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EVALUATION OF NEW AND OLD METHODS FOR CONSOLIDATION AND DESALINATION OF LIMESTONE
CASESTUDIES; RENAISSANCE SCULPTURES IN LIMESTONE

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CASESTUDIES; RENAISSANCE SCULPTURES IN LIMESTONE

ABSTRACT

The thesis discusses the methods for consolidation of weathering limestone based on compatibility of consolidants with limestone. I base my essay on literary investigation, two case studies, and to some extend experimental work.
The case studies represent two lunettes made by the sculptor Nicola Firentinac 1450-1500; Lunette on St: Ana Church, Island Hvar, Croatia and Lunette on St: Klara Church, Trogir, Croatia.
This bachelor thesis discusses difficulties in decision making with slat laden reliefs in limestone and methods that can demonstrate effect of combined treatments; cleaning, desalination, consolidation and fills. The methods to be evaluated are: calcium hydroxide, barium hydroxide, ammonium carbonate, ammonium oxalate, new developments of nano-lime techniques, and alkoxysilanes.

Except for the alkoxysilanes, which are important part of the discussion because of their wide usage and commercial availability, the methods discussed here can be considered as preventive measures. The experiment based on research of methods of consolidants' specific qualities and use is judged visually, with SEM (scanning electronic microscopy) and by water absorption. The tests which include water porosity on the untreated limestone, THEOS treated sample, and the penetration depth of barium hydroxide are performed on limestone from Gotland. The SEM results show that the penetration of barium hydroxide is directly proportional to the low porosity of the material and that the penetration is possible. Other methods have been judged visually or by microscopy. Due to the same nature of consolidate and substrate, SEM cannot distinguish between materials and provide any results for the methods using carbonates and oxalates. The tests also show that THEOS doesn’t influence hydrophobic behavior of limestone.

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CHAPTER 1

1. INTRODUCTION AND BACKGROUND

During my internship, I encountered a problem with desalination of renaissance sculptures carved in limestone. The sculptures of high historical and artistic value were acutely treated for harmful salts and consolidated. In this case it was also important to protect the trace of painted surface during the desalination process. We used Lewin's desalination method using $Ba(OH)_2$ and urea. Since the method is not used in Sweden, I became curious about the processes and the chemistry used by the method. In some cases, when the stone did not exfoliate, we used the method with ammonium carbonate which is also known as method for consolidation, cleaning and desalination of wall paintings.

In the case of stone polychromy, the ethical approach and conservation problems are often focused on the trace of color, which is left from deterioration or previous conservations /restoration: there are not many reliefs/sculptures that actually have traces of color left. To be extra cautious in the examination of reliefs / sculptures of high historical value, we should broaden our knowledge of paint and protection during a process of cleaning / desalination / consolidation.
My interest was not in the polychromy as a particular separate subject, but as one of the problems one might face during the whole process of consolidation/conservation of the stone objects attacked with salts.

I became more interested in consolidation methods/ processes, and not just one consolidated agent or materials. During my investigation on this subject, I realized that chemistry of these particular methods works on concept of compatibility with lime stone and other calcareous surfaces. And the reason I chose to look at this subject closely is also my observation that ethyl silicate (or its different modifications /alcoxysilanes / siliceous acids ester/ethers), which is based on siloxane bounds, has often been recommended as the treatment for lime stones although is not compatible with limestone.

1.1 PROBLEM DEFINITION AND ISSUES

The demands with which the consolidation medium must comply have already been defined (Hansen & Doene (2000) p.1). But the consolidation of stone includes a range of different issues: the diagnosis, cleaning, desalination, and material reinforcement. To give an accurate diagnosis a salt measurement should be performed before the consolidation process. If the stone is suffered extensive damage, even a pre-consolidation has to be performed. If we find traces of pigment, the difficulty of consolidating is even more complex: some pigments or only traces of pigment may be sensitive to preserving liquids and a certain pH.

Does a consolidation method include a salt-reducing effect and how does this mechanism work?
Which methods are the most compatible with the limestone chemical compounds and which are the reasons why we use silicic acid ether with a Si-O- Si structure (siloxane bonds) even on the limestone?

Since water is a good cleaner and desalination agent, but not at a high concentration of few soluble salts or traces of pigment, I wanted to find out which chemical methods could possibly merge cleaning, desalination and consolidation on the limestone.
How to protect polychromy during desalination?

1.2 AIMS AND OBJECTIVES

This investigation should broaden my knowledge about various consolidation techniques, advantages and disadvantages, the study of salts, analysis of different concentrations of salts, other investigative methods which are suitable for stone analysis and provide a summary for the various degradation factors in different environments.

The purpose of essay is to evaluate the consolidation of different methods, based on the concept of compatibility with the material.

Another purpose is to discuss modification of techniques for better adaptation to the material and new discoveries in the field.

The final purpose is to evaluate the consolidation methods used on limestone and hopefully provide useful information for the students and practitioners in the field of stone conservation.

1.3 LIMITATIONS

The discussion is limited to sculpture and sculptural objects in limestone: it examines the various problems during consolidation especially desalination.
There are several references to a case study which I have worked on during my internship. Some consolidation methods have been applied to both limestone and wall paintings, due to similarity in chemical structure. But the limitation of this thesis does not provide enough space for research in paint and pigments or techniques used on painted stone / calcareous surfaces.

The essay does not investigate the stone consolidations agents, such as acrylic, silicic, organic or inorganic ones. The methods discussed here can be seen as preventive, which is the limitation of this essay. But not all preventive methods are discussed here, since I have left out the consolidation with bio-mineralization, crystal-grow inhibitors or sacrificial layers.

Due to the limitation of this thesis, the most of the research is focused on the inorganic compounds such as ammonium carbonate and barium hydroxide.

The alkoxysilanes are partly organic and partly inorganic products, commercially available, and have apparently been used on limestone too. I found it important to evaluate even this consolidant, which is sometimes used on lime stone, although it is not compatible with it.
The essay does not investigate any cleaning methods, such as laser cleaning and its impact on stone and pigments.

1.4 METHOD

With references to two case studies I have been working on and have had the opportunity to follow the conservation progress thereof, I do a literature investigation concerning degradation factors and use of various consolidation techniques. I do base my essay on experimental studies to some extent.

The essay deals with an experimental feature of the limestone in which 5 consolidation methods are tested and evaluated. The experiment based on research of methods or consolidants specific qualities and use are judged visually (ocular), tested with SEM and by water absorption. Those tests which include water absorption on THEOS treated sample and the penetration depth of barium hydroxide are performed on limestone from Gotland. The other methods: ammonium oxalate, ammonium carbonate and calcium hydroxide, have been judged visually/ocular or by microscopy.

1.5 PREVIOUS RESEARCH

There is no specific selected literature for the conservation of limestone. In my investigation I found valuable information about consolidation methods used previously in Master of Science thesis written by Oztiirk Isil 1992, "*Alkoxysilanes consolidation of stone and earthen buildings materials"*, University of Pennsylvania. It is a historical overview of consolidation agents' use in conservation of stone and their chemical properties and qualities.

In my literature studies I used the scientific articles from *ICOMS* stone congresses (2004, 2006), the articles from catalogs *"Studies in Conservation"*, and *BCIN*. The articles support information from yearly catalogs of Getty Conservation Institute. For the experimental part I followed the standards from *ICROM* manual for the conservators and laboratories work.

I found some very interesting and contradictory information about limestone conservation in an article written by Getty -conservators from 2000 which was later printed in *"Studies of conservation 2003"*, namely "A review of selected inorganic consolidants and protective treatments for porous calcareous materials". The article in some ways supports the idea of more preventive conservation on limestone and calcareous surfaces in generally, discussing both old and new methods. The authors are known scientists in the field of stone conservation, i.e. Hansen Eric, Doehne Eric, Fidler John, Larson John, Martin Bili, Matteini Mauro, Carlos Rodrigues Navaro, Sebastian Pardo Eduardo, Price Clifford, Alberto de Tagle, Teutonico Jeanne Marie and Weiss Norman.

The methods on which this thesis focuses have not been actually used in Sweden, but in yearly reports of Swedish National Heritage Board (Raä) I found interesting introduction written by Svahn Garreau, Hélène (2010) " *Removal of damaging conservation treatments on mural paintings: a research and development report from the workshop".*

The report from the workshop evaluates the different methods for cleaning, desalination and protection of mural paintings in several Swedish churches. This was important information for the evaluation of "ammonium carbonate method", which was introduced by Professor Piero Baglioni here in Sweden (2010). The method is sometimes called "Ferrino – Dini" method and it is also combined with nano-lime technique. To certain extend, it is an interesting introduction to "Nanoscience for the Conservation of Cultural Heritage".

