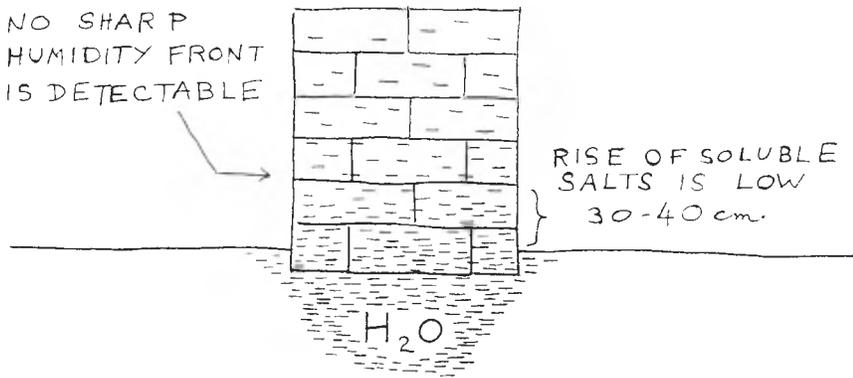
8.4 WEATHERING OF MUD-BRICK STRUCTURES

The main weathering agent is rain. Excess of water completely disperses the clay, and the material is washed away. This can happen directly under exceptionally strong rain, but more frequently in an indirect way through the formation of running streams or pools in contact with masonry.



The second weathering agent of importance is wind, which acts mainly by sand-blasting.

Capillary rise is low in mud-brick, contrary to the case of fired brick; in general it does not surpass 30-40 cm. The moisture content varies slowly with the height of the wall and no humidity front is detectable.



Therefore capillary rise and crystallization of soluble salts do not constitute a major danger for mud-brick masonry except in special cases.

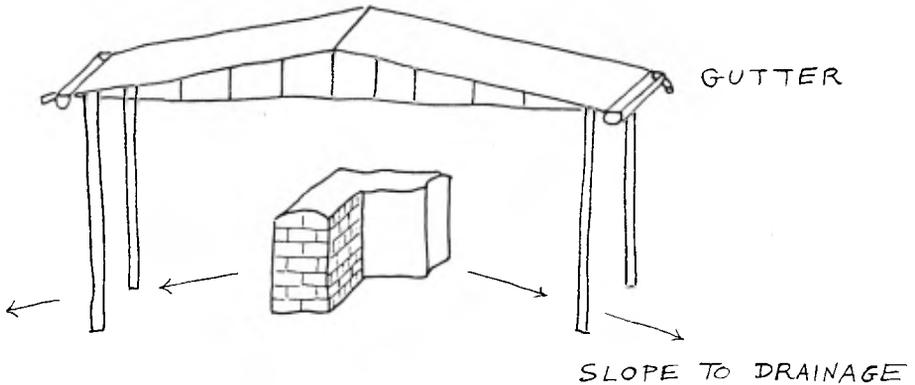
Snow is a potential deterioration factor if it is allowed to accumulate near walls and then eventually melts.

8.5 PROTECTION OF MUD-BRICK STRUCTURES

8.5.1 Archaeological excavations

Mud-brick structures are well preserved when buried in the ground. They must be protected as soon as they are discovered.

a. Total protection - shed



Formation of water pools near the walls must be avoided by providing suitable slopes and drainage systems.

b. Total protection - re-burial

c. Partial protection

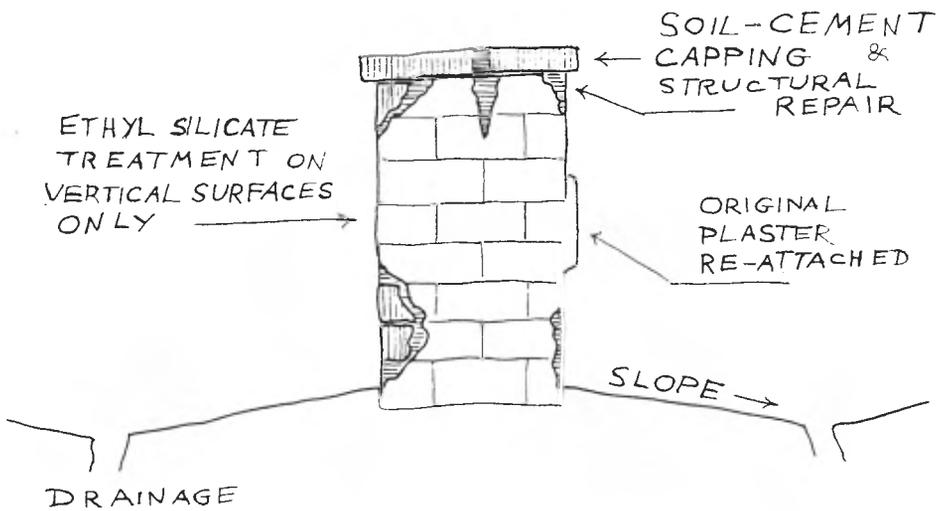
- (i) Capping and repair made in soil-cement.
- (ii) Surviving plaster consolidated with adhesives (e.g. polyvinyl acetate emulsions).
- (iii) Rainwater drainage provided.
- (iv) Treatment of vertical surfaces (only) with ethyl silicate.

Soil Cement

Clay-rich soil	8 parts (volume)
Sand	1 part
Portland cement	1 part
Straw (chopped short)	
Water	

The clayey soil must be left under water a few days; the other components are then added. If soil-cement is used in the form of bricks these are moulded in open-bottom moulds and kept damp for one week to allow the cement to set. They are then left to dry in the sun.

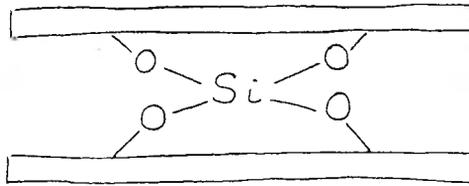
Soil-cement can also be used as a stucco for minor repairs or a thin capping layer.



Rainwater disposal must be carefully studied and adequate gutters, slopes and drainage channels provided.

Ethyl silicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ is hydrolyzed by water in the presence of a catalyst (an acid) and forms hydrated silica $\text{Si}(\text{OH})_4$ which can bridge the gap between the clay wafers, cross-linking them.

The cross-linked clay becomes non-dispersible in water.



8.5.2 Structures above soil level

Buildings built in mud-brick can survive only if subject to continuous maintenance. The key points for maintenance are:

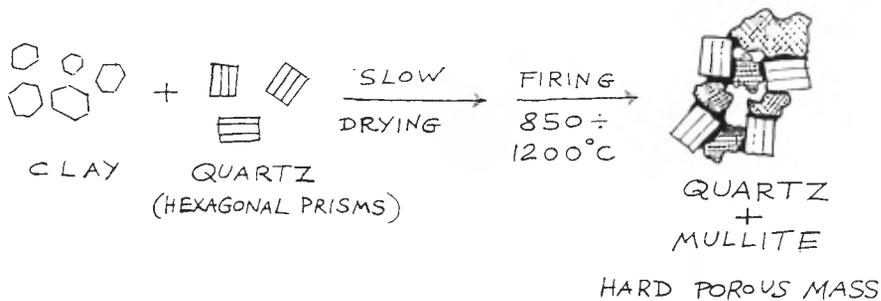
- roofs
- rainwater disposal systems
- plasters (to be renewed frequently)
- bases of walls (damaged by rain splash or rising damp)

Any shear stress caused by settlement of structures results in cracks due to the weak tensile strength of the materials. Such cracks are extremely dangerous if water is allowed to enter them; immediate repairs are therefore required.

