Characteristics and technologies of archaeological materials - Alterations and decay processes - Environmental impact on archaeologic heritage

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for ICCROM Documentation diagnosis and planning course - Sirmium, Serbia, 28 August - 23 September 2006

Unit 1.3 to 1.5: August 29 to September 2, 2006

1. PREVENTIVE CONSERVATION

1.1. BASIC PRINCIPLES. Soon or later, every material decays. Most of metals oxydize, wood dries and shrinks, stone and ceramic materials loose their binders, and so on.
As we cannot expect that any material will last forever, current conservation tries to elongate the life expectancy of materials that humankind perceives as “cultural heritage”. The perception of cultural heritage will be dealt further on by Varoli Piazza.

Conservation is a “system”. Every conservation activity must consider this as a complex reality. One cannot argue about, say, “conservation of stone” in itself. He has to analyze the material, its working technique AND the environment in which conservation will (or must) happen. Materials are the principal “actors” of the system, environment is the scene, and the combination of the two produces the drama. There is another component in the system, of the most unpredictable: mankind and human activities.

During this session these components will be analyzed in order to establish a grid to understand how the sub-components interact and play a role in the weathering processes.

1.2. SYNERGIES AND CONFLICTS. As we will see later on in depth, the most dangerous moment for buried materials is when they are excavated. In the very moment in which they are brought in contact with athmosphere, many crucial events start, and they can quickly lead to destruction of the find. It is then important to make a difference between conservation DURING excavation, and AFTER excavation.
Organic materials are highly fragile, and they can be destroyed in minutes (or hours) after disinterred, but every material suffers at this stage. The environmental conditions of exhumation are of great importance even for long-term conservation, as the physical (and chemical) processes that start at this moment affect life of every material. Even materials that survive exhumation are prone to mid- (or long-) term decay.

Conservative activities may interfere with the excavation schedule. For example: if an amphora is found and partially disinterred, a conflict may arise.
The conservator will try to avoid major damage by sheltering it, while the archaeologist will tend to stop excavation for documentation needs (drawn recording, photographs, and so on). The amphora is half buried in wet (or, anyway, stable) soil, and half in open air, with harsh and sudden changes in temperature, humidity and so on (this will be seen in detail later, see § 7).
As excavation activity cannot be stopped at any moment for every find, it is important to establish a mutual recognition of competences between archaeologists and conservators. The working team should tend to a synergic effort to proceed with excavation and, at the same time, to secure the best conservation of finds, in the given budget and timetable. Dealing with budgets (money), conflicts are likely. Archaeologists want to use a maximum of money to excavate, while conservators fight to do their job and retreive finds in a conservative perspective. In general, if field conservation is put into practice, the initial cost for it is widely retrieved with lower costs for “*restoration*” of finds, and lower information loss. A decayed material holds less information than a good conserved one.
1.3. PLANNING PREVENTIVE CONSERVATION. Conservators can often ascertain that archaeologists fear their presence, as they immagine that conservation will slow consistently excavations. Field conservation MUST be quick for at least two reasons:

❷ it must have a MINIMAL interference with archaeologic activity
❷ it has to face quick phenomena (drying, shrinking, salt efflorescences, etc)

Once again, mutual recognition is crucial. Conservators have the responsibility to make conservation feasible, effective and quick. They have also the responsibility to make archaeologists aware that well preserved finds enhance the quality of their work at a bearable cost of time and money.

Planning preventive conservation means that some basic materials and tools must be available on the excavation, as well as trained people to use them. This does not mean that a conservator/restorer must be **permanently** present. Archaeologists and archaeological diggers can (and should be) trained to basic field conservation, with a global improvement of the excavation activity.

As we admit that conservation actions cannot be done at any step of the dig, it is useful to identify priorities as on the following grid:

RISK

HIGH

WATER-LOGGED WOOD
LEATHER
BONE, IVORY
GLASS
METALS

WOOD
PAINTED PLASTERS
PLASTERS
BRICKS AND TERRACOTTA

POROUS STONES
NON POROUS STONES

GOLD

LOW

1.4. COMPATIBILTY. As archaeological activity proceeds, more and more materials emerge … and problems with them. A constant evaluation of risks should be made by a joint team of archaeologists and conservators. For example: if a soil is discovered and workers have no other choice to walk upon it, a SIMPLE conservation action (a shelter of proper material and resistance) must be put in place to protect (and not simply to hyde) the soil. Another example: a wall needs a support (prop) not to crumble. Will this interfere with excavation activities? If YES: could the excavation activity be delayed for 1 or 2 days to provide structural consolidation? If NO: could the wall be lost after documentation? If NO: props and/or consolidation are unavoidable and excavation plans must be varied.
In this case, note that the responsibility of the choice is to the archaelogist. If the archaeologist states that the wall cannot be lost, the conservator CAN act and find the most effective way to attain this object.

1.5. IDENTIFICATION OF POTENTIAL DANGERS. An excavation rarely begins after having installed preventive conservation measures. Every site should be studied before excavation in order to identify potential dangers. Studying of the topography of the site gives elements to foresee what can endanger the archaeological activity and finds. The following elements must be considered:

- A) SLOPE
- **Excavation is higher than the surrounding soil** ------> assure proper drainages to send rainwater downhill
- **Excavation is lower than the surroundng soil** ------> install interception drainages upstream to prevent excavation flooding

- B) ORIENTATION. Check the position of excavation to install temporary shelters to avoid direct (or excessive) sunlight. This is useful to limit thermal stresses to materials (and diggers!).

- C) WIND. If it is known from where prevailing winds come, the installation of windbreaks may avoid dust build-up and quick drying.

- D) RAIN. Try to get informations about the frequency and intensity of rainfalls in the region. If rain is frequent in the region, provide quick shelters to be used in case of.

- These are some of the main components of the “environmental system”. If they are considered BEFORE excavations start, a lot of what I call “the *predictable* unpredictable events” can be avoided.

For instance, an excavation in desertic region will hardly have to face rainfall, but winds may fill the dig with sand in few hours, and light will be so hard that thermal variations quickly alter or damage the hardest material. On the opposite, an excavation in Central Europe in autumn has an high probability of rain, dew in the morning, subdued light and gentle temperature changes.

1.6. CLIMATIC MISHAPS EXPECTANCY. Common attitude consider strong winds, rainstorms, hail (and so on) to be “*exceptional events*”. Once more, weather statistics give important informations about their frequency. In continental climate, it rains, statistically, one day every four. For anyone who witnessed what is a flooded excavation, it is clear that a storm can cause, in a quarter of an hour, a severe halt to archaeologic activity, a deep hole in the budget and a considerable (and irreversible) loss of information.

After a flooding, you have to pump out water. You have to wait that mud dries. The excavation is not anymore the one you have drawn and photographed. Stratigraphies are altered. Landslips have occurred. Everything has to be cleaned again. Porous materials have been soaked with polluted water. A simple calculation of the cost of flooding will convince any archaeologist that shelters save time, money and scientific accuracy.

2. MATERIALS AND BUILDING TECHNIQUES

2.1. GENERAL FEATURES. Materials that form archaeological finds are classed, as most of materials present on Earth, in two main chemical classes: **organics** and **inorganics**.

Inorganic materials have mineral origins (e.g.: stone, ceramics, metals), and have the following general features:

❷ if heated, they generally do not burn
❷ in general, they are little or not sensitive to light
❷ microbiology do not develop easily on them. When it happens, life does not develop at the material's expense
❷ some stones and some ceramics are porous. During the burial they can absorb capillary water and salts dissolved in it. When unburied, the salts present in the capillary system can loose moisture and crystallize, thus weakening the mechanical resistance of porous materials.

Organic materials have vegetal or animal origins (e.g.: wood, fabrics, ivory, leather, wool):

❷ if heated, they generally burn
❷ they are sensitive to light, that modifies them
❷ they can be colonized by live organisms, that develop at the material's expense (organisms use the material as '*food*'). This leads to the weakening of the material and modifies its aspect and structure.
❷ they are hygroscopic, they quickly absorb and release moisture, changing their dimensions
❷ they tend to keep their dampness (Relative Humidity, see § 4) in equilibrium with the environment. If they are dryer than air, they absorb water, increasing in weight and dimensions. If they are more damp than ambient air, they release water loosing weight and volume.

2.2. BUILT STRUCTURES. Having in mind that conservation means analyze a "system", we look at built structures as to "systems" composed by different elements. The combination of these elements gives the material its physical features and determines its weathering behaviour.

Practically, every built structure is a "composite" of different materials.
Mudbrick (or '*adobe*') is one of the simplest and oldest building material, is made of clay, straw or manure. Straw helps to limit shrinkage and cracking during dessication and provides a sort of fibrous "*skeleton*" to the structure. Being organic, straw is prone to decomposition. After decomposition of straw, mudbrick is more porous and weaker.

Modern building materials, like concrete, are made of cement and iron.
Walls of cooked bricks are a system composed by the bricks and the mortar that holds them together. The mortar itself is a system composed by a binder and a filler. The filler ("sand") is the result of erosion of mountains or shorelines, and it is generally composed by several kinds of stone, more or less resistant, more or less porous, and so on.
The same can be said for stone walls, where stones of different origins are held together by a mortar.