The other literature which provides information about contemporary conservation in stone is written by Doehne, Ferguson & Price (2010)," *Stone conservation: an overview of current research*", Getty Conservation Institute.

The "barium hydroxide method", which is considered separately, has been introduced by Lewin, S. Z., and Norbert S. Baer (1974), "Rationale of the Barium Hydroxide-Urea Treatment of Decayed Stone", in the form of an article in "Studies in Conservation" from 1974.

An interesting experiment and evaluation of ammonium oxalate method is introduced by Cezar Tody M. (2006) in Master of Science thesis," *Calcium Oxalate: a Surface Treatment for Limestone*", The City and Guilds of London Art School.

1.6 SOURCE OF CRITICISM

According to certain literature; Enzo Ferroni (1921–2007), a chemist at the Florence University, developed together with the conservator Dino Dini a method for consolidation of mural paintings and reduction of gypsum on salt loaded limestone, named the "Ferroni-Dini method" (or the "Florentin" method). According to some other litterateur the chemistry of this method has been introduced by scientists Mori, Philippotu and Matteini. (Malinar H.2003, p. 78) In Sweden the method has been known through an introduction by Professor Piero Baglioni. (Svahn Garreau, 2010, p. 16)

CHAPTER 2

CONSOLIDATION VALUES AND METHODS TO BE DISUSSED

Although a lot of research has been done in conservation of stone it is necessary to question and search for other sources then we already know. With understanding that each situation is unique and in order to find best possible course of action, it is important to have greater knowledge of investigative methods and of different rock types and consolidation characteristics, and how they interact with each other and with the prevailing environment and climate.

2.1 VALUES

According to known principles in conservation, the important understanding is issue in this thesis; "*Consolidation should not be considered as a single operation. It is a part of a series of processes which include diagnosis, cleaning, pre-consolidation, consolidation, surface protection, and maintenance. Additionally, consolidation should be performed only in specific cases when the degree of deterioration threatens the integrity of the material and after considering other less invasive treatment options.*" (Oztiirk, Isil 1992, p. 2)

Consolidant properties to be considered when evaluating a consolidant system:
consolidating value (surface reinforcement)
depth of penetration
effect on appearance
compatibility of consolidant with substrate
durability of treatment
effect on liquid water and vapor permeability (moisture transfer)
effect on stone porosity
biological resistance
ease of application
health and safety issues

(Hansen & Doehne 2000, p. 1)

2. 2 MATERIALS

Different agents and materials have been selected and used for consolidation of stone: some more due to their availability than due to their predetermined qualities. (Doehne, Ferguson & Price, 2010, p.38)
A major problem is to find materials which are compatible with the components of the substrate. Some other problems are the depth of penetration and long term stability.
The development of inorganic consolidates has been dominated by organosilicon agents which work mostly as impregnation coatings. The methods in focus are compatible with a limestone and other calcareous surfaces and also permit a reduction of soluble salts. The methods which are discussed are: calcium hydroxide, barium hydroxide, ammonium carbonate, ammonium oxalate, the new developments of nano-lime techniques and alkoxysilanes.

The use of polymer and silica gel consolidants (alkoxysilanes) for porous limestone and other calcareous surfaces is well documented in the conservation literature, while the materials and methods previously mentioned, (the old and new methods) are not that well represented, despite their potential usefulness particularly in case of salts attacks. (Hansen & Doehne 2000, p. 1-32)

The organic polymers have been tested and mostly used as stone consolidants, but several inorganic materials need to be mentioned as they operate quite differently, for example: calcium hydroxide (lime water) and barium hydroxide.

2.2.1 Calcium hydroxide

The aqueous solutions of calcium hydroxide (known as a limewater) have been used for centuries to treat limestone. Calcium hydroxide readily reacts with atmospheric carbon dioxide and forms insoluble calcium carbonate, which may bind particles of calcareous stones together.

Isil Oztiirk, in his Master of science thesis in 1992 “Alkoxysilanes consolidation of stone and earthen buildings materials” wrote:” *Despite more than a hundred years of experience in the application of various chemical substances to consolidate stone, little success has been achieved with inorganic materials*.” (Oztiirk, Isil 1992, p.10)

2.2.2 Barium hydroxide

The method combines techniques for desalination/reduction of gypsum and consolidation on lime stone. The latest development of this method has come from the field of wall paintings, presented by Philippotu, Matteini and Mori (1991). They are conservator scientist whose work is often related to science center “*Opificio delle Pietre Dure*” Florence, Italy or to Getty Conservation Institute.

S.Z. Lewin (1970) has developed a barium hydroxide technique by adding urea and glycerol for the work “in situ”.

2.2.3 Ammonium carbonate

The pronominal treatment to the barium hydroxid method seems to have developed in the field of wall paintings, where Philippotu, Matteini and Mori (1991) have suggested that the barium hydroxide method should be preceded by the use of ammonium carbonate, in order to dissolve the calcium sulfate. (Malinar H. 2003, p. 79)

According to C.A Price (1996), the use of this procedure on stone is still experimental. A result of this method has yet to be reported. (Price C.A.1996, p.18)

2.2.4 Nano-lime / Colloidal calcium hydroxide sols

It seems that the development of Matteini’s or Ferroni-Dini method -ammonium carbonate method for stone and calcerious surfaces is followed by the new nano-lime technology. The nano -lime method is one of the steps in the sequences of conservation of the wall paintings which professor Baglioni presented here in Sweden. The “two steps ammonium carbonate method” is combined or developed with nano compounds of carbonates. (Svahn Garreau 2010, p.16) The technique is developed since 2000 (Giorgi, Dei, and Baglioni 2000; Ambrosi et al. 2001; Dei and Salvadori 2006; Adolfs 2007; Ziegenbalg 2008). (Svahn Garreau 2010, p. 16)

2.2.5 Ammonium oxalate

Calcium oxalate is patina which according to some sources naturally occurs on the stone. Once it has been taken away it takes centuries to repair. There are different opinions about the origin of this patina. It can appear in the presence of lichen, but it could also have been artificially made by the earlier conservations. The method is based on conversion of calcium sulfate and carbonate to the more durable calcium oxalate by ammonium oxalate. (Cesar T. 2006, p. 3)

2.2.6 Polychromy

How much polychromy has been used as a protection for the stone surfaces is an actuality in Swedish restorations polemics right now. One of the few written documents in Sweden was the examination of Cecilia Strömer, Heléne Arthursson *“Stormaktens Polykroma stenskulptur”* 2006 and Raä report written by Claesson & Henningsson 2011, *“Painted* *stone in Swedish heritage: a study of color as the surface protection and history of Swedish stone conservation and restoration"*. The text covers discussions and attitudes towards painted stone in contemporary Swedish restoration of the heritage and an evaluation of the paint compatibility with the underlying material, in particular with the silicone harts' paint. (Claesson & Henningsson 2011, p. 8)

2.2.7 Alkoxysilanes

Nowadays the organosilicon compounds find a wide application as stone consolidating agents for historical monuments. The most commonly used alkoxysilanes are tetraethoxysilane, triethoxymethylsilane and trimethoxymethylsilane. The lack of bounding to calcareous materials has long been an issue and an important subject of investigations. "Siliceous consolidants have been used to consolidate sandstone and limestone based upon the principle that formation of silica or insoluble silicates occurs within the pores of the stone." This means penetration ability depends of particularly low molecular weight. (Oztiirk Isil 1992, p. 2)

Except for the alkoxysilanes, which are important part of discussion due to their widespread use and commercial availability, the methods discussed here can be seen as preventive measures. This methods and materials will be closely described later on in chapters 4, 5, 6 and 7.

