Mechanical properties of masonry with environmental degradation

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ABSTRACT:

The exposition to environmental actions produces several degradation patterns in masonry textures, mainly as a function of the chemical reactivity of the masonry materials. Blistering of the bricks and powdering of the mortar can reduce locally the thickness of structural elements and introduce eccentricity of the thrust path.

In the paper, the results of a preliminary analysis of typical degradation and repair situations is presented. By comparing existing experimental data with site data acquisitions it is possible to link the main data of salt concentration, humidity and temperature ambient variation and rate of pulverization of brick faces and mortar decay. The role of initial porosity is pointed out and some data on the increase in porosity due to salt attack are useful to define an analytical relationship among parameters.

Finally, two examples of site investigations in Venice and Ancona sea front zones are presented in order to highlight the role of rheological properties and weather conditions as driving factors of the observed decay patterns.

Keywords: Masonry, degradation, mechanical properties, salt attack, rehabilitation

NOTATION

C-A-H	hydrated calcium aluminates;
C-S-H	hydrated calcium silicates;
RH	relative humidity;
T	temperature;
p	porosity;
ρ_p	radius of pores;
f_{cm}	compressive strength of mortar;
E_m	Elastic modulus of mortar;
Δm	mass loss;
f_{cb}	compressive strength of brick;
e_V	void content;
δ_{dep}	annual stock factor;
$Day_{fav,\%}$	annual percentage of days with favourable condition for dust or salt spray deposition;
$Day_{unf,\%}$	annual percentage of days with unfavourable condition for depositions;
C^{year}_{cl}	stocked salt, p.p.m. for a time slot of one year;
C^{year}_{so4}	stocked dry deposition of SO_4^{2-}, p.p.m. for a time slot of one year;
PM10	air pollution particles with diameter smaller than 10 μm;

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D_{mortar} width loss in mortar due to weathering (millimetres);
D_{brick} brick thickness converted in powder due to salt action (millimetres).

1 INTRODUCTION

The structural skeleton of historic buildings is, for the most part, composed of clay or stone bricks or blocks bonded with mortar to compose a large variety of textures. The structural performances of masonry elements have evolved during time as the technical knowledge and the materials' science.
In historic ages, several different recipes for the bricks bonding agent were developed and employed: gypsum has been the first compound to be used (2500 B.C.), followed by lime mortar. Afterwards, (900 B.C.), thanks to Phoenicians, the very first hydraulic mortar was discovered by mixing lime, sand and stone slivers. Roman and Greece construction masters obtained later the same result by mixing lime mortar and pozzolanic sand coming from volcanic sites. The hydraulic mortar with fully hydration hardening was set by Andrea Palladio (1570), but a fully reliable bonding compound with consistent strength was obtained only in the 18th century. In the 19th century, with the preparation of Portland cement, different mortar types have been defined by appropriately mixing cement, lime, sand and water. In recent times special additives were prepared in order to modify the rheologic properties of special mortars.

The availability of ovens with even larger temperature capabilities, has led to an increase of hardness and strength of bricks and clinker products for cement production [1].

Therefore, it is important to point out that in the history the components of the masonry structures varied considerably in terms of physical and mechanical properties leading to a wide spectrum of results in terms of durability of the masonry.

Leaving out structural collapses, the construction material deterioration is driven by chemical and physical processes [2] specific of the different components.

2 MORTAR DETERIORATION BY CHEMICAL CAUSES

2.1. Damage on hydraulic mortar

Mortars based on pozzolanic components (either natural or artificial) and hydraulic cements are both characterised by the formation during hardening of two important by products of the mixture: calcium hydro aluminates and silicates, which are responsible in turn of the medium term and long term resistance of the paste. As is well known [2], they suffer both of the sulphate attack by SO_4^{2-} ion, which is capable to convert these phases in reduced strength salt crystals. These last are dissoluted by water and conveyed as sulphate products into the mortar giving rise to the chemical reactions acting on C-A-H and C-S-H macro molecules.

