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## DOCTORAL PROGRAM IN PRESERVATION OF ARCHITECTURAL HERITAGE

Chair:  
**Prof. Carolina Di Biase**

Interventions on the built environment and more generally on buildings of the past, including the recent past, and their management call for fine-tuned knowledge and organization skills in all the related areas, from planning to maintenance. In Italy, even today, these activities are frequently dealt with – by public authorities and private individuals alike – in inappropriate or inadequate ways, considering the present state of know-how, historic and archaeological discoveries, sophisticated surveying and diagnostic techniques, and recent studies on the materials and structures of old buildings. The PhD course sets out to mould operators who will make a significant impact on the project as well on the practices of conserving, maintaining and managing our built heritage. Special, and separate attention is paid, on one hand, to older and historic buildings and structures, on the other to “modern and contemporary” architecture, in both cases in constant contact with developments in studies elsewhere in Europe

### Teaching aims

Knowledge is an essential step towards protecting and preserving, especially for conservation of the built environment. Only through awareness it is possible to understand complex aspects of creation, transformation and heritage’s condition; we can understand what could be lost: “you don’t lose what you are unaware of or uninterested in owning”.

A building or structure cannot be explained by instruments alone, even with the technical instruments of architecture: its documentary dimension lies in its material substance, in its meaning developed in society that should be evaluated when news condition and significants are defined. Familiarity with the built environment is necessarily aided by historical research, “stories of days gone by” and every other kind of useful contribution as well as, obviously by experimental science. As far as knowledge and intervention on the built heritage are concerned, the “human sciences” and historic disciplines are indissolubly linked with the relevant applied sciences. For there can be no “truthful”, exhaustive diagnosis of old buildings that fails to consider the dimension of time, and the reconstruction of past usages and transformations. Conservation of built environment founds on transversality of knowledge, on people able to catch the questions which can be solved with contribution of different discipline.

### Coursework

The PhD is intended to offer a broad range of courses which combine theory and practice to stimulate advances in multidisciplinary research, a necessity in the field of conservation and maintenance of historic buildings. The basic teaching program is organized with seminars held by Italian and foreign lecturers who introduce the most advanced research methods and results in four major disciplinary fields:

- The *Culture and experiences of preservation* is approached as part of the history of culture, and it is linked to present days. In particular, the topic is studies as history of the change of ideas and preservation’s limits; it’s also the expression of different cultural and institutional aspects. The preservation is considered also as history of new criteria and types of project, up to the introduction of intervention techniques and new materials, between XIXth and XXth century.
- *Material history of buildings* explores the issues of recognizing buildings as a historic source, interpreting how events unfolded at building sites and how production was organized, and showing how construction techniques of the past evolved thanks to the technical know-how of architects and builders, on one hand, and the methods of archaeological stratigraphy, also in elevation, on the other. In parallel students conduct workshop analyses and learn to interpret their findings.
- *Historical research methodology* addresses its subject on a more general level: the history and geography of documentary sources, the history of institutions which with their activities have changed the landscape and erected and used the buildings; in this respect going beyond the traditional 19th-century perception of history of art, the importance of history of architecture should be reconsidered.
- *Strengthening of historical building* of structures and materials deals with analytical and experimental methods for testing the efficiency of structures, including those at particular risk. It includes study and calibration of non-destructive investigative techniques for structural diagnosis, as well as theoretical and experimental study of appropriate non-invasive techniques, amongst them compliance with safety standards for buildings in seismic zones.

### Research organization and topics

One of the distinctive features of the PhD course is that it explores issues as yet seldom addressed in the sector of conservation, as



1. Resistograph text



2. House of Balilla in Forlì, Arch. C. Valle. Windows of the gymnasium (1936)

a means of developing new contributions to scientific output. Particularly among the subjects identified in recent years and currently being researched, there are analysis of materials of contemporary buildings and their decay, the research of intervention techniques respecting the cultural heritage; the topic could be extended, starting from monumental building, to the wider field of common ones; the heating and plumbing systems of historic buildings, "building physics" (already studied in Germany and France) and the consequent documenting of innovative installations in old buildings with the parallel study of old installations in individual buildings and at urban level. This is one of the most original and promising subjects of contemporary historic research, and it also highlights the environmental dimension of conservation. Particular attention is focused on wooden structures, considering the different structural types and finishes, and the material and its state of preservation. While

extensive studies on this sector have been conducted in the rest of Europe, literature in Italy is scant, limited to precise geographical areas and frequently of debatable content. Experimental and workshop activities about famous buildings (Arena di Verona – S. Andrea a Mantova) or less known (Rocca di Spilamberto, Modena) are in progress in the DiAP, Laboratory of Analysis and Diagnostic Evaluation Building, DIS, and in collaboration with