CHAPTER 3

MOISTURE AND SALTS AS A FACTOR OF DEGRADATION OF LIMESTONE /STONE

Salts are widely recognized as a major contributor to the loss of the world´s architectural heritage and other engineering structures as well as outdoor sculptures and museum objects. The damage is the result of salt crystals growing, from solutions, within porous structure of materials such as stone, ceramic or concrete. Salt weathering requires not only the presence of the salts but also sources of moisture and suitable environmental conditions. The crystal growth can occur as a result of crystallization from supersaturated solutions, of changes in hydration state, or more rarely of chemical reactions. (Prikryl R. 2002, p. 175)

3.1 LIQUID WATER AND MOISTURE

Liquid water has a number of effects. Dissolution of calcite by absorbed carbon dioxide in rainwater is an issue. Dissolution of marble is increased by acidic precipitation from gaseous pollutants. Water also produces wetting and drying cycles of stone creating destructive effects of salt crystallization cycles. It seems that calcareous stones like limestone or marble become more susceptible to this form of damage as it ages. (Torraca G. 1988, p.15)

Rain may damage a stone in two ways. The first way is when rain falls on the stone. It works by striking the stone which damages it mechanically. Weaker related particles erupt from the surface and thereby change the relief of the stone. Thus, this mechanical effect is called *erosion*.
Another way is when rainwater erodes limestone by chemical reaction. Rainwater has in itself the dissolved carbon dioxide (CO_2) which makes carbonic acid ($H2CO_3$). Although this is a weak acid, it breaks down calcium carbonate into soluble hydrogen- carbonate. This degradation process is called *corrosion*. (Malinar H. 2003, p.19)

The speed of deterioration of limestone depends of the binder. This reaction is revertible. Because of hydrogen- carbonate’s instability, in some environmental conditions, soluble hydrogen -carbonate will turn back into carbonate and build formations on stone surface. (Malinar H. 2003, p.19)

Except for the rain, the liquid water can damage stone by rising damp/ rising of ground water which enters the stone by *capillary moisture*. When the stone/wall is filled with 20% of moisture or more, the evaporation happens only on the surface.
In case when water does not evaporate, moisture will rise until maximum level which depends on pore radius and stone structure. Height of the capillary ascent in the building materials depends on the pore radius and the intensity of evaporation. The smallest capillary structure creates the highest capillary moisture. When the temperature of the outside air increases, it reduces the moisture in the wall and zone of crystallization withdraws to the interior of the wall. That causes damage to the wall material. (Torraca G.1988, p. 148, Malinar ,H. 2003 p. 17-23)

Condensation moisture depends on the difference between outdoor and indoor temperature, cold surfaces and hot air, when warm air in springtime moves into unheated houses. Point of condensation is a dew point which depends on the relation between relative humidity and temperature.

3.2 HYGROSCOPIC SALTS

This moisture is related to high relative humidity, fluctuating temperature and high level of hygroscopic salts in the stone. The growth of damaging salt crystals is usually attributable to crystallization, caused by the evaporation or cooling of salt solutions within the stone. In the past, there was much reference to “hydration damage,” building on the fact that some salts can exist in more than one hydration state. The prime example is sodium sulfate, one of the most damaging of soluble salts, which can exist as the anhydrous salt thenardite (Na_2SO_4) or the decahydrate mirabilite ($Na_2SO_4 \cdot 10H_2O$). (Malinar H. 2003, p.19)

Thenardite increases in volume by more than three times upon conversion to mirabilite, and it has been argued that this growth in volume was the cause of so-called “hydration damage”. (Doehne, Price 2010, p. 19-30)

Salts in the stone may be of different chemical composition and origin. The most common are sulfate groups (polluted atmosphere or ground water), chloride (from the sea, blown by the wind) and nitrate (polluted atmosphere, agricultural and microbiological sources). Air pollution is a major source of sulfates and nitrates. (Teutonico J. M. 1988, p.21)

When coal was used for heating it composed a large percentage of sulfur that released SO_2 by burning. Sulfur dioxide further oxidizes to SO_3, which together with water gives sulfuric acid. The acid destroys the calcium carbonate from limestone and converts it into calcium sulfate $CaSO_4x2H_2O$ - gypsum. (Doehne, Ferguson & Price 2010, p.18)

The sources of salts can be building materials themselves (sand, bricks, mortar) or other external sources. Other sources include the soil, from which salts may be carried into masonry by rising damp (some already mentioned); salts blown by the wind from the sea or the desert; deicing salt scattered on roads in winter; unsuitable cleaning materials; incompatible building materials; garden fertilizers or products generated by metabolism of micro-organisms. (Borrelli E. 1988, p. 3)

Salt damage does not occur only in an outdoor environment, where the stone is subjected to cycles of rainfall and subsequent drying. It can also take place indoors, through the hygroscopic action of the salts. Severe damage to stonework held in uncontrolled museum environments is not uncommon. (Rodriguez-Navarro H. et al 1984-1998, p. 15)

3.2.1 Salts

The biggest questions in consolidation process are the salts and the hygroscopicity of material before and after conservation.

Moisture content in a material depends on relative humidity of the air and of hygroscopicity of salts. Most of the soluble salts are much more hygroscopic then stone/ sand, bricks, mortar. But salts do not move if the temperature and RH is stable, and not all salts generate decay. This depends on their solubility, hygroscopicity, mobility and the hydration level or their crystalline form.

After a prolonged watering, with a change of temperature the stone begins to dry. Emergence of moisture evaporating through the pores of the stone evaporating leaves the soluble salts behind. The solutions/soluble salts become more concentrated with repetitive evaporation changes in RH (relative humidity) and the temperature. When the concentration of salts reaches the highest possible level (depends on the material and pores) and the solution of salts is supersaturated the salts become crystallized.

This can create a white powdery appearance on the surface which we call *efflorescence.*

A critical moment occurs when the volume of crystal becomes equal the size of the pores, creating stress (crystallization pressures that are transmitted to the pore wall); and the crystals grow below the surface layer. This manifestation of salts we call *sub-efflorescence*. These pressures can reach very high levels which results in spalling and dispersal of materials. (Borrelli 1988, p. 3 ; Malinar H. 2003, p.20)

Salts of nitrates, chlorides, carbonates and hydrogen carbonates crystallize at the surface of the stone as efflorescence, and the sulfates and oxalates crystallize with sub-efflorescence. It is very important to know the salts content of deteriorated surfaces to understand the causes of decay and to plan the conservation strategies. (Malinar H. 2003, p.20)

3.2.2 Sulfates

The combustion of fossil fuels releases sulfur dioxide. Sulfur dioxide under the influence of ultraviolet rays oxidizes to sulfur trioxide. Sulfur trioxide in the reaction with water from the atmosphere turns into sulfuric acid acting on calcium carbonate turning it into damaging calcium sulfate:

a) $S+O_2$ ---- SO_2
b) SO_2+O2------SO_3
c) SO_3+H_2O------H_2SO_4

Creation of sulfuric acid in the atmosphere can be interpreted in this way: SO2 in contact with water is converted into sulfurous acid, H_2SO_3, which with the molecules of ozone O3 oxidized to sulfuric acid, H_2SO_4.

$$SO_2+H_2O\text{-----------------}H_2SO_3\xrightarrow[H_2O_2]{O_3}H_2SO_4$$

The oxidation of SO_2 to SO_3 can also occur by actions of sulfur oxidized bacteria. (Mestrovic & Saran 2010, p. 89)
A black crust is most common form of sulfate deterioration.

3.3 FROST

The collection of water generally within the sedimentary stone masonry of standing walls or ruins can lead to spalling of face stonework. The moisture penetration at the top, in most materials, permeates down toward ground level. Frost damage is often limited to the base of the wall masonry which remains wet for a long period of time. If the ground of the wall has not fully dried out the bases of these structures become susceptible to frost damage.

The combination of frost and salts damage occurs often because of the unbalanced and fragile ecology when groundwater raises salinity level. This is a major reason why some of the worst “salt damp” problems occur. Typically the lower masonry in the historic structures suffers almost complete collapse into powder. (Ashurs J. 2007, p. 22- 24)

From the above, it is obvious that moisture has an indirect and direct role in deterioration of stone. To repair a damaged stone we need to make a proper diagnosis. It consists of an overview of stone, determining the cause of wetting and chemical analysis of soluble salts. The decision on the process of conservation is made based on the types of salts in the stone.

3.4 DETERIORATION MECHANISM OF SOLUBLE SALTS

Solubility of the salts is in direct relation with the damaging effect on the material. We can distinguish between three types of salts, based on their solubility.
Practically *insoluble salts* (mostly carbonates) do not crystallize, mostly because of their poor solubility.
Slightly soluble salts generally cause more decay. Because of their low solubility, they often crystallize just below the surface and cause bulging, detachment and loss of fragments. Among these, sulfate *gypsum* is the predominant salt ($CaSO_4$-$2H_2O$).
Highly soluble salts are mostly chlorides and nitrates (sodium chloride NaCl, sodium nitrate $NaNO_3$, potassium nitrate KNO_3). They can accumulate and reach very high concentrations. Their hygroscopic salts in humid environments remain in solution producing a dark patches. Because of high solubility, the crystallization requires a strong evaporation that takes place especially on the surface causing limited damage. When the crystallization occurs, efflorescence appears, but sometimes crystallization spreads below the surface layer, affecting cohesion – subefforescence. (Borrelli E. 1988, p. 5)

Another parameter for evaluating the danger of salts is their hydration properties. I have already mentioned $NaSO_4$-$10H_2O$ (mirabilite), which is an extremely soluble salt and according to previous explanation should not be too dangerous, but it is. It derives from hydration of $NaSO_4$ (thenaride), and increases in volume for about 400%.