Ruins in mud-brick must be protected by re-forming a roof and a water disposal system over them. As an alternative proposition, the partial protection suggested for archaeological excavations might also be adopted.

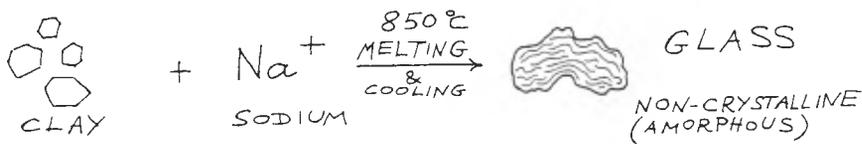
8.6 FIRE BRICK - TERRACOTTA - PORCELAIN

Fired bricks and terracotta are manufactured from mixtures of clay (mainly montmorillonite and illite types) and sand (quartz type).



The clay crystals are destroyed and mullite (a crystalline aluminium-silicate) is formed together with more quartz.

The presence of sodium or potassium in the clay causes some melting of the clay.



Upon cooling, the molten clay does not re-form a crystalline structure. A hard, non-crystalline, mass is formed instead (glass, vitrified material).

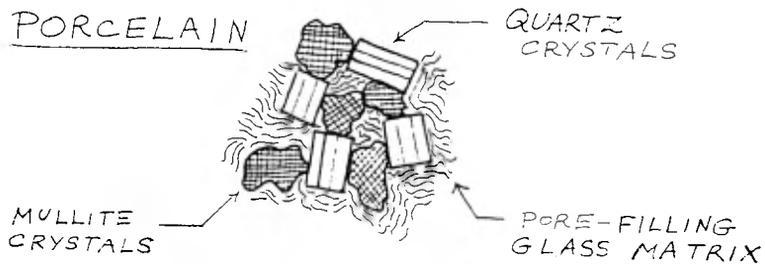
The glass acts as a cement between crystals of quartz and mullite.

As a general rule glass is formed whenever a silicate melts.

The amount of vitrification and the strength of the brick depend upon the temperature reached during firing (and the composition of the mixture). The higher the temperature the stronger the brick.

As clay also contains some iron, the baked material is yellow if fired at lower temperatures and red if fired at higher temperatures and in an oxidating atmosphere (excess of oxygen).

Porcelain is manufactured from very pure clays (of the kaolin type, no sodium and no iron) mixed with sand (quartz type) and feldspar (a silicate containing much potassium). When this mixture is heated at about 1200°C , mullite formation takes place together with extensive melting (due to the potassium). On cooling, the amount of glass is sufficient to fill the spaces between the crystals almost completely. Therefore porcelain is not porous.



Materials of this class are called ceramics. They are partly crystalline and partly vitreous. The extent of porosity and the strength depend upon the type of clay, the addition of sodium or potassium-containing materials and the firing temperature.

Chapter IX

CONSERVATION AND DETERIORATION OF MASONRY

9.1 MOISTURE IN MASONRY

Water can gain access into porous masonry either in the liquid phase (suction from wet materials, rainwater infiltration) or in the vapour phase (condensation, interstitial condensation, adsorption) but it leaves masonry almost exclusively in the vapour phase (evaporation).

Therefore the moisture content of a wall is determined not only by its contact with water sources but also by its water vapour balance (evaporation versus condensation and adsorption). Due to this fact, most walls undergo a seasonal cycle in temperate climates with a maximum water content in late spring (after condensation periods in winter and spring) and a minimum in late autumn (after prevailing evaporation conditions in summer and early autumn). Such cycles constitute an added complication when the efficiency of processes devised to reduce moisture is evaluated, even more so because of change from year to year, due to climate variation. Surveys of moisture content in masonry should either follow the entire cycle, if possible for more than one year, or should be repeated every year at the same date.

The removal of plaster or impervious paint layers also improves evaporation rates and causes a reduction of moisture content.

Frequently, rehabilitation works in old damp buildings are carried out in the good season: plaster is removed and special provisions against moisture are taken. When the works are completed in autumn, analysis of moisture content normally shows a good improvement with respect to samples taken before the works (in

spring) so new plaster is applied and everybody is happy, but it is obvious from what was said above that in such conditions no effective evaluation of the provisions taken against moisture is possible. It will take some years to prove whether they were effective or not.

This is to emphasize the importance of an accurate diagnosis of the troubles that affect a building before provisions are taken for the drying of the masonry.

Unfortunately, diagnosis involves measurement of temperature and humidity in the air and in the masonry, in several points and in several seasons; it is, therefore, a long and costly job that many prefer to cut short using some guesswork and relying on experience rather than on figures. However, in moisture problems (as Mr Massari says) reality often runs counter to plain good sense, the first guess being frequently wrong; and the cost of failure can also be very high.

9.2 SOLUBLE SALTS IN MASONRY

Soluble salts can be present in the original materials from which the masonry was made (sand, bricks, mortar) or can gain access when water climbs in walls from the soil, or when acid gases of the air react with the wall surfaces.

Deterioration theory indicates that they can cause damage in at least two ways.

- a) Soluble salts *attract* liquid water (osmosis) or water vapour (hygroscopicity); they cause an increase of the critical moisture content and in general hinder the drying of masonry.
- b) Soluble salts *crystallize* upon evaporation of water and cause efflorescences and disgregation of surfaces.

In cities with significant salt problems, like Venice, there is a tendency to remove all the masonry affected by soluble salts and to replace it with fresh brick courses which are protected from new salt

invasion by a damp-proof course placed below them. Such systems are very costly and it would be desirable to develop cheap salt extraction systems.

A successful experiment was carried out in the Tower of London some years ago, using a clay poultice. Paper or clay poultices are also used in archaeological conservation to remove salts from objects found in salt-laden soils. A wet poultice is applied to the object to be de-salted and is allowed to dry. Salt crystals concentrate in the evaporation surfaces, which are in the poultice, so that when the poultice is dry it can be brushed off, carrying away the salts it contains. Repeated treatments are required for thick objects and it is still not clear whether walls can be economically de-salted by such techniques as a matter of routine.

Intensive washing with salt-free water is another possibility, and I know of one experiment which was not completed. A drawback of this method is that the water added to the masonry can prove to be as bad a problem as the one it is meant to cure because its subsequent removal might be costly and difficult.

Electrodialysis and electrolysis have been tried only occasionally for salt removal in conservation technology as they are successfully used for other purposes and look promising; however, difficulties are likely to be met in the practical application of these electrical systems to the case of building masonry.

9.3 PLASTER (RENDERING) AS A SACRIFICIAL PROTECTIVE LAYER

The surface layer of masonry is exposed to the most efficient deterioration processes: thermal shock, salt crystallization, frost and attack by acid gases.

If a porous, hydrophilic layer is applied over the masonry, most of the destructive effects of the environment are concentrated in this layer while the masonry core is protected.

A constant practice in the past was to apply plaster (or rendering) over masonry; the wall material was seldom left exposed although, occasionally, stone, mosaic or facing brick was used for decorative purposes as a surface lining.

Plaster acts as a sacrificial protection layer and should be renewed periodically when it has lost its functionality because it is too deteriorated. Plasters on historic buildings, however, carry important information and should be preserved with as little renewal as possible; this can be achieved by the use of appropriate conservation techniques.

Unfortunately, in recent times, it has become fashionable to remove ancient plaster and leave the masonry structure of historic buildings exposed to view. This practice is obviously objectionable from the conservation standpoint, apart from the loss it implies of potential information stored in the original plaster layers.

When new plaster is applied, in partial or total replacement of the old, it must be remembered that it can carry out its sacrificial protective action only if its pore system is accessible to water, in liquid and vapour form.

