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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

Salts

SALTS

ARC
LABORATORY HANDBOOK

VOLUME 3/99

Ernesto Borrelli

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors** to periodically update the texts;*
- ***users** to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes** to be gradually added in line with developing needs.*

1998 - 99 volumes:
*(1) Introduction, (2) Porosity, **(3) Salts,** (4) Binders, (5) Colour specification and measurement*

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Rome, 1999

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① : Footnotes
📂 : Bibliographic references

1 INTRODUCTION

The presence of water-soluble salts in porous building materials is one of the principal conservation problems. Their crystallization is in fact the cause of those phenomena of deterioration that so often appear on surfaces: lack of cohesion, scaling, flaking and bulging *(photo 1)*.

Sources of salts can be the building materials themselves (sand, bricks, mortar) or external sources (soil, materials used for conservation treatment, pollutants in the atmosphere, sea spray, de-icing salts scattered on roads in winter, products generated by the metabolism of micro-organisms). Salts are transported into porous materials by rainwater, rising damp, infiltration or condensation 🗀**1**.

Almost all masonry contains soluble salts, principally ***sulphates, nitrates, chlorides and carbonates of sodium, potassium, calcium, magnesium and ammonium*** and so all liquid water present in walls is more or less a diluted salt solution 🗀**2**.

But not all salts generate decay. This depends on their solubility, hygroscopicity, mobility and the hydration level of their crystalline form.

When the water transporting the salts through porous materials evaporates, due, for example, to changing climatic conditions, the solution becomes more concentrated. As soon as it becomes supersaturated, the salts crystallize giving rise to both efflorescences on the surface and/or sub-efflorescences below the surface layer 🗀**3**.

It is very important to know the salt content of deteriorated surfaces both to understand the causes of decay and plan conservation strategies. The nature of the salt provides us with information about its origin and therefore indicates the possible conservation treatment to adopt 🗀**4**. For example, the presence of nitrates is generally attributed to the infiltration of sewage water or to the proximity of burial sites while sulphates are often due to the effect of atmospheric pollution particularly in urban areas.

1 Marble deterioration due to sulphates

colour print on inside back cover

2 BASIC SALTS CHEMISTRY

Ions

When a salt is dissolved in water, it is dissociated into ions.

e.g. $\underset{\text{sodium chloride crystals}}{NaCl} + H_2O \longrightarrow Na^+ + Cl^-$

Ions are electrically charged atoms or groups of atoms. If positive, they are called <u>cations</u>:

e.g. Li^+ *(lithium)*, Na^+ *(sodium)*, K^+ *(potassium)*, NH_4^+ *(ammonium)*, Ca^{++} *(calcium)*, Mg^{++} *(magnesium)*, Fe^{+++} *(iron)* ....

If negative, they are called <u>anions</u>:

e.g. F^- *(fluoride)*, Cl^- *(chloride)*, NO_2^- *(nitrite)*, NO_3^- *(nitrate)*, SO_4^{--} *(sulphate)*, CO_3^{--} *(oxalate)*, PO_4^{---} *(phosphate)* ....

Salts

Compounds formed by the crystallization of a solution deriving from the reaction of an acid (e.g. HCl) with a base (e.g. NaOH).

$$HCl + NaOH \longrightarrow H_2O + Na^+ + Cl^-$$

hydrochloric acid + sodium hydroxide → *water + sodium chloride solution*

$$Na^+ + Cl^- + H_2O \xrightarrow{evaporation} NaCl \text{ (crystals)}$$

Solubility

The maximum amount of solute (salt) that will dissolve in a given amount of water. It is usually expressed in g/l or g/100 ml at a given temperature. Solubility is constant at a constant temperature and generally rises with an increase in temperature. *(Table 1)*

SALTS	FORMULA	SOLUBILITY (g/l)	
Calcite	$CaCO_3$	0.015	(25 °C)
Magnesite	$MgCO_3$	0.106	(20 °C)
Gypsum	$CaSO_4 \cdot 2H_2O$	2.58	(20 °C)
Halite	NaCl	264.0	(20 °C)
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	363.4	(20 °C)
Natrite	$Na_2CO3 \cdot 10H_2O$	486.5	(20 °C)
Hydrophilite	$CaCl_2$	595.0	(0 °C)
Nitronatrite	$NaNO_3$	921,0	(25 °C)
Nitrocalcite	$Ca(NO_3)_2 \cdot 4H_2O$	2660,0	(0 °C)

Table 1: Examples of the solubility of a number of salts

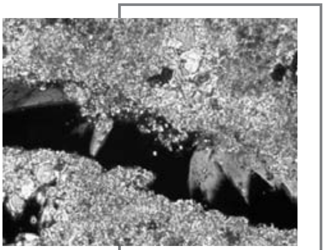
Saturated solution

A solution containing the maximum equilibrium amount of solute at a given temperature. In a saturated solution, the dissolved substance is in equilibrium with the undissolved substance. In other words, the rate at which solute particles crystallize is exactly balanced by the rate at which they dissolve. A solution containing more than the equilibrium amount of solute is said to be supersaturated (and can be formed by slowly cooling a saturated solution). Such solutions are metastable; if a small crystal seed is added, the excess solute crystallizes out of solution.

Crystallization *(photo 2)*

This takes place when conditions for a salt to remain in solution no longer exist: at this point the solution is supersaturated.

On porous building materials crystallization can take place 🗁5:



2 Gypsum crystals
colour print on inside back cover

- WITHIN THE PORES of materials if the solution becomes supersaturated, that is, if the concentration of salts exceeds solubility.
- ON SURFACES of materials in relation to the humidity level of the environment. It is very important to know the **temperature** and **relative humidity** conditions that induce phase transformations of the solutions, particularly for indoor environments where it is easier to control climatic conditions 🗁6.

  Within the masonry, each saturated solution of a given salt at a given temperature corresponds to the "equilibrium relative humidity"①. When the ambient relative humidity becomes lower than the equilibrium relative humidity of the saturated solution, evaporation from the walls takes place, the solution becomes supersaturated and the condition for crystallization is reached②. This is what happens, for example, when a room is heated or ventilated. To avoid crystallization, it is always necessary to maintain the **ambient relative humidity** at a higher level than the **equilibrium relative humidity** of the salts inside the masonry *(Fig. 1)*.

① This means that the humid air in contact with the surface influences the equilibrium between salt, solution and vapour and therefore conditions crystallization and dissolution

② However we are generally dealing with systems containing a mixture of salts and so both "solubility" and "relative humidity" of pure salts cannot be applied, as they only represent indicative values 🗁4. For example, salt efflorescences on walls containing complex salt mixtures have been observed at considerably lower relative humidity levels than would have been expected from those of pure salts.

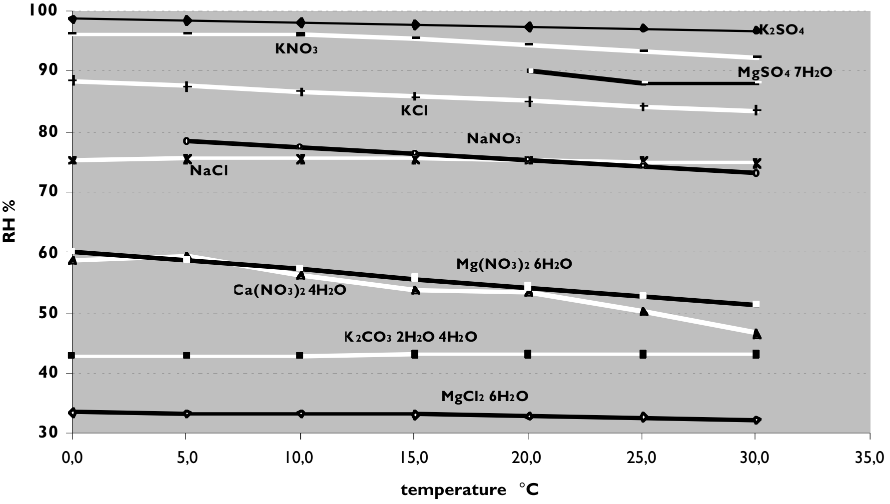


Fig 1. Equilibrium relative humidities of salts commonly found in walls 🗁**7.**

3 DETERIORATION

There is a relationship between the **solubility** of salts and their **disruptive action** on materials 🗁8:

- **Practically insoluble** salts do not produce phenomena of dangerous crystallization. Even though their poor solubility enables them to reach saturation inside materials, the concentrations at saturation are minimal and insufficient to cause conspicuous damage.
- **Slightly soluble** salts are generally more dangerous. Due to their low solubility, they often crystallize just below the surface layer and cause bulging, detachment and loss of fragments. Among these, *gypsum* is the predominant salt ($CaSO_4 \cdot 2H_2O$), which crystallizes even in humid climates③ , becoming the principal cause of deterioration.
- **Highly soluble** salts (principally chlorides and nitrates, e.g. sodium chloride NaCl, sodium nitrate $NaNO_3$, potassium nitrate KNO_3), can accumulate and reach very high concentrations of highly hygroscopic salts which therefore remain in solution in humid environments producing dark patches. In drier conditions (e.g. inside heated buildings), when crystallization occurs, efflorescences appear. However due to the high solubility, crystallization requires strong evaporation that takes place especially on surfaces causing limited damage. Sometimes the crystallization is so abundant that it spreads below the surface layer affecting cohesion.