The principal sources of sulphate ions are pyrite contaminated clay bricks, capillary rising water, and SO_2 deposits due to air pollution. In a first phase sulphate ions interact with water and calcium anhydrite in the mortar resulting in gypsum formation; then, gypsum enters in the C-A-H and C-S-H decomposition leading to ettringite and thaumasite formation.

Ettringite is a non soluble salt with large volume increase due to wetting, and therefore is responsible of cracks in the mortar joints and swelling (rendering mortars), but in general the decay of the alluminate phase do not involve a large strength reduction of the mortar. High concentrations of sulphate ions not converted by calcium anhydrite lead to a direct attack to C-S-H phase (resisting skeleton of the paste), with a noticeable reduction of the mechanical properties of the mortar.

The simultaneous diffusion of gypsum and calcium carbonate (as fine fraction), gives start to thaumasite formation, an insoluble salt. This reaction is not acceptable at all, since as a consequence the complete disruption of the material skeleton is obtained. In general the two salts appear in subsequent deterioration stages with ettringite preceding thaumasite formation; temperatures in between 0°C and 10°C accelerate the decay process, but humidity in excess of 95% is necessary to complete the path to thaumasite formation. Figure 1 shows the schematic damage patterns resulting to a sulphate ion exposition of a masonry solid volume.

Sabbioni [3][4] completed a comparison study on cement and lime mortars by highlighting a similar sensitivity of the two compounds to degradation by air pollution and salt formation, although the natural pozzolan sand can reduce the reaction speed.

The thaumasite formation is a peculiar risk mainly for the cement mortars because the calcium carbonate of that mixture is in a very reactive fine dispersion form. This fact is supported by experimental evidences of historic constructions in wet zones experiencing cold winter and high air pollution content, as Venezia and Ancona in Italy. These sites show a very high decay rate of the cement plasters arriving to fall even in few years after hardening [5].

2.2. Damage of lime mortar

Calcium carbonate, the final by product of the oxidation of air set mortar is in essence subject of the sulphate attack; it is however to point out the fundamental role of the sulphate crust deposition of the polluted atmosphere. The combination of powder, humidity and ozone is an aggressive fast converter of the chemical calcium into gypsum, as illustrated by Martinez – Ramirez [6].

In Figure 1.b is presented a schematic representation of masonry wall damage resulting from this type of chemical reaction.

3 PHYSICAL PROCESS LEADING TO DECAY PHENOMENA ON MASONRY

The results of freeze – thaw cycles on geo materials were known also in the past and therefore in very important works materials with low porosity were provided. The vulnerability to salt attack is however more subtle with relation to porosity. In fact, sea front masonry structures suffer of the pulverization of the wall face; this slow but unavoidable process is caused by the crystallization of the salt brought by the wet breeze on the wall face. In each crystallization cycle the external pores are filled and expanded forming a detaching powder which has no immediate evidence. However, the superposition of a large number of cycles in a long duration can result in a total disruption of either the bricks or the mortar.

Even low porosity natural geo materials can suffer of pulverization; by example, Theoulakis and Moropoulou [9][10] discuss in detail the aging effect of the salt breeze impelling on the medieval masonry belt of the city of Rodi, composed of bio calcarenite stones.