2.3. FINISHING LAYERS. Before the use of modern building materials (concrete, concrete/glass) the core of every building was generally covered by finishing layers, with two main roles:

❷ to even the surface
❷ to protect the masonry

Finishing layers were meant to be renewed when altered. Nowadays we consider those layers of the uppermost importance, as they represent the '*original*' finishing and are often decorated. Finishing layers are enlightening about the aesthetic sense of ancients and their decorative techniques, so we want to conserve them indefinitely.

Renderings are layers several centimeters thick (up to 10) with little or no aesthetic role. They are used to egalize an uneven masonry and to receive further, and more sophisticated, layers. They are generally composed of coarse sand and lime (or other binder).

Plasters are layers some centimeters thick(up to 3) and may be finished with decorative patterns, as *stuccoes* or *frescoes*. They are made with fine sand and a binder, but may contain very fine fillers, as crushed marble or stone, to obtain a smooth surface and a specific colour.

Coatings are very thin layers (rarely more than 1 mm) which determine the final appearance of the plaster. Coatings may contain very fine powders (pigments) with a binder (lime, animal or vegetal glue, etc), and are often polished to reach a glossy aspect.

The thickness of finishing layers determines its chance of survival and the difficulties to conserve it.
In an excavation, is more likely to find a rendering than a plaster, and a plaster rather than a coating. If paintlayers still exist, they are the most fragile component. Every exchange with atmosphere will happen on this layer, that will decay first. Alteration always starts from the surface, where all the physical phenomena act: light incidence, mechanical stresses, changes in temperature and humidity, evaporation, salt crystallisation etc.

2.4. FLOORS. It is impossible to summarize all the variants of floors that can be found. In general, floors have been consumed by passage, and well conserved ones are the ones that have been suddenly buried by a rapid event (collapse of the roof, volcanic ashes, mud, etc.). It is also evident that well manufactured floors have far more chances to survive than poor ones. In humble buildings, floors were often made of a thin layer of earth compacted with little lime, so their life expectancy is low. By contrast, floors of rich buildings (public buildings, churches, *villae*) were made with great care and were considerably thick. For example, roman imperial soils were manufactured following precise rules and are composed of several layers:

❷1) *Rudus*: pebbles aligned to form a nearly-flat surface, thichness up to 20 cm
❷2) *Statumen*: a layer of mortar, often hydraulic, thick up to 10 cm, to hold the *rudus'* pebbles and flatten the surface
❷3) *Nucleus*: a further hydraulic layer, thick up to 5 cm, perfectly flat
❷4) *Subtilius*: or final layer, made of 1 to 3 cm thick mortar, with colored pebbles and/or *tesserae*, to achieve the decorative project; polished and smoothed.

The resulting final thickness of such a floor can reach or exceed 40 cm. This building technique is noteworthy because the arrangement of pebbles of the *rudus*, leaving wide hollows between them, stops capillary rise. The global thickness gives good thermal inertia and high resistance. This technique, even if modified, evolved till the 18th century, notably in the Venitian *terrazzo*.

Opus sectile and ***opus signinum*** are variants of the above described technique, having the final layer made of hydraulic mortar, decorated with pebbles of different colour and tiles of polychrome marbles, that were sunk on fresh mortar.
When mortar started curing, it was beaten with huge wooden or iron trunks, to help residual water to surface and to close cracks. When dry, the surface was treated with a tool named '*bear*' (italian word: **orso**), consisting in a great slab of soft limestone. Handed by two men, the '*bear*' was pushed and pulled on the surface covered with fine sand. The resulting abrasion made visible the decorative pattern, and sealed the microporosity. (In italian texts, this operation is known as '***orsatura***')

2.5. DIFFERENT MATERIAL, DIFFERENT BEHAVIOUR. Once again, all the described layers are "systems". They are more or less thick or coarse, but they are all composed by different materials that behave differently.

A wall composed of siliceous stone, limestone, and mortar, has an extremely varied behaviour. siliceous stone has in general a low porosity; limestone medium or high; mortar generally high. In case of rain or condensation this kind of wall is, initially, evenly wet. Porous materials absorb water quickly, while siliceous stone won't. So, siliceous stone dries before the other materials. Porous materials have absorbed water and also pollutants that water dissolves: soluble salts, organic products of vegetal and animal decomposition, etc. All this stuff fills the capillary system of the stones, carried in by water. When water evaporates, pollutants stay in the material, altering its equilibrium. Soluble salts, when drying, form crystals that exert a considerable force on the pores' walls. Salt crystallisation is one of the most frequent causes of decay of porous materials (see § 6.3.1.).

A floor in *opus signinum* is composed of lime, crushed brick or *pozzolana*, sand, pebbles of different origins. The *tesserae* of a mosaic may be composed up to 30-40 different types of stone. Porosity, expansion coefficient, hardness of these materials are very different, so their behaviour is. If those materials have been soaked an dried (and surely they have), water movements, and the related pollutants, have followed preferential ways. That is to say that porous materials have endured more water movements, and they are probably more weathered than non porous, or less porous, ones. If the floor has been exposed to fire, the more rigid materials may have cracked, while the softer ones have better chances to survive uncracked. If the floor has suffered a collapse of the surrounding building, the hardest pebbles may have provoked cracks around them, acting as chisels.
Further on this course you will have thorough lessons about OOA (Object Oriented Analiys), so try to look at every material NOT in itself (floor, wall), but as a complex system. At a close look, you will notice that often decay occurs at the interface between two different materials. Look at it, describe what you see, record it. This is the way to understand **where, how and how much** decay has worked and is working.

3. MORTARS.

3.1 WHAT IS A 'MORTAR'? From a dictionary: "*A mortar is a mixture of a setting substance (lime, gypsum or cement) with water and sand, wich hardens in more or less time. It is used to join stones or bricks to form walls and renderings. It can harden in contact with air (**aerial** mortars) or with water (**hydraulic** mortars)*".

This definition gives us enough topics to develop, as it refers to "*setting substance*", from now on named '**binder**', and to "*sand*", from now on named '**filler**'.

These are the components to know in order to understand what a mortar is and how it works. It is nearly impossible to list all the different types of archaeologic mortars, as their range is nearly endless. What is important to know, is the mechanism of mortar' setting, the importance of fillers, and how they decay.

The definition distingushes between '***aerial'*** and ***'hydraulic***' mortars, indicating a different '*catalyst*' to their setting. Aerial binder sets in contact with 'air'. One could think that setting is due to simple drying. This is true only for clay. In facts, the most important of aerial binders, lime, sets due to a chemical reaction with some of the components present in the air.

On the other side, inside hydraulic binders, water activates chemical processes that would not be possible in the dry state.

3.2. AERIAL BINDERS

3.2.1. **Clay**. Clays are minerals widely spread on the planet, coming from the alteration of stones. They are generally found as natural deposits formed by the wind (scientific name: ***Loess***) or by the rivers. The main components of clay are Silica Oxyde (SiO_2) and Aluminium Oxyde (Al_2O_3). These elements are thin crystals, whose dimension is about 2-4 microns. Every crystal is composed by several hundreds of "sheets", each composed of two or three alternated layers of silica and aluminium oxyde. The clay's "sheets" are weakly held together by electric forces. Water, being a ***dipole*** (it contains both negative and positive charges), can easily win the attractive force between the "sheets", penetrating them, and causing a general swelling and softening of the clay mass. In excess water, clay looses its cohesion and dissolves completely.

Wet clay has a plastic behaviour that has always been used to shape objects (pottery, bricks). As wet clay is higly adhesive, it has been used to cover walls, too.

When clay dries, the original electrical attraction forces re-estabish, conserving the shape of the mass, that is prone to contraction and loss of volume. As a building material, clay is always mixed with other minerals (sand) or with organic materials (straw, vegetal or animal fibers, manure, etc.), to contrast or reduce shrinkage and to improve its mechanical strenght.

Clay is easily eroded by water flow, and 'washing' is the main cause of decay of clay-built structures.

On the contrary, capillary rise is inhibited by the swelling of clay, when wet. The capillary pores are closed by the swelling, and becuse this behavior some clays are used to stop capillary rise.

3.2.2. **Aerial (or Slaked) Lime.** Aerial lime is obtained by the firing of limestone. Limestones are a very various family of stone, containing mainly Calcium Carbonate ($CaCO_3$) and impurities (Silica, Aluminium, Iron oxydes).

Ancient romans, that perfectly knew the lime technology, suggested the use of river sandstone to achieve the best results. The firing (or '*cooking*') of limestone is summarized by this reaction:

$$CaCO_3 + 42{,}5\ \text{cal} = CaO + CO_2$$

CaO is Anhydrous Calcium Oxyde, or **quicklime**, CO_2 is carbon dioxyde.

The firing of limestone produces a loss of 44% in weight and 20% in volume of the original Calcium Carbonate, due to the loss of Carbon dioxyde.

Quicklime is a white, light powder that reacts violently with water, wich is immediately absorbed, causing the swelling of the mass and producing heat, up to 300°C.

If excess water is added, the mass starts cooling, becoming a plastic and soft paste.

This reaction, called '*sleaking of lime*' is chemically defined as follows:

$$CaO + H_2O = Ca\,(OH)_2 + 15{,}6\ \text{cal}$$

where $Ca\,(OH)_2$ is Calcium Hydroxyde.
Traditionally, quicklime is soaked in excess water, producing a paste sold as '*slaked lime*'.
In modern factories, each part of lime is mixed precisely with 3,22 parts of water, producing a dry powder sold as '*hydrated lime*'.