Another parameter for evaluating the danger of salts is their hydration properties. $Na_2SO_4 \cdot 10H_2O$ *(mirabilite)* is a particular example as it is highly soluble and therefore, according to the above explanation, should not be dangerous when in fact it is. Mirabilite, deriving from the hydration④ of Na_2SO_4 *(thenardite)*, increases in volume by about 400% causing considerable stress within the pore structure.

The presence of soluble salts in walls can cause their deterioration in at least three ways:

- soluble salts attract water and produce phenomena of osmosis⑤ and hygroscopicity, causing an increase in the moisture content which always leaves the masonry damp;
- due to microclimatic variations, the saline solutions present in walls give rise to dissolution and crystallization cycles. If they are frequent, even daily, they produce mechanical stress and consequent crumbling of the material;
- when salts crystallize close to the surface, they form efflorescences and sub-efflorescences.

③ *Gypsum has a very high deliquescence humidity (>99%) which diminishes considerably in the presence of other salts (it increases its solubility). We can therefore find efflorescences of sulphates also in moderately humid climates (e.g. relative humidity of 70-80%).*

④ *This phenomenon is caused by a change in temperature. At <24.3 °C mirabilite is the stable form, while at t >32.4 °C thenardite represents the equilibrium. This range in temperature is normal on surfaces in temperate climates.*

⑤ *Osmosis is a physical phenomenon: in this case it happens when water (solvent) flows through the porous material from a weaker to a stronger solution increasing the moisture content of the wall.*

4 MAIN CHARACTERISTICS OF SOME SALTS

Sulphates SO_4^{--}

Origin 🗀9

They are generally found in walls in the form of dihydrate calcium sulphate ($CaSO_4 \bullet 2H_2O$ *gypsum*), sodium sulphate ($Na_2SO_4 \bullet 10H_2O$ *mirabilite*) and more rarely as magnesium sulphate ($MgSO_4 \bullet 7H_2O$ *epsomite*).

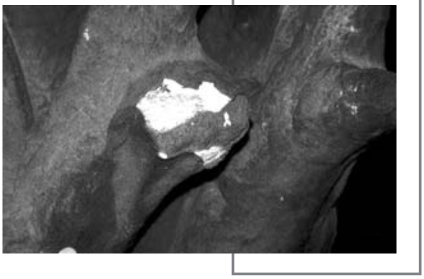
The most important source of sulphates is **atmospheric pollution**. Wet acid deposition from sulphur dioxide and humidity in the air attacks calcium carbonate in masonry to form calcium sulphate, but according to some authors sulphates can also be deposited on the surface from particulate matter existing in the air (dry deposition) 🗀10.

Other sources include

- AGRICULTURAL LAND: (ammonium sulphate) from which sulphates can penetrate masonry through capillary action;
- ORIGINAL OR ADDED MATERIALS: inorganic binders like cement contain sulphates which can be mobilized by water. Portland cement normally contains about 4% of calcium sulphate and certain grouting binders contain sodium sulphate as an impurity when plasticizers are added;
- SEA SPRAY: which contains low concentrations of magnesium sulphate that can be found mainly on surfaces;
- MICRO-ORGANISMS: sometimes present in calcareous materials, able to metabolize compounds containing reduced forms of sulphur and oxidize them to sulphates 🗀11.

The most common forms of deterioration

Black crusts *(photo 3)* are generally found on the calcareous material of buildings sheltered from the rain but exposed to the attack of atmospheric pollutants. Their composition is essentially gypsum and the black colour is due to the accumulation of carbon particulate matter present in polluted air. Apart from disturbing the aesthetic appearance of the surface, they can also conceal damage extending well below the surface layer 🗀12.



3 Black crusts
on marble
colour print on inside back cover

Efflorescences are particularly evident on mural paintings and generally appear in three forms:

- GYPSUM DUST: a whitish deposit (from a few micrometers to 0.1 mm) mixed with small fragments of the paint layer and lightly attached to it.
- WHITE DOTS: between 0.1 and 1 mm in size, they are well attached to the surface and are usually found close to small imperfections (e.g. cracks); they are made up of clusters of gypsum aggregate.
- WHITENING: whitish or transparent layers which can detach themselves from the surface in flakes; they are typical of areas with increased humidity and can become gypsum dust if humidity decreases.

Pitting: gypsum is easily adsorbed in the macro-porosity of mortars forming minute sub-efflorescences and consequently detaching microfragments from the surface.

Chlorides Cl^-

Origin 🗀13

The most common source is **sea spray** (above all NaCl *halite*). Chlorides can also originate from impurities present in building materials used, for example, from sand for preparation of mortars; from de-icing salts spread on roads in winter and from emissions into the atmosphere of hydrochloric acid coming from certain types of industrial activity.

The most common forms of deterioration

Chlorides are highly soluble salts and this enables them to even penetrate very deeply into materials inducing alterations. Since they are highly hygroscopic (especially calcium chloride $CaCl_2$), their presence in a material induces a higher moisture content at equilibrium compared to one where they are absent. The high water content in the walls, following the freeze-thaw cycles, leads to the formation of **cracks** and **crumbling**.

Corrosion of steel reinforcement in concrete can occur if cracks allow chlorides to penetrate the structure. Calcium cloride ($CaCl_2$) is particularly dangerous 🗀14.

Nitrites and Nitrates NO_2^- NO_3^-

Origin 🗀15

Nitrites are produced by the **organic decomposition** of nitrogen-containing products and may therefore be found where there is infiltration of sewage water or proximity to burial sites. The tendency for nitrites (NO_2^-) to oxidize to nitrates (NO_3^-) makes it difficult to find them in masonry.

Nitrates can have the same origin but can also come from **agricultural land** (fertilizers) or from the **photochemical smog** typical of highly polluted areas with long periods of sunshine. Nitric acid (from nitrogen oxides in the air) attacks calcium carbonate in masonry to form calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$ *nitrocalcite*).

Another source of both nitrites and nitrates is **microbiological**: nitrous and nitrobacteria can transform nitrogen compounds into nitrites and nitrates in metabolic processes 🗀16.

The most common forms of deterioration

Nitrates, like chlorides, are highly soluble. The most serious damage is due to high moisture content in the masonry caused by the hygroscopicity of the nitrates. This leads to **decay phenomena** that generally occur in masonry with permanent high moisture content.

The other alteration is from nitric acid formed under particular atmospheric conditions: **corrosive action** attacks the mortar and causes loss of material in calcareous stone.

Carbonates CO_3^{--}

Origin 🗀17

Calcium carbonate ($CaCO_3$ *calcite*) is a constituent of both calcareous stone and mortars, and though being practically insoluble in water, can be transformed into the **more soluble bicarbonate** $Ca(HCO_3)_2$. If there is a higher than normal quantity of carbon dioxide (CO_2) in the atmosphere (as a result of industrial activity or due to the presence of a large number of people in a closed space), carbonic acid (H_2CO_3) can be formed in the presence of water and reacts with calcium carbonate to form calcium bicarbonate.

Equilibrium exists between these two compounds:

$$2\,CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2$$

The soluble bicarbonate comes to the surface where evaporation shifts the equilibrium to the left again forming insoluble $CaCO_3$ which is deposited on the surface.

Another source can be the soluble alkali content of cement in masonry from which the highly soluble $Na_2CO_3 \cdot 10H_2O$ (*natron*) can be formed. Sodium carbonate (Na_2CO_3) can then be transformed into sodium bicarbonate ($NaHCO_3$), again due to the presence of a high quantity of CO_2 in the atmosphere. Both can be found as $Na_2CO_3\ NaHCO_3 \cdot 2H_2O$ *(trona)*.

4 Calcareous concretions
colour print on inside back cover

The most common forms of deterioration

Accumulation of calcareous material in the form of encrustations and concretions mainly on protruding parts of buildings (where crystallization occurs) *(photo 4)*.

A mixture of $Na_2CO_3 \cdot 10H_2O$ and $NaHCO_3$ has a very disruptive effect on building materials.

Oxalates $C_2O_4^{--}$

Origin 🗀18

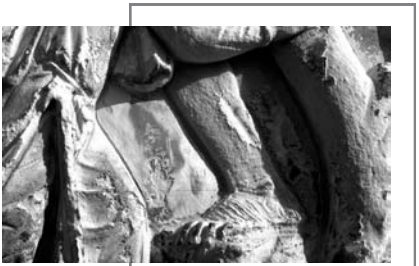
Among the various suggested mechanisms for the formation of these salts, the following two are usually cited:

- the biodestruction by certain micro-organisms of complex proteins (such as casein and egg white) sometimes applied in conservation treatments of the past.
- the presence of oxalic acid ($H_2C_2O_4$) secreted by lichens, reacting with the calcite ($CaCO_3$) on the surface, generates calcium oxalates (CaC_2O_4) with different hydration states like *whewellite* ($CaC_2O_4 \cdot H_2O$) and *weddellite* ($CaC_2O_4 \cdot 2H_2O$). These are both highly insoluble, unlike most of the other salts so far taken into consideration.

There are, however, other interpretations about the formation of oxalates, the most recent involving the presence of carbon monoxide in the air as a pollutant 🗀19.

