Historic Mortars: Characterization and Durability. New Tendencies for Research

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1. INTRODUCTION

A mortar is a material resulting of the intimate mixture of sand grains, a binder (lime, cement, etc.) and water. The properties and characteristic of the mortars mainly depend on the nature of the binder component. That is the reason for which, its evolution with time has been very related to the development of artificial cementitious materials. So, with the consolidation of the Roman civilization the use of lime mortars was generalized and extended. Since the XVIIIth century, hydraulic binders begun to partially replace the lime. These new materials hardened more quickly and developed higher mechanical strengths. In the XIXth century, the invention of portland cement revolutionized the world of building materials, completely displacing the use of lime in all type of civil and military constructions.

With the purpose of modifying and/or improving some of the properties of the mortars, traditionally they have been mixed (together with the basic components), some different products or additional constituents. These products have evolved along the time. At the beggining the admixtures were composed of natural substances (blood, egg, fig juice, pig grease, manure, etc.). The current admixtures are generally industrial by-products, like fly ashes or blast furnace slags ..., or other more elaborated products, like organic polymers, acrylic resins, epoxi resins, etc.

Since a long time ago mortars, as constructive element, have had a double mission: on one hand to make the link between other materials (fundamentally rocks or bricks); and on the other hand to cover and protect the surfaces of columns, walls, facades ... They have been, at a certain extent, the skin of the building. It is obvious that these functions are vital for the conservation of the “monument”, and they reveal the importance of these materials in the Historical Heritage.

Some characteristics of the mortars (mainly those related with the heterogeneous composition and high porosity) can affect its durability by making them easily attackable for external agents, and so to contribute to the unstability of materials in contact with them. Also, some of those characteristics, can stimulate the access of polluting agents that act as initiators of the deterioration of the materials that mortars are protecting or binding.

All this clearly explains the role of the mortars in the conservation of the buildings and constructions of the Heritage.

The interest for the systematic study of ancient mortars is relatively new. In 1981 a first tentative arises (favoured by the ICCROM) for establishing a investigation strategy of ancient mortars as well as of repair mortars. In Spain that interest has also been declared since more than one decade. Different groups of investigation from CSIC (basically those working at the Eduardo Torroja Institute), together with other investigators from Spanish Universities (Navarra, Seville, etc) are working hardly in some running projects. Additionally, just a few months ago a Thematic Network on Cultural Heritage was constituted at the CSIC ... Among those objectives of the Network it should be emphasised the multidisciplinar study of Historic mortars. It demonstrates the strategic importance give in our country to these materials.

The studies about ancient mortars have been mainly centered in the characterization and identification of their components (from a quantitative point of view) in order to date them (information that has been used in many occasions to differentiate the constructive steps of the studied construction). Also a lot of time and effort has been invested for deeply studying the processes of deterioration of mortars and the influence of such alteration on the adjacent materials. In all these studies some more or less conventional methods have been applied, but occasionally the use of sophisticated techniques has also been explored.

At present, investigations are advancing on the application of technics and treatments of conservation on ancient mortars (already experienced in stony materials). Criteria of selection of the most appropriate treatments for each mortar should be stablished as well as a methodology for evaluating the effectiveness of such a treatments. Repair mortars are a valid and coherent solution but not forgetting that its design should be based on sustainable and durable approaches.

Next a state of the art on the present knowledge on mortars of the Heritage is presented. Types of mortars, characterization, durability, methods of conservation, etc are discused. In a final section some future topics for investigation in this field are suggested.

2. TYPE OF MORTARS

RILEM established a first classification of mortars as a function of its technical application:

1. Mortars for plasters.
2. Mortars for the application of facings:
   - (i) paviments/floors,
   - (ii) walls,
   - (iii) other arquitectural elements.
3. Mortars for decoration:
   - (i) layered,
   - (ii) reliefs.
4. Mansory mortars:
   - (i) bedding,
   - (ii) pointing,
   - (iii) sealing,
   - (iv) stiletto work,
   - (v) repairs.

And a second classification as a function of the nature of the binder:

1. Mortars based on lime.
2. Mortars based on lime and pozzolanic materials.
3. Mortars based on hydraulic binders.
4. Mortars based on gypsum.
5. Mortars based on clay binders.
6. Mortars based on organic binders.
7. Mortars based on more than one binder.

Most of mortars forming part of the constructions of the Historical Heritage have been found to be constituted by lime binders or lime + pozzolana or portland cement. This is the reason for which this text will basically refer to those particular cementitious materials

2.1 Mortars based on lime

The binder used in lime mortars is calcium hydroxide which produces $CaCO_3$ when carbonated (compound responsible for the hardening of the material).

In general terms, building limes are defined as binders which main constituents are calcium oxide and calcium hydroxide (CaO, $Ca(OH)_2$), magnesium oxide and hydroxide (MgO, $Mg(OH)_2$), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). Building limes can be classified into two groups:

1. Air lime. It is fundamentally constituted by calcium oxide (unslaked lime) and/or hydroxide (slaked lime).
2. Hydraulic lime. The hydraulic limes consists predominantly of calcium silicates, calcium aluminates and calcium hydroxide.

The main difference between the air and the hydraulics lime, resides that in the first case the addition of water has the only objective of facilitating the mixture of the components and placing the mortar, but it does not intervene in any chemical reaction. The process of hardening of the mortar carried out with air lime, takes place for the reaction of the $Ca(OH)_2$ with the atmospheric CO_2 producing $CaCO_3$. This product provides, to the lime mortar its physical, chemical and mechanical properties.