The setting of lime is based on its reaction with Carbon dioxyde, as in the reaction:

$$Ca\,(OH)_2 + CO_2 = Ca\,CO_3 + H_2O$$

where Calcium Hydroxyde and Carbon Dioxyde form Calcium Carbonate and Water. The initial chemical form of limestone ($Ca\,CO_3$) is retrieved. This reaction is called '*carbonatisation*' and is the chemical mechanism of hardening of lime-based mortars.

3.3. HYDRAULIC BINDERS

3.3.1. **Gypsum**. Under this definition are classed several materials formed by Calcium Sulphate ($CaSO_4$) + a variable quantity of molecular water. These are:

- ❷ Dihydrated Calcium Sulphate: $Ca\,SO_4 \cdot 2H_2O$. This is ***Selenite***, very common in nature as a crystalline stone, with grey and trasparent crystals. Heating Selenite, different materials can be obtained, following the heating temperature.

- ❷ Anhydrous Calcium Sulphate: $CaSO_4$. Called ***Anhydrite II***, it is a white, compact, crystalline stone. When exposed to moisture, it is prone to hydratation, and transforms slowly in Selenite, increasing volume. It has been widely used in the past for artistic sculptures. It is easily worked and looks like marble or alabaster. For that matter it is often (improperly) called '*gypsum alabaster*'.

If heated up to 128°C, Selenite looses 1,5 molecules of water, becoming Hemi-hydrated Calcium Sulphate ($CaSO_4 \cdot 1/2\ H_2O$). This is quick-setting **gypsum**, used by dentists, or to make casts; it sets in few minutes (1 to 4), producing heat.

If heating of Selenite continues up to 163°C for enough time, the compound looses the rest of its molecular water, becoming Anhydrous Calcium Sulphate:$CaSO_4$. This is the traditional '*mason's gypsum*' with a much slower setting time (15-20').

Other kinds of gypsum may be obtained heating up to 1300°C, but they are of no interest for historical building.
As the stable form of gypsum is the Dihydrated, hemi-hydrated and anhydrous forms tend to absorb water to reach the Dihydrated Calcium Sulphate form.
If gypsum, in its less stable forms, is mixed with water, a plastic mass is obtained. This mass will initially heat an then harden, due to the formation of crystals.
Gypsum is water soluble, so it does not survive in damp environment or in contact with water. Widely used in the past, gypsum survives only in dry climates.

3.3.2. **Hydraulic lime** is obtained firing limestone containing silica and aluminium oxydes rich marls. The '*cooking*' temperature must be around 1000-1200 °C. The resulting powder is greyish or brownish, depending to nature and amount of oxydes. The hydraulic behaviour is proportional to the content of clay that, fired, produce highly reactive Aluminium and Silica anhydrous oxydes.

French chemist **Vicat** enunciated the '*Hydraulic Theory*' in 1818. He identifies the Hydraulic Index (***I***) with the following ratio:

$$I = \frac{\text{Acid Oxydes (} SiO_2, Al_20_3, Fe_2O_3)}{\text{Basic Oxydes (}CaO, MgO, Na_2O, K_2O)}$$

Following the value of ***I***, Vicat classed limes as follows:

Behaviour	***I***	complete hardening
Weakly Hydraulic	0,1 to 0,16	more than 30 days
Namely Hydrauic	0,31 to 0,42	2 weeks
Eminently Hydraulic	0,42 to 0,50	4 days

These criteria are still followed nowadays. When ***I*** exceeds 0,50 the compound cannot be considered anymore a 'lime': it is a Cement.

The anhydrous oxydes react with water, quickly forming (**hours**) hydraulic links between them and with CaO. CaO then hydrates (becoming Calcium Hydroxyde in some **days**) and reacts with Carbon Dioxyde of the atmosphere, forming Calcium Carbonate. The latter process is slower (**weeks**).

3.4. PORTLAND CEMENT.

3.4.1. **General features**. **Portland Cement** (P.C.) is a binder known woldwide for its mechanical characteristics. Its chemical nature is much less known, and constantly evolving. In a further section, the evolution of P.C. will be thoroughly exposed. It was first produced around 1860 in the town of Portland, U.S.A. Is use has become common since 1900.

C.P. is obtained by firing limestone rich in silicated and aluminated inclusions. The'*Cooking*' of this kind of stone above 1000°C, produces a greyish powder, named ***clinker***.

Clinker contains CaO, SiO_2, Al_20_3, Fe_2O_3, and is highly reactive with water.

We have already met all these compounds in hydraulic lime. The setting reaction is the same, but much quicker, due to the higher content of hydraulic components (Hydraulic index I = 0,66). Modern P.C. is not composed of clinker alone (see § 3.4.2.).

3.4.2. **Chemistry and evolution of Portland Cement**. Clinker was the base of early Portland Cements. As the hydraulic part of clinker could reach 40% in weight, early P.C. was a quick setting binder, with the tendency to shrink while setting. The basic composition of P.C. remained unaltered until about 1950.

As architects and engineers became more acquainted with P.C., their projects of concrete structures went more and more complex, and some features of P.C. got unsatisfying:

❷ too quick setting
❷ excessive shrinkage while setting
❷ too dark colour

The modification of P.C. started.

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In the seventies of 20th century, some European High Technical Schools were charged to enquire about the quick decay of modern concrete. Post-war concrete showed an embarassing sensitivity to freeze, presence of lots of soluble salts, rapid decay.

A) The researchers quickly realized that soluble salts were the main cause of decay. The mechanism of hydratation and crystallisation of salts inside the capillary system improved porosity and weakened the structure of P.C.
This statement did not explain why early P.C. didn’t have this behaviour.

B) Density, specific weight, compression strength (*quantitatitive* analyses) were then inquired. Analyses showed that mechanic features od P.C. were initially uneven, due to the differences of the minerals cooked. At the middle of the century, several laws stated the minimal requirements for the P.C., and features became more constant.
This was not enough to explain why ‘modern’ concrete behave differently than old ones.

C) Further *qualitative* analyses eventually gave satisfactory explications. The original formula of P.C. (made of pure clinker) had been progressively altered in the second half of 20th century. In order to modify some features and to easen its use, many additives were joined to clinker:

- ❷ Potassium Bichromate: to improve alcaline content, and help carbonatisation
- ❷ Calcium Sulphate (gypsum): to contrast shrinkage
- ❷ Sodium or Potassium Gluconate: as a fluidifier and to slow setting
- ❷ Polyvinyl Acetate: to improve ‘grip’
- ❷ Polyvinyl Alchools: to lower freezing point

The study of about 60 Portland Cements, in regular sale in Europe, showed that additives may reach 35-38% in weight.

All the additives have undesired effects on concrete:

- ❷ gypsum is water soluble. When wet, it causes sulphatation of iron and lime
- ❷ Sodium and Potassium form easily soluble salts
- ❷ Acetates (and PV) decompose and form acetic (vinylic) acid, corroding iron, lowering pH, and forming further soluble salts
- ❷ gluconates lower the compression strenght of concrete

D) Further enquiries were aimed to determine the filler/binder ratios. Some military buildings, where economy was surely **not** a priority, were analysed and showed surprisingly low filler/binder ratios:

- ❷ binder is in average present at 7% (70 kg/1000 kg)
- ❷ concrete shows evident macro porosity, but nearly no micro porosity
- ❷ iron structure is, in average, 12-15 deep from the surface
- ❷ the binder is pure clinker

On the other side, modern concrete has:

❷ binder is often in excess: in average 17,5% (175kg/1000kg)
❷ low macro porosity (‘*compact*’ aspect) but high micro porosity
❷ iron structure is, in average, 3-5 cm from the surface
❷ the binder is *clinker* (65-70%) and additives (30-35%)

Excess of binder, poor design and manufacture, too much additives, cause modern concrete to decay quickly.

3.4.3. **Why to avoid the use of Portland Cement in conservation**. P.C. based mortars behave in a different way, compared to ‘historical’ porous materials, as bricks, limestone, lime-based mortars.

❷ A) P.C. mortars are hard and rigid, and cannot follow the micrometric movemements of softer materials due to thermal dilatation and settling. As a result, the ‘hard system’ will soon or later separate from the ‘soft system’.

❷ B) Concrete can absorb liquid water, but is poorly permeable to water vapour. In other words, concrete is easily wetted, but it hardly releases moisture. When concrete is in contact with porous materials, the water absorbed by concrete migrates to the dryer zone (porous materials, that can absorb and release moisture easily), carrying soluble salts originated by additives. Water evaporation from porous materials causes soluble salts crystallization on/or inside the pores. This mechanism explains the disastrous effects of concrete when in contact with soft and porous stones.

❷ C) As concrete is harder and more resistant than lime-based mortars, in case of flowing water, the combination of A) and B) produces further decay.
❷

When restorers argue with archaeologists and architects against the use of Portland Cement, one of the most common arguments opposed to restorers is: “*With lime and pozzolanic fillers you achieve chemical features similar to P.C. So, why to make things more complicated and do not use P.C.?*”

The reasons against the use of P.C. are simple, physical, and definitive.