CNR G. Bozza, Department of Chemistry and other university centres mostly in Lombardy. Innovative studies are being conducted in this sector, thanks to new research tools: the particular subjects of interest are historic mortars (the earth-based mortars used in Italy and in Arab countries, though know-how, practices and conditions are not comparable), new mortars for masonry restoring and use of oxalate film to protect stone. The objective is to find out how they were produced in the past, something little is yet known about, and current possibilities for re-introducing their use. Other more usual subjects of research and specialized teaching are the economic aspects of conservation, legislation to cultural heritage, landscape conservation, history and conservation of historic gardens, museology and museography. The PhD program fosters contacts with government institutions – starting from the Ministry for Cultural Heritage, in its central and regional offices – and with organizations operating across the country in the sector of conservation and restoration. Within this framework several bodies have financed scholarships. Graduates of the PhD program have often found employment at progressively higher levels in public sector conservation institutions as well as in professional practice and in the business world, in specific specialized fields.



3. The monitoring of the microclimate. Distribution of temperature in the longitudinal section of the Rocca Rangoni in Spilamberto (MO)

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## COMPLEX WOODEN FLOORS AND COMPOSITE BEAMS BETWEEN LATE MIDDLE AGE AND MODERN AGE: ELEMENTS FOR AN INVENTORY IN MANTUAN AND BORDERING TERRITORIES

Juri Badalini

Considering the historical constructions techniques, wooden carpentry has not been faced in Italy in a diffuse and systematic way. Many researches, some of which very good, are often fitful, restricted to specific countries and without a protocol for collection, management and output of information and they do not manage to draw up inventories of carpentry useful to the knowledge of the persevered material heritage.

France, Great Britain and Germany, which past architectural heritage includes important and ancient carpentries with great consideration in technical literature since XVI to XVII century, are more interested in carpentry and produce a lot of detailed researches on wooden frameworks which can be considered a reference.

The bibliography ranges from the XV<sup>th</sup> century's treatises to the recent repertoire published by the French Centre de Recherches sur les Monuments Historiques, for example, or several groups interested in heritage conservation in England, and the yearbooks of the 315 research department of the University of Karlsruhe, Germany.

The Italian territory is not in absence of valuable wooden carpentry, but, in the Italian technical literature it does

not appear in specific books until the XIX century, when the publication of copy or translation of the most well-known European treatises encourages the appearance of manuals which were in various degrees indebted to these. Most information on traditional building techniques is contained in research to direct the works of conservation, with reconstructive purposes rather than informative. The "Manuali del recupero" (manuals of recovery) in the second half of the twentieth century, are a typical example, being a valuable repertoire of constructive solutions, but rarely dealing with the historical, economic and social aspects, which are faced, instead, in more in-depth researches by local construction techniques studies.

The aim of this study is not a critique of the literature on this subject, but is to recall the attention on the wooden carpentry in order to promote a possible method to draw up repertoires.

European methods are applied to sophisticated technology solutions that between the late medieval and early modern era spreads on most part of the Italian territory, although a proper interest is not gained on it: the wooden composite beam. The use of beams obtained by precise shape and assembled

small pieces of wood was spread and perfected in this region between the fourteenth and fifteenth century, a period in which large deforestation in Po Valley reduce availability of timber increasing, in Mantua, the import from Tyrolean and Trentine woods.

Construction of composite beams could be a solution to optimize material use, such as short beam ceilings "alla Serlio" or planks carpentry "alla De l'Orme", recurring in sixteenth century treatises but which origins are certainly more remote.

This research, starting from European repertoires and studies concerning composites beams in Ferrara, tries to identify possible sources and spread routes of the model in the Po Valley through the catalogation of a large number of composite beams in place, the study of the routes of supply of timber and the movement of workers. Local variations of models found in some showed cases strengthen the hypothesis that, while admitting a common origin, at the end of the Middle Ages and then in the Renaissance, the technology for the realization of beams through the joining of small pieces was integral part of the carpenter's knowledge. The beam in three pieces has also theorized by Leon Battista Alberti and models into four