Concerning hydraulic lime mortars, in this case the addition of water, besides favouring the fluidity of the slurry, it intervenes in chemical reactions with silicates and aluminates (both present in the raw materials) generating the formation of hydrated compounds that confer the mortar some different properties to those obtained in the case of the air limes.

The main properties and characteristic of lime mortars are the following:

1. Low mechanical strengths, due to the low affinity of the calcite and quartz crystal, as well as to the weak linkage among the calcite particles.
2. Easy workability, due to the slow process of setting (carbonation) that depends on the environmental conditions.
3. High capacity of deformation (low module of elasticity). It allows the material to absorb small movements of the adjacent materials.
4. High permeability to water and water vapour.
5. Low resistance to the freeze-thaw cycles.

No presence of soluble salts, what avoids the processes of dissolution-crystallisation of the salts, and therefore the appearance of eflorescences and subflorescences.

These properties can be relatively modified by altering the process of production of the mortar, the type of aggregate, the aggregate/binder and water/binder ratios, etc.

2.2 Mortars based on portland cement binders

The portland cement binder is a finely ground artificial product, of inorganic and mineral nature, which main property, when mixed with water, is to form a slug that harden and gives stable products with time.

The raw materials used in the manufacture of Portland cement are mainly constituted by four mineral oxides: lime, silica, alumina and iron oxide. These compounds interact one each other in the kiln. Four compounds are usually regarded as the major constituents of cement: C_3S[1] (tricalcium silicate); C_2S (dicalcium silicate); C_3A (tricalcium aluminate) and C_4AF (tetracalcium aluminoferrite). In the presence of water, the silicates and aluminates form products of hydration, which in time produce a stiff and hard mass: the hydrated cement paste. These products of hydration have a very low solubility in water.

The main product of the hydration of Portland cement is the C-S-H gel. This phase highly contributes to the mechanical strength of mortars. It is generated as a consequence of the hydration of the silicate phases according to the following reactions:

$$C_3S + H_2O = C\text{-}S\text{-}H + Ca(OH)_2$$
$$C_2S + H_2O = C\text{-}S\text{-}H + Ca(OH)_2$$

The main characteristics of a hydrated portland cement related with its chemical composition are:

1. Stability of volume. With the hydration process a mortar undergoes shrinkage due to a volume decrease of the hydrated cement phases. Additionally, the so called hydraulic retraction is also produced; it happens for the quick evaporation of the water of the plastic mass.
2. Resistance to the chemical aggression. If the mortar has been carefully elaborated (well compacted, no cracks, low porosity, appropriate binder/water ratio, etc.) then it will have good durability.
3. High mechanical strengths. They are mainly reached because of the formation of a high proportion of C-S-H gel.
4. Heat of hydration. The hydration reactions of Portland cement phases are exothermal. The fast development of heat in the system can lead to a quick evaporation of water which could give place to the formation of cracks in the mortar.

2.3 Mortars based on lime and pozzolanic materials

Pozzolanic materials are natural substances or industrial by-products having an amorphous or partially crystalline structure formed by silica, silico-aluminium compounds or a combination of both composition. Pozzolans do not harden when mixed with water, but when they are finely powdered and in presence of water, they are able to react with the calcium hydroxide at ambient temperature to form hydrated calcium silicates and developing suitable mechanical strengths. In fact the pozzolan-lime reaction is also a hydraulic reaction which main hydration product is C-S-H gel too (like in Portland cement).

The main properties of lime plus pozzolan mortars are the following:

1. Relatively low mechanical strength, although superiors to those in lime mortars.
2. Certain capacity of deformation (low module of elasticity).
3. Low resistance to the adverse climatic conditions.
4. Scarce presence of soluble salts.
5. Lower permeability to water than lime mortars.

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[1] Abbreviated symbols used in the cement chemistry: CaO = C; SiO_2 = S; Al_2O_3 = A; Fe_2O_3 = F. Likewise, H_2O in hydrated cement is denoted by H.

3. CHARACTERISATION OF MORTARS

From the scientific point of view the characterization of mortars is nowadays a quite well a resolved problem. The use of instrumental technics and analytic tools, usual in the study of materials, like for example XRD, DTA/TGA, SEM/TEM/EDX, NMR, FTIR, BET, Hg Porosimetry, etc., etc., etc., allows to settle down with enough precision the mineralogy and the microestructure of the constituent phases of mortars; it also allows to quantify the presence of this phases in the system and to detect the presence of minor phases attributable to the existence of degradation processes ...

However, the real problem to be solved when a study of mortars or any other cementitious material is approached in the framework of a construction belonging to the historical Heritage (from which no or scarce data exist), comes from the difficulty of identification of the material, or the identification of the constituents used in its elaboration, or the binder/aggregate ratio which was used in the moment of the mixing.

From a conservation point of view, the mortars' identification is a necessary step for the design of the repair materials, taking into account the compatibility that must necessarily exist between the original and the new materials.

The bibliography contains already examples of mortar analyses. Nevertheless, the accent is mostly put on pure lime mortars; in other words on materials with non-hydraulic binders. On the other hand, analysis carried out on cement mortars as found in literature and with standardised procedures does not seem to satisfy for historic hydraulic mortars. The main reason for this is, that all standards refer to the portland cement as a reference.