❷ a) the compression resistance of a good lime and pozzolana-based mortar can reach 40 kg/cm2. This is largely enough to hold together bricks and stones. The weaker concrete-based mortar has a compression resistance of 300 kg/cm^2, wich is higher than the brick’s one. The excessive strenght of the joint is a technical nonsense.

❷ b) lime and pozzolana mortars have an high vapour permeability. They can easily expell moisture from a wall. P.C. mortars keep moisture inside them. If they are close to a dryer, more porous, material, the dampness migrates, with pollutants, to the neighbouring materials.

❷ c) lime and pozzolana mortars are not as alkaline as P.C. ones. This means more difficult formation of soluble salts.

❷ d) Modern P.C., as already stated, is full of soluble salts or additives that produce efflorescences. If a mortar is made with lime, washed sand and pozzolana, the soluble salt content is near to zero.

There are some white cements, obtained by the cooking of limestone and Caolin (white clay) that are practically salt-free. They can be added, at very **low doses**, to lime, with good results (see § 11.3).

3.5. LIME: HISTORY AND CHEMISTRY

Ancient Romans defined severe rules to obtain lime for building purposes. Only the purest limestone had to be fired to get quicklime. Quicklime had to be slaked in big pools, where it had to mature for a long period (up to several years). In this way, even if a clay-rich limestone was cooked, the resulting quicklime, once slaked, would have set in water, and could not be used anymore. The control of lime-making was entrusted, at least for public use, to officials named by the State. The quality of roman mortars is astonishingly high, and its study leads to understand that 'making a mortar' was a science. The choice of fillers, binder/filler ratios, the thickness of coats, was scientifically precise, and nothing was left to fate.

As the Empire weakened, also the quality of lime (and mortars) declined. Supply of proper materials and quality control disappeared. Mortars of the 6th to 10th centuries have hardly survived and, if so, they are of poor quality and technology.

In the 13th century lime-making regained an acceptable quality.

During 14th and 15th centuries, lime-making is again a precise technology. Very often only white marble is fired to obtain "t*he purest and strongest lime*". Many roman monuments have contributed with their marble slabs to build Renaissance towns.

In convents and monasteries, the study of ancient texts (Vitruvius, Plinius), lead architects and scientists to understand how romans achieved such outstanding results. How to get a good lime, how to work it, is by then not anymore an "*ancient's secret*", but a common knowledge to masons.

3.6. POZZOLANIC FILLERS.

Since 3rd century, Romans tuned a technology to get water-resistant mortars. They needed mortars that would set in water, and resist to the action of water, wich is unlikely with slaked lime. Roman aqueducts, harbours, sewers, were all built with slaked lime, added with fillers that transform its behaviour from '*aerial*' to '*hydraulic*'.

As we have seen, the roman technology for making lime forbidded the discovery of 'hydraulic lime'. The 'hydraulic'component (oxydes of Al, Si, and Fe), would have set after slaking, during the ageing process.

Romans found that some volcanic minerals would react with slaked lime, and turn it to a water-resistant binder. The main mineral used was the sand found in Pozzuoli (Naples), near the Vesuvius volcano, and named '***pozzolana***'.

In the vast Empire, pozzolana was not always available, so roman architects found similar materials in Greece *(earth of Santorini*, volcanic sand), in southern Germany and Dacia (*trass*, a volcanic tuff), in Tunisia and Morocco (*diatomite*, sediments from shells). These are **natural** pozzolanic materials. If none of these materials was available, romans made use of artificial pozzolanic materials: crushed brick or tiles.

Chemically speaking, all the pozzolanic materials are formed by Silica, Aluminium and Iron Anhydrous Oxydes, that have endured very high temperatures.

During 16th century, some architects observed that firing clay-rich limestone, they obtained a brownish powder that cannot be aged in water. If this powder is slaked and already employed to make mortars, its features were 'superior'. This was the rediscovery of 'hydraulic lime'.

Only in the 19th century some chemists demonstrated that firing clay-rich limestones leads to a compound where Calcium Oxyde (quicklime) reacts with Silica, Aluminium and Iron oxydes. In this way the empirical statements of 16th century found a ‘scientific’ explanation, and hydraulic lime became available as an industrial product.

3.7. HOW TO PREPARE A GOOD MORTAR: FILLERS, WATER. Every mortar is composed by a binder, a filler and a certain amount of water.
Analyses of ancient mortars show that they were made following precise rules and proportions.

The physical features of fillers are important to determine the final strenght of a mortar. In general, **river sand** is to prefere because:

- ❷ it contains nearly no soluble salts
- ❷ its grains are coarse
- ❷ it originates from different kinds of stone, and has a varied granulometry

These features give the mortar a good behaviour, as the coarse surface of grains helps a strong link between filler and binder. The mineralogic variety limits the presence of porous sands. The varied granulometry minimizes shrinking during setting. The absence of soluble salts, obviously, avoids efflorescence.

On the opposite, **sea sands** have practically contrary features:

- ❷ high content of soluble salt (NaCl)
- ❷ the grain’s surface is smooth, due to the strong action of waves and winds
- ❷ granulometry is even, due to the restless action of waves
- ❷ mineralogic origins are generally uniform, linked to the erosion of coasts

The smooth surface of grains does not allow a strong link with binder. Uniform granulometry promotes cracking while setting. Soluble salts spoil the resistance of the mortar. In ancient buildings, mortars made with sea sand are very rare. Probably, if employed, they have decayed quickly. They are fragile, scarcely cohesive, and have an high salt content.
Sands containing porous limestones give low strenght, hygoscopic mortars.
Siliceous sands give hard and stiff mortars, scarcely hygroscopic.

****

To prepare a good mortar, siliceous sands with varied granulometry are preferred. It is important that sand grains are of various sizes, because this allows a better mix between sand and filler. The maximum diameter of grains can be settled with a sieve. In general, the maximum diameter of sand grains must be choosed according to the thickness required for the mortar’s coat. In ancient mortars the maximum diameter is very often equal to one third of the coat thickness. For exemple: max granulometry 4 mm = thickness of coat 12 mm. Sand has to be clean, exempt from clay.

Water has to be clean and fresh. Excess water spoils the quality of a mortar. It has to be added gently and progressively to obtain a plastic mass easy to work, but still keeping its form. ‘Liquid’ mortars contain too much water, this means excessive dilution of the binder and severe cracking while setting.

3.8. BINDER/FILLER RATIOS

Sand, when dry, contains a lot of air, trapped between its grains, that do not adhere perfectly one to each other. It is called **emptyness index**, and can be measured as follows. Fill a container of know volume (say: 1 liter) with dry sand. Then pour in water. Even if the container was full of sand, a lot of water is absorbed. When water is no more absorbed, all the air that was between the grains has been replaced with water. If the quantity of water absorbed is measured, we know the volume of 'voids' between the sand's grains.

A 'perfect' mortar is made with a given volume of sand and the quantity of binder equal to the voids.

Happily, the emptiness index varies slighly between different sands, and is in general 38-40%. A good mortar is obtained mixing 2,5 to 3 volumes of sand with 1 volume of filler.

4. THE CLIMATE

In conservation, 'climate' is the sum of environmental physical factors that act on any material, man-made or natural.

Tha main factors influencing climate are:

❷ temperature (T)
❷ relative humidity (RH)
❷ variations of T and RH, their frequency and intensity

4.1. TEMPERATURE. In physical terms, temperature is linked to infra-red (I.R.) rays activity.

Temperature affects many physical and chemical processes:

❷ chemical reactions accelerate as temperature increases
❷ heating causes expansion of materials; cooling generally their shrinkage (exception: water)
❷ in a certain range of temperatures, life can develop
❷ temperature affects directly relative humidity in the atmosphere, and then the equilibrium of materials with the surrounding environment

4.2. ABSOLUTE HUMIDITY AND RELATIVE HUMIDITY. What we call '*air*' is a mix of gases that may include some water in gaseous state (vapour). The maximum content of water vapour in the air is proportional to temperature. Warmer air can include more water vapour. The quantity of water vapour that can be included in a given volume of air at a given temperature, has been calculated and is called '**saturation line**'. This is the basic parameter of the **psychrometric chart**.

The saturation line is expressed in grams per cubic meter (g/m^3). The content of water vapour per cubic meter is called **Absolute Humidity (AH)**.

Beyond the saturation value, air cannot absorb more water vapour. Excess vapour turns to the liquid state: this is **condensation**.

Anyway, air is not always saturated. If we consider a cubic meter of air (say: a display box in a museum) at 10°C, we know (consulting the psychrometric chart) that saturation occurs with 10,5 grams of water vapour. If the box contains only 5 grams of water vapour, we can calculate the relative value compared to saturation, wich will be at 50% and is called **Relative Humidity (RH)**.

RH gives the percentage value of saturation and is expressed in %.
4.3. THE PSYCHROMETRIC CHART. The psychrometric chart has three parameters:

- ❷ Temperature (in our countries expressed in °C)
- ❷ Absolute Humidity expressed in g/m^3
- ❷ Relative Humidity expressed in %

Knowing two parameters the third can be calculated.

4.4. EFFECTS OF HUMIDITY ON DIFFERENT MATERIALS. On every material, the effects induced by humidity are various:

Organic and inorganic materials tend to reach an equilibrium with surrounding air. They will release or assume water vapour, depending to RH

As already seen, with water movements, also substances dissolved in water move. Soluble salts are between these substances, and are highly hygroscopic. They absorb water if air is damper compared to them, or release water if air is dryer.