Even environmental modifications can draw a salt attack to masonry materials. Lubelli [11] discusses the deterioration of masonry walls near sea shore in Holland. In this particular case, a number of sea floods on low lands salted the underground water streams. The capillary rise of near surface water led the dissoluted salt into the masonry walls, even in absence of contact with sea breeze. The case of Venice is the most important in the conservation of cultural heritage. A detailed analysis of the Venice major buildings has shown the ability and know–how of Venetian workmanship in avoiding capillary rise from buildings' foundations immersed in the lagoon water. In particular the knowledge of the role of the stone porosity led Venetians to select Istria's stone to build foundations and wall basements.
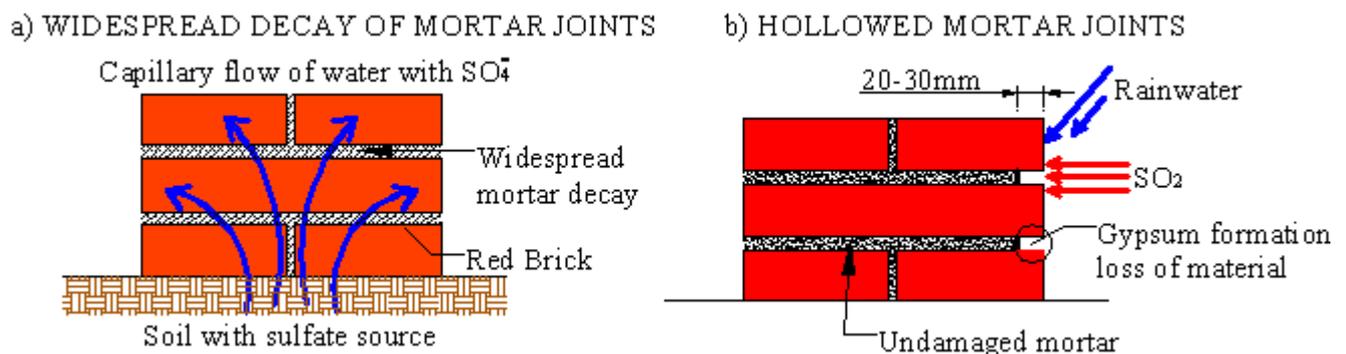

Figure 1.   Examples of mortar decay pattern as a function of sulphate ions source

Over this shield, masonry was composed with low porosity (high temperature cooked) bricks up to one meter above the ground level, and continuing the construction with cheaper porous bricks. In the meanwhile however, the sea level and the configuration of the lagoon have changed, and Venice flooding by the tidal growth ("acqua alta" in Italian), has increased the rate and the raised height. This outcome has nullified the Venetians' construction system care and increased dramatically the deterioration rate [12], so that the MOSE closing doors system for the lagoon embankment has been planned a long time ago (even not finished yet).

In Figure 2 some pictures related to the discussed degradation phenomena are presented: left, the Castrocaro fortress undergoes to heavy brick pulverization. Centre, the plaster is detached by salt crystallization in the interface behind plaster due to capillary rise. Right, sodium sulphate spots are present in the surface of bricks in a Venetian wall due to wetting and evaporation of flooding lagoon water.

3.1. Review of salt crystallization in porous materials

The formation of crystals inside pores of a brittle material can produce large pressures on the pore surfaces with micro cracks initiation and sliver detachment. When stone or clay bricks are the concern, the most dangerous salt types are sodium sulphate or chloride [9][11][12][13]; the problem is well studied, despite not easy to explain at a micromechanical level. The crystal form is function of temperature, relative humidity and evaporation rate, but due to irregular support where crystal deployment begins, irregular nucleation takes place with poor correlation to phase changes occurring near thermodynamic equilibrium as in a controlled experiment [9][14]. Obtained field data in any case suggest that pressures are generated by crystal growth and no effect is produced by solid salt hydration. Correns' theory [10] predicts that the pressure generated by the salt crystallization is directly proportional to the ratio of the solute concentration in the pore and the saturation concentration at a given temperature and evaporation rate.

Thus particularly dangerous situations happen when, due to fast evaporation, crystals are formed inside small pores with supersaturated concentrations of solute [14], [10]. Once the crystallization begins, the only mechanical property acting against internal pore pressure in order to avoid micro cracks formation, is the traction resistance of the bricks.

The experimental correlation of the analytical variables is a difficult task, due to the micrometric scale and the statistical variability of the process. It appears that a macroscopic evaluation of the damage as a function of the salt concentration is a more effective investigation tool, able to explain the observed behaviour in most cases. Through the phenomenological analysis of bricks and mortars subjected to salt weathering, the critical threshold of the major parameters is identified; among the others, the fraction of pores below a certain diameter plays a crucial role.

In general, high void volumes are necessary to absorb a sufficiently weight of diluted salt; as a consequence, a pore size distribution able to encompass high salt sorption and small pore diameters yields a fast and diffused damage.