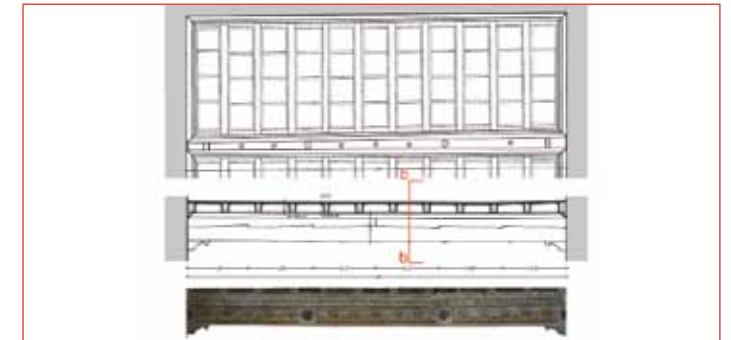
pieces can be found in the sketches of Leonardo da Vinci. Solutions to put right the inadequate timber size, or to improve the mechanical performance of the beams appear in many treatises in Italy, France, England and Germany since XV<sup>th</sup> century. This



1. Sketch by Leonardo da Vinci's "Codice Atlantico" of a three pieces composite beam and, below, similar beams in the castle of Pandino (XIV century)

availability of sources is not enough to explain the possible origins of this technique, the age of the specimens in place shows indeed that this is an older technology. The constant presence in bibliography testify the interest in composite beams, at least from theoretical point of view, but which could not match a real use in construction. Cataloguing of a large number of composite beams has partially overcome the lack of written sources, and is useful to determine different variants. Many buildings in Po valley built or substantially modified between the fourteenth and seventeenth-century contains composite beams: city and country residences, castles related to the Visconti, the Sforza and the duchy of Este in Ferrara and on

the Emilian Apennines. Cases found in Mantua, more than twenty at present, are dated mostly between the end of the XIV<sup>th</sup> and the XVI<sup>th</sup> centuries, period in which this technology could be defined mature, but we can not exclude cases previous or later.



2. Relief of a three pieces composite beam in Palazzo Gazini-Rizzini in Mantua (XV century)

The aim of this study do not give exhaustive answers to the initial questions and drawing a geography of Italian composite beams focused on not well identifiable diffusion paths; at the present time the boundaries are attested on the Rocca of Martino in Rio (RE) to the east and the castle of Vigevano (PV) to the west, Verona and the Alpine Arc to the north and the Apennines southward. The presence of composite beams in Florence and Venice, and some cases in France, confirms that the definition of 'habitat' of these structures is far from over. The reduced availability of timber involved several European regions between the Middle Ages and the modern age so, if the composite beam, in its various forms, was the most suitable solution to save timber,

this could have been improved at the same time in different regions, drawing on a common heritage of knowledge on the mechanical behavior of wood in place and systems of union of the pieces.

At the end of this study one can not say that composite beams

## FORTIFIED ARCHITECTURE AND PATRICIAN RESIDENCE IN MODENA BETWEEN THE FOURTEENTH AND SEVENTEENTH CENTURY

### The Rangoni fortress

Laura Balboni

The objective of the research is to show the passage between fortified architecture and noble residencies using the specific case of the Rangoni fortress. The fortress was the subject of an initial research with interdisciplinary results which made up the indispensable basis of this work and allowed to focus on the more general topics of this study. The thesis is structured with the thematic path which proceeds parallel with the timeline, in a continuous confrontation between the knowledge directly acquired from the artifact and indirect knowledge: the study of other architectonic projects chronologically and geographically close, or tied to the members and to the different branches of the Rangoni family; the information derived from archival investigations, and data gathered through various bibliographic sources.

#### The castle of Spilamberto between Modena and Bologna

The detection campaign clearly evidenced the geometries that today characterize the building, indicating the most antique structures inside modern era constructions. The individuation of wide walls, still present in the northern part of the building, allowed identifying

the remains of a tower before the construction of the fortress. This assumption forced to reread the most antique permanencies of the territorial context and the events which accompanied the foundation of the thirteenth century castle, to which the remains can be traced to: Spilamberto is in a system of villages in which the community looking for local settlement is given benefits to make communication routs secure as happening along the Panaro river. The development of towns corresponding to antique castles has cancelled the geometries and forms of antique defence systems; however, the medieval architectonic remains in their sizes and construction characteristics, in the morphology of the systems and in the location of the first turreted settlements, allowed to confirm the assumptions made on the case of Spilamberto, tracing the construction of the tower to the start of the thirteenth century.