The value of Humidity can affect the dimensions of several organic materials: wood, paper, bone, fabrics.

Glass and metals, even if they are not porous, once buried in wet soil can be chemically transformed (corrosion) by dampness. The products of corrosion are mineral salts, always sensitive to ambient humidity.

4.5. CLIMATIC DYNAMICS. Looking at the psychrometric chart, it is clear the close correlation between temperature and humidity.

- ❷ T is tightly linked to I.R. rays, and is directly proportional to the duration of sunlight. T variations are maximal with clear sky, reduced with overcast.
- ❷ A.H. of air is linked to waterfalls and to the evaporation of water from liquid surfaces or damp soil.
- ❷ R.H. is the result of correlation between T and A.H. The same value of A.H. (say, 10g/m^3) may produce saturation at 10°C or very low values of R.H. at 35°C.

Variations of T and R.H. are in nature cyclic and continuous. To assure a proper conservation to archaeological materials, it is of the uppermost importance to limit these variations.
Natural cycles may be very long (glaciations), long (seasons), short (day/night), very short (atmospheric events). Short and very short fenomena are the most dangerous to archaeologic materials, as they have little time to search, and eventually reach, an equilibrium.

If we consider the climatic recording of a **clear day**, we notice that:

- ❷ T variations are cyclic and broad
- ❷ R.H. variations are broad and in inverse proportion to T
- ❷ the highest R.H. value is at dawn
- ❷ the lowest R.H. value is in the afternoon

On the opposite, during a **cloudy day**:

- ❷ T variations are still cyclic, but not broad
- ❷ RH variations, always in inverse proportion to T, are also limited

In a **rainy day**:

- ❷ T variations are limited
- ❷ R.H. values are high and nearly constant
- ❷ The influence of daylight on R.H. is scarce

In a **shelterd excavation**:

- ❷ T and RH values are nearly stable during the day
- ❷ if you compare internal and external recordings, you notice that thermal inertia of the sheltering structure limits variations.

4.6. CONCLUSIONS ABOUT CLIMATE. Studying the climatic recordings of the most common situations (clear day, cloudy day, rainy day) we realize that climatic changes in the atmosphere are very dangerous for archaeological materials:

During a nice day, T and R.H. change quickly, at a cyclic pace. The cyclic phases are around 12 hours long (this may vary a lot at our latitudes). In one phase (tipically after sunrise), T quickly rises and, consequently, R.H. diminishes. In the other phase (in the evening), the opposite occurs. Every archaeological material will tend to reach an equilibrium at this daily pace, releasing vapour during one phase of the cycle, absorbing vapour during the other.
During a cloudy day, R.H. and T variations are less important: the danger for materials is diminished.
In a rainy day, materials directly exposed to rainfall are quickly soaked, with volume increase. As rain is often followed by winds and sunlight, evaporation of water endagers materials. Crystallization (of salts, or ice) is likely. If the rainfall (or snowfall) is in winter, and clear weather follows, T may fall very low, with the danger of freezing for wet materials. In this case the expansion of freezing water may destroy any material.

Following this analysis, you cannot expect that archaeologic materials exposed to open air survive without damage. As a consequence of this statement, archaeologic materials must be protected since the beginning of excavations. Every protection, of temporary or emergency type, has positive effects:

- ❷ avoids direct wetting
- ❷ avoids direct sunlight
- ❷ reduces thermal variations, then R.H. variations
- ❷ allows interventions even during atmospheric events

5. CLIMATE RECORDING

The importance of climate recording is often neglected. Systematic recording of T and R.H. values allows to:

❷ have a written proof of environmental situation
❷ identify the stresses affecting archaeological materials
❷ verify the effectiveness of temporary shelters
❷ know the climatic dynamics of the site

Climate recording is possible with recording instruments. They have an initial price, but they can serve for many years without any other cost, except some minutes of time required to download their datas or change a sheet of paper.

Recording intruments are of two main types:

❷ electronic (Data Loggers ™)
❷ mechanic (Drum Thermohygrometers)

Data Loggers ™ are small boxes (5 x 2 x 2 cm) that may record some parameters (in our case: T and R.H.) at a choosen interval of time. To download the recorded datas a laptop computer and a dedicated software are needed. The accuracy of recording is proportional to the closeness of data takes. More the time between two ‘takes’ is short, more accurate is the recording. Limited built-in memory does not allow takes closer than 10’. Anyway, the recording obtained with Data Loggers ™, **is NOT** continuous. Continuity between the takes is electronically extrapolated. They cannot be calibrated on the field: they have to be sent to the factory. They are powered by a built-in battery.

Thermohygrometers are big boxes (approx. 30 x 20 x 10 cm) containing: a clockwork drum, revolving in a stated time (24 hours, 7 days, or 31 days). A bi-metallic thermometer. An hygrometer.
Thermometer and hygrometer are linked to moving arms that trace a line on a sheet of paper fixed to the drum. The revolution of drum (and related paper) produces continuous lines indicating T and R.H. variations. Drum thermohygrometers may (and must, monthly) be calibrated on the field.
They produce a continuous recording. They are cumbersome and fragile. Their clockwork movement is mechanical or electrical (disposable battery).

Both types have advantages and shortcomings:

Data Loggers ™ shortcomings:

❷ no continuous recording: if a cyclic event coincides with the cyclic take, no variation can be noticed
❷ accidents (i.e.: electric breakdown) can be noticed only when the Data Logger ™ is downloaded

Data Loggers ™ advantages:

❷ they are small, they are stable albeit not very accurate.

Data Loggers ™ are ideal to survey the climate when this is already known in detail.
Drum Thermohygrometers shortcomings:

❷ difficult and frequent calibration is needed
❷ specific sheets are compulsory
❷ they need place and are fragile

Drum Thermohygrometers advantages:

❷ continuous recording
❷ accurate, if properly calibrated
❷ any climatic mishap can be seen in ‘real time’

Drum thermohygrometers are old-shaped, complicate to manage, but are the best instruments to know in detail the climate of a site.
Drum Thermohygrometers are recommended to record the basic climatic values of a site. When tendential climate is known. Data Loggers™ are good to survey climatic perseverance or evolution.

5.1. USE OF CLIMATE RECORDING INSTRUMENTS. To use recording instruments you have always to check some features.
On **Data Loggers™** check if;

❷ the instrument has recently been calibrated
❷ the battery check test is OK
❷ you have the dedicated software
❷ the required parameters have been choosen (T and R.H.)
❷ the take cycle has been established (the tightest possible depending on built-in memory)

On **Drum thermohygrometers**:

❷ calibrate the istrument (see: 5.1.1.)
❷ Wind up the clock, if mechanical
❷ Replace the battery, if the clock is battery-fed
❷ Be sure that the dedicated sheets are available (don’t use photocopies)
❷ Check if tracing pen-nibs trace correctly (ink may have dried)
❷ Check the drum revolution time (day-week-month). Program sheet change accordingly

5.1.1. CALIBRATION OF DRUM THERMOHYGROMETERS (practical exercise)

5.2. CHOICE OF RECORDING INSTRUMENT LOCATION. Every instrument, if poorly placed, will produce poor recording. When placing a thermohygrometer (electronic or mechanical) one has to ascertain that it is placed where climatic conditions are the ones he wants to record.

If archaeological structures to monitor are in open air, they are exposed to **ambient** climate. A single instrument is enough to record climatic changes. It has to be placed in a box that avoids direct rainfall but doesn’t impede a free flow of ambient air.
Recording external climate is warmly suggested to have datas to compare to sheltered or covered areas climate, and have an idea of a building’s thermal inertia.

In detail, the instrument has to be placed where:

- ❷ it is not exposed to light or air currents different from those who affect the studied material
- ❷ it is near, or at the same level, than the studied material
- ❷ it is not exposed to direct rainfall

5.3. SPOT RECORDING OF SURFACE TEMPERATURES. Measuring surface temperature needs a specific tool: **contact thermometer**. The surface temperature in itself means nothing.
If surface temperature is compared to ambient air temperature, one can realize what is happening to a structure.
Recording surface temperature has a sense only if compared to ambient air Temperature.

5.4. RELATIONSHIPS BETWEEN SURFACE AND AMBIENT TEMPERATURE
If a structure has the same temperature of ambient air, nearly no water movement occurs.
If a structure is cooler than ambient air, it is probably absorbing heat, and releasing moisture.
If a structure is warmer than ambient air, it is probably releasing heat and absorbing moisture.

6. EFFECTS OF ENVIRONMENT ON ARCHAEOLOGICAL MATERIALS

6.1. ORGANIC AND INORGANIC MATERIALS (A Quick Rewiew). As already seen, organic materials come from vegetal or animal life, they are composed by complex, unstable compounds: proteins. They naturally tend to DECOMPOSE, producing less and less complex molecules, till the original elements (mainly C, H, O, N) are delivered.
Inorganic materials come from the mineral world, and they scarcely decompose or change their chemical nature. They are prone to oxydation (metals, that react with oxygen) and to mechanical breakage.