The most common forms of deterioration

The presence of oxalates appears as chromatic modifications: generally a yellowish, reddish or brownish patina depending on the impurities it contains *(photo 5)*. They are usually well attached to the surface of the stone. Some authors suggest that they may even protect the stone surface.



5 Oxalate patina
colour print on inside back cover

Phosphates PO_4^{---}

Origin 🗀20

Bird excrement contains phosphate salts. The accumulation of excrement permits phosphates, which are soluble, to migrate over large surface areas under damp conditions. Another source of phosphates is fertilizers (ammonium phosphates).

The most common forms of deterioration

Dark black deposits and white patches which are rich in organic matter providing nutrient for microbiological growth and therefore increasing decay 🗀21.

5 SURVEYING AND SAMPLING

The first considerations regarding masonry damaged by salts must be made on site through an overall visual inspection and annotation of the following:

- type of masonry (brick, stone)
- orientation (north, south, etc.) and exposure (sun, shade) of the external surfaces
- indoor climate, existence of air-conditioning and/or heating systems, movement of air;
- identification of humid areas, rising damp and possible infiltration of water from roof or drainage system;
- visible deterioration caused by salts.

The result of this first inspection must be recorded on a plan of the building indicating the phenomena observed as a guide to planning sampling and future analysis relating to the presence of soluble salts.

Having completed a survey of the overall situation, photographic and/or graphic documentation must be carried out and if sampling is needed, a plan must be decided on.

6 ANALYSIS

With the exception of X-ray diffraction (XRD), the following types of analysis require the ground sample to be shaken in pure water to dissolve the soluble salt content and the analysis to be done only on the solution. They provide us with information about the ions and only indirectly about the salts.

This is often insufficient. For example, if dihydrate calcium sulphate ($CaSO_4 \cdot 2H_2O$) and decahydrate sodium sulphate ($Na_2SO_4 \cdot 10H_2O$) are present in a sample, the result with these methods will only show a certain amount of both calcium and sodium cations and sulphate anions. X-ray diffraction, instead makes it possible to identify the exact mineralogical composition of the compound so the result, in the above case, would show *gypsum* and *thenardite*. Furthermore, if $MgSO_4 \cdot 6H_2O$ *(hexadrite)* and $MgSO_4 \cdot 7H_2O$ *(epsomite)* are both present at the same time, only XRD can identify the two phases.

Simple tests

There are several very simple tests for the analysis of salts which require very little chemical know-how. Their cost is minimal and they provide semi-quantitative results in a few minutes. But there are no simple methods available for testing the presence of all the salts we may want to analyse (e.g. phosphates, oxalates) and the tests currently available are often not accurate enough for our purpose. If this is the case, it is better to resort to instrumental analysis (e.g. ion chromatography) at a specialized laboratory.

6 Microchemical tests

A) MICROCHEMICAL TESTS *(photo 6)*

These are laboratory tests that, through simple chemical reactions, make it possible to identify the type of anion (negative ion deriving from the dissociation of the salts, i.e. sulphate, chloride, nitrate, etc.) present in a solution. Even though they do not give quantitative information, they enable us to distinguish when there are negligible or massive quantities of the various anions and give a preliminary indication of the observed decay.

B) STRIP TESTS *(photo 7)*

These are plasticized strips with specific zones of reaction which are immersed in the solution to identify a specific ion⑥. If an ion is present, the strip changes colour at varying degrees according to the quantity.

Each type of strip test is sensitive to only one type of ion and they are available in boxes of 25 and 100 strips and cost approximately half a US dollar per strip.

The sensitivity varies according to the type of ion; there is a marked variation in range between one ion and another (e.g. sulphates 200-1600 ppm⑦(mg/l); nitrates 10 - 500).

7 Strip test kit
colour print on inside back cover

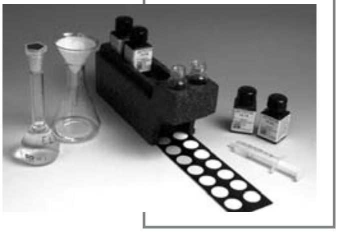
C) COLORIMETRIC KITS *(photo 8)*

These are based on reactions that lead to the formation of coloured compounds formed by each ion and its specific reagent. All the reagents and equipment necessary for analysis are inside the kit together with the instructions for their use.

As in the previous case, the intensity of the colour indicates the amount of ions present in the solution and the kit provides a colour card against which to measure the sample.

Each kit is sensitive to only one type of ion (and sensitivity varies according to the type of ion) and is sufficient to carry out at least 100 tests. One kit costs about 100 US dollars.

8 Colorimetric test kit
colour print on inside back cover



Instrumental analysis

A) MEASURING CONDUCTIVITY *(photo 9)*

Chemical compounds that in solution are totally dissociated into ions are called electrolytes. A characteristic of electrolytic solutions is that they conduct electricity through the ions. This property increases with the concentration of the ions in solution, and also depends on their charge, mobility and the temperature of the solution.

9 Conductivity measurements

For diluted salt solutions there is a linear dependence between ion concentration and specific conductivity (χ)⑧ *(Fig. 2).*

We can therefore use measurements of conductivity to provide us with information on the total content of ionic species and therefore of soluble salts even though we know nothing of the quality of these salts. The measurements can be effectively used both to give preliminary indications and to monitor trial treatment for the removal of salts from building surfaces 🗀22.

The measurements are expressed in microSiemens/cm (distilled water: about 7-8 μS/cm, tap water 300-400 μS/cm).

⑥*They can also be used on site by placing a wetted reagent strip directly against an efflorescence. Obviously the result in this case is only qualitative and only regards the outer surface in contact with the strip.*

⑦*Parts per million: yet another very much adopted way of expressing the concentration that for aqueous solutions is equivalent to mg/l.*

⑧*Specific conductivity (χ) is the reverse of its specific resistance (ρ)*

$\chi = 1/\rho = \mathbf{1/R} \times \mathbf{l/s}$

Where: **R** *= resistance of conductor expressed in ohm (Ω)*

1/R *expressed in Siemens (S);*

l *=length of conductor (cm);*

s *=cross section of conductor (cm^2);*

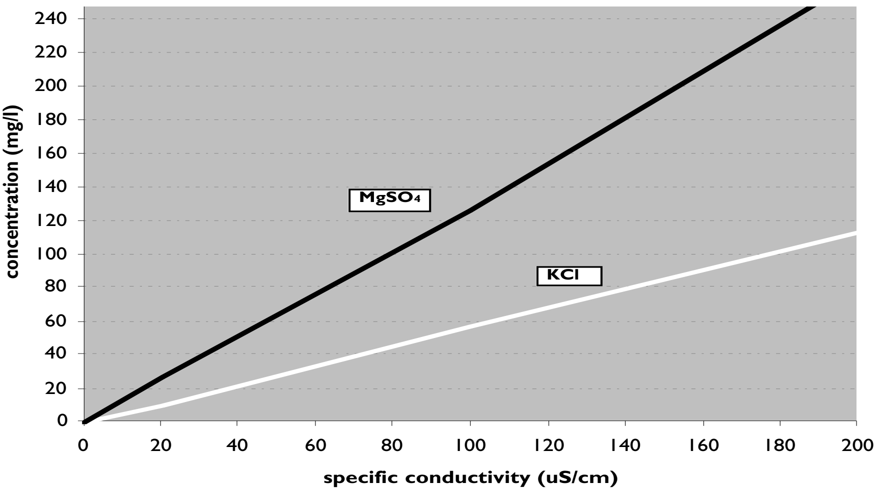


Fig 2. Specific conductivity curves

B) Ionic chromatography

Whenever diagnosis demands a more precise knowledge not only of the type but also the quantity of cations and anions present in the solution it is necessary to resort to more sophisticated technology.

Chromatography is used in chemical analysis to separate complex mixtures into single components based on the different velocities of migration (retention time) of the various components through a chromatographic column filled with a specific stationary phase.

From the retention time we can then recognize the anions and cations present in the solution and, calibrating the instrument with the standard solutions⑨ of anions and cations, we can calculate their precise concentration⑩.

The advantage is that the instrument is highly sensitive and can reveal ionic species in concentrations below 1 ppm in a short time but analysis must be done at a specialised laboratory at a cost of about 90 US dollars.

C) X-ray diffraction

X-rays provide information on the exact nature of the crystalline⑪ substances and not only on the ions, identifying the mineralogical composition of the compound.The minimum amount needed for the analysis ranges from 10 to 100 mg and the minimum percentage of crystalline compound detectable is about 3% of the mass of the sample, this limit depending upon the crystallinity of the compound.

One of the advantages of XRD is that the analysis must be done directly on the powdered sample without putting it in solution and therefore the sample after the analysis can also be used again for additional investigations.The analysis costs about 130 US dollars.

D) Infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) can be used with organic and inorganic compounds. Although inorganic compounds sometimes do not give clear readings, depending on the complexity of the mixture, FTIR has been widely used to analyse efflorescences, crusts and patinas on stone materials and is able to identify constituent materials and deterioration products. This technique is usually chosen because it only requires a tiny sample (1-2 mg). It costs about 90 US dollars in a specialized laboratory.

The relatively high cost of the last three types of analysis is obviously due to the high initial capital investment for equipment and the technical expertise necessary for their application.