Use of plaster impervious to water on old masonry creates a new situation which should be carefully analyzed before such a step is taken. Actually any impervious surface layer is likely to crack sooner or later, due to thermal movement, thus interrupting the continuity of the large water barrier. As a result the plaster will be bypassed by water which will spread in the masonry but will mostly tend to accumulate behind the impervious layer, through which it cannot evaporate easily.

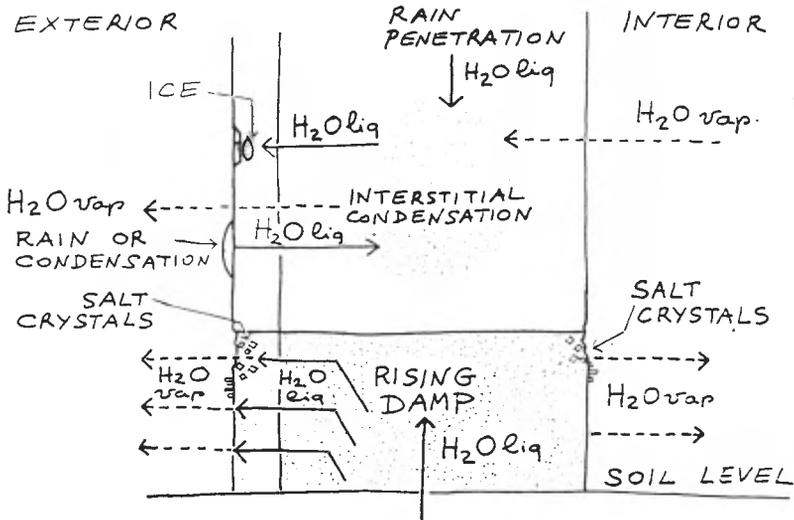
The final result might well be the development of internal stresses at the interface, because of frost or salt crystallization.

Another factor to be kept in mind is that, if the wall is affected by rising damp, moisture will reach a higher level after application of the impervious plaster, because evaporation is hindered.

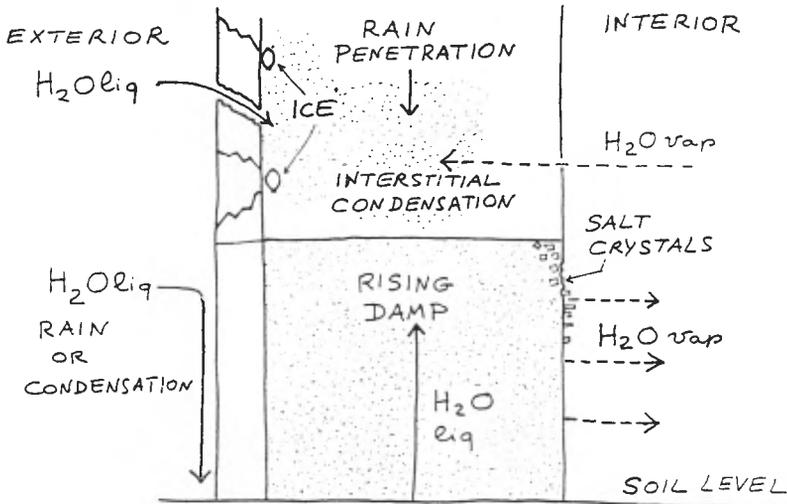
Properties of porous and impervious plasters are summarized in Figure 9.

FIGURE 9. PLASTER

a) POROUS SACRIFICIAL SURFACE LAYER



b) IMPERMEABLE SURFACE LAYER



9.4 DRYING OF MASONRY

Theory indicates that it is very difficult to remove moisture from the pores of masonry materials, even more so if soluble salts are present.

When walls are excessively damp, theory suggests that, in order to reduce moisture, water evaporation must be increased and/or water supply to the wall must be reduced.

There are obviously many ways of doing this, or attempting it. The first requirement, evaporation, can be met by means of heating or ventilation systems; provisions aimed to realize the second condition, control of water access, are more varied and depend upon a correct diagnosis of the source of moisture. Such provisions might include damp-proof courses, drainage systems, revision of rainwater disposal, avoidance of condensation, removal of salts and others.

In recent times, systems have been proposed with the claim that they could achieve drying in a very economic way and almost in every case. An examination of such systems in the light of theory, and a review of results recorded in the field by impartial observers, compels one to maintain a skeptical attitude even if one keeps hoping, against scientific evidence, that inexpensive drying were possible (just as in the case of perpetual motion).

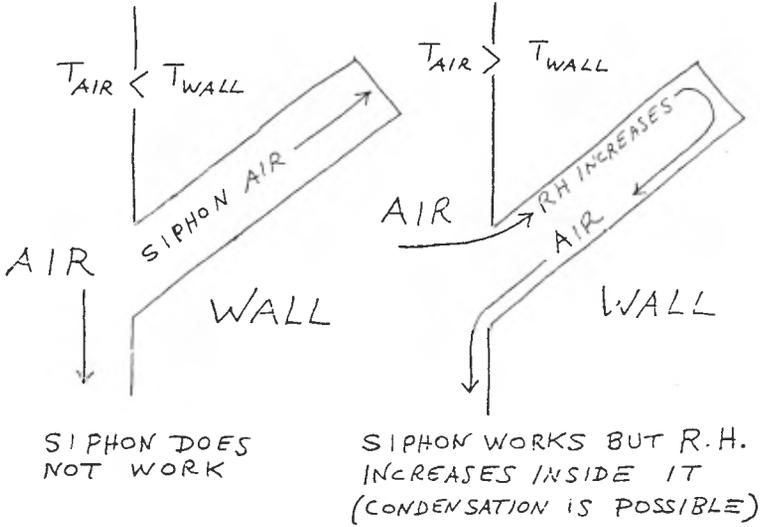
9.4.1 Atmospheric Siphons

Atmospheric siphons (also designated as Knapen siphons) are ceramic pipes inserted with a downward slope (from the end to the orifice, see Figure 10) in the masonry. Air circulation should originate inside them, resulting in an increase of evaporation from the wall.

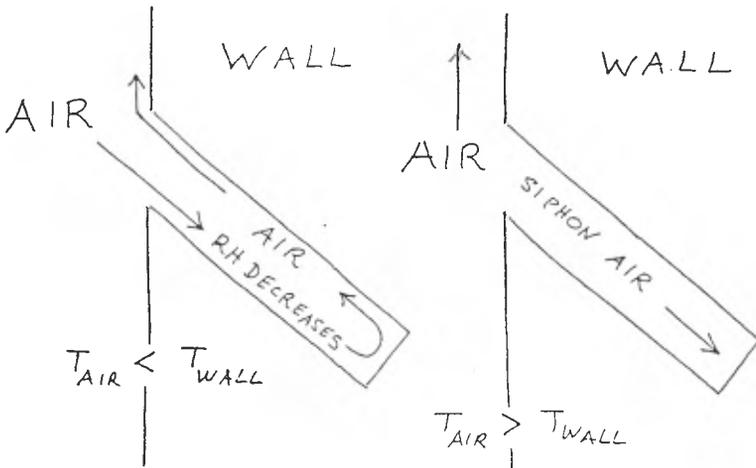
However, impartial observers in France, Great Britain and Italy have consistently reported that the effect of the siphons on moisture content of walls is almost irrelevant.

FIGURE 10. ATMOSPHERIC SIPHONS

a) THE DOWNWARDS SIPHON IS NOT EFFICIENT



b) THE UPWARDS SIPHON MIGHT WORK (BUT HOW LARGE SHOULD IT BE?)