The first issue is therefore the identification of the hydraulic or non-hydraulic character of the binder, which permits to operate a first basic distinction between the encountered mortars. Furthermore, the hydraulicity of a mortar might have different origins. It can be based either on the presence of pozzolanic admixtures reacting with lime or on the presence of calcium silicates. Thus, the identification of a mortar is a complicated procedure because:

- the initial mortar constituents have reacted, therefore it is very difficult to recognize them;
- the products of lime-pozzolan hydration or of cementitious materials are quite similar.

In a EU "Environment" project (EDAMM ENV-CT95-0096), ended in 1999 and participated by 3 research teams (one of them the Spanish group writing this state of the art) a procedure of identification of mortars was established. It is now described:

3.1 General description of the procedure

The first step in the setup procedure consists in the separation of the study of the aggregate type and the binder. The basic operations to be performed consist of: A visual analysis (this operation aims in the general description of the unknown sample); a complete optical microscopy study is the following step (this is the basic technique of the setup procedure, aiming in the identification of the aggregate and the study of the binder).

Schematically, the steps in which the setup methodology consists, are illustrated in Figure 1 below.

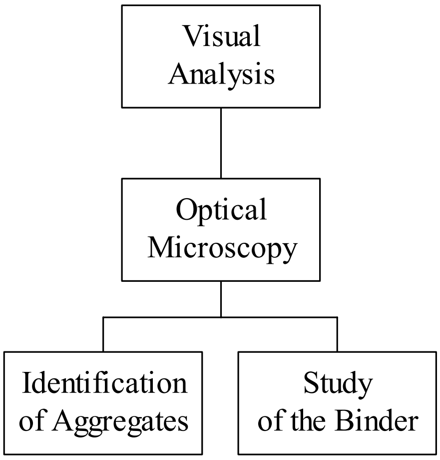

Figure 1 Procedure for mortar type identification

The study of the binder is also based on a combination of the aforementionned operations. However, the optical microscopy results may be confirmed through the use of complementary techniques:

- X-ray Diffraction;
- Chemical Analysis involving (a) a pozzolanicity test or (b) the determination of the soluble silica within the sample
- Thermogravimetric Analysis (DTA/TGA)

The binder identification procedure is presented in Figure 2. A first basic distinction permits the separation of lime mortars and hydraulic mortars. Indeed, if the sample is characterised by a carbonate matrix and the absence of minerals, such as pozzolan tracers (to be discussed further) or brick fragments, it can be concluded that it is a lime mortar. If this is not the case, then two cases are more likely to occur.

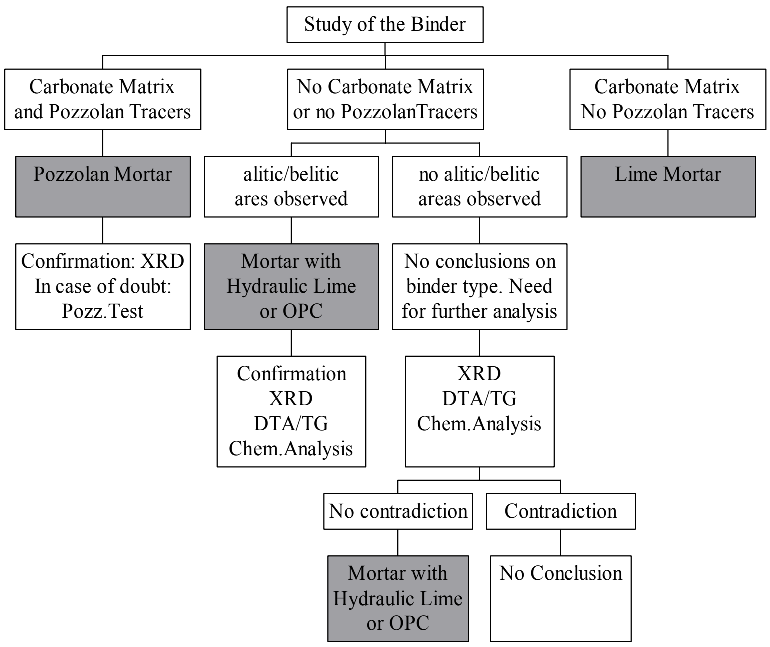

Figure 2   Flow-chart of the binder analysis procedure

In the first case, the presence of a carbonate matrix as well as the presence of pozzolan tracers or brick fragments is assessed. It may be concluded, that the mortar is a pozzolan one. This conclusion should be confirmed. The most appropriate technique is considered

The X-ray diffraction analysis, which aims in highlighting the presence of pozzolan tracers. In case of doubt, as it will be further explained in detail, additional tests, named pozzolanicity tests, should be applied.

In the second case, the analysis concludes that the material either does not contain a carbonate matrix or it does not contain pozzolan tracers. If, however, belitic or alitic areas are observed, then it may be concluded that the binder is hydraulic lime or Portland cement. As previously, this conclusion should be confirmed through one (or more) of the recommended techniques, such as X-ray Diffraction, DTA/TG and chemical analysis for the determination of soluble silica. Finally, if no alitic or belitic areas are detected, then no conclusions may be drawn; further analyses are required and may be performed by the combination of the aforementionned techniques. If no contradiction between the results arise, then the conclusion is that the binder is hydraulic lime or Portland cement. If, however, the results are contradictory , then no conclusion may be drawn.