⑨ Solutions with known concentrations.

⑩ In practice, as in any other measurement, there is always a margin of error.

⑪ Non-crystalline phases (amorphous) cannot be identified and in fact cause an increase in background noise and consequently a reduction in the sensitivity of the instrument.

PRACTICAL 1

PREPARATION OF SOLUTIONS WITH VARYING CONCENTRATIONS OF SODIUM SULPHATE

Aim

The aim is to gain confidence working with soluble salts and appreciate the forces in play. The prepared solutions will be needed for the second experiment which will involve observation of the damage caused by soluble salts on stone samples.

Equipment and chemicals

- 600 ml beaker
- 1 litre flask
- Deionized water
- Sodium sulphate decahydrate ($Na_2SO_4 \cdot 10H_2O$)
- Technical balance

Procedure

A) SATURATED SOLUTION AT ROOM TEMPERATURE.

Fill the beaker with 500 ml of deionized water and add the sodium sulphate decahydrate a little at a time, shaking gently, until it no longer dissolves (about 180 grams are necessary).

B) 10% SOLUTION W/V①.

Weigh 100 g of $Na_2SO_4 \cdot 10H_2O$, place it in the flask, bring it up to the volume of 1000 ml with deionized water and shake the solution.

① *The percentage composition is a way of expressing the concentration. There is generally an indication as to whether it is expressed as weight per volume (w/v) or weight per weight (w/w).*

PRACTICAL 2

CRYSTALLIZATION CYCLES②

Aim

The aim is to directly observe how salts can be transported inside materials, for example by capillary action, and how, over a period of time, the repetition of dissolution and crystallization cycles can lead to aesthetic and structural damage *(photos 10 and 11)*.

Equipment and chemicals

- Oven
- Glass or plastic tray
- 10% sodium sulphate solution
- Unaltered stone sample (preferably cube-shaped 5 x 5 x 5 cm)
- Stereomicroscope

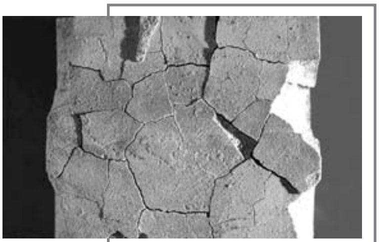
Procedure

- Dry the stone sample in the oven at 110°C for 24 hours.
- Leave it to cool.
- Put the sample in the tray totally filled with the solution of 10% sodium sulphate in deionized water.
- After 24 hours, remove the sample, blot excess water and dry it in the oven for 24 hours.
- Immerse the sample again in the sodium sulphate solution and repeat the cycle at least three times or until some evident alteration is visible.

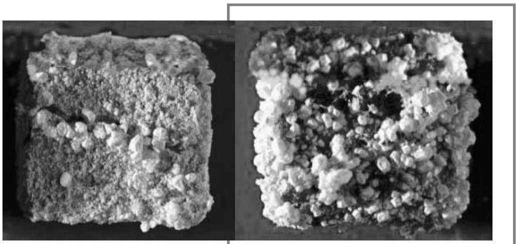
The number of cycles necessary to achieve physical change varies according to the type of stone material.

Naturally, the experiment can be done under more drastic conditions so as to heighten its effect, for example, by using solutions with higher concentrations.

It is very useful to study the macroscopic variations of the sample with a stereomicroscope and learn to recognize the macroscopic effects typical of the crystallization of the various salts.



10 Disruptive action of 10% sodium sulphate solution on mortar sample
colour print on inside back cover



11 Two phases of prolonged disruptive action of saturated solution of sodium sulphate
colour print on inside back cover

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②*Movement of salts in porous materials and observation of their deterioration.*

PRACTICAL 3

SAMPLING

Aim

The aim is to learn correct sampling procedure and technique.

Equipment

- Scalpel
- Paper pulp
- Plastic bags and small containers for samples
- Identification cards for samples
- Adhesive tags
- Camera

12 Sampling kit

Procedure

- Once the overall situation has been assessed and the need for sampling verified, photographs must be taken and a sampling plan decided upon.
- Before taking any samples, photograph the sample point (indicating it with the scalpel and putting a label on it specifying the identification number of the sample).
- It is advisable to take at least two photos for each sample: a general one that gives an overall view of the area and a close-up of the precise sampling location.
- Each sample taken with the scalpel (about 100 mg are sufficient③) is recorded on its data sheet with all relevant data (position, aspect, reason for taking sample, assumptions, analysis to be carried out); the sample container must be marked to avoid mixing up samples.
- Whenever the taking of samples is not possible, as in the case of mural paintings, the alternative is to use pulp poultices④ (suggested size: 10 cm^2, thickness approximately 5 mm, ratio of pulp to water about 1/6 or 1/8 in weight soaked in deionized water and applied to the wall so that it sticks to the surface *(photo 13)* 🗀*23*.
- After a certain time (a day, for example) the pulp poultice is removed and analysed in the laboratory. It must be remembered that, depending on the solubility of the salts, the efficiency of the extraction can vary. To ensure reliable results, more than one extraction may be necessary.

13 Sampling salts using pulp poultice
colour print on inside back cover

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③ In the specific case of pure salt efflorescence the amount can be even smaller, the sample being constituted only of salt.

④ These must be carefully chosen preferably with the assistance of a conservator as they must guarantee adherence to the surface even after the water has evaporated. They must neither contain impurities nor leave visible traces of fibre on the paint layer.

QUALITATIVE ANALYSIS OF SULPHATES, CHLORIDES, NITRITES, NITRATES AND CARBONATES (microchemical tests)

Aim

The identification of salts present in masonry, though it may only be qualitative, provides information that assists us in understanding phenomena of deterioration and may be the only instrument available in field laboratories, such as those on conservation worksites.

Equipment and chemicals

- Mortar and pestle
- Test tubes
- Filter paper and a small glass funnel
- Diluted hydrochloric acid (HCl 2M)⑤
- Diluted nitric acid (HNO_3 2M)
- Diluted acetic acid (CH_3COOH)
- Sulphamic acid (HSO_3NH_2)
- 10% solution of barium chloride ($BaCl_2$) in deionized water
- 0.1M solution of silver nitrate ($AgNO_3$)
- Zinc powder
- Griess-llosvay's reagent

14 Microchemical analysis: glassware

Procedure

PREPARATION OF SAMPLE TAKEN FROM WALLS

- Grind part of the sample (0.1 gram is more than enough) to a fine homogeneous powder.
- Put half⑥ of the ground sample in a test tube and add about 5 ml of deionized water and shake it gently to dissolve the material.
- Wait a few minutes so that the insoluble residue is deposited at the bottom of the tube. The solution must be clear. If not, filter it using filter paper and a small funnel.
- Keep the test tube containing the insoluble part for the analysis of carbonates and divide the clear solution above into another 4 small test tubes to use for testing for sulphates, chlorides, nitrites and nitrates.

PREPARATION OF PULP POULTICE SAMPLE

If indirect sampling with pulp poultices must be carried out:

- Take a small piece (about 1 cm^2) of the detached poultice and shake it in a beaker with deionized water. Wait till the cellulose fibres have sunk to the bottom and use the clear solution to do the tests on the next page.

Safety precautions

When working with these reagents always wear safety gloves and observe the safety precautions recommended for dealing with *corrosive* materials

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⑤ *M indicates the molarity, frequently used in chemistry to express the concentration of a solution. It signifies the quantity of moles of a certain substance in a litre of water. The mole of a compound corresponds to the quantity in grams equal to its molecular weight, for example, in a 1M solution of NaCl (molecular weight 58.44), there will be 58.44 grams of NaCl dissolved in 1 litre of water.*

⑥ *The other half can be used to repeat the analysis in case of doubt or error.*

For each of the following tests a simultaneous test should be carried out on approximately 1ml of deionized water so as to compare these so-called "blank" results with those of the sample.

Analysis of sulphates (SO_4^{--})

Add 1 or 2 drops of **HCl 2M** and 1 or 2 drops of a 10% solution of **barium chloride** to the first test tube.

The appearance of a white precipitate of barium sulphate, insoluble in nitric acid, indicates the presence of sulphates. Gently stroking the walls of the test tube with a glass rod helps the nucleation of the crystals, and therefore the formation of the precipitate.

The reaction can be
summarized as follows:

$$(SO_4^{--}) + BaCl_2 \rightarrow BaSO_4 \ \textit{(prec.)} + 2\ Cl^-$$

The sulphate present in the solution precipitates as it reacts with barium chloride forming the insoluble salt barium sulphate.

Analysis of nitrites (NO_2^-)

Add 1 or 2 drops of **CH_3COOH 2M** and 1 or 2 drops of **Griess-Ilosvay's reagent** to the third test tube.

The appearance of a more or less intense **pink colour** indicates the presence of nitrites.

Analysis of chlorides ($C1^-$) *(photo 15)*

Add 1 or 2 drops of **$HNO_3$2M** and 1 or 2 drops of a 0.1M solution of **silver nitrate** to the second test tube.

The appearance of a whitish-blue gelatinous precipitate of silver chloride indicates the presence of chlorides.

The reaction can be
summarized as follows:

$$Cl^- + AgNO_3 \rightarrow AgCl \ \textit{(prec.)} + NO_3^-$$

The chloride present in the solution precipitates as it reacts with silver nitrate forming the insoluble salt silver chloride.