Figure 2.   Examples masonry walls decay induced by salt weathering

The literature containing experimental and site data on the vulnerability of masonry materials to different exposure conditions allow to establish a defined framework for the durability analysis.

As a result, the crystallization of sodium chloride is possible at temperatures larger than 20°C even with a relative humidity *RH* smaller than 75%, while for the sodium sulphate, the very dangerous form thenardite [14], is formed only around *T*=32°C but with *RH* less than 40%. The wind pressure is capable to activate an evaporation front several millimetres inside the solid material; in this case material pulverization can be substituted by blistering or even sliver detachment.

3.2. Mortars vulnerability to salt weathering

The following data are gathered from different sources and encompass the work of a number of different research teams [7][8][15]. By assuming a paradigmatic case with sand / cement ratio of 3:1, in Table 1 the hardened paste mechanical properties of various mortars types are summarised.

Table 1. Mortars' properties

Mix	p %	ρ_p (μm)	f_{cm} (N/mm^2)	E_m (N/mm^2)
Cement	16.68	0.01	37.0	20000
Lime	29.88	0.21	4.12	7052
Air set	40.15	2.53	1.95	2430

In Figure 3 the pore size distribution and volume are presented for a practical range of mortar compounds and construction ages. The proposed diagrams point out noticeable differences of the rheological properties of the mortars.

The different sensitivity of mixture to salt crystallization is clearly depicted by an experimental study of Maravelaki [15]; through measurements of mass loss after 30 cycles of sodium chloride exposition, it is found that air set mortar has a Δm = 6% decrease while lime and cement hydraulic mortars have a swelling larger than 3%.

The sensitivity of air set mortar is induced by a number of micro pores working as reservoir for the critical ones with pore diameter less than 0.1 μm approximately. In hydraulic mortar, the lack of small micro pores and large ratio of diameters ρ_p larger than 0.2 μm gives to the paste the highest deterioration resistance. The presented results confirm the damage patterns of Figure 2, where the masonry courses made with highly porous hydraulic mortar in historical constructions do not show any pulverization effect.

3.3. Brick vulnerability to salt weathering

A general framework discussing brick vulnerability to salt weathering is presented in [1][12][13]on the basis of a number of experimental evidences. Larsen and Nielsen [13] measured the pore size distribution of medieval and modern bricks by considering both undamaged and damaged units (Figure 3). In general, we define as bricks with high risk of deterioration those characterized by a large void content (e_V > 40%) and a large amount of pores with diameter in the range ρ_p = 0.2 ÷ 2 μm (Elert et Al. [1]). In experimental tests, units of this class posed in a saline environment, showed a mass loss in the range Δm = 6% ÷ 15%.

In Figure 3 the results of the available tests are put in comparison, with a general agreement on the observed behaviour. In particular the range of critical pore diameters defined in the laboratory study

confirm the field measurement of mass loss for exposed walls in Holland. Both studies report an average porosity $p > 30\%$. Void volumes beyond this threshold can be interpreted as ongoing attack.

Finally, it is to mention that pulverization of the bricks pertaining to high risk class in terms of reduction of wall thickness per year is in direct proportionality to the duration of the temporal window in which temperature and humidity enter in the critical ranges.

The salt attack due to contaminated water capillary rise is discussed firstly, by using data from a Venice building which is a paradigmatic example; as shown in Figure 2, the worst outcome onto the wall surface is confined in the wall strip in which the water head is oscillating during time (1.2 ± 0.2 m above ground). Then, the weathering due to marine spray exposition is explained by using evidences from a decay survey of Vanvitelli's mole in Ancona [16]; for this peculiar case, the effects of climate changes and increase in air contained contaminant chemical species are investigated in detail.

3.4. Residual mechanical properties of the brickworks in Rio piccolo del Legname

Venice is taken as a fundamental case of study with relation to the importance of its architectural heritage and the presence of both key factors promoting the decay process: air pollution, (the city is nearest to industrial zone of Marghera), and salt water. The degradation patterns of some historical masonry buildings and the inefficiency of restoration works (sometimes out of service in only few years due to incompatibility), are a proof of the importance of physical and chemical processes discussed before.