As it has already been mentionned, research has focused on the development and testing of two operationnal procedures. The first is part of the study of lime-pozzolan binders through pozzolanicity tests, whereas the second is related to the determination of soluble silica coming from a hydraulic reaction. Both procedures are presented in the paragraphs that immediately follow.

3.2 Identification of lime-pozzolan binder

Natural pozzolans are tufaceous volcanic rocks, which are incoherent, pulverulent and rich in amorphous phases. They are due to the alteration of lavas rapidly cooled by the water vapor emitted by volcanoes, giving rise to the formation of grains, which are subsequently lightly cemented. The literature reports numerous references to the chemical and petrographical characteristics of pozzolan [7-12].

The basic hypotheses relative to the setup of a methodology for the identification of a lime-pozzolan binder can be summarised as follows:

1. each pozzolanic material is characterised by specific mineralogical phases;
2. if those phases are detected, the pozzolan (whose typical tracers are those phases) is in fact present inside the material;
3. however, the absence of these peaks is not a sufficient indicator of the absence of pozzolans and can lead to uncertainties.

As a consequence, there is a need for complementary procedure (pozzolanicity tests) in order to verify whether the lime is still reactive with the mortar components. It has to be underlined that, if fine ground bricks or tiles are identified, then only the pozzolanicity test is applicable. The reason is, that brick fragments are artificial pozzolans made of clayish materials, therefore they do not contain pozzolan tracers. Thus, the procedure of identification of pozzolan tracers is not applicable.

3.2.1 Pozzolanicity tests

In order to develop a procedure that would reliably ascertain whether a binder is lime-pozzolan or not, two methods have been tested. The first method (A) employs acid and basic attack to eliminate carbonates, silicates and aluminates, leaving a residue mainly composed of the crystalline phases of the pozzolan, which are more easily XRD detectable with respect to the original mortar. The second method (B), based on a pozzolanicity test which is limited to pozzolanic cements, consists of treating the mortar with a saturated solution of $Ca(OH)_2$, and evaluating the mortar pozzolanicity from the amount of lime reacting with the mortar components. In both cases, a preliminary preparation of the samples is necessary (the objective is to enrich the sample with the binder component by separating coarsest aggregates).

3.3 Identification of a "modern" hydraulic binder

In mortars and concretes, silica proceeding from a hydraulic reaction is soluble in acidic means. However, silica from aggregates is not. Consequently, through the analysis of the silica from the hydraulic reaction and, if possible, by determination of the amount of water belonging to the binder fraction, it could be concluded whether or not an unknown material is a hydraulic binder.

An important problem can arise when attacking the sample, if part of the silica of the aggregates is solubilized together with the silica from the hydraulic reactions. Therefore, the research objective consisted in finding a procedure of attacking the sample strongly enough, so as to solubilize the SiO_2 of the binder, but not too strong either, for not altering the aggregates. Soluble silica is measured in Spanish cements following the instructions given in UNE 80-223-85 standard: the sample is attacked with a hot solution of hydrochloric acid [HCl/H_2O ratio of 1:9 in volume] [12]. Additionally, Takashima [13] found a method through which it was possible to selectively dissolve silicates and free lime of cement clinkers leaving unaltered the rest of the clinker phases. In this case, the dissolvent is a mixture of salicilic acid in methanol. This dissolvent dissolves also the C-S-H gel. If it is shown that this method is not so strong so as to attack the aggregate, then the obtained soluble SiO_2 may be attributed to the C-S-H and the material may be considered hydraulic.

4. DURABILITY

Mortar deterioration occurs through different chemical, physical, mechanical, biological, etc., processes. Very often, more than one alteration mechanism takes place simultaneously and also frequently chemical processes or biological processes, etc., have physical or mechanical effects; it means that is quite difficult to establish a classification of the deterioration mechanisms of mortars. So, we will point out here some of the processes of deterioration commonly observed in this kind of materials.

4.1 Dissolution and leaching of the components of hydrated mortars

Pure waters (proceeding from the condensation of the fog or of the water vapour) and the soft waters (rain water or melted snow and ice) contain little or nothing of calcium. When these waters get in contact with the hardened mortar they spread through the porous system of the material and dissolve the hydrated phases which are rich in calcium.

The $CaCO_3$, main constituent of lime mortars and lime plus pozzolana, has an equilibrium pH of 9,93 which is moderately far from the neutral. Then, when $CaCO_3$ it is put in contact with water, this product will be dissolved until reaching the equilibrium. If waters also contain dissolved CO_2 the solubility of the $CaCO_3$ will be very superior. In turn, $Ca(OH)_2$ is the most soluble constituent of Portland cement and hydraulic lime pastes (1230 mg/l) and it is therefore the most easily phase to be leached.

The dissolution of the mortar binder can cause an increment in the porosity of the system and consequently in the permeability giving place to the decrease of mechanical strengths and to an increase of the susceptibility for being attacked by other aggressive agents.

Leaching process of calcium salts from mortars can also have other undesirable effects from the aesthetic point of view. Frequently, the leachate ($Ca(HCO_3)_2$) precipitates on the surface of the material or even on adjacent materials giving place to white efflorescences of $CaCO_3$.

4.2 Interaction of the mortars with the atmospheric pollutants

The air contains pollutants in three states: gassy, solid particles and substances dissolved in drops of water. The most important pollutants are: SO_2, NOx and CO_2. During the last decades the problem of the acid rain has acquired serious dimensions in a large part of Europe and of Northern America. The pH of the rain uses to be between 4 and 4,5. This acidification is due, in principle, to the effect of the HNO_3 and the H_2SO_4 that are respectively formed for reaction of SO_2 and NO_2 with the water. These acid waters in contact with the mortars and concretes give place to the formation of calcium nitrates, sulphates, bicarbonates, etc. Some of these salts are highly soluble and easily leached.