Both materials are sensitive to **TEMPERATURE**, albeit in different ways.
Organic materials, if freezed, become hard and brittle. If heated, they first change in colour and then burn, decomposing totally.
Inorganic materials vary their dimension with temperature changes, and if the amount of heat is sufficient, they melt, changing their physical state without chemical alteration.

Both classes of materials are influenced by R.H. changes. Organic materials have an highly porous structure in which water, in its liquid or gaseous form, gets in, modifying their dimension and hardness. Water can also solubilize (*hydrolisis*) some of their components, and speeds up decomposition.

Also inorganic materials, depending on their porosity, are sensitive to water and R.H. changes, but in an indirect way. Water **does not** affect them, but promotes **physical** events that may destroy their structure: freeze/thaw cycles, salt crystallisation.

LIGHT, and expecially its IR and UV components, affects organic materials.
IR radiations promote temperature changes, then dimensional stability and water content. UV radiation may break the long molecules of organic materials, altering their appearance and their physical features.
IR radiations heat also inorganic materials, causing tensions that may produce flaking, breaking, etc. UV rays may cause the fading of some mineral pigments.

Organic materials are often colonized by BIOLOGICAL LIFE, and living organisms **feed** with chemical components of the host, leading to their destruction.
Inorganic materials cannot be “eaten” by living organisms, but they may be a good support for their lives. In this way also inorganic materials may become colonized by biological life, altering their appearance (mosses, lichens, see § 6.3.3.). Some forms of life may induce chemical decay with some methabolytes containing acids, that leat to pitting. Superior plants, with their invasive root system may displace stones or whole walls.

6.2. WEATHERING MECHANISMS. No material can be damaged by **one single** climatic event. For instance, if we freeze an organic material (say, a fish) it keeps its natural features for a long time. If the frozen fish is thawed there is no other choice to cook it, as if we freeze it again the freeze/thaw cycle will accelerate decomposition. If we soak an inorganic material (say, a brick), and we keep it soaked, no alteration will occur. Foundations of bridges are perpetually soaked, and they don’t show decay. If a water-logged brick is dried, no damage will be noticed. If dry/wet cycles are repaeated indefinitely, even the hardest material decays.

Weathering is **always** the result of cyclic changes and repeated events.
Weathering is **always** a complex system in which water plays an important role.

6.3. ALTERATION AND DECAY: CAUSES AND PROCESSES.

6.3.1. **Soluble salts**. Soak a brick in distilled water. Its capillary system is filled only with water. We can hardly measure a dimensional change, but the change in weight is significant. If the brick dries, this means that water evaporates from the capillaries, leaving it in the same shape and weight than before soaking. The only way to damage a soaked brick is tho freeze it. Water crystallisation builds up crystals of ice that have a much higher volume than liquid water. The expansion of ice crystals exerts very high forces on the capillaries walls, breaking some of it. **Decay** has started. If the freeze/thaw cycle is repeated many times, the brick may be destroyed.
Soak now a brick in salty water. Apparently, things appear to be the same as for the brick soaked in distilled water. But in this case, the brick’s capillary system is filled with a salty solution. If the brick dries slowly, water evaporates, leaving on the surface crystals of salts, appearing as a white powder. This is an **alteration** called ***efflorescence***. If the brick is soaked again in salty water, the surface crystals dissolve and go again into the capillary system, adding to fresh salts already dissolved in water. The salt content inside the brick will be higher. Further drying produces more crystals on the surface, partially occluding the pores. If this cycle continues, salt build-up inside the structure of the brick reaches a treshold where:

- ❷ water is **saturated**, and salts crystallize **inside** capillaries
- ❷ surface pores become obstructed by salt crystals
- ❷ water evaporation continues, causing further crystallisation inside capillaries

The capillaries walls are rigid, and salt build-up exerts high pressures on them, the rigid structure of the brick finally breaks.
This is a **decay** called ***sub-efflorescence***. This kind of decay can be recognized by the powdering of the brick and the presence of salt crystals under the powdering surface. The breaks in the ceramic structure improve the absorption, accelerating the decay process, that ends with the total destruction of the brick. There have been no chemical changes in the nature of the brick, but it is reduced to powder.

6.3.2. **Freeze/thaw cycles.** The same mechanical stresses induced by salt cristallization happen when water freezes. In this case the crystals are of ice, instead of salt, but the results are the same. Water crystallization implies volume growth and extremely high cristallization forces, that can break every material. (i.e. cast iron of engine blocks). Freeze/thaw cycles are very dangerous as in every freezing event some capillaries break, improving water absorption. In this way the quantity of freezing water is progressively bigger, leading to complete failure of the material' structure.

6.3.3. **Biology**. Consider a wall made of stone ashlars linked with a mortar. Even on the smoothest surface some depressions are present, and soon or later some dust deposits on them. Dust is hygroscopic, then a build-up of moisture follows. Dust and moisture are an excellent ground for a pollen, or a spore, to grow. The simplest forms of life appear: lichens. This is an **alteration**. Plants modify the background, leaving on the stone some organic material: died parts of the plant that decompose. This is "food" for other, and more complex, plants: mosses. Mosses develop, live and die, retaining within their structure more moisture or even liquid water. Mosses have thin roots that go inside the microscpic cracks of the stone (due either to their nature or to the shaping process). Due to presence of roots, microcracks are partially filled with water. If freezing occurs, water crystallizes, widening the crack, that can room more roots and water. At this stage, superior plants (grass) can colonize the stone, developing more roots and retaining more 'dust' and moisture. Dust and roots begin to form a true 'soil'. This process leads to the complete colonisation of the wall, where 'trees' or climbing weeds (like ivy) grow. Such plants have strong roots that displace stones and break the mortars of the wall, that soon or later will crumble. This is **decay**.
Biologic life is impossible without water. In extremely dry climates (desertic), no biologic decay exists.

6.3.4. **Chemical pollution**. Human activities produce lots of pollutants that float in the air. Dust deposition brings pollutants in contact with any material. Rain and dampness react with pollutants generating extremely aggressive compounds. One of the most common (and aggressive) pollutant is Sulfuric acid (H_2SO_4) that reacts with Calcium Caarbonate (as already seen, present in limestone and mortars) following the classic reaction:

$$Ca\,CO_3 + H_2SO_4 \text{------>} CaSO_4.2H_2O + CO_2$$

The reaction is called **sulphatiation** and transforms Calcium carbonate in soluble gypsum.

6.3.5. **Erosion**. Winds and water may produce abrasive effects. The flow of water or dust-laden winds wears the surface of stones, bricks or mortars, improving their porosity and modifying their shape.

6.4. 'ENVIRONMENTAL EQUILIBRIUM'. Following physical laws, every material tend to 'share' temperature and dampness, till there is no difference between the material and the surrounding environment and no exchange is anymore possible (1st principle of thermodynamics). This is called '**environmental equilibrium**'.

6.5. OBJECT INTERRED. OBJECT DISENTERRED.

Every object or material, of any nature, when buried, is in an environment different from the one in which is was made. The underground environment has some peculiar features:

❷ absence of light
❷ absence of air, and expecially oxygen
❷ presence of soluble salts
❷ soil may be more or less corrosive
❷ temperature is very stable and changes slowly
❷ relative humidity is very stable

Buried in such an environment, the object slowly transforms. Transformation may affect the shape, the weight, dimensions and even the chemical nature of objects, and often leads to their complete destruction. In other cases, the object is not destroyed because the trasformation has led it to a new environmental equilibrium.
When the object is disinterred, this equilibrium is broken, and the new environment is very different:

❷ there is light, that may activate oxydizing processes
❷ there is air, containing oxygen and acid gases (CO_2 e SO_2)
❷ temperature and relative humidity have great and quick variations

The sudden change of environment is always traumatic for the materials, and triggers processes that can destroy them in few hours. To minimize the effects of this change, it important to know the state of the material when it is disinterred and the transformations occurred when it was buried.

7. THE ‘EXPOSED’ ARCHEOLOGICAL MATERIAL’S BEHAVIOUR

7.1. MOISTURE MOVEMENTS - DRY/WET CYCLES. When exposed, a material tends to reach an equilibrium with the new environment. This implies temperature and humidity changes.
If the material is wetter than air, it looses moisture, with the consequences already studied: efflorescences, shrinkage, etc. If the material is dryer than air, it absorbs moisture (and pollutants) with the known consequences: weight and volume increase, etc.
If the material stays in open air, it is prone to condensation during the colder (and damper) hours of night and dawn. When the day comes, evaporation is unavoidable. These cycles are very dangeraous for a worn material, that can collapse during the effort of reaching equilibrium at this daily pace.

7.2. DIMENSIONAL VARIATIONS. Moisture movements and thermal variations affect particularly organic materials, that are quicker to absorb or release moisture. Dimensional variations are so important for wood, bone, ivory etc., that they can be destroyed in few hours. Also porous inorganic materials (ceramics, bricks, clay) may be affected by important dimensional changes during wet/dry cycles.

7.3. WEATHERING OF ‘COMPOSITE’ STRUCTURES. As already seen, many structures are composed by different materials. A wall is, macroscopically speaking, composed by different kinds of stone and mortar. A mortar is, microscopically speaking, a mix of different kinds of gravel or sand and a binder. All these components have different behaviour as to temperature and dampness. When disinterred, all the components start to react to thermohygrometric changes following their nature: thermal conductivity, porosity, dilatation modulus and so on. The structure, till then in

equilibrium with a stable environment, tends to the separation of its components. Sand tends to separate from the binder, mortars tend to separate from the stones.
If the composite structure has both organic and inorganic materials, the difference of behaviour of these classes of materials is more marked, and weathering is quicker.