In Figure 4, left, is summarized a study of Bakolas et Al. [12] in which a detailed monitoring (porosity & salt content) of an ancient Venetian wall is presented. The porosity distribution along the vertical direction points out the ability of ancient mason constructors who graded bricks with diminishing solidity with the elevation as in Figure 4 (dashed line).

The growth in tidal condition in the venetian lagoon has caused the increase of the water table with larger water pressure on foundations. As a consequence the capillary rise has jumped up to a new elevation (1.20 m) where bricks had an initially larger porosity ($p > 35\%$); at this height, the balance between rising and evaporating water leads to salt accumulation, promoting saturation and finally crystallization, so that the property decay is localised in two or three brick rows with rheological properties insufficient to withstand salt attack. Hence, in a short period, the porosity of this layer has grown by 17% due to salt crystallization.

Since brick low porosity is linked to high temperature and duration of the coking phase, it is easy by using data of Elert et Al. [1], to evaluate a relationship between porosity and compressive strength. The data reconstructed for the Venetian wall under examination are presented in Figure 4. The initial strength is defined by means of the initial porosity, while the strength decay is obtained as a proportion to the difference between initial and final porosity.

As a first suggestion, we can consider that the shear strength of walls during earthquakes and the out-of-plane resistance of the wall are function of the local masonry strength, and therefore this type of localised damage could be very detrimental to the overall seismic behaviour of the construction.
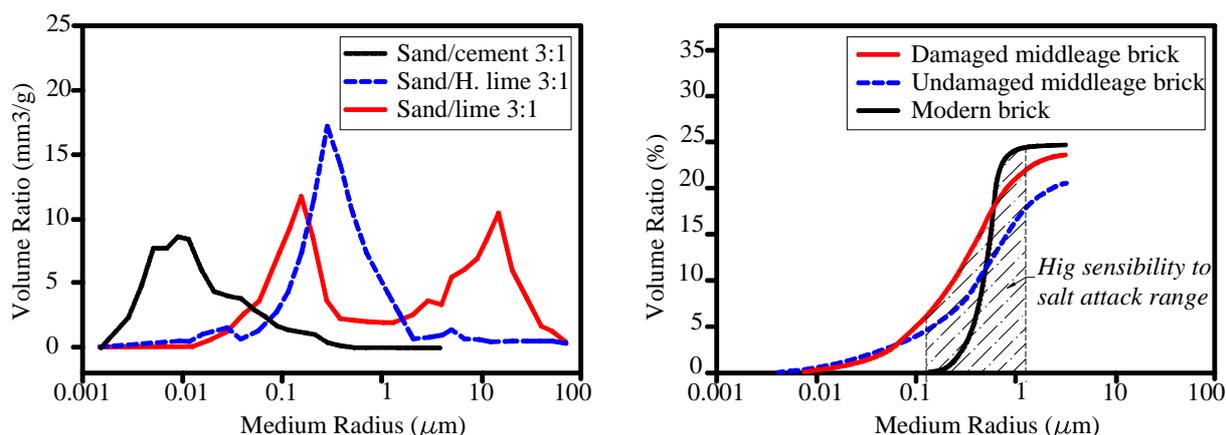
Figure 3. Pore size distributions for mortars [7] and bricks [13]

4 A CASE STUDY: WEATHERING ON THE VANVITELLI'S MOLE IN ANCONA

In the following, making use of an existing database of climatic parameters in Ancona, the frequency of environmental conditions bursting the decay phenomena of the Vanvitelli's brickwork is evaluated for the period occurring from the final construction stage to today. Tanks to this information, empirical laws for damage evaluation on mortar and brick are finally proposed.

This military building was erected in 1750 onto an artificial island in a strategic site inside the Ancona's harbour, by creating a very strong masonry fortress wall of clay brick units. The wide exposition to sea breeze and the high air contamination level of the harbour neighbourhood led in the Mole's life to an accelerating degradation of the construction materials. This trend obliged to deliver diffused interventions since 1860. At that time bricks already had falling layers and the mortar wythes showed losses and cavities.