15
Microchemical
test for chloride
identification.

Analysis of nitrates (NO_3^-)

A) If the test for nitrites was negative add a small quantity of **zinc powder** to the same solution. In this way, if there are nitrates, they will be reduced to nitrites which, reacting with the Griess-Ilosvay's reagent already in the solution, will give rise to a more or less intense pink colour.

B) If the test for nitrites was positive add a small quantity (1 or 2 crystals) of **sulphamic acid** to the fourth test tube to eliminate the nitrites (make sure you have eliminated all the nitrites by carrying out the test for nitrites on a small portion of the solution).

Add 1 or 2 drops of **CH_3COOH 2M**, 1 or 2 drops of **Griess-Ilosvay's reagent** and a small quantity of **zinc powder**.

The appearance of a more or less intense pink colour indicates the presence of nitrates.

Analysis of carbonates (CO_3^{--})

Add 1 or 2 drops of **HCl** to the test tube with the insoluble residue. Bubbles of gas (CO_2) indicate the presence of carbonates.

The reaction can be summarized as follows:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_{2\,(sol.)} + H_2O + CO_{2\,(gas)}$$

The insoluble calcium carbonate is attacked by the chloride acid forming a soluble salt (calcium chloride) and developing carbon dioxide.

Recording results

As this analysis is only qualitative it is not necessary to weigh a fixed amount of the sample and add a precise volume of water. The results are therefore recorded on a table expressing the different intensities of the reaction observed in the tests through the use of symbols:

–	indicates the absence of an ion
±	indicates the presence of an ion at the limit of perceptibility
+	indicates the presence of an ion
++	indicates the presence of an ion in relative abundance

PRACTICAL 5

SEMI-QUANTITATIVE ANALYSIS

The remaining powdered sample can be used to prepare another solution for the analysis with the strip test⑧.

Equipment

- Strip test
- Kit test
- 100 ml flask
- Deionized water
- Analytical balance

Procedure

A) PROCEDURE FOR POWDERED SAMPLE TAKEN FROM WALLS

Weigh 100 mg of sample and put it into a small 100 ml flask. Bring it up to the indicated volume with deionized water and shake it for 10 minutes.

Briefly immerse the reaction zone of the test strip in the solution and after about one minute⑨ compare the reaction zones with the colour scale or use an ion kit test *(see section 6 c - p. 10)*.

CALCULATION

Since in this case you are dealing with semi-quantitative analysis it is advisable to express results in a precise way. In fact, in this practical the amount of the sample is weighed and the water volume added is precise.

The ion content (A^-%) is expressed in percentage weight of the initial dry mass of the sample:

$$A^- \,\% = \text{recorded } A^- \text{ concentration (mg/l)} \times 0.1$$

where A^- is a generic anion (*sulphate, chloride, etc.*)⑩.

B) PROCEDURE FOR PULP POULTICE SAMPLE

Use a section of pulp poultice of 5 x 10 cm^2 in size (see Sampling Practicals) and immerse it in a beaker with 200 ml of deionized water *(photo 16)*.

Wait until the cellulose fibres have sunk to the bottom and do the measurement on the clear solution.

CALCULATION

The ion content A^- is expressed in milligrams of ions per 100 square centimetres of pulp poultice.

$$A^- \text{ (mg/100cm}^2\text{)} = \text{recorded } A^- \text{ concentration (mg/l)} \times 0.4$$

where A^- is a generic anion *(sulphate, chloride, etc.)* ⑪.

16 Dried pulp poultice

DISCUSSION PROPOSALS

Depending on the data obtained, sum up the results of the analysis carried out, and proceed as follows:

- Draw a map of the distribution of soluble salts at different heights on the walls.
- From the information obtained about the composition of salts found in the wall, try to indicate the provenance of the salts.
- On the basis of the analysis results and broader considerations, come up with a diagnosis.
- Propose how to remedy the actual deterioration of the materials and how to intervene in order to limit the infiltration of salts.

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⑧ *If salt content in the sample is very low, use the more sensitive kit test.*

⑨ *Check the instructions which vary slightly for the different strip tests.*

⑩ *If the dilution volume (Vd) is different, apply the formula:*

$$A^- \,\% = \frac{A^- \text{ (mg/l)} \times Vd \text{ (ml)}}{1000} \times \frac{100}{\text{sample mass (mg)}}$$

⑪ *If the dilution volume (Vd) is different, apply the formula:*

$$A^- \text{(mg/100 cm}^2\text{)} = \frac{A^- \text{ (mg/l)} \times Vd \text{ (ml)}}{1000} \times \frac{100}{\text{sample size (cm}^2\text{)}}$$

8 CASE STUDY

SALT AND MOISTURE SURVEY ON MASONRY AND MURAL PAINTINGS IN THE CHURCH OF S. ELIGIO DEGLI OREFICI – ROME

(The author acknowledges the kind contribution of W. Schmid, ICCROM)

Background

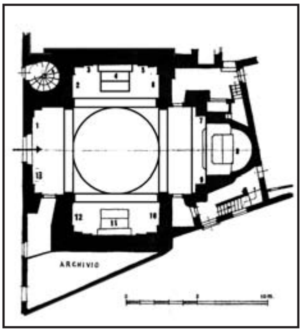
This survey was organized in May 1998, as part of the International ICCROM Course on the Conservation of Mural Paintings and Related Architectural Surfaces (MPC 98). The limited time frame of the course did not allow for the collection of further historical data, the monitoring of the micro-climatic parameters over a longer period and an overall building analysis. Only the integration of these elements would have made it possible to draw effective conclusions.

Description

"S. Eligio degli Orefici" is a small church, in Greek cross plan *(Fig. 1)*, whose design has been attributed to Raphael. It is situated between Via Giulia and the River Tiber in Rome.

The building material is brick covered with plaster. In the apse of the central chapel and in the two lateral altars there are mural paintings (16th century) mainly done in fresco technique: "Madonna con Santi" attributed to Matteo da Lecce, "Adorazione dei Magi" by Francesco Romanelli and "Nativita' di Gesu' Cristo" by Giovanni De Vecchi.

Fig 1



Survey

The church is close to the river and has adjoining civil buildings on both sides that show a uniform level of rising damp up to about 1.5 m. This probably dates back to when the water table in this area of the town was much higher before the construction of the Tiber embankment in 1870.

The plaster indoors shows isolated patches of decay in all the lower parts of the church. A white veil covers the paintings up to 4 metres from ground level.

The case study refers mainly to the fresco "Nativita' di Gesu' Cristo" on the left of the altar whose alteration (a patchy white veil) suggests the presence of crystallized salts. Traces of infiltration are visible on the ceiling to the right of the altar. The interior of the church, although repainted in 1983, appears to have deteriorated in many areas, due to lack of roof maintenance.

Sampling

Three types of samples were taken to provide information about moisture and water-soluble salt content.

1. Six powdered samples of the plaster and/or masonry were collected by drilling gently into the pilaster strip to the left of the painting at heights of 1, 2 and 3 metres and at a depth of between 0-3 cm (samples "a") and 15-18 cm (samples "b").
2. Pulp poultices were applied, on two successive occasions, on the right side of the mural painting at three different heights *(photo 17)* and removed after drying was complete. In this way, soluble salts were extracted from the surface for a total of six samples.
3. One sample was obtained by gently scratching the whitish surface veil on the painting.

17 Church of St. Eligio: Salts analysis on mural painting

colour print on inside back cover

Experimental

A) SALTS ANALYSIS

The **salt content** of the samples described in points 1 and 2 was measured by ionic chromatography according to the Italian standard "UNI Normal U84000050. Beni culturali. Materiali lapidei naturali ed artificiali. Determinazione del contenuto di sali totali".

The **moisture content** of the powdered samples (point 1) was measured by weighing them before and after drying at 60°C in an oven until constant weight was reached. The weight loss corresponds to the moisture content and is expressed as a percentage of the dry mass of the sample.

The surface sample *(point 3)* was analysed by X-ray diffraction to determine its **mineralogical composition**.

B) MICROCLIMATE MONITORING

The **microclimate** (relative humidity and air temperature) was monitored both inside and outside the church by using two thermohygrographs.

The first one was on a shelf *(photo 18)* very close to the fresco, and the second, in the church courtyard but protected from direct sunlight. A data logger ⑫ inside the church was also used to measure air temperature, relative humidity and surface temperature of the walls. The measurements were carried out over a period of two weeks between April and May 1998.

⑫ *A portable instrument for the collection and processing of environmental data*

18 Church of St. Eligio: Climate monitoring

colour print on inside back cover

Results

- ***Salts and moisture analysis***

A) POWDERED SAMPLES

Data relative to the moisture and anion content of the samples taken close to the surface (depth 0-3 cm) and samples taken inside the wall (depth 15-18 cm) are summarized in Fig. 2 and Tables 1, 2, 3.

If we take nitrates, the most abundant salts, as an example, two trends can be observed:

1. In the "a" samples (depth 0-3 cm), the salt concentration is related to the moisture content and diminishes with height; the higher the sample, the lower the concentration.
2. In the "b" samples (15-18 cm inside the wall) where the moisture content is constant, the trend is vice versa; the higher the sample, the higher the concentration, according to their mobility.