#### Control and defence of the feud: Rangoni fortress

The genealogies and heraldry present the Rangoni at their entrance into the history of the territory on the border of the Panaro. But the role of the family was considered in a wider context tied, first, to the creation of the Estense states and after

to the control and the defence of the Modena borders, and of the territories located along the foothills. In this sense the study of the private Rangoni Machiavelli archive allowed to individuate an important *post quem* term, after which to date the construction of the fortress. The donation in 1394 by Niccolò d'Este in favour of Jacopino Rangoni with "*merum et mistum imperium*" brought to reread the event in relation to the Estense family. The role of Jacopino in the military expeditions emerged and a probable connection between his settlement in the feud of Spilamberto and the construction of the fortress. As in other cases recorded in the territory examined, the new presence of important lords controlling territories automatically determines the construction of fortresses for their defence. The fortress conserves the signs of this passage of power: a portion of the Rangoni coat-of-arms is still on a battlement, today hidden by the coverings of the central west tower. The extension of the fortification can be fully understood by the layout of the wall, and specific elements that connote the military architecture of the period are recognizable, also thanks to the confrontation with other fortified architecture cases located on the territory in question.

#### Noble residence in the fortress

A series of rooms are still in the fortress that bear characters and decorations belonging to the end of the fifteenth century. The research lingered on such permanencies which marked the passage from military outpost to aristocratic residence: the courtyard with the two colonnades represents the first welcoming area for the Rangoni lords and their guests. The thesis attempted to recognize the residence of the leader Niccolò Rangoni and of his wife Bianca Bentivoglio both through the signs individuated by the stratigraphic analysis and in relation to coeval examples and in the light of new archival findings: the inventory written in 1501 upon the death of Niccolò, found in the private archive, proved diriment for the reconstruction of the building phases. The data interlacement made it possible to more precisely individuate environments, their distribution, furnishings and decoration. The inventory also evidenced that for the Rangoni family the residences multiplied in the feud and in the main cities tied to the family history and activity, as happens with other noble houses. The role of the different houses were confronted, interlacing the data emerged from the various investigations;



1. The Rangoni fortress. West façade with the indication of transformation phases

today it seems possible to interpret the interventions as wanted by the feud to show off power and prestige through architecture, also increased by the wedding with the daughter of the Lord of Bologna. Even though the construction work, in Spilamberto like in Modena, was of large importance in the late fifteenth century local context, the feudatory continued to live in Bologna, mainly using the Modena houses for short stays or for holiday locations.

#### The residences in the feuds during Modena capital. The house of Bianca Rangoni

Traces of a second intervention have been recognized, before the seventeenth century reforms of Guido IV. Searching the reasons which brought about this transformation, various archives were examined, especially the correspondence of the family;

after periods of long absences of members of the family it is at the end of the sixteenth century that the presence of the Rangoni in Spilamberto is once again recorded, in particular the presence of Bianca, called to carry out territory government tasks in the absence of her husband. The village becomes the centre of a small country court and inside an intense religious construction and "proto-industrial" activity is recorded which gives the small centre back vivacity. And it's here that the stratigraphic signs of the transformations recognized in the fortress can be read as tracks of an intervention with the objective of widening the apartments, in consideration of the larger receptive necessities given the tight relationship with the ducal court in the new capital, evidenced by the visits of members of the Este family.

## POLICIES OF CONSERVATION AND PROTECTION OF ARCHITECTURAL HERITAGE IN THE CITY OF BUENOS AIRES AND FUTURE POSSIBILITIES FOR THE RECOVERY OF THE "BARRIO LA BOCA"

Silvana Basile

The research is based on two targets strictly related each other. The first one is intended to provide an analysis of the safeguarding instruments to be developed both at a local and national level. The second one, is aimed to identify a possible recovery project of La Boca district, through different intervention works to be carried out in distinct steps (covering all aspects from legislation to the institutions involved) to solve the complex reality of this specific part of the Argentinean territory. To discuss the topic of the existing instruments for the protection of the architectural heritage, a preliminary analysis of the state of the national and local legislation has been done, starting from the first regulations up to the most recent ones. The purpose was to analyze the laws and evaluate their limits, how they developed over time and to provide an evaluation of the effectiveness of the technical and specific solutions proposed. Finally, a set of principles have been elaborated and proposed for the Argentinean Republic, so as to define a common base for the activities to be performed by of all the operators and institutions involved in the protection of architectural heritage. This document is intended, in the first place, for the Argentinean specialists involved in conservation. A



1. "Calle Garibaldi e Magallanes". Typical boquenses houses. Fonte: AGN, Departamento documentos fotográficos, Argentina. Caja 42, sobre 22, negativo B45901, inventario 9842

second, but nonetheless very important objective, is to provide architects, civil servants and politicians with a mean to understand the architectural heritage and the measures needed to guarantee a long lasting conservation. The second part of the research analyzed the structure and how the "barrio La Boca" was developed, in order to identify specific buildings targeted for the program of conservation, protection and value enhancement within this area. This district has been chosen because of its important historical value, being the first settlement in the city of Buenos Aires, close to the river Riachuelo. The river was a source of wealth, the first big colonial port of the city was established here, and it marked the political and physical limit of the city of Buenos Aires.