It is interesting to note that on theoretical grounds a siphon would be inefficient if it is turned downward (it is turned that way in present practice to avoid filling by rainwater), as shown in Figure 10. In fact, when the wall is warmer than the atmospheric air, the cold air cannot enter the siphon from below, so it does not work.

When the wall is cooler than the air, the siphon movement is operative as cold air flows down, out of the wall, while warm atmospheric air ascends in the pipe; unfortunately, in such a condition, the relative humidity of the air rises sharply when it enters the siphon and cools down to the wall temperature. Condensation can take place occasionally, otherwise the drying efficiency would be in general low.

An upwards siphon would work much better because air circulation would take place when the wall is warm (see again Figure 10) as we can see in chamber tombs in Tarquinia and Thebes. Some calculations would be required to evaluate the evaporating surface that should be installed to achieve a significant result, but it is the writer's personal impression that such a surface should be much larger than the one offered by the present siphons.

9.4.2 Passive Electro-osmosis

Passive electro-osmosis is based on a principle that is not accepted by the theory outlined here. The assumption is that water is drawn up in the masonry by a difference in electrical potential existing between the earth and the masonry.

Earthing of the walls in an efficient way would presumably inhibit the rise and allow the water to go back to the soil, or to evaporate. Apart from the fact that it is doubtful whether such a difference of potential exists at all, according to the present theory, water suction is caused by hydrogen bonding of water molecules to hydrophilic surfaces and does not require any superimposed electrical potential to explain it. Therefore, earthing of a wall would not affect the capillary rise to any great extent.

9.4.3 Active Electro-Osmosis (or Electro-Kinesis)

Active electro-osmosis (or electro-kinesis) is based on the well-known fact that water can be pushed to the negative pole by an electric field in a hydrophilic porous body. However, as has been shown here, removing water altogether would require far more energy than displacing and substituting it with new water molecules.

The energy required for drying would be of the order of magnitude of 1 kW Hour per kg of water. One does not see how low-voltage, low-current systems could provide in a reasonable time the energy required to dry out large masses of water; actually a section of wall 60 cm thick, 4 m long and 2 m high with a moisture content of 10% contains about 1 ton of water and 700 kW Hours would be required to cut the moisture content to 3%. On the other hand, high-voltage systems would be difficult to operate and to maintain.

Another difficulty suggested by the theory is constituted by the fact that when drying brings the moisture content below the critical level (level III), there are enough interruptions in the network of water-filled pores to stop the passage of the electric current between the poles. Drying by electric means could not, in principle, proceed beyond level III.

The presence of soluble salts could influence the course of the electric treatment, possibly in a positive way, because the ions could carry hydration water more efficiently than the large negative ones.

The effect of electrolysis of water should also be favourable but it would be important only if large amounts of energy were provided. On the contrary, polarization of the electrodes might hinder water movement after some time.

Surprisingly enough, the electrokinetic transfer of substances suspended or dissolved in water has received little attention in this domain. It could be exploited to create water barriers inside porous bodies, for instance by deposition of suspended molecules carrying a positive charge which might be able to enter the small pores, because

of the electric displacement of water molecules, and to form an internal hydrophobic coating. Another possible line of research might be the precipitation of gel-like substances as a result of the electric migration of soluble silicates or aluminates; such precipitates, it is hoped, might obstruct the pores and form a kind of damp-proof course.

9.5 IMPROPER MASONRY CONSERVATION PRACTICES

In the light of a general theory of deterioration, as outlined here, several techniques currently applied in dealing with old masonry appear to be objectionable.

A first case is that of the cleaning of brick or stone masonry with strong acids or alkalis. The fact that acids can damage lime mortars or limestone is quite obvious because calcium carbonate (an essential component of both materials) is rapidly attacked by acids. What is less obvious is that any chemical reaction used for the cleaning of any porous material constitutes a potential danger because the secondary products of all reactions are soluble salts which, if not removed, can later crystallize in the pores. Alkali (e.g. caustic soda) will invariably produce carbonates (e.g. sodium carbonate) which can crystallize into hydrated crystals that produce strong internal stress, as discussed above.

Also *mechanical cleaning* was shown to be the possible cause of deterioration processes through the formation of surface cracks. The theory shows that the good condition of the surface is an essential factor in determining the resistance of building materials to environmental attack.

Cleaning practices should avoid, insofar as possible, introducing new defects in the treated surfaces. Where many defects already exist, the use of consolidants or protective coatings should always be required.

Water used with cement for mortars, or concrete, being in contact with the setting reaction, is rich in basic materials (hydrated

lime, caustic soda) and soluble salts (sodium silicate, sodium carbonate, sodium sulphate).

Such a solution can cause serious damage if it is allowed to enter the pores of nearby old masonry materials, such as brick, stone or mortar. Efflorescences and crystallization stresses are a frequent consequence of the use of cement mortar or concrete in the repair of old masonry.

The use of *strong mortars*, made of *cement concrete* or *synthetic mortars* (e.g. epoxy resins), in the repair or re-pointing of old masonry can cause damage for mechanical reasons.

These materials show good adhesion on old masonry but their thermal expansion coefficients are twice as large (even more for the synthetic resins) as those of most old building materials.

Thermal movements therefore result in contrasts and stresses and, since the old material is weaker than the new, it is invariably on the losing side of the contest; microscopic and visible cracks develop around the section where the old material joins the new, ready to play their role in future deterioration processes.

In general one can state the principle that *the material used for repair should be of strength comparable with (or even lower than) that of the original material*. As the theory shows, if the new material is stronger than the old, it is very likely that the deterioration of the old parts that are in contact with the new repairs will be accelerated, which is the contrary of what the aim of sound conservation practice should be.

9.6 HYDROPHOBIC TREATMENT OF HYDROPHILIC SOLIDS

If all pores in a hydrophilic solid could be coated, by *deep impregnation*, with a hydrophobic substance, the material would become practically impervious to water, even if the pores remained open. It is possible to achieve good distribution of an impregnating

substance in the pores, if they are dry, by the use of suitable techniques; the problem, however, becomes more difficult to solve if the pores are already full of water.

Suspensions or emulsions in water of hydrophobic substances exhibit limited penetration into small pores because the suspended particles are large. Water-soluble siliconates (sodium derivatives of silicones) have been used for creation of damp-proof barriers by injection into masonry.

A possible source of trouble, in this case, is that the diffusion of the solution in the water that fills the pores is slow, and good distribution might be difficult to obtain if the material contains a high proportion of small pores.

Solvents that are rather polar (so they can be attracted to the polar surface) but not miscible with water (because they are unable to form hydrogen bonds), e.g. chlorinated hydrocarbons, might be able to displace water from the pore surfaces, exploiting in part the strong tendency of water molecules to form drops (high surface tension); such techniques are successful for the application of organic coatings over wet surfaces but there is no proof that they would also work in deep impregnation.

Surface hydrophobic treatment of porous solids is easier and, in general, successful. It is subject, however, to at least two important limitations: the first is the ageing of the hydrophobic material, while the second is the possible accumulation of water or salts behind the surface film, resulting in damaging internal stresses.

Ageing of surface films. All molecules containing hydrogen and carbon (organic materials) are subject to oxidation when they are exposed to the air. This process is normally triggered by energy provided by light or ultraviolet radiation and is, as a result, very active on the surfaces. Oxidation results in the breaking or cross-linking of molecules and in the addition of oxygen which creates polar hydrophilic groups, such as $C^+ O$ and $O^- H^+$.

Frequently, the result of oxidation is a change in colour, a reduction of mechanical strength and the loss of hydrophobic action; in the later phases of oxidation, the material can even become water soluble. The best hydrophobic materials have an expected useful life of 8-10 years when directly exposed to light and the atmosphere; the life inside a pore should, however, be much longer because light is absent and oxygen less available.