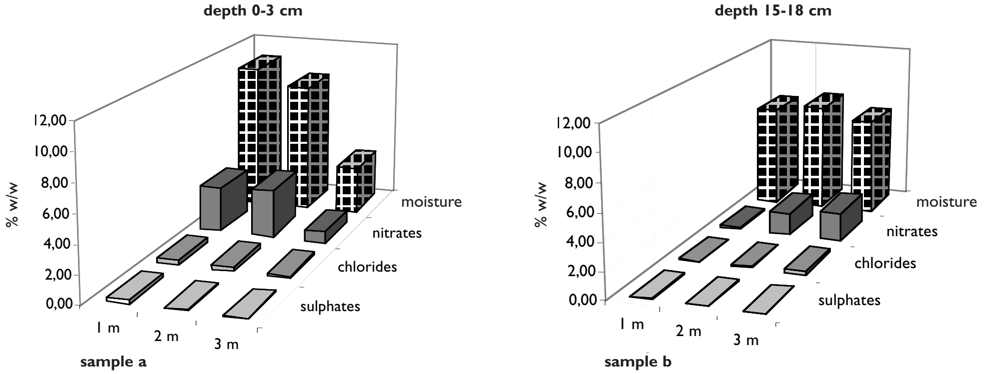


Fig 2. Church of St. Eligio - Rome. Powdered samples taken at different depths

b) Pulp poultice samples

Data for the salts extracted with poultices are summarized in Fig. 3 and Tables 4, 5. These also indicate that nitrates are the most abundant anions (followed by chlorides and, in much lower concentrations, sulphates and phosphates) and that there is a general decrease in concentration between the first and second extraction except for the sample at 3 metres that shows the opposite trend. The corresponding cations are principally calcium and sodium with a much lower quantity of potassium and magnesium.

C) Efflorescence sample

The XRD analysis indicates that it is made up of a significant amount of gypsum ($CaSO_4 \bullet 2H_2O$) together with some traces of calcite ($CaCO_3$).

- ***Microclimate monitoring***

Relative humidity and temperature showed normal daily fluctuations outside the church while inside there was no variation. The inside temperature was constant at 14°C during the first week of rainy weather and increased from 14 to 17°C during the second week of sunny weather. Inside relative humidity increased from 75% to 95% during the first week and was constantly higher than 90% during the second week.

The surface temperature of the wall was generally in equilibrium with the air temperature and also remained stable during sudden indoor climatic fluctuations, for example, when the church was opened for worship on Sundays.

Sample		Height (m)	Depth (cm)	Moisture content (% w/w)
1	a	1	0-3	10.62
	b	1	15-18	7.64
2	a	2	0-3	9.43
	b	2	15-18	8.12
3	a	3	0-3	3.49
	b	3	15-18	7.27

Table 1 - Moisture content of powdered samples

Sample		Height (m)	Depth (cm)	NO_3^{--}	Cl^{--}	SO_4^{--}
1	a	1	0-3	3.30	0.33	0.23
	b	1	15-18	0.12	0.03	0.04
2	a	2	0-3	3.50	0.33	0.07
	b	2	15-18	1.70	0.1	0.05
3	a	3	0-3	0.86	0.12	0.02
	b	3	15-18	2.11	0.23	0.01

Table 2 - Anion content (% w/w) of powdered sample

Sample		Height (m)	Depth (cm)	Na^+	K^+	Mg^{++} b	Ca^{++} 3
1	a	1	0-3	1.45	0.82	0.10	1.46
	b	1	15-18	0.34	0.32	0.04	0.66
2	a	2	0-3	0.49	0.87	0.09	1.81
	b	2	15-18	1.00	0.95	0.09	0.9
3	a	3	0-3	0.10	0.38	0.07	0.98
	b	3	15-18	0.35	0.79	0.14	1.47

Table 3 Cation content (% w/w) of powdered samples

a = plaster
b = masonry

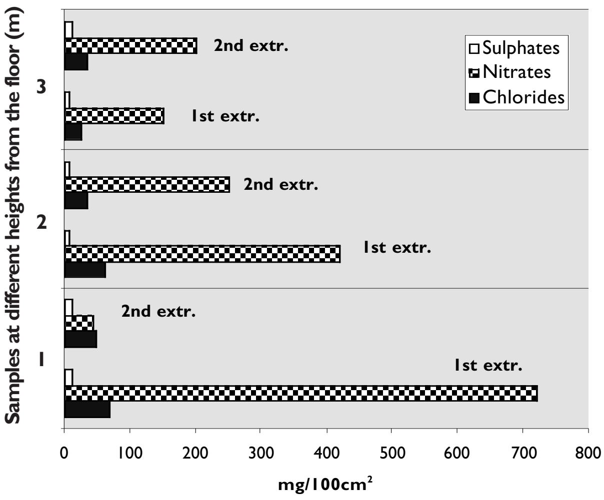


Fig 3. Church of St. Eligio - Rome. Salts extraction by wet pulp poultice application

Sample		Height (m)	Extraction	Cl^-	NO_3^-	SO_4^{--}
1	a	1 m	first	68	719	3
	b	""	second	48	44	2,6
2	a	2 m	first	61	420	2
	b	""	second	34	250	1
3	a	3 m	first	25	150	1
	b	""	second	35	200	3

Table 4 - Anion content (mg/100cm^2) in wet pulp poultice samples (paint layer)

Sample		Height (m)	Extraction	Na^+	NH4$^+$	K^+	Mg^{++}	Ca^{++}
1	a	1	first	59.7	21.7	34.7	27.9	142.4
	b	1	second	59.3	n.d.	32.0	25.4	110.5
2	a	2	first	40.7	7.4	36.9	18.6	132.9
	b	2	second	21.8	4.4	21.5	14.7	89.7
3	a	3	first	17.0	n.d.	14.5	7.5	62.8
	b	3	second	22.9	n.d.	17.6	10.0	74.2

Table 5 - Cation content (mg/100cm^2) in wet pulp poultice samples (paint layer)

Conclusions

1. Soluble salts.

   These are concentrated mainly inside the first 3 cm. Therefore it is advisable not to plan to extract salts from this wall because there is no serious danger of crystallization due to the high levels of indoor relative humidity.

2. Humidity in the wall.

   This is attributed mainly to the high hygroscopicity of the deliquescent salts (mainly nitrates) within the wall. Capillary action, which was considerable in the past, is now present only at a lower level.

3. Condensation on the mural painting.

   If this occurs, it could be very dangerous due to the presence of gypsum on the paint layer (whitish veil) which could become partially dissolved, penetrate the plaster and begin the crystallization cycle. In this case study, there was no risk of condensation as the monitored surface temperature was the same as the air temperature.

Proposals

First of all, constant monitoring throughout the whole year is recommended in order to obtain data relating to all seasonal variations.

As salts are above all present inside walls in the form of highly soluble salts (mainly nitrates due to the fact that the area was inhabited in ancient times), there is no reason to desalinate the walls.

In order to avoid condensation principally on the paint layer, it is necessary to reduce the relative humidity inside the church. Levels of 85-90% are obviously too high but also a drastic reduction is dangerous because it could activate the crystallization of soluble salts inside the wall. The optimum level of relative humidity should be studied further.

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STANDARDS

RILEM tests (Réunion Internationale des Laboratoires d'Essais des Matériaux)

Test n.V.1a: Crystallization test by total immersion (for untreated stone)

Test n.V.1b: Crystallization test by total immersion (for treated stone)

Test n.V.2: Crystallization test by partial immersion

Test n.VI.4: Electrical conductivity

NORMAL documents (Commissione Normativa Manufatti Lapidei)

UNI NORMAL U84000050: Determinazione del contenuto di sali solubili totali

NORMAL 1/88 : Alterazioni macroscopiche dei materiali lapidei: Lessico

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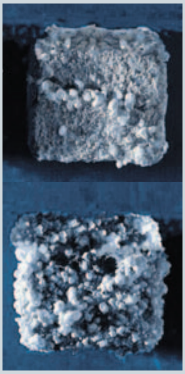
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Binders

BINDERS

ARC
LABORATORY HANDBOOK

VOLUME 4/99

Ernesto Borrelli

The ICCROM ARC Laboratory Handbook is intended to assist professionals working in the field of conservation of architectural heritage and historic structures. It has been prepared mainly for architects and engineers, but may also be relevant for conservator-restorers or archaeologists.
It aims to:

- ***offer an overview of each problem area combined with laboratory practicals and case studies;***
- ***describe some of the most widely used practices and illustrate the various approaches to the analysis of materials and their deterioration;***
- ***facilitate interdisciplinary teamwork among scientists and other professionals involved in the conservation process.***

The Handbook has evolved from lecture and laboratory handouts that have been developed for the ICCROM training programmes. It has been devised within the framework of the current courses, principally the International Refresher Course on Conservation of Architectural Heritage and Historic Structures (ARC).

The general layout of each volume is as follows: introductory information, explanations of scientific terminology, the most common problems met, types of analysis, laboratory tests, case studies and bibliography.