8. PREVENTION OF BIOLOGICAL ATTACK

“*The term* ‘biodeterioration’ *refers to any undesired change in material properties due to the activity of microorganisms and/or organisms belonging to various systematic groups.***”** (from: CANEVA, NUGARI, SALVADORI - Biology in the Conservation of works of art. ICCROM, Rome, 1991).
This definition asks for some clarification. Microorganisms or organisms play an important role in the ageing and decaying processes, that goes far beyond ‘*undesirable changes*’. Biological attack, soon or later, causes loss of cohesion and transformation of materials. Biodeterioration is never alone: it is tightly linked with other decay processes of chemical and physical nature.
When biodeterioration is associated to physical and mechanical processes, there is **disintegration**. Wen associated to chemical processes, there is **decomposition**.

Prevention of biological attack has the aim to restrain or to slow the growth of biological colonies. Prevention may be obtained with **indirect methods,** that’s to say modifying the environment**.** **Direct methods** modify the physical and chemical state of the substratum, that’s to say of archaeologic materials.

8.1. DIRECT METHODS. Direct methods imply the use of chemical compounds named **biocides**. The aim of a treatment is the complete suppression of deterioration agents. The results are obviously related to the products and the methods employed. One have to bear in mind that, if life has developed, the environmental conditions were in favour of it. After a treatment, if the environmental conditions stay the same, soon or later biological life starts again. In other words, the causes promoting the biologic developement have to be removed (see: § 8.2. Indirect methods) to achieve a durable success.

Direct methods are of different nature.

Mechanic: this is the removal of the visible forms of life. If spores or pollens are present, they stay in place. This method has very low effectiveness.

Physical: Gamma Rays and Ultraviolet Ray have showed good results on laboratory tests. Unhappily the wavelenght of these radiations causes dacay to most archaeological materials. This method is not recommended.

Biological: The method is based upon the use of a species antagonist to the parasite. The method may be effective, but the risk is that the new species replaces the former.

Chemical: Modern chemistry offers a practically endless range of biocides, that have to be choosen accurately. To choose a biocide, verify:

❷ the compound has to be toxic for the species responsible of decay
❷ low toxicity for mankind
❷ no interaction with the materials treated

- highly biodegradable (it does not stay for a long time in the soil, and does not reach the watertable)

8.2. INDIRECT METHODS. In general, the factors that promote biological life are:

- high RH
- high T
- poor ventilation
- light
- organic material on the substrate

Once again, high humidity is the main factor promoting life. Before any direct treatment, it is advisable to:

- limit capillary rise
- verify the effectiveness of rainwater collectors (gutters and sewers)
- drain the excavated area

High temperature favors the growth of many deteriorating agents and insects. High T associated to high HR may origin condensation when T drops.

8.3. STRATEGY

8.3.1.**To promote an effective control** of biodeterioration the following steps are suggested:

- Ascertain the biological attack. This is often associated with:
  presence of dampness
  colonies produce further dampness (droplets)
  some microorganisms have a pungent smell
  microorganisms may have different colours, depending on their state (active or quiescent)

- Identify the nature of biodeteriogen (lab culture)
- Identify a specific biocide
- Remove dust, if compatible with archaeological works
- Limit water access
- Limit light
- Plan a calendar to check the effectiveness of treatments

8.3.2. **Operational guidelines**. The identification of all the species present on an archaological site may need a long time. This is often in contrast with the archaelogic and conservative work.
To slow the developement of biologic life, a **wide spectrum biocide** can be used. This will produce the following consequences:
A first state of **quiescence**, when the colonies absorb biocide and stop to grow.
Biologic life stops. At this stage, the soil is filled with decaying organic material, that may promote the developement of species resistant to the wide spectrum biocide. Those species have a lot of ‘food’ available, without antagonists.
The growth of new colonies is possible and generally starts where the conditions are most favorable (dampness, light, microclimate, etc.). It is a **local** growth.

It is suggested **at this stage** to sample the biodeteriogens and send them to the lab analysis. The identification of a specific biocide allows local treatment.

8.4. CLASSIFICATION AND USE OF BIOCIDES. See joined documentation (from: CANEVA, NUGARI, SALVADORI - Biology in the Conservation of works of art. ICCROM, Rome, 1991).

9. PROPS AND SUPPORTS

During excavation, a structure may need some intervention to avoid further decay, or to allow the archaeological activity to continue without danger (for structures or workers).
These interventions are related to circumstances of digging, and they must:

- ❷ be quick, when made and when removed
- ❷ be reversible, to allow archaeological work's progression
- ❷ have little or no chemical interaction with the archaeologic material or structure

Most common field interventions are mainly of three types: static, mechanical, conservative.

9.1. STATIC INTERVENTIONS (PROPS). During excavation some structures may need to be propped to avoid crumbling or collapse. In this case, solid props, generally wooden, are used to contrast the gravity force. These are **props**, and they must be put in place following these rules:

- ❷ The prop has to support the widest area around the critical zone. This helps to spread gravity forces and avoids concentrated stresses
- ❷ When organic materials are used for props (typically: wood), the interface between the archaeologic material and the prop has to be treated with a biocide, and protected with a vapour-permeable, moisture-resistant stuff. This avoids condensation and the growth of micro-organisms between the archaeological structure and the prop.
- ❷ Buttresses are often unavoidable to secure the prop against the structure. They must not interfere with the neighbouring activities.

9.2. MECHANICAL INTERVENTIONS (SUPPORTS). Some archaeological elements, in general renderings or coatings, may be found during the excavation completely separated from the wall or the floor on wich they are laid. In general they still stick to the main structure because an adhesive layer of wet clay or earth. When dry, clay looses most of his adhesive power and the coating can fall. To avoid any loss of material a temporary support is needed. Supports must hold in place the material during the unavoidable consolidation. These supports are generally made with light structures that exert a gentle pressure against the endangered layer. The variations of this kind of support are practically endless: hereafter are listed some of the commonest cases.

9.2.1. **Small fragments of rendering**. If the rendering has to be saved, its consolidation has to be done as soon as possible. The support has to stay in place only for few hours, and can be made with wooden boards. Place between the boards and the rendering an isolation coat (polythene bag, transparent film used for wrapping food, '*Domopack*'). Once supported, the rendering can be reattached to its support with lime and pozzolana injections.

9.2.2. **Large fragments of rendering**. In this case the amount of rendering to support is larger, and the support will inevitably interfere with some archaeological activity. The support must allow both archeologists and restorers to do their job. This is the typical case in which synergies (cf. § 1.2.) are fundamental. A suggested technique is as follows:

❷ protect the surface to support with polythene or aluminium foil
❷ install the wooden boards, protected with polythene, at about 1-2 cm from the surface to save
❷ fill the hollow space between boards and rendering with polyurethane foam
❷ let P.U. foam swell and harden
❷ cut excess foam from the sides

This kind of support has no chemical interaction with the material supported, it helds properly the rendering during consolidation, and can be removed without any mechanical stress.

9.2.3. **Dislocated or weak mosaic's *tesserae*.** If tesserae are mobile, they have no more mortar retaining them. They are covered with medical gaze, glued with acrylic solution (exemple: Paraloid B-72 at 10% in Acetone). A fast-evaporating solvent (like Acetone) accelerates setting and quickens the conservative action.

10. SHELTERS

When archaeologic activities end, a difficult choice has to be made. What to do to conserve the structures? **Any choice has consequences**, and implies dangers in the mid- or long-term.
In general two main guidelines are possible: reburial or shelters.

10.1. REBURIAL. To cover again an archaeological site is often an axcellent way to conserve it.
Reburial is often the best solution when a suitable budget for effective shelters is not available.
Reburial may also be a correct choice waiting for appropriate funding.
If waterfall is abundant, or water table can submerge the excavation, reburial has to be done as soon as possible. If reburial is temporary, it is useful to cover the structures with plastic nets (agricultural types, in P.E.) or unwoven tissues to keep them separated from the filling material. Nets have to follow the structure' shape and not to be stretched, to avoid concentration of tension or stresses. Covering with plastic sheets must be avoided, as well as every material promoting internal condensation.
Filling material has to be devoid of soluble salts and metallic impurities.

10.2. TEMPORARY AND FINAL SHELTERS.

This topic is too huge to be thoroughly treated here. Some basic principles are anyway proposed.
Too often excavation are intended to be '*open to public*', at any cost. This is a false step for conservation.
Before any decision, many elements should, and must, be evaluated.

❷ Which are the environmental conditions?
❷ How much will cost conservation?
❷ How maintenance can be assured?
❷ Is it worth that people visit such an excavation?

If these elements are not considered in advance, most excavations decay in a quick and irreversible way, without having a true interest for visitors. Managing an '*open to public*' excavation is a matter of money, monitoring of state of conservation, availability of trained personnel to stop or slow decay. If none of these activities is predicted, decay and ugliness quickly remove any residual value to excavated sites. Many archaeological sites are scientifically interesting, but they do not deliver any fascinating ‘message’ to visitors. Many archaeological sites are so poorly managed that they had become dumps. More than ugliness, poor management, or unsuitable projects, produce definitive destruction of finds, when a correct reburial would have ensured the survival of this heritage.