It is important to note that resistance to oxidation depends partly upon the purity of the materials, as small amounts of easily-oxidized impurities can start the chain reaction and transmit it to the more resistant molecules. Because of this, it is necessary to test each single commercial material for ageing, and it is impossible to rely on general statements about entire families of chemicals (such as "silicones are bad", "acrylics are resistant").

Water accumulation behind films. Water can accumulate behind a surface coating because it can penetrate into the porous material in so many possible ways that sooner or later one of these possibilities is going to be realized. Water can gain access by capillary rise, or rainwater can infiltrate through joints or defects in the coating or defective gutters; interstitial condensation can also take place behind the film if it is applied on the external surface of a wall and the interior atmosphere is much warmer than the exterior one. If the film is, partially or totally, impervious to evaporation, the accumulated water can eventually freeze, causing internal stress. If evaporation does take place slowly, dissolved salts can crystallize behind the film, causing internal stress also in this case.

Application of a surface coating to a porous material therefore requires a preliminary study of circulation of liquid water and water vapour in the masonry to avoid the dangers mentioned above.

Chapter X

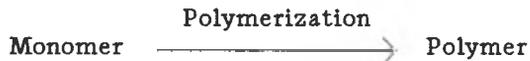
SYNTHETIC PLASTICS

It is convenient to divide synthetic plastics into two main groups:

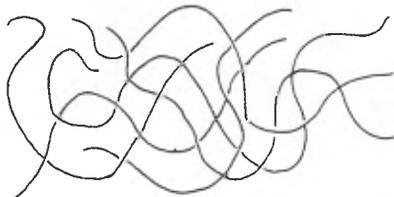
- a. Thermoplastic resins
- b. Thermosetting resins

10.1 THERMOPLASTIC RESINS

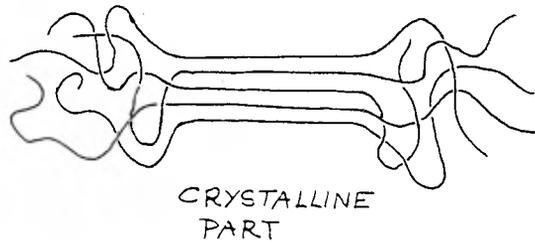
Thermoplastic resins are molecular solids (that is, they are composed of molecules). The molecules are very long and are synthesized starting from a small molecule (monomer) which can be added to itself for a great number of times (polymerization) to yield a long chain of atoms (polymer).



The long chains are flexible and can be disposed in complete disorder

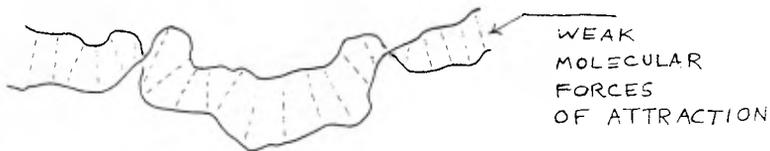


or partially arranged in parallel fashion (crystalline parts - crystallites).



The crystalline part is harder but stiffer, while the disordered (amorphous) structure allows the absorption of mechanical shocks thanks to the flexibility of the chains.

The long chains are attracted to one another by weak molecular forces



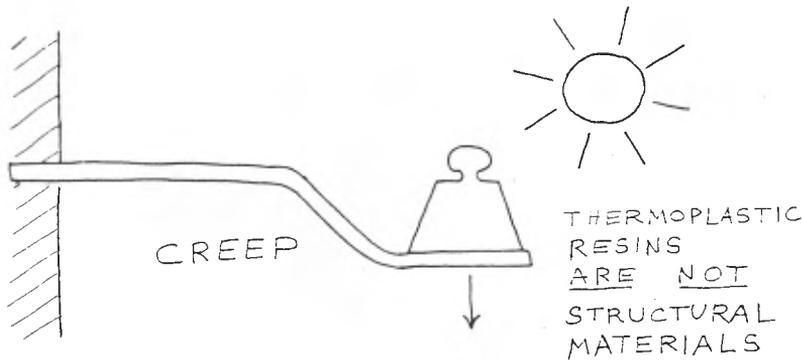
which allow easy deformation of the material at moderate temperature and under moderate compression.

Below a given temperature (*glass temperature*) thermoplastic resins become stiff as glass because the chains are no longer flexible. Thermoplastics that are glassy at room temperature are used as substitutes for glass (e.g. methacrylates, Perspex).

Flexible thermoplastics (e.g. polyethylene, nylon) have very low glass temperatures and are used as high resilience (shock resistant) materials or in fibres and films.

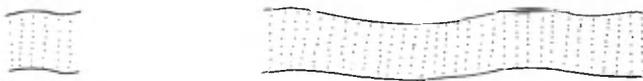
Adhesives are made from both types of thermoplastics.
Polyvinyl acetate and acrylic resins are the most common choice.

Thermoplastic resins are not structural materials, that is they cannot carry heavy loads for long periods.



This is due to the weakness of the forces binding the molecules together; they give way slowly under sustained stress, causing deformations of the plastic material which continuously increase in time and can lead to complete failure (*creep*).

Longer molecules show better mechanical behaviour than shorter ones; hardness and strength increase as the chains lengthen because the force of attraction between two molecules is equal to the sum of the forces of attraction between all their atoms.

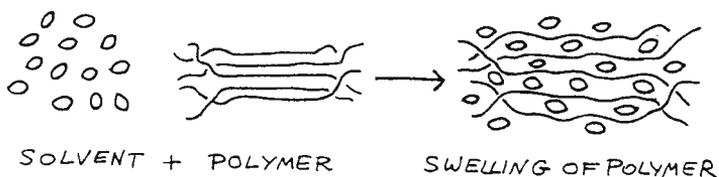


THE FORCE OF ATTRACTION BETWEEN MOLECULES INCREASES WITH THEIR LENGTH
(and so does mechanical strength)

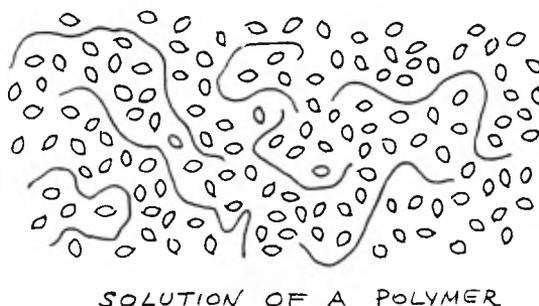
Solubility of thermoplastic resins

Long molecules are not dissolved easily because solvent molecules are delayed in their penetration between them.

In the dissolution of thermoplastic resins there is always an intermediate stage in which the material swells and becomes soft.



Complete dissolution takes place when the molecules are completely separated from each other.



Solutions of polymers are viscous because the long molecules attract each other and hinder the flow of the liquid.

Very long polymer molecules can be almost insoluble (e.g. polyethylene and nylon); those which are still soluble form solutions that are extremely viscous.

Polymers made of smaller molecules are easier to dissolve and their solutions are less viscous, but their mechanical strength in the solid state is lower. They are more suited for penetration in porous materials (impregnation).

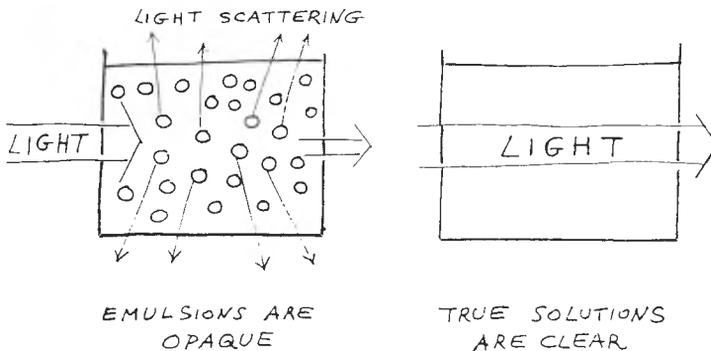
In *conservation of building materials*, acrylics and polyvinyl acetate are the most useful thermoplastic resins.