The La Boca neighborhood is located at the margins of the metropolitan area even if it is not far from the city centre. Until recent years, the land was marshy and often flooded from the river Riachuelo. It was inhabited mostly by immigrant sailors coming from Genoa; in fact, even today the inhabitants of La Boca are called "xeneizes" (Genoese in the Italian dialect). The Xeneizes created an urban space characterized by its very poor architecture but with particular connotations. According to Marco Zanuso, this typology of architecture was able to solve "problems that the modern architecture raises, but has not yet solved" (1958). With the closing down of the port activities, the economic importance of La Boca became marginal. However, it maintained a privileged role

within the city due to the vicinity to the city centre. The study surveyed the current urban conditions, the transformation of the area and the impact of the lack of investments in maintenance, requalification measures and the general perish caused by economic decline and the loss of shipping activities. Despite the aforementioned situation, this area has a strong character not only due to the presence of its peculiar architecture but also due to a strong feeling of "belonging" which overcomes the apparent phenomenon of social disintegration. The work links the evolution of the residential population fabric to the territorial configuration, the state of the local economy, the structural decay (frequently with inadequate hygiene conditions), the availability of services, schools and employment, and the presence of speculation in the real estate market which is focused on demolition rather than conservation. The project deals with very delicate problems not only related to the social degradation, but also to the constraint that the very poor materials used in the characteristic construction give in terms of the standards required and expected of modern residences.



2. Casas conventillo de chapa y madera

This intervention would try to put into practice the principles addressed in the "Carta di Amsterdam" (1975) which states the importance of the integration between the restoration works and the urban requalification considering the need to improve the social environmental conditions as well as suggesting investments to improve overall social conditions. Some proposals were foreseen, starting with the identification of policies for conservation and valorization of the whole area, up to the definition of hypothetical legislation, so as to give indications for a recovery of a building by examining the specific problems which might be encountered in a typical building chosen as a representative example. The aim was to point out some methods of interventions which could be used to improve the

urban environment, the mobility, the commercial structures and the security to revitalize the economy using tourism as an important pillar of the development strategy. The future perspective is oriented to a strictly conservative philosophy, preserving the physical handicrafts, aware of the limits that modern lifestyle imposes. This is the main goal of any restoration work: to combine the technical requirements, the valorization of the historical and aesthetic features with wellbeing. The interest for conservation has to be envisaged within the strong sense of belonging which is an integral part of this specific area. This allows the adoption of successful criteria of planned maintenance which can positively contribute to the quality of the local economy.

## MODERNITY AND WINDOWS: THE PRODUCTION OF METAL WINDOWS IN ITALY, 1920 – 1940

**Maria Conte**

In Italy during the period between the two World Wars, the use of metal windows was not so diffused as far as house buildings or public works are concerned. It was in fact mainly connected with meaningful works of Modern Architecture. It was during this period that metal windows made several technical and productive headways.

The purpose of the study is to see if and how the metal window differentiates from the past in the planning, making, use, spreading and in the interpretation of the age-old relation that windows established between the inside of a building and the outside world; to research into the organizational structure of its production cycle and to reconstruct the manufacturing process from raw materials to end product; to consider the hypothesis that we can think the production cycle as an interpretative key of the role that the metal windows had as to *modernity applied to windows*; to illustrate the history of some famous buildings in Milan. The reading of architecture magazines and also journals specialized in fields such as metalworking and mechanics, has had different merits: on one hand it has been useful to outline the profiles of the discussions that with more

intensity had tried to define the significance and the use of the metal windows; on the other it has made possible to gather the expectations of architects and firms in the light of a new potential market and at the same time to draw up a list of the main protagonists involved in the production of metal windows which were the result of two different productive phases. The first phase was the profiles making: the big industry produced *special profiles* in order to make windows frames. The second phase was the profiles assembling which took place in specialized workshops by carrying out mechanized operations based on a rational planning. The research points out the existence in Italy, from the middle of twenties to the beginning of forties, of two main experiences: the national production of *special profiles* of steel and the use of aluminium and of its light alloys in architecture thanks to the scientific evolution in this field as well as the economical situation of the country. Although the conservation of the industrial archives of the firms involved in these experiences was generally fragmentary, the contribution from the ILVA documents kept inside the Ansaldo Foundation has been all the