Among the gassy atmospherical pollutants the most dangerous one is SO_2 while the nitrogen oxides were generally considered, for a long time ago, no important concerning its aggressive effect. However, it has been recently proven the strong synergy effect produced by SO_2 and NO_2 when they are together:

$$SO_2 + NO_2 + H_2O \text{------>} H_2SO_4 + NO$$

The degree of interaction between atmospheric SO_2 and the mortars binder is a complex factor very difficult to be determined, as there exist a lot of variables affecting that process and influencing it at different levels (the concentration of the gas in the atmosphere, the direction of the wind, the intensity of the rain, etc). Concerning the effect of SO_2 on the mortar, this is a function of the capacity of self protection of said material (nature of the binder, microstructure, porosity, permeability, etc.).

In general, it is accepted that the interaction mechanisms between atmospheric SO_2 and building materials take place through very well known processes of dry deposition and wet deposition (acid rain).

The most recent investigations are those carried out using climatic simulation chambers and analysing the effect of the dry and the wet deposition. Martinez-Ramirez et al. reports that in the case of the dry deposition of SO_2, the rate of reaction between the lime or hydraulic mortar components and the atmospheric gases increases attending the following order:

$$SO_2 < SO_2 + O_3 < SO_2 + H_2O < SO_2 + O_3 + H_2O$$

The chemical reaction of SO_2 with the cement mortar components in presence of water and an oxidant element is 35 times faster than in absence of those elements; while it is two order of magnitude quicker if the reaction takes place between SO_2 and lime mortar phases. This author also shows that for mortars exposed to a polluted environment, the rate of conversion of SO_2 to sulphate increases when the binder/water ratio of mortars decreases. In the case of the acid rain the increase of the water/cement ratio involves the increase of the gypsum formation on the surface of the affected specimens. Additionally, the author indicates that the dry deposition of SO_2 generates a low proportion of SO_4^{2-}, meanwhile when humidity conditions are appropriated, SO_4^{2-} is formed in large amounts.

It is commonly accepted that gypsum is the only stable compound formed in the mortar-SO_2 interaction even when laboratory tests have shown that some sulphated salts (very soluble or unstable ones) can also be found. The produced gypsum is a consequence of the oxidation/hydration of SO_2 and the later interaction of the sulphuric acid with the $CaCO_3$ in the substrate.

Zappia et al. through climatic chamber experiments using lime, lime plus pozzolana and cement mortars, confirms that SO_2 - mortar interaction occurs following two mechanisms: a) Formation of $CaSO_3 \cdot 0.5H_2O$ followed by its oxidation into sulphate and b) direct formation of sulphate. The authors indicate that the amount of sulphate and sulphite formed depends on the properties and on the physical and chemical characteristics of the tested mortar and it is independent on the $CaCO_3$ content.

In summary, although this subject has not been sufficiently studied, most of the authors have concluded that gypsum is the only stable salt formed during the interaction of SO_2 with hydraulic mortars or concrete. Other authors have recently explored the possibility of formation of Thaumasite and Ettringite in hydraulic mortars when they are exposed to an atmosphere containing SO_2. Thaumasite formation process in carbonated hydraulic mortars due to the interaction of the material with SO_2 at 5ºC, has been reproduced in hydraulic lime and cement mortar samples. Gypsum is the first product formed as a result of the interaction. Subsequently, gypsum reacts with calcium carbonate and C-S-H gel giving place to thaumasite. However sulphur dioxide gives rise to the formation of syngenite $CaK_2(SO_4)_2H_2O$, as the first and main phase formed by sulphation of lime-pozzolan mortars, which decompose along test.

Blanco-Varela et al. tried also to reproduce ettringite formation in hydraulic mortars (lime and lime plus pozzolan ones) due SO_2-mortar interaction. They proved that all of the tested mortars reacted with SO_2 and also that the sulphation process occurring on hydraulic mortars depended on the composition of the binder and on the total porosity. No gypsum crystals were observed by SEM after 12 months exposure, although chemical analyses indicated that sulphation occurred.

Sulphation of mortars mainly produces insoluble S-species (surely ettringite), while the amount of soluble S-species is the lowest. In all of the exposed samples, the soluble S-species were found in form of sulphites and sulphates. The presence of sulphite indicates that, in addition to the direct formation of sulphate, sulphite is an intermediate product in the sulphation process, also occurring by oxidation/hydration of the dry deposition of SO_2.

4.3 Crystallisation of soluble salts

The crystallisation of soluble salts in the porous system of the mortars frequently produces deterioration. Salts are produced from the ions that water have extracted from altered rocks, floors, mortars, concretes, bricks, etc. The aerosols of marine environment and atmospheric pollutants of industrial or urban environment, contribute to the deposition of salts in those mentioned materials. The metabolism of alive organisms can also be the source of some ions.

Given the porous nature of building materials, the ions penetrate and circulate through them as diluted solutions. A salt will crystallise when the water evaporates and the activity of ions in the solution overcomes that of saturation; but also when the relative humidity of the atmosphere in the surroundings of the material is inferior to that of equilibrium of a saturated solution of this salt. In this way, in a porous system containing accumulated salts, they will crystallise and they will be dissolved again depending on the relative humidity of the air.