They can be dissolved in organic solvents and their solutions can be used as adhesives (to carry light weights) or to form protective coatings on stone, stucco or mural paintings.

Occasionally they are also used to impregnate and consolidate wood, mortar or stone.

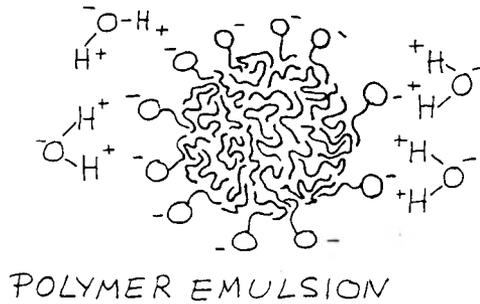
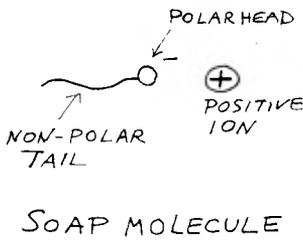
Emulsions of thermoplastic resins

Acrylics and polyvinyl acetate are also available as emulsions in water which are easily distinguished from true emulsions because they are not clear but white and opaque, like milk. Emulsions are opaque because they contain clusters of agglomerated molecules of polymer, suspended in water, which scatter the incident white light.



In the true solutions, the single molecules are separated from one another and do not cause scattering because they are much smaller than the wavelength of the light.

The emulsion is made possible by the use of a soap that coats the droplets of the polymer molecules, which are not soluble in water.



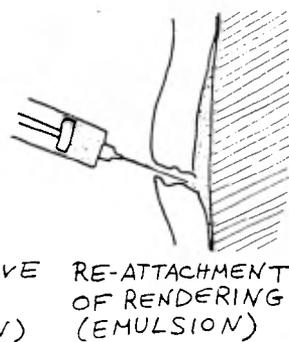
The polar head of the soap attracts water molecules and does not allow the droplets of polymer to join again.

The use of emulsions in conservation is limited, however, by the fact that they contain soap and other additives whose behaviour on ageing is not reliable.

Also emulsions cannot be used for impregnation of porous materials because the large clusters of molecules do not penetrate easily into the pores.

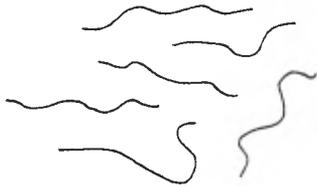
In conservation, the most frequent use of thermoplastic emulsions is as adhesives to reattach plasters that have become detached from walls, or as additives to lime, gypsum or cement mixes to increase flexural strength and decrease fragility of the mortars.

USES OF THERMOPLASTIC RESINS IN CONSERVATION



10.2 THERMOSETTING RESINS

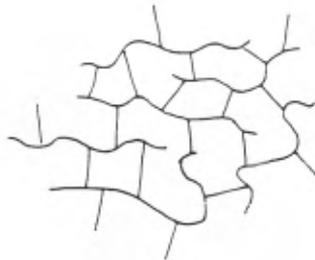
Thermosetting resins are always manufactured in two stages. In the first, a rather long chain molecule is prepared by a chemical process:



THERMOSETTING RESIN
FIRST STAGE
VISCIOUS LIQUID

In the second stage, a chemical reaction or the action of heat (or both) causes a cross-linking of the chains, which join together to form a hard brittle mass (setting of the resin).

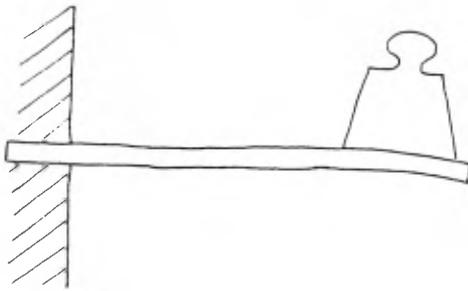
THERMOSETTING RESIN
SECOND STAGE
HARD, BRITTLE SOLID



The most popular thermosetting resins are the epoxies (e.g. Araldite) and the polyesters. Both are viscous liquids which can harden, without heating, by addition of a liquid "hardener" or "catalyst".

In the set resin, the chains are kept together by strong chemical bonds (not by weak molecular forces as in the thermoplastics). The consequence is that the chains are not easily flexed nor can the material be deformed with pressure and heat.

Thermosetting resins are harder and stronger than thermoplastics but they are also more brittle. In order to improve the mechanical properties of thermosetting resins, fillers are always added to the liquid resin before setting. Fibrous glass reinforcement is widespread and yields materials that show improved resilience and *can be used as structural materials*, as thermosetting resins are far more resistant to creep than thermoplastics.



REINFORCED
THERMOSETTING
RESINS ARE
STRUCTURAL
MATERIALS

Epoxy resins adhere very well to most materials (exceptions: polyethylene, nylon, greasy surfaces, silicones) and are resistant to water and several chemicals. Adhesives based on epoxy resins are widely used in conservation of building materials to repair broken stones, to seal cracks in concrete, to connect reinforcing bars to masonry, etc. Epoxy resins, like most thermosetting resins, are insoluble in all common solvents.

Polyester resins are less resistant chemically than epoxies but also less expensive. Glass-reinforced polyester is extensively used for lightweight sheds or structural elements. A highly-filled polyester resin is used in the Massari technique to build a damp-proof course in old masonry. Injection of very fluid polyester permits consolidation of very fine cracks.

Both polyester and epoxy resins are used to cast exact copies of sculptures from latex moulds obtained from the originals.

10.3 WEATHERING OF SYNTHETIC PLASTICS

Environmental action causes the deterioration of synthetic plastics as well.

The main agent of deterioration is oxygen, particularly in the presence of light (ultraviolet light is the most dangerous radiation).

The oxidation of synthetic plastics follows two apparently contradictory routes:

- the splitting of molecules and the formation of smaller, oxidized fragments
- the cross-linking of separate chains.

The results of these quite complicated processes are:

- discoloration
- loss of tensile strength
- brittleness.

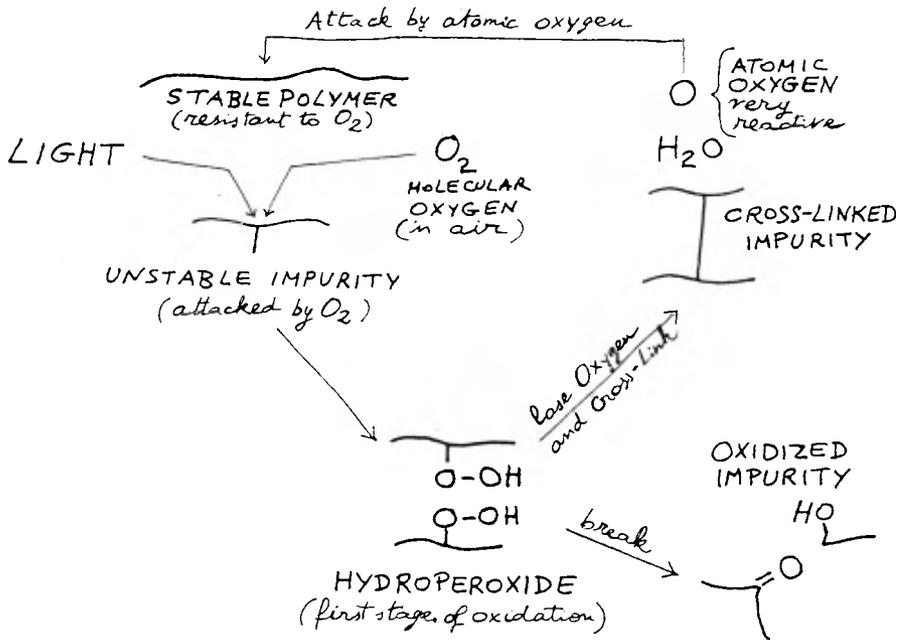
Often the material becomes soluble in water and is easily washed away from exposed surfaces (polyester from polyester-glass roofing).