Conclusion:

Presence of soluble salts affects decay of stone in the following ways:

- Soluble salts dissolve in humid air and produce phenomena of *osmosis* and hygroscopicity, causing an increase in the moisture content in material.
- Depending on microclimatic variations, frequent changes give a rise of salt concentration, which creates crystallization cycles of saline solution. This produces mechanical stress and consequent crumbling of material.
- When salts crystallize close to the surface, they form efflorescence and sub-efflorescence.

The slightly soluble salts do the most damage as they expand below the surface and can push surface off. Very soluble salts usually crystallize at the surface and can be brushed off. The insoluble salts stay either on or below surface. (Borrelli E. 1988, p. 3-7)

CHAPTER 4

COMPATIBILITY OF CONSOLIDANTS AND METHODS WITH LIMESTONE

4.1 INORGANIC CONSOLIDANTS AND METHODS

“The use of inorganic materials as consolidants is an effort to produce a decay- resistant phase in the pores of deteriorated stone from aqueous solutions. The deposition, that will bind stone particles together, can result from evaporation of the solvent or chemical reactions with the stone”. (Oztiirk Isil 1992, p. 12)

4.1.1 CALCIUM HYDROXIDE - LIMEWATER

The aqueous solutions of calcium hydroxide (known as limewater) have been used for centuries to treat limestone. When saturated in a solution, the calcium hydroxide readily reacts with atmospheric carbon dioxide and forms the insoluble calcium carbonate, which may bind particles of calcareous stones together. (Clifton J. R. 2010, p. 3)

$Ca\ (OH)_2 + CO_2\text{------}\ H_2O + CaCO_3$

There are doubts about calcium hydroxide’s ability to bond detached stone particles together. Some improvements in the application of limewater have been achieved at the Wells Cathedral in England by Professor Baker, 1970, known as the "lime method", or ”Baker" or "Wells " method. The treatment is divided in several steps: cleaning, consolidation, repair, and surface coating. Baker was using a 38 mm thick slime of slacked lime during three- week period, which was then removed followed by fresh diluted limewater which was stroking about 40 times. There have been different and conflicting opinions by conservators, about the effectiveness of the limewater method.

The limewater compatibility with a limestone meets consolidation requests well, but the application is often difficult and many times depends only on conservators’ skills. (Oztiirk Isil 1992, p. 12 and Price 1996, p. 32).The method has mainly been criticized due to a lack of deep penetration and the hard, shallow surface in the outer grain of stone, which gradually exfoliates. (Hansen , Dhoene et.al 2000, p. 9)

The solubility of calcium hydroxide in water is very limited, the solubility scale is 1 (meanings 1 gram of calcium oxide in 1 liter water).
The other problem is when the reaction with CO_2 happens to soon and carbonization takes place only at the surface. Those are the main reasons to increase the concentration of calcium hydroxide in the solution.
Addition of different substance has been suggested as a solution to this problem; sugars, carbohydrates or other organic materials, and lately it has been suggested to include small amounts of crystallization inhibitors. A method of precipitation from *homogeneous solutions** has been developed in order to obtain deeper penetration of stone by some inorganic consolidants. Or by introduction of carbon dioxide by carbonated water, or by carbamates (urea) which produce carbon dioxide by chemical reaction in the homogeneous solutions. (Clifton James 2010, p. 4)

**A method, referred to as precipitation from homogeneous solutions, has been developed to obtain deeper penetration of stone by some inorganic consolidants (carbamates).*

4.1.2 BARIUM HYDROXIDE

S.Z. Lewin and Sayre (1970) have developed a barium hydroxide method including also addition of urea and glycerin but more important was the length of absorption, and the length of the carbonization (periods of about 20 days) which they believed, ensured a slow growth of well formed barium carbonate crystals within the stone. It combines the processes for the desalination/reduction of gypsum and consolidation on lime stone. (Lewin S. Z. 1974, p. 24-35) In order to precipitate barium carbonate and barium sulfate deeply within a stone Lewin and Sayre have developed a method based on a process known as "*precipitation from homogeneous solution*". "In this process the material to be precipitated and the precipitating chemicals are present in the same solution. For example, barium carbonate is precipitated from an aqueous solution of barium hydroxide and urea."(Clifton J. R. 2010, p. 3) Lewin suggested that this method is very suitable for certain types of calcareous stone, because although certain whiteness appears after drying , it is otherwise safe and effective in consolidation when applied to an appropriate stone using a suitable technique.

4.1.2.1 Process with 7% Barium hydroxide and 4% urea

Similar to calcium hydroxide, barium hydroxide reacts with carbon dioxide resulting in the precipitation of insoluble carbonates. (Hansen et.al 2000, p. 6)

After years of atmospheric attack by sulfur dioxide, stone loses its molecular cohesion and under a destructive influence of polluted atmosphere degrades into gypsum.
What actually happens in this process besides reduction of gypsum (desalination), is a consolidation, even though $Ba(OH)_2$ compounds are not consolidation agents.
The easily soluble sulfate gypsum (calcium sulfate dimhydrat ($CaSO_4$ $(H_2O)_2$) converts into more stable compounds, insoluble and non-harmful barite $BaSO_4$ (barium sulfate), and calcium dihydroxide (lime - $Ca(OH)2$) which, in contact with CO_2 is transformed into carbonate (calcite), $CaCO_3$. Urea accelerates the reaction with CO_2. Urea undergoes process of hydrolysis and slowly dissociates into ammonia and CO_2 carbon dioxide.

$CaSO_4;2H_2O$ (calcium sulfate gypsum) + $Ba(OH)_2$-----$BaSO_4$(non harmful barite) $Ca(OH)_2$(lime) +$2H_2O$
+ CO_2 (atmospheric)
$Ca\ (OH)_2+CO_2$-----$CaCO_3$ (calcite)+H_2O
CO_2 in a soluble condition penetrates pores and accelerates the reaction.

"The liberated ammonia and carbon dioxide dissolves in water forming ammonium carbonate which raises the pH of the solution. When a certain pH is reached, barium hydroxide reacts with the carbonate ion and barium carbonate is precipitated". (Clifton J. R, 2010, p.4) The process can be controlled by slow formation of barium carbonate which is the main reason for using a cellulose pulp after immersion in barium solution (Levin's method 1974). Both processes should take two- to three weeks, which means that the whole process takes a minimum of one month. This approach has been reported to give a crystalline solid solution with the calcite crystals of calcareous stone. (Hansen & Doehne ,2000, p.16)

First phase: $CaCO_j + Ba(OH)_2 = BaCO_j + Ca(OH)_2$
Ion exchange
Second phase: $Ba(OH)_2 + COj$ (atmospheric) $= BaCOj + HjO$
Carbonation of Surface
$Ba(OH)_2 + CO(NH_2)_2$ (urea) $= BaCOj + 2NH_3$
Carbonation of Interior

4.1.2.2 Shortened conservation process

The pulp with $Ba(OH)_2$ and urea is applied and remains wet for ten days. During this period the pulp should be replaced at least three times and kept wet. After three weeks, the cellulose pulp should be taken away, stone brushed off of the barium white layer and washed with vaporizer.

4.1.3 AMMONIUM CARBONATE

According to Mori and Philippotu Matteini, the painted stones with calcium sulfates have been treated with a solution of ammonium carbonate, because it is alkaline and does not constitute a threat to some dyes. They have also suggested (1991) that the barium hydroxide method should be preceded by the use of ammonium carbonate; in order to dissolve the calcium sulfate (Malinar H.2003, p.19)
The method is used on limestone and other calcareous surfaces as well. The principal is based on carbonation process of degraded material, reduction of gypsum/salts and the consolidation on lime stone. It is a two step method with ammonium carbonate and barium hydroxide known as the “Florentin” or “Ferroni- Dini” or “Florian” method.

4.1.3.1 Presentation of method

The method applied in two steps:
Step 1) application of ammonium carbonate which reacts with the gypsum and creates the calcium carbonate and water-soluble ammonium sulfate,
Step 2) application of barium hydroxide which makes the sulfur insoluble (barium sulfate).

Step 1: In this reaction, reduction of gypsum takes place, and then soluble ammonium sulfate forms along with the insoluble calcium carbonate. It is important to prevent and remove the possibility of a negative effect of $(NH_4)\ 2SO_4$. The ammonium sulfate can be removed the same way as chlorides; both chlorides and ammonium sulfate migrate to the surface of stone covered with cellulose pulp and emerge in some distillate water.
The ammonium sulfate as an extremely soluble substance, readily reacts with water, migrates to the surface and soaks in cellulose pulp.