In a thorough study based on x-raydiffaction completed in 1980 by Collepardi et Al. [16], the mortar composition along the depth was considered. The analysis results pointed out that the external 25 mm contained cement mortar but gypsum contaminant was present up to a depth of 100 mm. Moreover, the external zone in contact with cold air and carbon dioxide included also ettringite particles due to the presence of conditions sufficient to activate the gypsum conversion.

In Collepardi's work several zones lacking of mortar repair are listed, defining finally a mortar width average loss of nearly 20 mm. In 1930 however, a significant seismic shake did fall the degraded zones, which were subsequently thoroughly restored.

Again, in 1970 a further partial repair has been carried out on the most damaged zones; it can be concluded that time intervals in between subsequent intervention works are even shorter in the Mole's life span, which means that the conditions boosting the chemo – physical degradation are increasingly stronger during time.

The present study is aimed to explain the relationship between climatic factors as temperature T and relative humidity RH and the observed chemo – physical material degradation. Starting from the available data in the period 1973 – 2010 an extrapolation of the variables in the whole previous life span 1750 – 1973 is sought by using a linear regression. Then, the time windows with weather conditions favourable to salt crystallization and ettringite and thaumasite formation are listed.

Concerning average yearly temperature, the values range from 10°C in year 1750 to 13,3°C in 1980, with a sharp increase in 2009 up to 15,5°C. The trend in relative humidity is more complex, encompassing an increase from 73,5% during initial construction up to 80% in 1980, while a strong reduction as low as 72% is produced finally in 2009 due to global warming.

The observed trends allow the definition of the reference values for the examined sites; the mean temperature in the service life is $T_r = 12,9°C$, whereas the mean relative humidity is $RH_r = 79,68\%$.
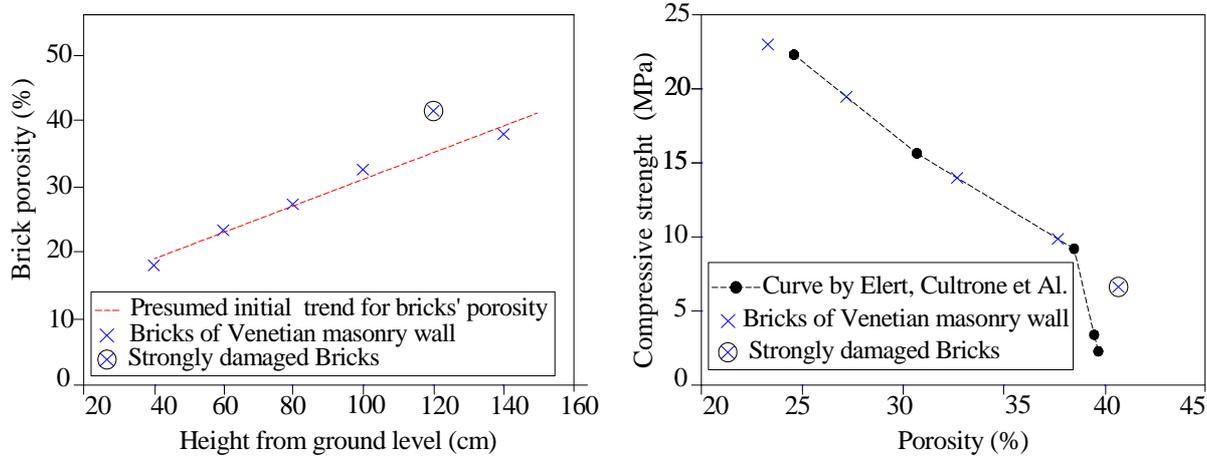
Figure 4. Study on ancient wall in Venice: pore size distribution, bricks compressive strength

The year 1980 is a turning point in the climatic evolution of Ancona. Through a fit of the meteorological data by a bilinear distribution (Figure 5.a), it is easily understood that the global warming is increasing the periods promoting salt crystallization while conversely ettringite formation is withstood. Regarding thaumasite, the formation conditions are not matched at all, and this is in close agreement with observations that no chemical evidence of its presence has been inferred in the latest surveys completed on the Mole.