same outstanding. In fact they have allowed to outline the context which originated the first *special profiles* of steel produced in Italy together with the project to come, this time inside of the same company, to a standardized production of metal windows. The reference of the Montedison Archives has finally helped to reconstruct the events of the "MONTECATINI General Company for Mining and Chemistry Industry" and its consociate companies, that saw the research and the production of *special profiles* extruded of light alloys in the hands of the big companies, while the windows making was again a prerogative of specialized workshops. The situation of these specialized workshops has been mainly investigated through a detailed analysis of the magazine advertisings which are frequent sources of technical drawings, information about possessed tooling, executed consignments, adopted patents, but also through the documentations about expositions and the files which can be found at Chambers of Commerce. This work has documented their geographic concentration in Lombard areas and the progressive apply, from the beginning of the thirties, to windows productions with *special profiles* of aluminium

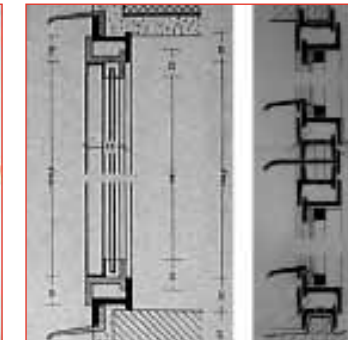
(ex: Anticorodal) according to a program aiming at extending the catalogue placed at specialized people's disposal. Finally the technical manuals, in their attempt to meet the new market requests, brought themselves up to date on technical evolution, the

industrialization. As to the national context in the period between the two world wars, the research includes the analysis of magazines and technical manuals. The second part is dedicated to the characteristics of the Italian production due to economic

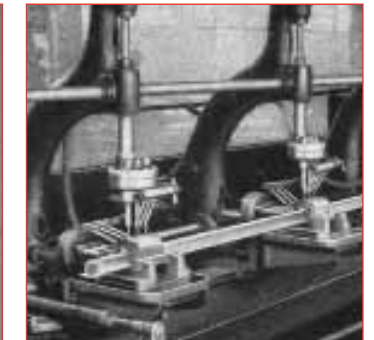
Two appendixes are enclosed: a glossary that collects definitions and more detailed examinations than the research on the whole; a catalogue of magazines and specialized journals that, as to themes which have been developed, lists the main references to papers, magazine



1. Iron window of commercial profiles (1909)



2. Vertical sections of steel windows: the window frames are created with special profiles with parallel and conic flanges (1932-1933)



3. Combined punch in a specialized workshop (1940)

architect's role and the building yard economy. Until the first half of the twenties, technical manuals continued fundamentally to seem an instrument to provide recommendations useful for a correct execution and to explain examples which helped to understand the rules given about the topic; from the thirties it is possible to see the presence of pieces of information more useful to choose from different constructive systems or to end products already put on the market; the manufacture's or the patent number were often mentioned. The research is divided into three parts. The first part includes an international analysis, covering a large period of time, of the main architectural events connected to the employment of metal windows and the building

situation, the developments of the metal industry and those of specialized workshop; the third, referring of Milan, consists of specifications about consignments executed in famous building yards where it was present the name of the manufacturer. The material data analysis even if carried out in a limited way, has nevertheless allowed to underline that also for significant buildings, the direct document of the history of productive technique, has often been cancelled or compromised; the common procedure of the last decades has indeed seen the metal window to be replaced in the event of damage or if it is not more respondent to present requirements, which brought to the loss of the original technical characteristics of the building itself.

advertisings, monographic issues and technical pages.

## DURABILITY OF COMMERCIAL MORTARS FOR THE CONSERVATION OF ARCHITECTURAL HERITAGE

**Davide Gulotta**

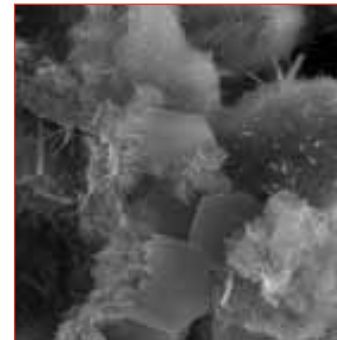
The preservation project is a complex issue that requires contributions and expertise belonging to different scientific fields. It involves practical interventions on aged artifacts, which are usually made of heterogeneous materials and show a precarious state of conservation. A deep knowledge of materials characteristics, in terms of chemical, physical and mechanical features, is a preliminary requirement of paramount importance during the planning of any kind of operation on the built heritage. At the same time, all interventions should be aimed at preserve every trace, stratification and significant sign of the past on the historic surfaces.