$CaSO_4$, $2H_2O$ (sulfate) gypsum + $(NH_4)\ 2CO_3$ ---- $(NH_4)\ 2SO_4$ (aq) soluble in water + $CaCO_3$ +$2H_2O$

Step 2: A more effective method or another step in preventing harmful effects of $(NH_4)\ 2SO_4$ is by the neutralization with the cellulose pulp containing $Ba(OH)_2$. This we do by adding a new /second layer of cellulose pulp containing barium hydroxide which additionally binds ammonium sulfate and builds barium sulfate (not deleterious). Thereafter the packaging can be removed only in a dry state. This is not recommended for exfoliated surfaces.

$(NH_4)\ 2SO_4$ + $Ba(OH)_2$ ------ $BaSO_4$ (insoluble barite /not deleterious) +$2NH_3$ +2 H_2O (ammonia and water evaporates)

The principle of application: The ammonium carbonate mixed with cellulose pulp is applied on the stone and kept wet for a few days under controlled temperature of 15 degrees C.
Consolidation reaction:

$Ba(OH)_2 + CaCO_3 \rightarrow Ca(OH)_2 + BaCO_3$
and $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

4.1.3.2 Quick process with ammonium carbonate and barium hydroxide

Spray with 15 % $(NH_4)\ 2CO_3$ in distillated water; let stay for four hours before adding $Ba(OH)_2$. The stone must sustain moisture during the whole process so as not to let barium dry and crystallize, or clog pores before deeper penetration takes place.
The pulp with 7 % $Ba(OH)_2$ is applied once, and holds until it dries (or it has to be repeated in wet conditions). After three weeks, the stone can be brushed off and washed with vaporizer.

Step 1 $(NH_4)2CO_3 + CaSO_4.H_2O \rightarrow (NH_4)2SO_4 + CaCO_3 + 2\ H_2O$
Step 2 $(NH_4)2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2NH_3 + 2H_2O$

4.1.3.3 Important reminder

The pulp is sprayed with the $Ba(OH)_2$ solution. The cellulose pulp must be covered or the moisture maintained by regular spraying.
- Removal of the cellulose pulp with distilled water is carried out when the pulp is in dry condition.
- Removal of cellulose pulp with ammonium carbonate is carried out only when the pulp is in wet condition. It reduces the risk of dragging bits of more fragile parts during the removal.
- The use of those methods without proper safety precautions may be seen as hazardous to human health.

4.1.4 NANO-LIME METHOD

Nowadays, a new development in the field of nano technique has led to the development of the calcium hydroxide method into “nano-lime”. The colloidal calcium hydroxide nano particles are stable when dispersed in different alcohols (ethanol, iso-propanol, isopropyl). In a way similar to the traditional treatment of limestone, after evaporation of the alcohol, the nano-lime results in the formation of solid calcium hydroxide, which converts into $CaCO_3$ (calcite) by reaction with atmospheric carbon dioxide. The nano technique improves not only pervious method, but can be used with ammonium carbonate method; although it is still in investigating stage. (Svahn Garreau, Hélène (2010), p. 16)
This technology suspends nano-scale calcium hydroxide particles in alcohol, permits a deep penetration in the limestone (calcareous surfaces), and at the same time limits carbonation by CO_2 before the particles are deposited in the porous stone. (Doehne & Price 2010, p. 38)

$Ca\ (OH)_2 + CO_2 \longrightarrow CaCO_3$ (calcite) : Carbonation Process

The lime with high concentration of calcium hydroxide particles in nano size is much more reactive than lime slaked in water. The particles are dispersed in alcohol to prevent carbonation before the application. There is a product which has been commercially available since 2006 under the trade name CaLoSiL, a some products are compatible with silicic acid ether (ethyl silicate) or combined with it. (Piaszczynski & Wolf 2010, p.2)

4.1.5 AMMONIUM OXALATE

“Naturally occurring calcium oxalate patina, called “Scialbatura” had been found on stone, wall-paintings, other works of art and on natural outcrops of limestone and marble.” (Cezar T. M. 2006, p 6) There are different opinions about the origin of this patina. It can appear by presence of lichen, but it can also be artificially made by previous conservations.

The painted stones and marble sculptures in heavily polluted environments attacked by calcium sulfate can be repaired and coated with a solution of ammonium oxalate. Thus the insoluble calcium oxalate (mineral- monohydrate whewellite* and dehydrated weddelite*) occurs, which is an excellent protection of stone. (Malinar H. 2003, p.79)

Matteini, Moles, and Giovannoni (1994) have proposed this technique after observing a natural oxalate patina on stone surfaces known as "scialbatura". (Malinar H. 2003, p.80)

This natural conversion of calcium carbonate to calcium oxalate has led to experiments in "*Opificio delle Pietre Dure"* in Florence (Italy), using an artificially induced conversion to protect stone and lime plaster. The treatment relies on the controlled use of a naturally occurring chemical process using ammonium oxalate as a chemical compound. (Cezar T.M. 2006, p. 8)

The conversion of calcium sulfate and carbonate to the more durable calcium oxalate ($CaC_2O_4 \bullet 2H_2O$) by ammonium oxalate can be present as passivating action and as consolidation action.

$CaCO_3 + (NH_4)2C_2O_2$ aq ---------------- $CaC_2O_4 \bullet 2H_2O + NH_3 + CO_2$
(Calcium oxalate dehydrate)

Weddellite* - calcium oxalate dehydrat ($CaC_2O_4 \bullet 2H_2O$)
Whewellite* - calcium oxalate monohydrate ($CaC_2O_4 \bullet H_2O$)

Desulfating action: $CaSO_4 + (NH_4)2C_2O_4$---------- Ca $C_2O_4 + (NH_4)2SO_4$

This method converts both calcium sulfate (gypsum) and calcium carbonate into a thin, protective layer. (Matteini Mauro 2012, p.22)

Unfortunately, these chemical conversions cannot eliminate nitrates, and if chemical analyses have been performed on the stone, they can be removed only by immersion in a water bath, rinsing with water or with wet compresses. (Malinar H. 2003, p.79)

"Scialbatura" provides passivating barrier as well as sacrificial surface and it is highly resistant to acid attack. The solubility studies show that the dissolution of calcium oxalate is not as pH dependent as the calcium carbonate." (Cezar T.M. 2006, p.6-12)

It is used mostly in acidic environment as the protection from acid rain, and is often applied directly to the stone surface. Some researches discuss this method ass a problem of the future conservation.

4.2 ORGANOSILCON CONSOLIDANTS

Nowadays the silane-based materials, in general the organo-silicon compounds, are available on the market a wide range of facilities and under different names (ethyl silicone, ethyl silicate, methyl silicone, silicic acids ether or ester) as they are widely used as the stone consolidating agents for historical monuments.

4.2.1Alkoxysilanes

Alkoxysilanes are monomeric organo-silicon compounds containing silicon, oxygen, carbon and hydrogen atoms. They react with water to give a solid polymer.

Among these compounds of synthetic organic monomer, the following ones are most commonly used and known: tetraetoxysilane(THEOS), methyltrimethoxysilane(MTMOS), methyltriethoxysilane(MTEOS) and ethyltriethoxysilae (ETEOS). The final product of their consolidating effects is a polymer network (gel) formed through the process of hydrolysis and condensation to the polymers chains. Silica –gel is produced by the polymerization (cros-linking reaction) of silicic acid ethers (monomers THEOS, MTMOS, ETEOS). (Oztiirk Isil 1992, p. 31-33)

Thorough the bounding process with silicic based materials (sandstone) those monomers create strong bound building a cross-linking network inside the pores. This reaction does not have the same bonding ability on limestone or marble.

The process of polymerization (hydrolysis and condensation) takes place in the moment of deposition on the stone, creating formations of siloxane linkages (-Si-O-Si-) which are responsible for the strengthening effect. A byproduct of this reaction is alcohol.

If ethyl silicate in resin meets moisture in the air, ethanol and silicone gel is produced by the reaction between ethyl silicate and the moisture. Ethanol is evaporated from the surface of stone and silicone gel is consolidated in the stone. (Shin G. H. 2004, p. 473)

Si(OEt)4 + 4 H2O-------- SiO2 aq + Catalyst ----------4EtOH
Ethyl silicate Water Silica gel Alcohol

The rate of polycondensation and the structure of the formed products depends on amount of water used in the reaction, the type of catalysts, the type of hydrocarbon group (methyl, ethyl), which is attached to the silane and the type of solvents, as well as the temperature and the RH (relative humidity) during deposition.