Owing to define the time variant accumulation law of the salt on the Mole surface, the yearly deposition coefficient δ_{dep} is considered. This factor helps to take into account the number of raining days in which not only no salt deposit is added but also due to solubilisation some accumulated salt is lost by flooding water on wet walls.

From the gathered data, it is possible to state that raining days are almost constant along several years with an average value of 125 days per year, i.e. 35% of the running time window. A more empirical assumption concerns the salt removal capacity of falling rain; with some arbitrariness we assume that one raining day removes a two day deposit. Therefore we have:

$$\delta_{dep} = Day_{fav,\%} - 2Day_{unf,\%} = 100 - 2 \cdot 35 = 30 \tag{1}$$

The concentration increase of chloride crystals is defined by using (2) as a function of the ratios among average yearly temperature and humidity with the reference service life values on the site.

$$C_{cl}^{year} = \left(\alpha \frac{T}{T_r} \right) \cdot \left(\beta \frac{RH}{RH_r} \right) \cdot \delta_{dep} \tag{2}$$

The proposed relationship contains two scale factors α and β which can be determined by fitting the available chloride concentration measurements with the cited law. The proposed formula is a sort of parameterization of the site severity in terms of average aggressive conditions. By using an incremental time integration, the time varying chloride accumulation is obtained on the basis of the subsequent annual values.

$$C_{cl}^{i+1} = C_{cl}^{i-1} + C_{cl}^{year} \Delta t \tag{3}$$

The starting accumulated value in the erection period is fixed as 550 p.p.m. and the evolution is integrated without jumps until a major repair intervention. After one of these events, the very degraded portions are demolished and substituted, and therefore the accumulation starts again with an uncontaminated raw material. In the year 2008 the Urban Conservation Administration of the Ancona City completed a thorough survey of the Mole surfaces including also chloride

measurements. The final determined value was around 20000 p.p.m. [17]; by using the final tail of the accumulation integral curve the well approximated value of 20160 p.p.m. is computed.

The same reasoning chain can be applied to the sulphate ions SO_4^{2-} deposition induced by the dry powder accumulation coming from car exhaust gases. In this case a very important driving factor is the fraction of particles smaller than 10 μm. All Italian administrations use pollution control systems trying to contain PM10 fraction under a threshold able to protect the public health.

Once the average reference PM10 value is fixed to 34 μg/m³, the dry yearly deposit of SO_4^{2-} is computed by using eq. (4).

$$C_{so_4^{2-}}^{year} = \left(\mu \frac{PM10}{PM10_{ref}} \right) \cdot \delta_{dep}$$ (4)

Again, the amplification factor μ = 5 is obtained by a fit of existing data [17]. The incremental calculation runs as for the chloride computation; the concentration C_{SO4}^{2-} is defined for a given year through an integration starting in year 1900, in which pollution due to exhaust gases is thought to begin after birth of car industry.

Once the surface concentrations of aggressive ions are known, the reduction of the mortar and brick thickness can be evaluated by using a pollution dependent damage rule.

In case of ancient mortar with high pozzolanic content and low mechanical properties, we assume that both salt crystals and gypsum formation (repeatedly washed out by rain), promote a mass loss of the wall materials, which can be expressed in thickness reduction (5). On the contrary, for bricks, only the face deterioration due to sea breeze is considered (6).

$$D_{mortar}^{i+1} = D_{mortar}^{i} + \left[\left(\varepsilon \cdot Day_{fav,perc} \cdot C_{cl}^{i+1} \right) \left(\vartheta \cdot C_{SO_4^{2-}}^{i+1} \right) \right]$$ (5)

$$D_{brick}^{i+1} = D_{brick}^{i} + \left(\gamma \cdot Day_{fav,perc} \right) \cdot \Delta t$$ (6)

We assume ε = 0,0015 , θ = 0,0055 e γ = 1,7.