Lime mortars and lime and pozzolan mortars, are in general quite porous and permeable materials, consequently they admit a considerable amount of solution in the porous system and they facilitate the evaporation process. It is deduced therefore that mortars are weak materials susceptible of deteriorating for crystallisation of salts. Hydraulic lime mortars and cement mortars are much less porous and permeable than lime and lime plus pozzolan mortars (specially if the former ones were submitted to a good curing process), then the volume of liquid circulating through them and the access of soluble salts are inferior than in these later materials.

On the other hand, the point where the crystallisation takes place is determined by a dynamic balance between the rate of evaporation of water from the surface and the rate of access of the liquid to this point.

If the access rate of the liquid to the surface of the material is a slightly superior to that of evaporation, then the salt crystallisation takes place on the surface giving place to the characteristic efflorescences which are not harmful but are indicating that in another point an internal crystallisation is going on. If the rate of migration of the liquid from the inner porous system of the material till the surface is not superior than the evaporation rate, then a fair dry area will be developed under the surface. The solid crystals will precipitate inside the material (in the interface among the dries off areas and humid areas), giving place to flakes, bladders... etc. Finally if the rate of access of the liquid is slow, regarding that of evaporation, the deposits gather inside the material and no superficial deterioration is observed; however successive cycles of crystallisation-dissolution can mechanically destroy the mortar.

During the crystallisation process high pressures are generated due to the growth of the crystals and due to its hydration. The destructive effect depends both on the mechanical characteristics and on the porous structure of the material.

The higher the mechanical strength, the higher the resistance to crystallisation pressures. In this sense it is evident that cement mortars are stronger materials than lime or lime and pozzolan mortars and therefore they will be less susceptible of deterioration.

In turn the crystallisation pressure is inversely related with the radius of the pores in such a way that materials with high volume of small pores will be submitted to very intense crystallisation pressures capable of destroying the material. Lime and lime and pozzolan mortars, in general, present higher porosity and pore size than those of cement and hydraulic lime mortars; then the internal pressure due to salt crystallisation is not a very important alteration factor for lime and lime plus pozzolan mortars.

4.4 Effect of the freeze-thaw cycles

The increase of specific volume (9%) that takes place in the water when passing from liquid to ice, generates pressures in the pore walls of the mortars that can produce its cracking and breaking. Mortars are fragile against the action of ice (especially if they develope low mechanical strength, if its coefficient of saturation of water is high and also if they have hogh total porosity with small pore size. Lime and lime and pozzolan mortars are much less resistant to freeze-thaw processes, than hydraulic limes and portland cement mortars.

4.5 Expansive reactions

Hydration of CaO and MgO

When the slaking process of lime is not enough intense, the final product could contain some crystalline *CaO and MgO* (magnesium coming from dolomites). Also hydraulic lime and portland cement can contain this crystallised oxides (as a consequences of bad dosages, incomplete clinkerization, etc). The reactions of hydration of MgO and CaO (to give portlandite and brucite) are slow and expansive and they can cause cracking problems and even the break down of mortars or hardened concretes.

Ettringite formation

Ettringite is formed as consequence of the chemical reaction between the sulphates and aluminates usually present in the hydration products of portland cement. Ettringite crystallisation involves a high increment of volume. But mostly, this takes place during the first stages of hydration, before the hardening of the cement slurry. In these initial stages the system is in plastic state and it is able to absorb that increment of volume. However, if ettringite is formed when the system is hardened, then an expansive phenomenon can take place with mortar disintegration (cracking and loss of mass).

The damage produced in cement mortars due to the ettringite formation depends on different factors: a) composition of the cement (aluminates content), b) amount and origin of sulphates, c) quality of the mortar ... The best way to increase the resistance to the sulphate attack is the reduction of the porosity of the system but it is also important the modification of the chemical composition of the cement in order to reduce reduction the C_3A content.

Thaumasite formation

Even though it is obvious that formation of thaumasite in portland-cement mortars cause important damage, there is no general agreement in the literature on the mechanism that causes deterioration.

Thus, according to some authors, thaumasite formation can be the result of different mechanisms: it can be the consequence of the evolution of ettringite by incorporating Si^{4+} in its structure, substituting Al^{3+} ions within the columns $Ca_6[Al(OH)_6]_2$ and the interstitial replacement of $(SO_4)_3 \cdot 2H_2O$ by $(SO_4)_2(CO_3)_2$. According to others scientists thaumasite can be the result of the interaction of sulfates and carbonates (present in the aqueous phase of the concrete) with C-S-H gel. Both mechanisms might simultaneously develop within the same material.

According to some authors the destructive effect of thaumasite formation is due to expansion mechanisms very similar to those described for ettringite formation, while according to others thaumasite formation involves the destruction of C-S-H gel and therefore the decohesion of the material.

4.6 Volume changes due to thermal variations or water presence

The temperature variations can produce dilations and contractions in the material and so creating tensions. The rendering of walls with several layers of renders of different characteristics was an usual practice in the past and it still is at present. Frequently this different materials possess different thermal or hygric expansion coefficients. Under certain circumstances tensions can take place in the materials, giving place to cracking and breaking down of the layers.