The best resistance to oxygen and ultraviolet is shown by the acrylic resins. Epoxy resins discolour very rapidly and in general should never be used on the surface of materials.

Epoxies and polyesters are quite resistant to ageing if shielded from light and oxygen, as they are when they are used as structural adhesives or damp-proof courses.

Oxidation of synthetic plastics is made easier if impurities that are easily attacked by oxygen are present. In the course of the oxidation of impurities, some fresh oxygen is developed which is more active than atmospheric oxygen and acts more rapidly, even on the more resistant molecules.

OXIDATION OF POLYMERS IS MADE EASIER BY UNSTABLE IMPURITIES



Oxidation of synthetic plastics is a chain reaction in which oxygen is recycled in a more active form.

For this reason, synthetic materials should be very pure and have a constant high quality. All commercial products should be individually (and repeatedly) tested. Chemical similarity to other successful (or unsuccessful) products cannot be accepted as evidence of good (or bad) ageing behaviour.

Chapter XI

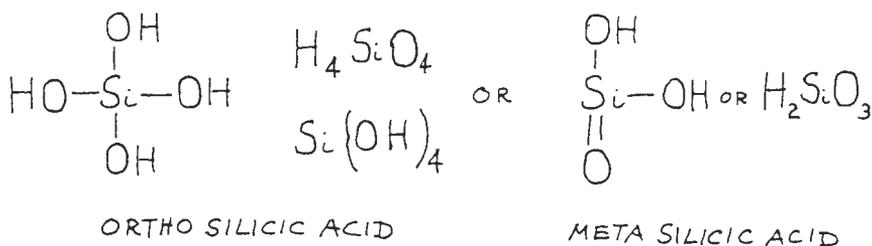
SILICATES AND SILICONES

11.1 SILICA AND SILICATES

The element silicon (Si) forms an oxide called silica (SiO_2).

Silica is found in nature in several forms (e.g. quartz) but also in amorphous states (e.g. silica glass and silica gel).

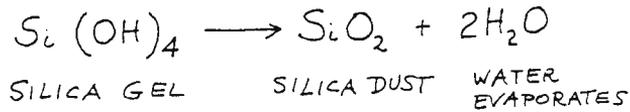
Hydrated silicon oxides (i.e. silica plus water) behave as weak acids:



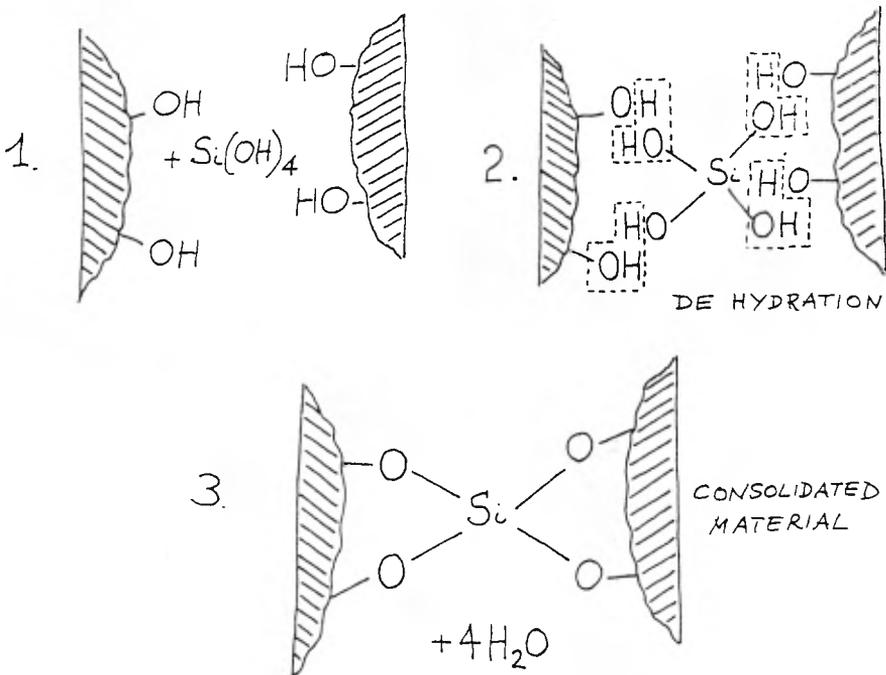
They form salts that are called silicates; for instance, sodium silicate or "soluble glass" (Na_2SiO_3) or potassium silicate (K_2SiO_3) which have both been used in the past as consolidants for stone, wood and other materials.

Reaction of sodium and potassium silicate with water (this type of reaction is called "hydrolysis") results in silicic acid and sodium or potassium hydroxide. Both hydroxides are strongly alkaline and are better known under the names of caustic soda and caustic potash.

The silicic acid freshly formed in the hydrolysis reaction is responsible for the consolidation of materials. If left alone, the acid forms a gelatinous mass (gel) which undergoes progressive contraction as it loses more water until it is transformed into silica dust.

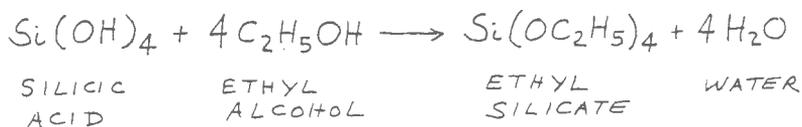


If the silicic acid is formed inside a material that carries hydroxy (OH) groups on its surface, as is the case with wood, brick, clay and several types of stone, dehydration takes place between the acid and the material, causing the formation of chemical bonds that improve the cohesion of the material.

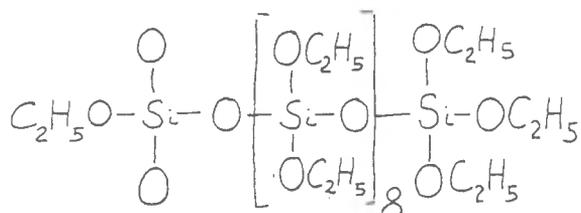


A drawback of the use of silicate salts as consolidants is constituted by the caustic materials formed in the hydrolysis which can damage organic materials and cause efflorescences on inorganic porous materials.

Silicic acid, like all acids, can react with alcohol to form esters which are also called silicates or, better, *silicate esters*.



Silicate esters are available under various trade names (e.g. Silester). Some types are composed of molecules such as the one shown above whose complete chemical name is "tetra-ethyl-ortho-silicate". Other types contain longer molecules formed by the condensation of several single molecules; an example is "ethyl silicate 40", formed by the condensation of about 10 molecules.



ETHYL SILICATE 40

The condensed types form more silicic acid from the same volume of liquid.

The silicate esters can also be used as consolidants because they can be hydrolyzed if an acid catalyst is used and they form silicic acid, which can bring about consolidation as in the case of the silicate salts.