The concept behind the Handbook is modular and it has been purposely structured as a series of independent volumes to allow:

- ***authors*** *to periodically update the texts;*
- ***users*** *to work selectively with the volume relating to the particular problem they are facing*
- ***new volumes*** *to be gradually added in line with developing needs.*

1998 - 99 volumes:
(1) Introduction, (2) Porosity, (3) Salts, ***(4) Binders****, (5) Colour specification and measurement*

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CONSERVATION OF ARCHITECTURAL HERITAGE,
HISTORIC STRUCTURES AND MATERIALS

ARC
Laboratory Handbook

Binders

Ernesto Borrelli

ICCROM

Rome, 1999

CONTENTS

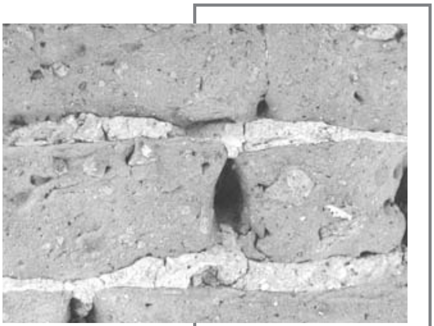
① : Footnotes
🗁 : Bibliographic references

1. INTRODUCTION

For thousands of years the availability of raw materials has been the main factor influencing building traditions. In the past, building tradition was always strictly linked to the geographical and geological nature of the different areas of civilisation.

The use of *clay*, *gypsum* and various types of *lime* as binder material are the traditional expression of certain ancient cultures.

It is well-known that solid mud constructions such as the Egyptian mastaba tombs *(photo 1)* reflect the presence of alluvial material from the Nile, and the use of gypsum as the principal binder again in Egypt is the result of the wide distribution of gypsum rocks in the region. The development of lime technology and the natural presence of materials such as pozzolana in the Mediterranean Basin were the main reasons for the excellence of Roman architecture.


1. Mud blocks

From the fall of the Roman Empire until the 18th century, there were very few innovations in the use of materials and construction techniques. Gypsum, lime mixed with sand, with pozzolana or with brick dust, had been used for centuries, following almost identically the ancient methods handed down in architectural treatises from Vitruvius① to those of the 15th and 16th centuries.

John Smeaton② (1750) was the first to experiment in the production of a new type of lime. The 18th century saw the beginning of a new phase in the development of new binders ranging from hydraulic lime to modern-day cement.

2. BASE TERMS

Binders

Natural (inorganic) and/or artificial materials that, if mixed with water, permit the preparation of a plastic mixture that hardens to form a solid mass.

Materials which bind sand particles or crushed stones together to obtain mortars (i.e. gypsum, lime, cement, etc.)

Mortar

A combination of binder and other components such as sand, crushed stones and water to form a paste.

Mortars are used because of their capacity to fill all the gaps between masonry material and for their quality of adhering strongly and hardening to form a whole with the stone or bricks to which they have been applied③.

Aggregate

Materials added to binders to prepare mortars. They can either be natural such as sand and crushed stones④ or artificial such as crushed bricks or pottery shards. In the majority of cases the aggregate is an inert material (e.g. sand); in other cases, it can be chemically reactive (e.g.

① *The ten books of architecture 10 B.C.*

② *J. Smeaton. A Narrative of the Building and a Description of the Construction of the Edystone Lighthouse, London 1791.*

③ *Further classification and types will be presented in the volume on "Mortars"*

④ *Usually defined as fine aggregate*

crushed bricks or natural materials such as pozzolana⑤). Occasionally fibrous material may be added as reinforcement (i.e. vegetable fibres, straw, etc.).

Admixtures (additives)

Added substances which modify properties such as the workability of the mortar mixture that cannot be obtained using basic binders (i.e. casein, oils, or synthetic resins, water reducers and setting time retarders).

(Both aggregates and additives will be further described in the volume on "Mortars")

3. CLASSIFICATION

The most common binders used in the past and still recommended today for restoration purposes can be classified

either according to their **origin** as *natural* or *artificial* (modified inorganic materials)

or according to their **setting process** as *dehydration/hydration-setting*, *air-setting* or *hydraulic-setting*.

4. MAIN BINDERS

A) CLAY

Natural origin

Clay is a natural binding material and was the first used for building not only in the preparation of hand-made mud bricks but also as a binder of the masonry.

Clay is the finest fraction of the soil. It has a significant content of clay minerals of the aluminosilicate group with a sheeted layer crystal structure and micrometric dimensions⑥.The minerals give plastic properties to the soil when mixed with the right amount of water.

B) GYPSUM 🗀1

Artificial origin

Gypsum is a mineral primarily consisting of hydrated calcium sulphate (or calcium sulphate dihydrate) commonly found in the form of selenite⑦, alabaster⑧ or compact gypsum stones.

$$\boxed{CaSO_4 \cdot 2\ H_2O}$$

gypsum

When heated gypsum loses water at a moderate temperature (130-150 °C) passing from the dihydrate ($CaSO_4 \cdot 2\ H_2O$) to the hemihydrate:

$$\boxed{CaSO_4 \cdot 0.5\ H_2O}$$

the dry powder better known as plaster of Paris.

Setting process

The hardening of gypsum is due to a process of *hydration*. The hemihydrate (plaster of Paris) when mixed with water, sets rapidly to form hardened gypsum:

⑤ Of volcanic origin, used by the Romans and still in use in the South of Italy (pulvis puteolanus). Trass in Germany and gaize in France are the same class of substance.

⑥ This will be further illustrated in the volume on "Earthen Building Materials".

⑦ Macrocrystalline - a variety of gypsum occurring as colourless and transparent crystals or large crystalline masses.

⑧ Microcrystalline – fine-grained massive gypsum, normally white and often translucent.

$$CaSO_4 \cdot 0.5\ H_2O \quad + \quad \text{water} \longrightarrow \underset{\text{hardened gypsum}}{CaSO_4 \cdot 2\ H_2O} \quad + \quad \text{heat}$$

$$\text{plaster of Paris} \quad + \quad \text{water} \xrightarrow[\text{set}]{} \text{hardened gypsum} \quad + \quad \text{heat}$$

It neither shrinks nor requires aggregates. As calcium sulphate is slightly soluble in water (2.5 g/l), gypsum is not used normally on exposed surfaces in damp climates. It is not very hard⑨, and in the presence of water it has a slightly acid reaction so that any iron imbedded in it is easily corroded.

c) LIME 🗁2

Artificial origin

Lime is obtained through the decomposition of natural stone material *(photo 2)*: limestone (calcareous deposits of calcium carbonate $CaCO_3$).

If limestone is heated at ~900 °C, it decomposes into calcium oxide (CaO) which, when slaked with water, forms hydrated lime $Ca(OH)_2$.

2. Limestone stockpile

Lime is a general term which includes the various chemical and physical forms of

Quicklime *Hydrated lime* *Hydraulic lime*

Quicklime (calcium oxide) is obtained by heating limestone, which is composed essentially of calcium carbonate, in a suitable kiln at 850 ~900 °C.

$$\text{Limestone} \xrightarrow{850\ \sim 900\ ^\circ C} \text{Quicklime}^{⑩} \quad + \quad \text{gas } CO_2 \nearrow$$

$$\underset{\text{calcium carbonate}}{CaCO_3} \longrightarrow \underset{\text{calcium oxide}}{CaO} \quad + \quad \underset{\text{carbon dioxide}}{CO_2}$$

~**12** kg of charcoal are necessary to decompose *(burn)* **100** kg of limestone, from which **56** kg of quicklime are obtained.

The use of lime for building has a very ancient history⑪, and so the type of kiln used to produce quicklime has become more and more refined, improving with the building tradition and developing technology.

Today *rotary kilns*, *(photo 3)* which allow continuous production of quicklime are widely used, but more traditional kilns such as *flare kilns* *(photo 4)* and *open* or *batch kilns* *(photo 5)* are still quite common. 🗁3

Some problems still arise when using traditional kilns, as they do not generate the required heat uniformly within the whole mass of limestone

3. Rotary kiln

4. Flare kiln

5. Batch kiln

⑨ Mohs scale 2

⑩ Due to the high reactivity of quicklime this product is an irritant and special safety measures must be adopted when handling it (i.e. protect skin and eyes from accidental contact).

⑪ The earliest use of lime dates back to 1700 B.C. in Mycenaean and Minoan civilizations; in Egypt, it was adopted much later in the Ptolemaic period (300 B.C.)

and part of the material may not burn especially if the stones are too large. On the other hand, overburned limestone produce nodules of sintered quicklime that react very slowly with water. They may hydrate at a later stage causing the mortar to expand and crack. In the past these problems were solved by sieving the slaked lime.
Slaking is the process of adding water to quicklime to obtain lime putty *(photo 6)*:

$$\underset{\text{quicklime}}{CaO} + \underset{\text{excess water}}{H_2O} \longrightarrow \underset{\text{slaked lime}}{Ca(OH)_2} + \text{heat}$$

This reaction also creates heat and must be carried out with care. Like quicklime, slaked lime is also caustic and strict safety precautions must be taken when handling it.

Lime putty is slaked quicklime stored in a pit *(photo 7)* and covered with an excess of water. Longer slaking encourages the formation of a soft, greasy mass and improves the plasticity and workability of the lime paste.

Most of the problems relating to inappropriate lime slaking procedures are linked to insufficient hydration and lumps of unslaked lime which can have a negative effect on the performance of the material when applied.