A number of experiences have been performed for a long time for the definition of adequate guidelines and shared protocols for the characterization of ancient mortars. All these examples provide significant information on several aspects related to the mortars composition and to the preparation techniques, although every single case have to be considered as a unique, due to specific geographic and chronological factors. Studies dealing with the methodology for the selection, the preparation and the application

of mortars for restoration and repair, based on traditional raw materials are available as well. On the other hand, new and innovative materials for the intervention on historic masonries have been scarcely investigated and exhaustive information about them are still lacking. Despite this, the use of commercial binders and pre-mixed mortars is increasing and these kind of products are currently available in the market with a large number of different formulations, while details of their characteristics and compositions are often poorly reported.

The research work presented within the thesis arises from the need for a deeper and more complete understanding of these products, achieved by the study and the characterization of a significant selection of the most diffused commercial mortars and binders. The selection has been made among products supplied for the bedding of bricks or blocks of the architectural heritage, strictly based on NHL - natural hydraulic lime binders, totally cement-free and with a very low soluble salts content. The main objective, beside the characterization of the raw and hardened materials, has been the evaluation of the overall durability and also

the identification of the main factors affecting it, paying particular attention on how to transpose the related results into practical indications for the decision-making process. The evaluation of compositional features, together with considerations arising from the significant differences showed by the different mortars, highlighted that commercial products intended for similar use are indeed quite heterogeneous from a compositional point of view. Hardened materials have been characterized in mineralogical-petrographical, microstructural and mechanical way by means of a multi-analytical approach: optical and electronic microscopy, x-ray diffraction, infrared spectroscopy have been used and compressive strength test has been performed. The mortars durability to salt decay has been evaluated as well, focusing on sulfatic attack. This latter part of the research has been aimed at identify the correlations between significant compositional, mechanical and microstructural parameters and the damage evolution. Salt decay has been chosen as a damaging factor because it is widely considered as one of the main phenomenon which can seriously compromise the conservation of porous materials of the cultural



1. SEM observation of the surface of a hardened mortar



2. Salt-induced damage of a mortar specimen



3. Salt crystallization on the surface of a walletoes

heritage. Its relevance is confirmed by the huge number of studies in the field, which investigate the decay mechanism, the deterioration patterns, the main damage factors and their influence on the compatibility of new intervention materials and treatments. Stone materials, bricks, mortars, plasters and stuccoes, traditionally employed in the built heritage are all porous systems, thus particularly vulnerable to the migration of water and soluble salts solutions within their matrix. Salt crystallization, in such conditions, can develop very high crystallization pressures and serious damage may occur. The durability of commercial products to salt decay has been experimentally studied in laboratory conditions by means of cubic mortars specimens and

also on walletoes that simulate the masonry system.

Results show that the research field may have further developments, especially for what concerning the potential transfer of experimental data to real cases and to the preservation practice. The current remarkable interest on commercial NHL binders and ready-mixed mortars is confirmed by the increasing number of products available in the market and requires a deeper knowledge. The overall durability of interventions, especially with respect to salt decay, can only be assured if quality requirements are fulfilled both for materials selection and for the application techniques. Moreover, durability is a very complex issue and it is strictly related to a large number of

parameters, all working at the same time. The definition of proper guide-lines for the choice of the most suitable material to be used in every different case, based on shared technical indications and aimed at the best compatibility, seems to be a more promising strategy rather than the definition of thresholds and numerical values for the risk assessment.



# CALCIUM OXALATE ON THE STONES AND PLASTERS OF HISTORIC BUILDINGS

## A comparison of analytical techniques for the identification of the substance originally applied

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It has been known for a long time that calcium oxalate, particularly in the shape of films, can be found on the surface of objects of historic and artistic value. The first studies date back to 1853 when Liebig analysed samples of oxalate films coming from the Parthenon marbles. Since the 1950's an intense debate started among scientists, architects, archaeologists and art historians aiming at investigating the chemical and mineralogical composition of those films and to understand whether their origin should be attributed to natural causes (lichens, algae, fungi, microorganisms) or rather linked to human activities (surface treatments applied for aesthetic or conservation purposes, whose organic component underwent in time a process of "mineralization" bringing forth calcium oxalate as the end product). Nowadays, it is believed that both origins are possible, although the anthropogenic derivation is considered to be most widespread. In the operative practice, determining what caused the insurgence of oxalate films in specific cases is paramount in order to choose the most appropriate conservation approach. Especially when the origin is related to treatments, it is of great interest to identify exactly which organic substance was