The shelter and the public exhibition of an archaeological site should be considered, following UNESCO’s advices of 1978, 1982, when:

- ❷ excavated areas may enrich visitor’s experience and awareness
- ❷ the site is easily accessible
- ❷ the state of conservation of finds may be monitored
- ❷ tools and technologies for basic conservation are available

Shelters and exhibition of archaelogic sites may be of mainly three types:

- ❷ open air
- ❷ under shelters
- ❷ inside existing (or purpose-built) buildings

10.2.1.**Open air shelters/exhibition**. Only big structures can be exposed, while it is impossible to exhibit objects and finds, that should be quickly damaged or stolen.

Open air exhibition needs the manufacturing of protective layers, or ‘blankets’ (in italian: ‘*sacrifice layers*’) that have to absorbe most of the stresses upon the structures to preserve.
In general, open air structures (namely, the top or surviving walls) are protected by masonry layers, that are espected to age more quickly than underlying (and ‘original’) structures. The italian word holds an acceptation (‘sacrifice) that inherently predicts their loss.
International agreements (**Athens 1936 e Venice 1968, ‘Carta Italiana del Restauro’ 1972**), state that those protective layers have to be different, and recognizable) from the original walls, and have to be ‘weaker’ than the material they have to protect.

As a consequence of this, open air exhibitions should be based on a constant survey of the state of conservation of structures and protective layers. This is , alas!, more theoretical than real.
Without a suitable program of survey, the protective layers can:

- ❷ age and disappear without being replaced, leaving the ‘original’ structure unsheltered
- ❷ be more resistant than the ‘protected’ layer, that decay more quickly than ‘protective’ one

In ‘open air’ context, long term conservation needs programming, budgeting, survey.

10.2.2. **Exhibition and conservation under shelters**. This kind of arrangement is possible when the excavation’s value and/or climatic conditions need a superior form of protection. Materials and structure's choice is again practically endless: from foliage to concrete. Anyway, a good shelter should fill these features:

❷ it has to protect a wider area than the archaeological one; to avoid that sloped rain may reach the archaeological materials

❷ it must reasonably resist to local climatic and atmospheric phenomena

❷ its maintenance must be easy and cheap (if maintenace costs are too high, the existance of the shelter is no more justifiable, and reburial is to prefer)

10.2.3. **Exhibition inside buildings**. This is a solution that can be adopted when:

❷ the archaelogical structures are **already** inside a building that cannot be taken away from public use

❷ the importance of the monument and environmental conditions make desirable a new building

Both choices need accurate planning and project. The features of the structure to build should be agreed on conservation musts, to avoid creation of an harmful (for conservation purposes) micro-climate inside the new structure. To achieve this, planning and building of the new structure must consider:

❷ proper drainage and piping of rainwater

❷ roofing with insulating materials: to avoid condensation inside the building and to reduce thermal dispersion

❷ proper climatic control to stabilize R.H. This is very important if the site is open to visitors. Visitors produce dampness: either climatic gear is able to control limitless presences, or the number of visitors has to be limited according to the climatic gear's power

❷ adapted lighting, with special attention to I.R. an U.V. rays content

❷ access control

❷ dedicated budgets to manage the site: ordinary and exceptional maintenance; personnel; climatic survey and maintenance of climatic gear

If these parameters are not thoroughly analysed and resolved by planning and building, the '*protection structure*' quickly turns to be a moisture-saturated room, where **all** the weathering factors act.

11. MASONRY PROTECTIVE LAYERS (*BLANKETS*)

The aestetic problem of protective layers is not in the aims of this section.
Blankets are protective layers of masonry that are superposed to broken walls, in order to protect them from atmospheric water, direct sunlight, human presence. As already stated, they are intended to be 'softer' than the masonry they have to shelter. Many types of blankets have been built in the walls' crest during the last century. At close examination, they usually show the following shortcomings:

❷ they are generally cracked and separated from the underlying (and 'original') masonry
❷ they are often made only (or predominantly) with mortar
❷ the binder is usually concrete
❷ they often are less decayed than the wall they had to protect

These shortcomings are mainly due to the materials employed and a poor building technique.

❷ Separation of the two systems (protective/protected) is mainly due to different dilatation modulus
❷ Cracking is the result of excessive thickness of the layer.
❷ Cracks widen quickly and let free passage to water, that embeds the underlying structure.
❷ Excess binder and its nature (Portland Cement), release soluble salts.
❷ Soluble salts and water cause erosion under the blanket

Instrumental recording has shown that, in a continental climate, surface temperature of a wall can exceed 30° daily and 65° between summer and winter. Uneven dilatation modulus between protective and protected layers brings to separation. So, theoretically, blankets should be:

❷ made mainly with materials similar to the original
❷ made with hydraulic lime to bind other materials

If the material used for the blanket is similar to the original, it can be used in smaller shapes to avoid that the protective layer is 'mimetic'.
If the blanket is madeonly with mortar, granulometry of fillers has to be varied and coarse (up to 15 mm). The maximum thickness of the coat has to be no more than 3 times the maximum shape of fillers (see § 3.7). In case of extreme climate, a very small quantity of salt-free, white cement (see § 3.6.), can be used (see further on).

11.2. HOW TO ADJUST THE BLANKET COMPOSITION. When deciding what will be the composition of a blanket, one has to evaluate three main factors:

❷ wich stresses it will have to bear
❷ wich kind of material has to be employed (limestone, brick, siliceous stone)
❷ thickness of the coat

11.2.1. Stresses that a blanked have to bear can vary a lot, depending for instance, of the exposition to rainfall, people walking upon, etc. As the 'best' mortar is the one that has the **minimal** resistance to fill his role, hydraulic binders can be avoided for use on **shelteerd walls**, as in this formula:

1)	washed siliceous sand	10 parts (volume)
	slaked lime	4 parts (volume)

Filler/binder ratio is: 2,5:1

For **sheltered walls**, in **damp climate** the former proportions may be varied in this way:

2)	washed siliceous sand	10 parts (volume)
	slaked lime	3 parts (volume)
	Hydraulic lime	1 part (volume)

Filler/binder ratio is: 2,5:1

Such mortars are perfectly adapted to their role. The addition of 1 part of hydraulic lime in the 2) formula allows a good setting even in damp climate.

To prepare good mortars to employ on **exposed walls**, the hydraulic binder can be improved, at the same time diminishing the filler/binder ratio, as follows:

3)	washed siliceous sand	12 parts (volume)
	slaked lime	2 parts (volume)
	Hydraulic lime	1 part (volume)

Filler/binder ratio is: 2,5:1

11.2.2. The composition of the mortar can be further adjusted, depending on the material to bind, that can be classed in three main families:

❷ bricks: very porous and capillary. Medium/low strenght
❷ limestones: average or poorly porous. Medium/high strenght
❷ siliceous stones: poorly porous. High to very high strenght
❷

A mortar for **blankets containing bricks** can be so formulated:

4)	washed siliceous sand	8 parts (volume)
	crushed brick	2 parts (volume)
	slaked lime	3 parts (volume)
	Hydraulic lime	1 part (volume)

Filler/binder ratio is: 2,5:1

This formula includes crushed bricks to enhance hydraulicity without affecting its vapour permeability.

For **blankets made mostly of limestone**, exposed, the formula suggested is:

5)	washed siliceous sand	8 parts (volume)
	slaked lime	1 part (volume)
	Hydraulic lime	3 parts (volume)

Filler/binder ratio is: 2,5:1. Notice, in this case, that the hydraulic binder is higher to have a good grip on limestone pebbles.

The mortar for **blankets composed mainly by siliceous stones**, exposed, will be composed so:

6)	washed siliceous sand	12 parts (volume)
	slaked lime	3 parts (volume)
	white cement	1 part (volume)

Filler/binder ratio is: 3:1

In this case, **one fourth** of the binder is salt-free cement instead of hydraulic lime. In this way the higher silica/aluminium content promotes a better link with the siliceous stones. At the same time the filler/binder is higher, to maintain good vapour permeability and to avoid excessive hardness.

11.2.3. The **maximum thickness** of mortar to apply is an important parameter to avoid cracking and excessive dilatation. The granulometry of fillers can be easily checked with graduated sieves. As already suggested, avoid single layers that exceed tree times the maximum granulometry. When employing a sand containing grains up to 10 mm, the layer's thickness must not exceed 30 mm.

11.3. PRACTICAL INDICATIONS: HOW TO PREPARE A WALL TO RECEIVE A MORTAR

To ensure a good adhesion of the mortar to the wall, some basic operations are compulsory:

- ❷ remove any form of biological life (insects, grass, seeds)
- ❷ wash thoroughly the surface to remove dust and loose mortar
- ❷ provide shelters to avoid direct sunlight

And, final tips:

- ❷ Spray again water on the surface just before spreading the mortar
- ❷ The wall has to be WET: neither slaked, nor drying
- ❷ **Resist the temptation of adding too much water to mortar!**
- ❷ A good mortar never drips
- ❷ Working a good mortar gives you satisfactory results and handsome foreharms!

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*Buon lavoro!**

Stefano Pulga

SUMMARY

8. PREVENTION OF BIOLOGIC ATTACK