There is a difference between impregnation (surface coatings) and consolidation; some alkoxsysilanes are both impregnating/hydrophilic and consolisating agents. Alkoxysilanes with methyl groups (CH_3) provide water repellency as well as consolidation (MTMOS). (Isil Oztiirk ,1992, p. 30)

Elastified silanes are modified nano particles of alkoxysilanes which have been developed to improve bonding processes probably for the limestone and marble. The nano particle-modified silanes are elastically modified ethyl silicate with fumed silica as filler. A commercial elastified version is known as Funcosil (KSA 500 STA) and also as
E. Wendler; Remmers KSE 500 E. (Skrdlantova Marketa 2004, p. 291-298)

4.2.2 Ethyl Silicate- Tetraehoxysilane (THEOS)

Ethyl silicate,THEOS, Si (OCH2-CH3)4 or [Si(OC2H5)4] is the best known alkoxysilane. It has also been used in the literature to refer to tetraethoxysilane, silicic acid ethyl ester, silicon ester, tetra(ethyl) orthosilicate (TEOS) ethyl silicate. Ethyl silicate has an extremely low viscosity that is lower than the viscosity of water which makes ethyl silicate more mobile than water. These phenomena describe a consolidant with excellent properties for penetration in porous materials. (Oztiirk Isil 1992, p. 10, p. 54-56)

4.2.3 Alkoxysilanes and hygroscopic salts

It was noted early that MTMOS cured and consolidated the stone in the presence of salts, but this was soon found incorrect. It was originally thought that the deposited gels would encapsulate and thereby deactivate salts. It has been found instead that salts break down the silane network. MTMOS treatment actually mobilized salts in limestone causing efflorescence. But surprisingly it was also reported that salts removal after treatment with MTMOS was possible. It has been reported that salts removal on sandstone is much more delicate and difficult due to the bond created between substrate and coating media. (Wheeler George 2005, p 74-75)

4.2.4 Properties

Two properties of alkoxysilane are often mentioned: its low viscosity and its ability to form siloxane bounds (Si-O-Si). The siloxane bonds, aside from the strengthening effect, have thermal and oxidative stability and resistance to ultraviolet solar radiation.
That means that alkoxysilanes keep their chemical properties independent of temperature or surrounding buildings materials (e.g. metals or glass).
The treatment with alkoxsysilanes is not reversible but allows new treatments, coating pores but not closing them, which allows material to breathe. They are hydrorepellent* /transpiring protective coatings, except for the MTMOS. Those materials inhibit the transfer of water in the liquid phase but allow the passage of water in the form of vapor.
Alkoxysilanes belong to low toxic consolidants.

Although this consolidant is mostly used in conservation of sand stone its use has also been attempts on limestone and marble. Those attempts will be discussed further in chapter 7.

CHAPTER 5

CASE STUDY I

5.1Renaissance relief 1450/ 1500 Sculptor Nicola Firentinac, Lunette; St:Ana, Hvar / Case study- sculpture in architectural environment with a trace of polychromy

Figure 1- Barium hydroxide method, Limestone, photo; Vinka Marinkovic 2011

The relief is part of a triptych and has long been on display in the exterior of the church as exhibit from their art collection. It is attributed to the architect and sculptor Nikola Firentinac 1450's, one of the greatest Renaissance masters in Dalmatia / Croatia, known for the building of the Cathedral in Sibenk.
The chemical analysis of the salts has shown presence of sulfides and chlorides. The analysis of pigments detected a presence of red pigment which now appears as black. A green pigment has been found on the shield and drapery, but the source of the color has not yet been identified. Master Firentinac has been known for polychromy with red and green. The brown-red patches on the stone are probably consisting of iron sulfide caused by the presence of mineral pyrite.

5.1.1 Difficulties in desalination process

In this case, the stone eroded just below the oxalate (epidermal) layer. Salts have built the crystals below the surface creating sub-efflorescence and blew up the stone in some places, mostly at the shoulders. The stone was pre-consolidated with Ba $(OH)_2$ + urea. The aim was to consolidate the most damaged parts and prepare the object for treatment with a total immersion in barium solution. Parallel to this, it was important to protect the polychromy during the treatment. Two possibilities were considered; one with temporarily consolidant cyclododecan (synthetic wax), and the other possibility was Paraloid B -72.
After the process of total immersion for three weeks and another three weeks of drying during the crystallization time, the stone has also been injected with acrylic emulsion in small cavities and porous parts with cracks.

5.2 Pre-consolidation

In order to protect a stone during consolidation by total immersion, the stone has been pre-consolidated with a local desalination/ pre-consolidation with the Ba $(OH)_2$.
At first, injections of barium hydroxide have to be repeated every 10 minutes in order to keep the stone wet. Thereafter one proceeds with the cellulosic pulp and $Ba(OH)_2$, but only on the solid surfaces preventing damage of the fragile parts. The object was kept in the moist condition covered by the PVC plastic and sprayed regularly (three times a day) during two to three days. The cellulosic pulp was kept on for 2 days. After two days, the relief was allowed to dry covered with a PVC cover. During this second phase, barium chemistry operates in 20 days. By adding any chemicals or water during this second part of the method, the stone can be seriously damaged. That is one of the difficulties during “in situ” conservation.


Figure 2


Figure 3


Figure 4

5.2.1 Step by step description

1. Pre-consolidation with $Ba(OH)_2$ and urea results in a white powdery film forming which was brushed away. *(Figure 2)*
2. As the salts have been formed just below the surface undermining the stone material, a gap filling was performed by injecting an acrylic emulsion (product name Adewat). One reason was to protect the stone during the total immersion with $Ba(OH)_2$. To break the capillary tension of the surface an alcohol-ethanol was used.
3. After the pretreatment with an acrylic emulsion (trade name Adewat), an “acrylic calcite concrete” (trade name “Margrip”) developed for that particular stone was applied. Acrylic emulsion was applied only around the fragile edges, where the stone had exfoliated the most. *(Figure 3)*
4. It was important to protect the polychromy. With a use of a high percentage (8%) of the Paraloid B-72* one has prevented this adhesive to be absorbed by substrate.

Paraloid B-72 is copolymer of ethyl methacrylate and methyl acrylate. Paraloid B-72 is soluble in acetone, toluene and isopranol.
In this case Paraloid B-72 was used as temporarily consolidant which was easily removed with acetone after the consolidation treatment.


Figures 5,6,7: Amplification with “acrylic calcite concrete” (“Margrip”) before immersion in the solution.

5.2.2 Consolidation/ desalination by total immersion

The solution with the barium hydroxide was heated up to 70 ° C – (7% $Ba(OH)_2$). 4% urea prevents the process of drying, retains moisture and accelerates the reaction with CO_2.

1. The object was immersed in the solution and covered with plastic during almost three weeks.
2. Afterwards it was allowed to dry under the plastic for another three weeks. During this second phase crystals growth occurs.
3. After drying the bariums whitish appearance were brushed off and washed away with soft brushes and distilled water.
4. Afterwards the barium was still visible. The object was treated again and re-fixed selectively with cellulose pulp and distilled water. The cellulose pulp with distilled water successfully removed traces of barium. *(Figure 4)*
5. A final reattachment was done with a 30% acrylic dispersion in small cavities and porous parts with cracks *(Figure 8).*The whole process took about 60 days.

5.2.3 Problems with the soluble salts and polychromy

The amount of sulfides was twice as many as chlorides. Since the chlorides are readily soluble salts they are highly mobile and migrate. They can be reduced in water, removed by the sacrificial layer or cellulose packing (pulp), with distilled water, synthetic laponite clay, etc. In this case, none of these methods were possible, because of the presence of sulfides and polychromy. Sulfides would react with CO_2, build crystals in the water and cause disruption of the surface. With this method a reduction of sulfides and chlorides was possible. The trace of pigment was successfully protected during immersion in barium/urea solution. An 8% solution of Paraloid B 72 will not easily penetrate into stone compared to 2% solution.

CASE STUDY II

5.3 Renaissance relief "Pieta", 1450/1500, Sculptor Nicola Firentinac, Lunette; St Klara, Trogir/Ciovo, Croatia

Figure 9 -Pieta, limestone, 150x90x11 cm, photo; Doris Bengtsson 2011

The Church of St:Klara is located between the sea and a highly trafficked road. The object is exposed to fluctuating humidity and temperature and high level of air pollution. The stone has suffered enormously from different granular disintegrations as sugaring, powdering, flaking, scaling and therefore had to be disassembled and acutely consolidate. During the process of dissembling, the relief was protected by the temporarily consolidant, cyclododecan*. The temporary consolidant facilitated the removal and transportation of the relief.