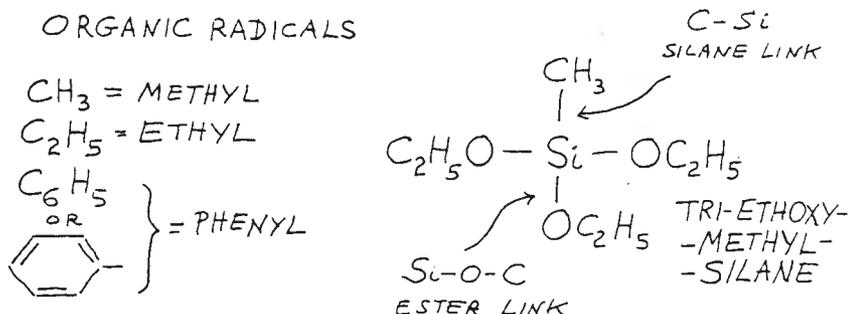
An advantage of silicate esters over silicate salts is the absence of caustic by-products in the hydrolysis reaction. In the case of ethyl silicate, the by-product is ethyl alcohol which evaporates and does not cause trouble.

Some disturbance can be caused instead by the acid catalyst if the material to be consolidated is sensitive to acids. The use of silicate esters is also complicated by the fact that they are volatile

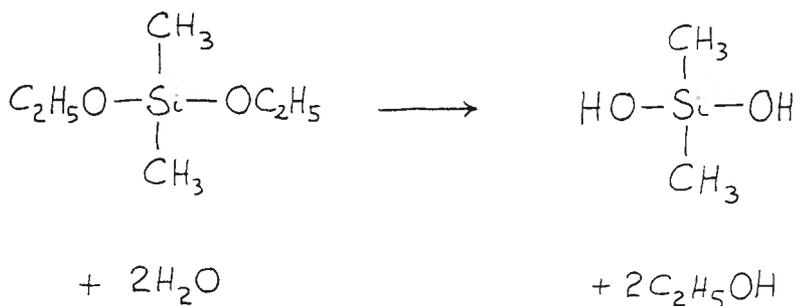
and care must be taken to avoid excessive evaporation before consolidation takes place.

11.2 SILICONES

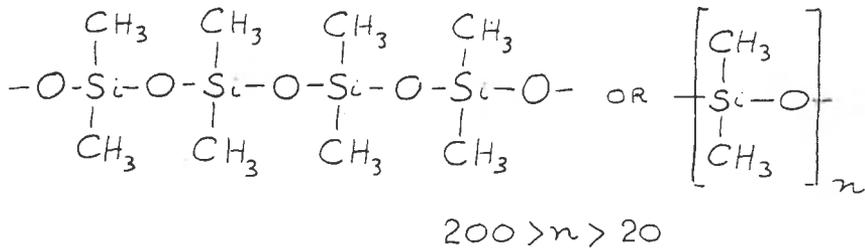
If organic radicals (i.e. groups of carbon and hydrogen atoms) are attached directly to silicon through a silicon-carbon link (Si-C), a class of compounds called alkoxy-silanes is formed. Some of them can contain silane and ester links at the same time.



Whereas the ester link is split by hydrolysis, the Si-C link resists hydrolysis. Therefore hydrolysis of compounds such as the one shown above (which are called ethoxy-alkyl-silanes) leads to products that still contain organic radicals.



Dehydration of such molecules results in the connection of several of them (20 to 200) to form long molecules that are partly organic and partly inorganic in character and are called *silicones*.

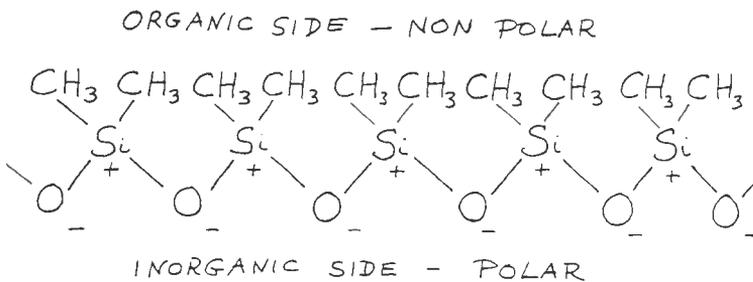


The silicone molecule shown above contains methyl radicals (CH_3) only, but silicones with phenyl radicals (C_6H_5) are also used.

Molecules that have a linear structure, such as the one shown above, are soluble in organic solvents. Insoluble silicones are also synthesized; they have a three-dimensional, cross-linked, structure.

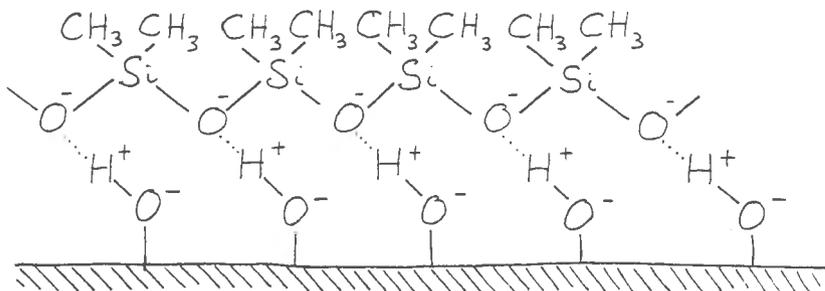
11.3 WATER-REPELLENCY OF SILICONES

The inorganic part of the silicone molecule ($\text{Si}-\text{O}$) is slightly polar, whereas the organic part (CH_3 or C_6H_5) is non-polar.



When a silicone is applied over a material that carries hydroxy (OH) groups on its surface (as in most building materials), the polar part of the silicone molecule is attracted towards the material. As a result, the non-polar organic radicals are oriented towards the air.

HYDROPHOBIC LAYER

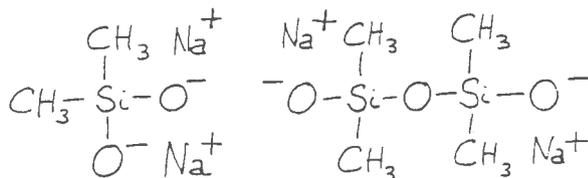


Therefore, over the surface of the material a non-polar barrier is formed which has no tendency to form hydrogen bonds with water molecules and is called "hydrophobic" or "hydro-repellent".

Water in the liquid state is unable to penetrate through such a barrier. However, enough empty space exists between the silicone molecules to allow isolated water molecules to pass. The silicone layer is therefore permeable to water vapour.

Silicones with a linear molecular structure are soluble in organic solvents but not in water. Water-soluble, hydro-repellent agents are based on silicones that contain some hydroxy groups (OH) transformed into sodium salts. For instance:

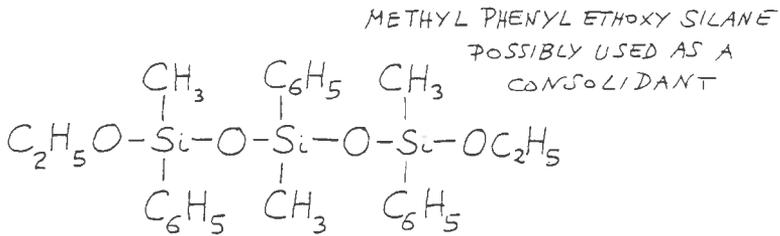
WATER SOLUBLE SILICONES



However, as water repellents, these appear to be less efficient than the solvent-soluble ones.

When silicones are applied as a surface layer, their effect is only temporary. The layer is very thin and can easily undergo mechanical damage or be destroyed by a chemical ageing process under the action of oxygen and light.

Alkoxy silanes containing both silane and ester links are used as stone consolidants in deep-impregnation processes as they can induce both water-repellency and consolidation.



The formula shown above represents the approximate structure of a silicone resin used in the conservation of weathered marble.

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