Macías et al. determined the coefficients of thermal and hygric expansion of samples of a render taken from the south facade of Toledo's Cathedral. The samples were formed by a microcrystalline dolomite with a low content in calcite rendered with a gypsum mortar and finally painted with a lime mortar. The value of the thermal coefficient of gypsum mortar at 50ºC was 10 times higher that that of the dolomitic stone and 100 times higher to that of the limestone. In this turn both gypsum mortar and dolomitic stone contracted when becoming wet, while the lime mortar layer did not experiment any modifications in its volume. The differences of both dilation coefficients justified the state of deterioration of the wall.

4.7 Deterioration due to biological causes

The bio-deterioration is the process of destruction of a material due to alive organisms or the products of its metabolism. The attack of natural materials through biochemical and biological processes as well as the influence that micro-organisms have in the formation of ground is well-known. The process of colonisation of a mortar is favoured by its characteristics (porosity, composition and roughness). These characteristics favour the retention of water in the material and the consequent growth of algae and ciano-bacteria. These last ones form a superficial bio-layer, similar to a mucous, favouring the retention of sand and powder and being an appropriate substratum for the growth of other alive organisms that can even promote the growth of superior plants.

To avoid the colonisation and the corresponding damage, some treatments with biocide products are used.

In the bibliography there are data on the bio-deterioration of mortars of the Mosaics of Italica and other Spanish archeological sites (Baelo Claudia, Medina Azahara, etc). One of the most interesting results of the STEP project CT90-0107 was the development of a lime mortar with biocide properties. In this mortar the biocide is adsorbed in sepiolite avoiding a quick leaching and increasing the effectiveness.

5. REPAIRING MORTARS AND CONSOLIDATIÓN TREATMENTS

5.1 Repairing mortars

Materials used in the repair of buildings (especially those belonging to the Cultural Heritage) should have one essential requirement: not to accelerate deterioration of the adjacent materials. The Symposium held at Rome in 1981 recommended that restoration mortars should be prepared taking into account the characteristics of the materials on which to be applied or to replace.

Numerous studies have been carried having the objective of determining the way at which the problem of repair should be approached; the errors made in the past (causing very serious damages in the Cultural Heritage) have stimulated these kind of investigations. In the previously mentioned Symposium of Rome the following main aspects were pointed out to keep in mind in the mortars used for restoration purposes:

1. Research should be carried out in parallel on both new and ancient mortars.
2. Characterisation of mortars from different points of view: physical, chemical, mineralogical, etc.
3. Methods for measuring the fundamental parameters should be standardised.

In 1981, for the first time, a tentative list of the characteristics of an ideal mortar for restoration was presented. These characteristics were:

i) Easy workability.

ii) Rapid and reliable setting in both dry and wet environments

iii) Slow shrinking during setting

iv) Mechanical and thermal characteristics similar to those of the mansory components (natural stones, bricks, etc.).

v) Soluble salts content as low as possible.

Rossi-Dorian indicated that repair mortars should be specifically designed for each particular case, and that some previous studies allowing to determine the mortar strength, its innocuous character, and the compatibility with the basic material should be carried out.

Lime pozzolan mortars have, in general, higher porosity and lower mechanical strength than Portland cement mortars. It makes lime pozzolan mortars to have better characteristics than other binders with respect to the compatibility with some building materials. However, from the mineralogical and chemical point of view both types of mortars (lime pozzolan and Portland cement) have a common component, which is an amorphous calcium silicate hydrate. Lime pozzolan mortars may even have an especially reactive alumina. Consequently, lime pozzolan mortars (the same as in Portland cement) may undergo sulphate attack and so producing gypsum, ettringite, thaumasite etc., and modifying its properties and characteristics.

An important characteristic of the repair mortars is determined by the colour. The white colour is usually, for aesthetics, very appreciated for this type of materials. Unfortunately, the colour of the white portland cement is due to the almost total absence of ferrites in the composition. It forces to white cement producers to increase the aluminates content, and it makes white cement to be specially sensitive to the attack of the sulfates. Blanco et al have developed a white portland cement resistant to the sulphates and the sea water, eliminating (almost totally) the aluminate phases of this cement and substituting them for phases that incorporate CaF_2.

5.2 Consolidants and water repelents products

Consolidants are products that have been used from the antiquity; however water-repellents are being used from the second half of the XXth century. The application of these type of products has been carried out fundamentally on stony materials in the field of the Conservation of the Cultural Heritage. There exist in the bibliography a lot of works explaining the way at which these products confer especific characteristics to the stony materials, as well as the modifications induced by them in the mechanical and micro-structural properties of the natural rocks (porosity and of pore size distribution, permeability to the water, variations of colour, etc).

Consolidation is understood as the application of a material that when penetrating through the pore system of the stone, improves its cohesion, and the mechanical characteristics and also the adhesion of the altered layers to the non altered substratum. The main consolidation methods are basically based on three processes:

1. Substitution of those constituents of the substratum that are open to the atmospheric attack, and precipitation of chemically resistant materials (into the pore system), in order to consolidate the grains.
2. Silica precipitation (proceeding from silicone esters) in the pores of the stone.
3. Impregnation of the stone with organic polymers in order to cement the altered grains and to waterproof and protect the stone from chemical, biological,..., attacks.

The main characteristics demanded to the consolidants are: consolidant value, depth of penetration, modification of the porosity, compatibility with the stony support ....