This relief is an interesting object from an art-historical point of view, but is also interesting as one of the most weathered items which the Croatian Conservation Institute had at the time.

5.3.1 Investigations and actions

Cyclododecan was dissolved in toluene, ratio 1:1. Samples with cyclododecan were first tested; dissolved in 50% toluene; dissolved in 50% Schatoll B; 100% melted at 70 degrees C. ("Cyclododecane is one of the so called volatile binding media. Volatile binders are non-polar organic compounds belonging to the class of saturated cyclic hydrocarbons.

They can be used as hydrophobic protective coatings for water-sensitive objects as consolidants for fragile objects during excavation or transport, temporarily sealing or consolidating fragile objects”). (http://cool.conservation-us.org/byform/)

A sulfide measurement was performed before, and after preservation in order to make the right diagnosis and follow the process of desalination.

Consolidation with $Ba (OH)_2$ + urea: 7% $Ba (OH)_2$ was heated to 70 ° C; addition of 4% urea which prevents premature carbonization.
The object was treated in a warm solution according to the conservator / scientist recommendations, as much as it was possible, in order to achieve a deeper penetration. The recommendation was to immerse the relief only to a half and spray the top part with just 2% $Ba(OH)_2$ for one month. Lunette was sprayed daily 2/3 times for about 2, 5 weeks and immersed in the bath for another week. From experience this process has shown good results and there was no reason for keeping relief in solution for a longer period of time due to fragile condition of the relief.


Figure 10- The moment relief was taken out of $Ba(OH)_2$ solution


Figure 10-11, photo; Doris Bengtsson

The looses parts were preserved separately shortly after the immersing in the solution with barium hydroxide ($Ba(OH)_2$) and urea (carbamide).
It was planned that sculpture should be vacuum impregnated with tetraethyl silicate (tetraethoxysilane) at the Conservator University of Split. The vacuum impregnation is application used to improve penetration and limit the evaporation. (Has not been preformed yet.)

5.3.2 Comments

2% solution has been recommended because some research has shown that more fragile surfaces will consolidate more easily with lower concentration of diluted consolidant.
The protection with temporarily consolidant cyclododecan, has saved a lot of time and difficult work during pre-consolidation in outdoor environment which is usually performed by injecting acrylic emulsion or Paralaoid B-72.

With a process of desalination and consolidation, the concentration level of sulfides and chlorides will be reduced with this method (barium hydroxide). And as the side-effect of the treatment, the surface reinforcement will also be achieved.

In my opinion this method was the best choice, because of the presence of both sulfites and chlorides which were determined in high and harmful level (Chapter 7- Discussion). It is necessary to measure the quantities of salts before and after the desalinations treatments and evaluate the process. This measurements show whether the salts are still present in the material in dangerous levels. This is done by quantitative and qualitative measurements of salts. The standards for measurement of damaging salts are not discussed here, due to the limitation of this thesis. ICROM laboratory manual can be very useful in this regard (Borrelli E. 1988, p. 1-45).

CHAPER 6

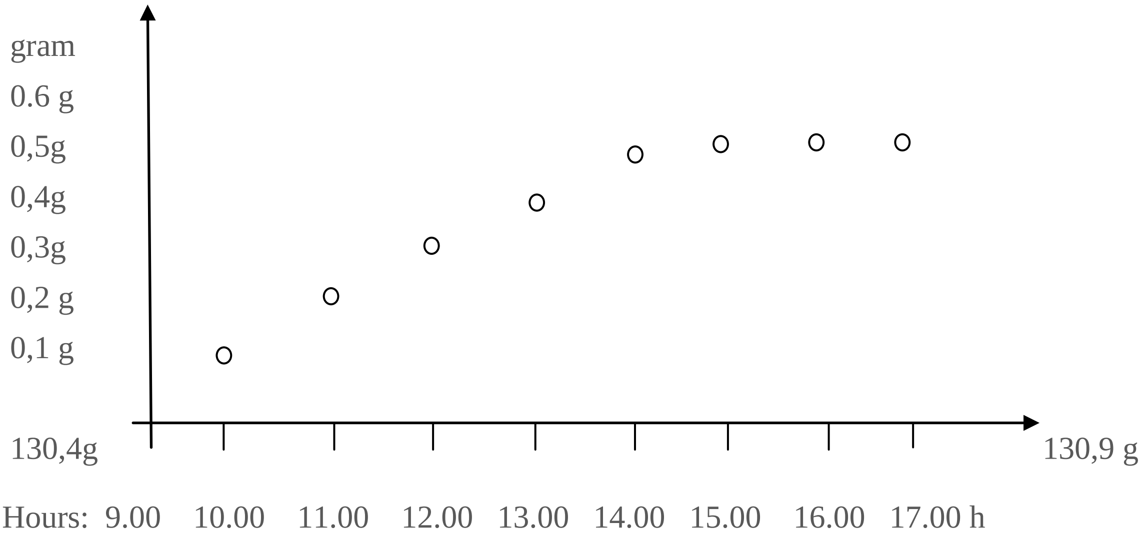
EXPERIMENTAL

6.1 MATERIALS AND METHODS

In the experimental studies the consolidating agents for the limestone were tested, and in order to find out how well they perform on Gotland’s limestone. The test of porosity of that limestone has been performed before and after consolidation according to ICCROMS Lab-manual. At first the samples were weighted and thereafter dried at 60 degrees C for twenty-four hours. A porosity test has shown good condition of those particular samples and extremely low absorption of water. The stone samples in general were in good physical condition.

The sample size: 3,5x2,5x2,5 cm.
Colour: Grey
Compounds: CaCO3, Al (presence of the clay minerals are typical for this limestone).

The table shows measurements taken during total immersion of sample in water.



During the period of six hours, the sample changed weight from 130, 4 grams to 130,9 grams. The same test was preformed twenty-four hours later and again six days later, without any change in a weight of the sample. This shows a particularly low porosity level.

6.1.2 Consolidating agents and methods tested:

- Calcium hydroxide Ca $(OH)_2$
- Barium hydroxid Ba $(OH)_2$
- Two steps method med ammonium carbonate NH_4CO_3
- Ammonium oxalate $C_2H_8N_2O_4$
- Silicic acid eter- tetraetoxysilane ,THEOS, Si $(OCH_2\text{-}CH_3)_4$ / product KSE 100

Particular attention has been given to the quality of penetration of barium hydroxide. According to literature it is not known enough about the quality and final results of processes which barium hydroxide undergoes during the process of penetration. It is not certain that any crystallization occurs, particularly in this case when stones/ sample are in very good physical condition.

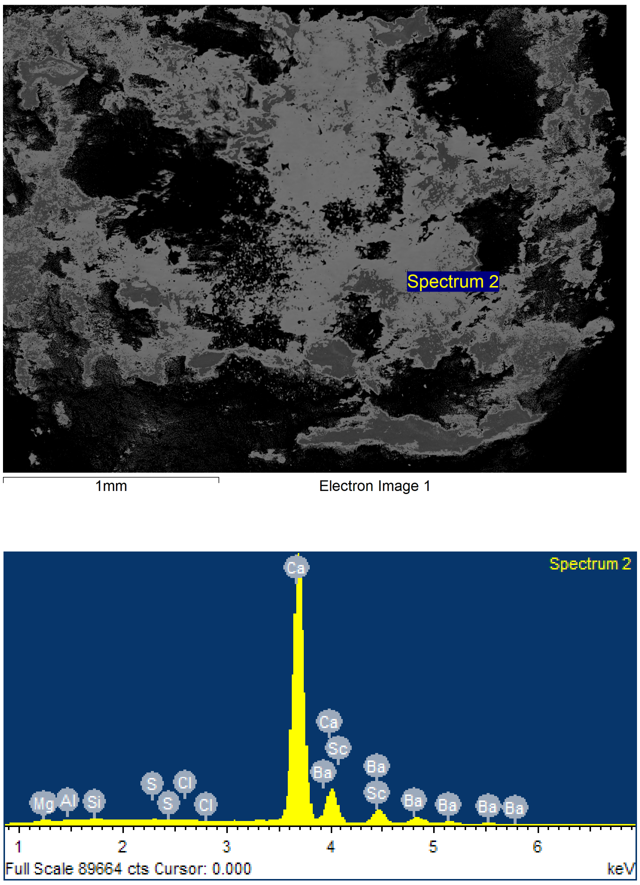
6.1.3 Method description: Table 1

	Treatment with optimizer	Elapsed time	Dry Weight - Before the treatment	Wet Weight - After the treatment
Sample1	5%Ca(OH)2 + 10% ethanol, (70C)	5.4-11.4 6 days-144 h	127,1g	127,1g
Sample 2	7%Ba(OH)2+4% urea, (80 C)	Från 30.3.kl 13.00 Till 11.4. kl 13.00, phase 2-från 11.4-22.4	126,1g	126,1
Sample 3	5%NaH4CO 3 7% Ba(OH)2	5.4-11.4 phase 11.4-16.4	127,8 g	127,8
Sample 4	4% Ammonium oxalate $C_2H_8N_2O_4$	11.4-16.4	128,6 g	128,6
Sample 5	Silicic acid ether , tetraetoxysilane /THEOS	10 minutes	125,3	125,3
Sample 5	Without treatment		125,2 g	125,2