Slaking problems also arise if the original limestone, used to produce quicklime⑫, contains more than 5% magnesium carbonate ($MgCO_3$) as an impurity⑬ . This leads to the formation, together with the calcium oxide (CaO), of magnesium oxide (MgO) which requires much longer to pass to the hydrated form $Mg(OH)_2$. The latter has a reduced capacity to develop into a greasy mass.

⑫ *It can be high-calcium, magnesium or dolomitic depending on the type of limestone used.*

⑬ *Good lime can be produced from magnesian limestone if the material is well understood and enough time is allowed for slaking.*

⑭ *Portlandite.*


6. Slaking lime

Vitruvius recommends storing the lime in a pit for at least two years and this is still considered the accepted method to follow when working in conservation:

aged lime putty ⟶ *growth of flat lime crystals*⑭

Hydrated lime $Ca(OH)_2$ is a dry powder obtained by treating quicklime (CaO) with enough water to combine chemically to form calcium hydroxide.

$$\underset{\text{quicklime}}{CaO} + \underset{\text{right amount of water}}{H_2O} \longrightarrow \underset{\text{hydrated lime}}{Ca(OH)_2}$$

In this process the dry calcium hydroxide powder is formed.

Limewash is obtained by adding a large amount of water to slaked quicklime or hydrated lime and is used as a paint-like coating.

Setting process

Lime sets by a process called carbonation.
Slaked lime is also called *air-setting* lime due to its hardening process.
The hardening of slaked lime takes place by reaction with carbon dioxide (CO_2) from the air and evaporation of water.

$$\underset{\text{hydrated lime}}{Ca(OH)_2} + \underset{\text{from air}}{CO_2} \longrightarrow \underset{\text{hardening}}{CaCO_3} + H_2O$$

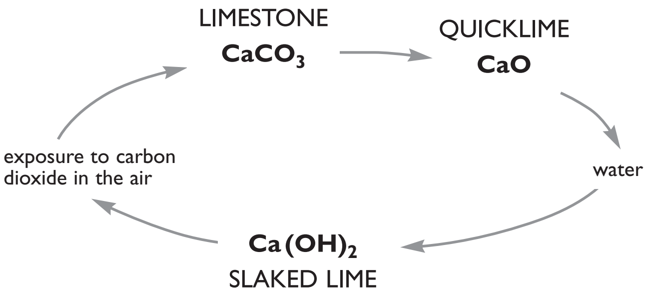
[a]

7. Lime putty pits

The *carbonation process* is rather delicate and varies according to the water evaporation rate and the presence of CO_2. The pore structure as well as the thickness of the mortar play an important role. 🗀4

In a lime mortar, hydrated lime is present during the setting process both in the form of solid particles and as a saturated solution. The carbon dioxide (CO_2) from the air reacts directly and exclusively with the saturated solution of calcium hydroxide $Ca(OH)_2$, working gradually from the exposed surface towards the internal layers and forming a thin crystalline surface layer of calcium carbonate ($CaCO_3$) . The subsequent shrinkage due to the evaporation of the mixing water normally leads to the formation of microfractures providing access routes to the carbon dioxide from the air and consequently restarting the cycle. As long as there is evaporation of water, carbonation takes place⑮ and the lime mortar becomes harder and harder as carbonation progresses gradually towards the inner layers. 🗀5

The lime cycle



Use of pozzolana or other "pozzolanic"materials

When hydrated lime is used in combination with volcanic earth (i.e. pozzolana) a different setting process takes place:

pozzolana⑯ contains a certain amount of silica (SiO_2) and alumina compounds (Al_2O_3) in a reactive state (glass). These react with calcium hydroxide and water to produce new compounds: **calcium silicate hydrate** and **calcium aluminate hydrate** which are responsible for the chemical setting of this type of mortar. 🗀6

$$\boxed{Ca(OH)_2 + H_2O + \text{pozzolana} \longrightarrow CSH + CAH}$$

where:

CSH stands for calcium silicate hydrate
CAH stands for calcium alluminate hydrate⑰

The speed with which this reaction occurs is certainly greater than that of the carbonation process when hydrated lime is mixed with inert sand (calcite, quartz, rock fragments, etc.). That is why a pozzolanic mortar hardens more rapidly. This process of hardening defined as hydraulic in principle⑱ does not require the presence of air and therefore of CO_2.

The capacity of lime-based mortars and pozzolana to harden within a formwork with scarcely any contact with the air even under extremely wet conditions was well known to the Romans. It was in fact the discovery of the special properties of aggregates such as volcanic earth (pozzolana), ground tiles or pumice⑲ that permitted them to construct hydraulic works.

slaked lime + pozzolana + cleaved tuff stone = Roman concrete

Reactive aggregates coming from other geographic areas such as trass (from the Rhine region), volcanic earth (from Santorino in the Aegean), gaize (from France) containing silica (SiO_2) and alumina

⑮ *It must be emphasized that the carbonation reaction frees a water molecule that considerably aids the solubilization of further calcium hydroxide which is gradually exposed to the action of the CO_2.*

⑯ *The name derives from the town of Pozzuoli, near Naples.*

⑰ *CSH and CAH are cement chemistry abbreviations for more complex formulas.*

⑱ *The reaction between lime and alumino silicates does not exclude the simultaneous carbonation process as in the reaction [a] p.6*

⑲ *A light-coloured cellular glassy rock of volcanic origin which is highly porous.*

(Al_2O_3) in a reactive form are classified as hydraulic aggregates or pozzolanic additives. These are still in use today though modern technology also uses silica fumes and blast furnace slag from industrial processes. 🗀7

D) HYDRAULIC LIME

Hydraulic lime is a dry product obtained by burning limestone containing silica and alumina (marl●) at a temperature above 900 °C.

Origin

As a product obtained through the transformation of another, its origin can be classified as *artificial*, but if hydraulic limes are made from limestone containing natural clay minerals (e.g. attapulgite, kaolinite, montmorillonite) in varying quantities, they are commonly known as *natural hydraulic limes*.

It was already known in the 16th century that impure limestone from some quarries would produce quicklime, which when mixed with water, hardened quite rapidly●. It was in 1756, however, that John Smeaton, experimenting with lime and additives obtained a new lime by burning limestone containing about 11% clay impurities.

In 1796, Parker obtained a hydraulic lime, patented as Roman cement, produced by heating limestone with a high clay impurity content at ~1100 °C.

Only later, in 1818, did Vicat● first demonstrate the possibility of producing hydraulic limes **"artificially"** by burning limestone with clay added purposely to improve the hydraulic performance of the final product.

Hydraulic lime production is the result of complex thermal and chemical processes 🗀8 with the direct formation in the kiln of calcium silicates and aluminates as shown below, in simplified steps that take place at around 500 °C, 850 °C and 1000 °C.

Thermal decomposition of the clay material starts when the limestone and clay mixture is heated gradually up to 500 °C:

$$\text{CLAY} \xrightarrow[500\ ^\circ\text{C}]{} \underset{SiO_2}{\text{SILICA}} + \underset{Al_2O_3}{\text{ALUMINA}} + H_2O$$

Limestone starts to decompose at around 850 °C:

$$\text{LIMESTONE} \xrightarrow[850\ ^\circ\text{C}]{} \text{QUICKLIME} + CO_2$$

At 1000°C

$$\text{QUICKLIME} + \text{SILICA} \longrightarrow \textit{di-calcium silicates}$$
$$\text{QUICKLIME} + \text{ALUMINA} \longrightarrow \textit{calcium aluminates}$$

In cement chemistry the above-mentioned compounds are often represented in an abbreviated form:

CS for calcium silicates and **CA** for calcium aluminates.

Limestone Clay impurities	
Kiln 1000 ÷ 1100 °C	
calcium oxide	(CaO)
di-calcium silicate	(C_2S)
calcium aluminate	(CA)

● *A sedimentary rock consisting mainly of a mixture of clay and calcium carbonate in varying proportions.*

● *Palladio mentions this limestone.*

● *J.L.Vicat, Recherches experimentales sur les chaux hydrauliques, les bétons et les mortier ordinaries, 1818.*

Setting process

The setting process, in this case, is due to the hydration of both calcium silicate and calcium aluminate to form a network of fibrous crystals of calcium silicate hydrate **CSH** and calcium aluminate hydrate **CAH** which are mainly responsible for the hardening (without excluding the carbonation of the calcium hydroxide formed by the hydration of the existing CaO).

Based on the work carried out by Vicat in 1837, varying degrees of setting and strength are usually defined as:

Feebly hydraulic lime (produced from limestone containing under 12% clay)

Moderately hydraulic lime (produced from limestone containing 12% to 18% clay)

Eminently hydraulic lime (produced from limestone containing 18% to 25% clay). [9]

E) PORTLAND CEMENT

A hydraulic cement produced by pulverizing a clinker obtained by firing clay and limestone at temperatures above 1400 °C. It consists essentially of hydraulic calcium silicates and aluminates, and contains a small amount of calcium sulphate added to reduce the setting rate. [10]

Portland cement has only been briefly mentioned in this volume as it is considered unsuitable for repairs in historic buildings and monuments. It is almost incompatible with old masonry, its main disadvantages being its high mechanical resistance, its soluble salts content and its low porosity .

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