1. Area of the Arena in Verona where the analysed specimens were sampled (arcovoli VIII, XIX, X)

turned into oxalate during the centuries. The ordinary analytical techniques utilised in diagnostic investigations can identify with precision the presence of calcium oxalate, but they are often not sensitive or specific enough to detect the low amount of residual organic matter or to disclose its exact composition. After giving a detailed account of the scientific literature about calcium oxalate from the last thirty years, this thesis reports original results obtained on film samples from the Arena of Verona. Preliminary tests (optical microscopy and X-ray diffraction carried out at ICVBC-CNR "Gino Bozza", Milan) confirmed that calcium oxalate is present in all specimens and correlations between the morphology and chemical and physical characteristics of the films were proposed<sup>3</sup>. In

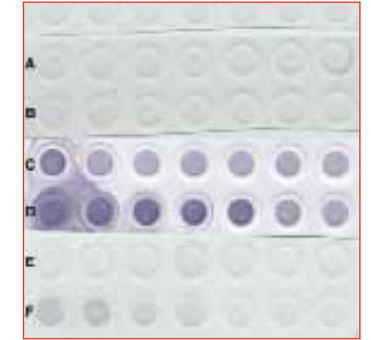


2. Calcium oxalate films on red limestone on the exterior stone lining of the Arena in Verona

particular the relative abundance of either form of hydration (weddelite and whewellite) was considered. Subsequently two analytical methods were applied to the study of the organic components. First of all infrared spectroscopy (FT-IR, c/o Dip. di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano), a general-purpose technique, able to detect a wide range of substances both organic and inorganic, and thus frequently employed in the diagnostic phase of conservation works. The second technique was gas chromatography–mass spectrometry (GC-MS, c/o Dip. di Chimica e Chimica Industriale, Università di Pisa), commonly used to investigate painting media, as it is a very sensitive and effective method for the detection of proteinaceous and lipidic materials, even when they are only left in

traces. Furthermore, this thesis introduces immunoassays (experiments conducted at DISTAM – Dip. di Scienze e Tecnologie Alimentari e Microbiologiche, Università degli Studi di Milano) which, albeit often employed in several fields of application (biomedical diagnostics, food industry, forensics, quality checks), are not as common in Cultural Heritage and were hardly ever reported in connection to the study of oxalate films. This very sensitive methodology is based on the highly specific matching of antigens and antibodies and is only suitable to identify proteins, which are in any case the most important class of organic compounds in this field. This thesis describes a dedicated home-adjusted immunoassay protocol for detecting the proteins most frequently involved in the art techniques and historic recipes for surface treatments (casein, ovalbumin and collagen, found in milk, egg and animal glues). The protocol was tested on laboratory constructs and real specimens to evaluate its detection limits and the influence of contaminants (lime, gypsum, pigments) or protein ageing. The laboratory constructs were samples of fresh proteins, commercial restoration products, and paint replicas on plastered boards, artificially aged; the real specimens were

taken from mural paintings dating back to the late '700 and gildings from the Basilica di Sant'Andrea in Mantua. The oxalate films from the Arena of Verona were sampled in such a way that they would be representative of all the typical characteristics described in the literature: they were abundantly found on the calcareous lining of the exterior walls either on continuous and extended surfaces or in tiny speckles; color ranged from ochre to dark grey according to their degree of exposition to atmospheric agents. Analyses of the inorganic component (XRD and FT-IR) demonstrated that whewellite was prevalent, especially on ochre films: this is interesting because even though whewellite is the most chemically stable calcium oxalate in normal conditions, it is generally less widespread on monuments. As far as the organic component is of concern, FT-IR carried out both on powdered samples and on suitable solvent extracts was not able to identify the composition of any organic substance, albeit potentially present in traces. GC-MS could not detect any proteins, while evidence of an animal fatty substance was obtained, although that was considered a contaminant of unknown origin as its presence could not be linked to any specific material.



3. Specimen of mural painting treated with calcium hydroxide and egg white, sampled from the apsis of the Basilica of Sant'Andrea in Mantua. Scanning of the blot membrane after staining of the immunoassay: antibodies against animal glue (A-B), egg white (C-D) and casein (E-F)

The immunoassay protocol gave positive preliminary results both on the laboratory and real specimens, particularly in connection with casein and ovalbumin which were detected down to concentrations in the order of nanograms. It seems that neither the co-presence of foreign materials in the samples or protein ageing (be it natural or artificial) had any adverse effect on the sensitivity and specificity of the devised protocol. Coupling traditional techniques with promising innovative methodologies such as the proposed immunoassay could lead to improved opportunities to identify ancient treatments on monument surfaces.