In Figure 5.b the obtained damage evolutions of the mortar are reported according to the preceding incremental rules. The computed values are compared to the experimental measured losses recorded in the service life, as collected in the historical documents, in the Collepardi [16] and Corinaldesi [17] surveys. Concerning the brick units, according to the presented thickness reduction law, a fallen down layer of 15 mm is estimated starting from the last overall intervention in 1970. This outcome is in fairly agreement with the measured average damage.
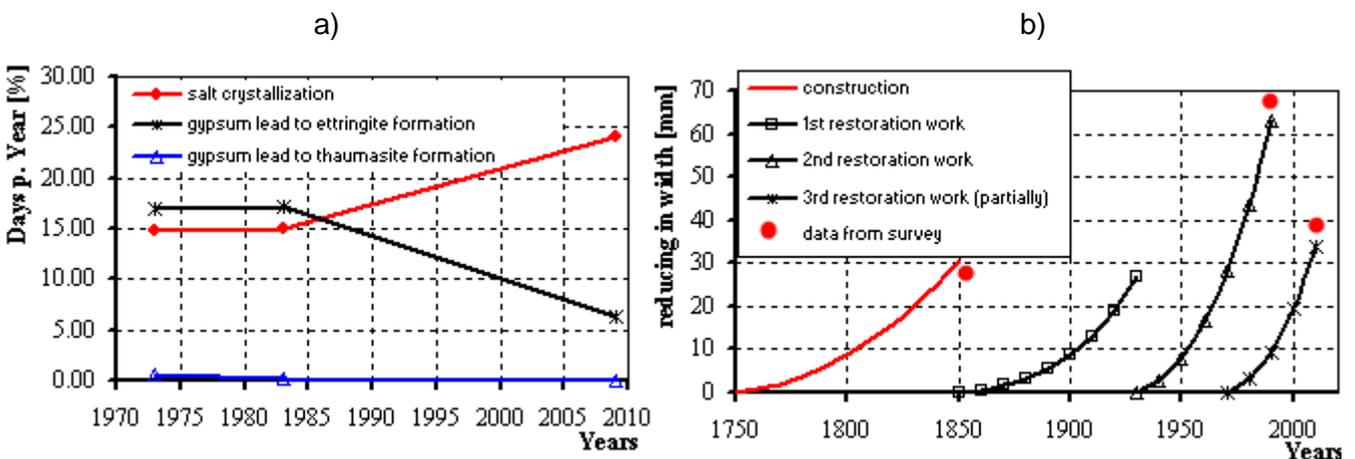
a)   b)

Figure 5. a) trend yearly intervals promoting decay, b) reduced width of mortar, estimation & data

5   CONCLUSIONS

Experimental observations show that masonry structures suffer a wide spectrum of aging phenomena resulting from chemical phase changes and mechanical deteriorations of stones, clay bricks and mortars.

The ambient conditions that turn on these effects are a consequence of aggressive environment and pollution increase, but the porous nature of the traditional construction materials is a key factor in the chain of events leading to brick pulverization, blistering and mortar rendering. Although the mass loss in a single cycle is in general very small, the number of cycles per year and the service life can be sufficient to superpose a noticeable deterioration, promoting finally a mechanical damage of the structure due to stress concentration. The possibility to prevent such aging phenomena, is linked to the translation of the available recorded data into analytical formulations that can be incorporated in a finite element analyses.

In the paper, some correlations between salt content, porosity and compressive strength have been presented. The conversion of the presented data into chemo – mechanical limit surfaces could allow computing aged structures acted on by accidental actions such as earthquakes. A more complex and practical problem is the strength of deteriorated and restored structures as a function of the residual strength and the properties of the added repair material.

The problem presented is a very important one in the preparation of a strategy for the protection of the architectural heritage. A number of field data reports and experimental tests gave the knowledge basis for further scientific assessment of the durability problem, but until now procedures for the implementation of the presented knowledge into numerical methods are still lacking.

The presented data are however very clear in pointing out that climate changes are producing dramatic durability issues, as the case of Venice is presenting a really fast evolving situation which poses the risk of losing very important masterpieces.

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