Consolidants have different chemical composition and they can be classified in the following way:

1. Inorganic consolidants. They have been used from the antiquity. Basically they are: $Ba(OH)_2$; $Ca(OH)_2$; alkaline silicates and some fluorine compounds (fluo-silicates).
2. Organo-silicic consolidants or alcoxi-silanes. Its action as consolidants consist on the formation of a structure similar to that of the silica. They are classified under the following nomenclature: alkyl-silanes, alcoxi-silanes, alkyl-alcoxi-silanes, siliconates, poly-alkyl-alcoxisilanes and alkyl-aril poly-siloxanes.
3. Organic consolidant produts or synthetic polymers. They are the products more extensively used from the sixties. The main organic consolidants are the waxes, acrylic polymers, epoxy resins, resins of estirene polyester, vinyl polymers, polyuretans, nylon, etc.

In turn the water-repellent products that are applied with the main purpose of avoiding water to get in contact with the construction materials, and therefore to prevent deterioration.

The properties that an effective water-repellent should have are: No permeability to water, minimum influence on the optical properties of the material on which is applied, no modification of the appearance, stability against the chemical agents, permeability to the water vapour, good adhesion to the construction material, good capacity of impregnation, enough penetration depth and easines of application.

When a water-repellent product is going to be applied, it is important to keep in mind the following aspects:

Product choice. It should resist the pH of the mortars.

- Product concentration. It usually will oscillate between 2.5 and 5%.
- Application method. It is generally applied with brush or crusher.

- Penetration depth. In porous materials it has been observed that it can reach up to 20 mm.
- Control of the treatment. Monitorization of the efficiency of the product with the time and influence of the environmental conditions.

The water-repellent products more usually used at the present can be classified as follows:

1. Siliconates. These compounds have the general formula R-Si-O_3H_2Me, where R is a alkyl radical and Me is an alkaline metal. They are soluble in water.
2. Organo-silicic products. Among the water-repellent compounds, the organo-silicic ones are those showing the best advantages. They form very thin layers characterized by an excellent waterproof property as well as durability and resistance. Those trade products usually called *silicones* belong to three groups:
   - Monomers. They are organo-silicic molecules of small size that give place to a hydrolisis and polycondensation reaction.
   - Oligomers. Due to their composition they can be placed between monomers and polymers. Their partially polymerised molecules, react on the materials in the same way that the sylanes do: forming silicone resins.
   - Polymers. They are similar products to the previous ones. They are applied entirely polymerised. The waterproof action is obtained by adhesion to the stone of molecules with hydrophobic groups

Water is an agent of deterioration involved in a lot of physical (salt crystalisation, hygric expansion, freezing etc), chemical (disolution, SO_2, NO_x interactions etc.) or biological (bacteria, fungi etc.)processes. Recently it was shown that mortars are very bioreceptive materials when compared with limestone or sandstone, being easily colonized by bacteria, fungi and lichens. Microorganisms not only attack building materials but also chemicals products used for their conservation. All these phenomena have a common element: **water**. This is the reason why, for last 20-30 years, the use of biocides and water-repellent products have often been applied in order to protect our Cultural Heritage. There is a wide diversity of water-repellents; among them, probably silicones are the most frequently used.

In addition, the application of water-repellent products provides to the treated materials with a higher resistance towards aggressive agents. Accordingly, the behavior of different materials treated with silicones against freeze-thaw cycles, salt crystallization, temperature changes, etc. has been evaluated in the bibliography. The main deteriorating element of water-repellent products is ultraviolet radiation, which acts on the hydrophobic part of silicones.

At present more durable silicones are being designed in order to improve their resistance against UV radiation. In the ENV-4-CT-97-0707 project, four new formulation (two silicones and two mixes silicones + biocide) have been developed. The new formulations were characterized by FTIR, ^{29}Si RMNMAS, Raman Spectroscopy before and after a laboratory reticulation process as well as after their application on lime and lime-pozzolan mortar surfaces.

Modification of properties of lime an lime-pozzolan mortars (color, hydro-repellence degree, porosity, etc.) due to the application of the new formulations as well as durable behavior of such a mortars (UV stability, salt crystallisation, freeze-thaw and wet-dry cycles, etc.) have been also studied.

Authors concluded that water repellence reached by lime mortars and lime-pozzolan mortars is excellent after the chemical treatments. Porosity decreases in both types of mortars due to the application of chemical treatments, although in lime mortar, this descent is higher when chemicals do not contain biocide. Treatments mainly make the volume of pores sized between 1 and 0.01 μm to decrease. The saturation coefficient of mortars decreases with all treatments, but it is more considerable in lime mortars. Application of treatments does not provide mortars with remarkable color changes. In both type of mortars, damage from aggressive agents are evidenced at the interface (treatment/mortar): the 2 mm superficial layer which correspond to the treatment depth, gets loose and fall down. Treatments are not attacked by ultraviolet radiation after a 2000 hours exposure.

6. SOME IDEAS ON FUTURE RESEARCH TOPICS RELATED WITH MORTARS AT THE HERITAGE

1. Cleaning methods for the elimination of salts.
2. Interaction of atmospheric pollutants with mortars. Influence of mortar characteristics on the velocity of interaction.
3. Mechanisms of formation of expansive products in mortars (ettringite and thaumasite).
4. Repairing mortars: development of new formulations. Use of organic admixtures. Correlationship between rheological properties of mortars and mechanical and microstructural characteristics.
5. Development of analytical and instrumental methods that permit a correct evaluation of conservation treatments. Accelerated ageing tests. Standard methods.
6. Validation of the EDAMM identification mortar method through an inter-laboratory test. Aplication of the EDAMM methodology to a high enough number of samples permitting to establish the method limitations.

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