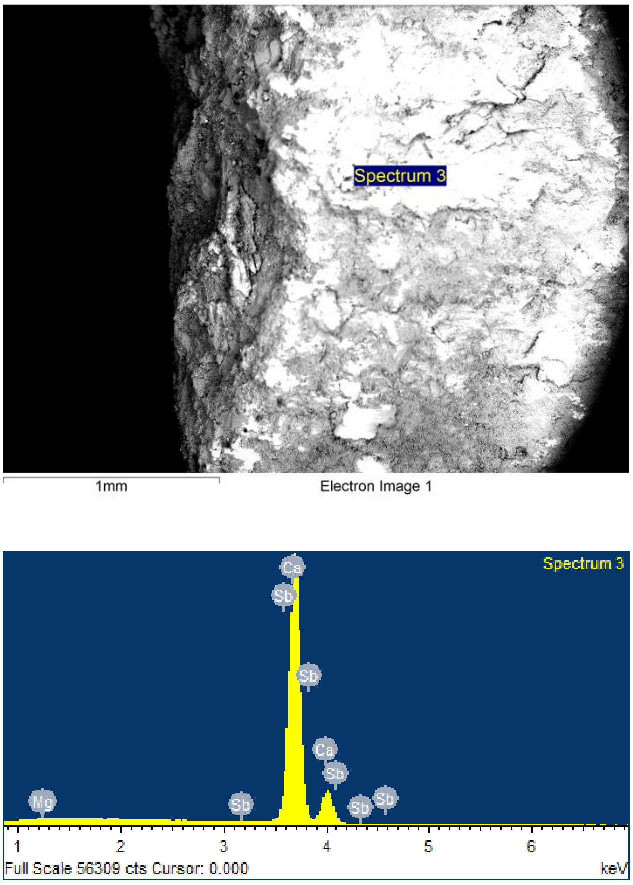
6.1.4 Results- Table 2

	Treatment with optimizer (ethanol or crbamide/urea)	pH of solution	Change in appearance: colour	Change in appearance: luminance
Sample1	Ca(OH)2 + 10% ethanol	pH11,5	some	non
Sample 2	7%Ba(OH)2+4% urea	pH 12,5	some	non
Sample 3	5%NH4SO 4 7% Ba(OH)2	pH 8,5 pH 12, 5	non	non
Sample 4	5% Ammonium oxalate $C_2H_8N_2O_4$	pH 5	some	some
Sample 5	Silicic acid ether/ tetraetoxysilane THEOS	pH 3/4	non	non
Sample 5	Without treatment			

6.1.5 Chemical analysis – SEM- Scanning Electron Microscopy



Comment:Barium metod, andefined position 90 c
Figure 12- SEM, Result 1



Comment:Barium metod, inner position 90 c
Figure 13-SEM, Result 2

SEM shows that barium has entered the stone sample to a depth of 1.5 mm (Result 1). At the depth of 3 mm barium compounds were not found. The earlier measurement of water absorption of the Gotland limestone was extremely low, and these results were anticipated.

The weight of the stone did not significant change after consolidation.

6.1.6 Scanning Electron Microscopy

“The SEM permits the observation of materials in macro and submicron ranges. The instrument is capable of generating three-dimensional images for analysis of topographic features.” (Herguth, William R. 2005, p. 2)

6.1.7 Application methods and comments

All the samples were treated according to previous explained methods in chapter 4 and 5 following the prescription. All the methods were performed by total immersion of samples in the solution for the suggested period of time (Table 1-2), following the description of method. The sample immersed in ammonium oxalate was treated for the period of five hours following the suggestion in article of Cezar Tody M., 2006, “Calcium Oxalate: A Surface Treatment for Limestone”.
In some cases I have tried two different percentages of solutions elements, particularly in the case of ammonium carbonate. The aim was to test the pH in the solution because of the fact that ammonium carbonate influences the solubility of the sulfates (gypsum) and

increases penetration of barium hydroxide and barium carbonate in the weathered limestone. The samples I used were not weathered, and this is the reason why it was not possible to follow or to see any consolidation effect, but it was still possible to test the penetration depth with a SEM (Scanning Electron Microscopy).

Before the treatments with homogeneous solutions (barium hydroxide and ammonium carbonate), the samples were treated with 98% ethanol. Ethanol was used to reduce the capillary tension on the surface of the stone permitting a better penetration (case study). The barium hydroxide was prepared by heating (at 80 C) because of its low solubility.

The calcium hydroxide was also prepared by heating. In order to raise the concentration level of compounds in the solution, the calcium hydroxide was prepared by heating of 5% solution to 60 degrees C. After some cooling the ethanol alcohol (10 % of complete solution) was added. The particles dispersed in alcohol prevent carbonation before the application. Although those particles were not dispersed in alcohol the addition of alcohol could slow down the carbonating process.

6.1.8 Porosity test

Porosity test on untreated stone shows good quality of Gotland's lime stone. The treatment was tested simply by measuring of the "dry-samples" (24 hours in 60 degree C) and "wet-sample" weight and time it takes the water to accumulate in stone sample.

6.1.9 Water absorption – THEOS

Tetraethoxysilane THEOS is tested for water permeability*, comparing water absorption on treated and untreated stone samples. The test is performed with total immersion in THEOS for the short period of 10 minutes. The treatment has not been repeated.

Measurement of water absorption after consolidation with alkoxysilane THEOS does not show any significant change compared to untreated sample.
The penetration depth of THEOS was not questioned by thesis, but mostly compatibility.

6.2 Fault sources

Due to samples' low porosity and good condition, the results are not very usable in evaluation of the methods or consolidants. To do this test properly one should have a deteriorated stone sample and perform the tests over the longer period of time. The limitation of the time and equipment might cause the imprecise results of this experiment.

By the visual judgment it is very difficult to observe any change in surface reinforcement by THEOS or any other method, mostly due to samples' good condition. It was not possible to convert unstable calcium sulfates to more stabile compounds with the samples chosen in this experiment.

CHAPTER 7

DISCUSSION:
EVALUATION OF CONSOLIDANTS / METHODS COMPATIBILITY WITH LIMESTONE

Teutonico et al. (1997) defines compatibility as follows: *"the introduced treatments or materials will not have negative consequences"*. (Athuman M. K. Ngoma 2009, p. 10)

7.1. Alkoxysilanes- silicic acid esters/ethers

Alkoxysilane THEOS was recommended as the water repellent or consolidation agent after the treatment with $Ba(OH)_2$ for the Relief on the church of St:Klara, Trogir, Croatia.

The polymerization process of akoxysilanes produces strong silicon-oxygen-silicon bonds which results in a high strengthening effect.
Alcohols as by-products of hydrolysis instantly evaporate and leave the solid polymer in the stone without any deleterious effect on it.
Another positive characteristic of alkoxysilanes is water permeability*. In its solidified form, akoxysilane does not fill the entire pore space, but instead coats the pores, and therefore allows the stone to absorb further treatment and transmission of moisture.
Alkoxysilanes require normal outdoor temperatures.

There are also some disadvantages with alkoxysilanes as consolidating agents.
Alkoxysilanes are likely to evaporate from the surface before hydrolysis can take place and the treatment requires precautions. The consumption of material is high in order to achieve a sufficient penetration which makes the treatment rather expensive. This characteristic might restrict the use of alkoxysilanes to small objects and limited surface areas.
Changes in the color as an initial darkening or formation of white spots on the stone surface can appear on the treated stone.
The use of alkoxysilanes without proper safety precautions may be seen as hazardous to human health. They can cause injury to the eyes leading to blindness and kidney damage.
Alkoxysilanes are not stabile in presence of salts.
Consolidation with alkoxysilanes is not reversible, but permits retreatment.

Aloxysilanes are not compatible with marble or limestone and do not create a stable bond with these substrates which eventually can create micro cracks and detach from substrate. Otherwise on silicate containing materials (sand stone) this consolidant creates a bond with the material, coating pores but not closing them, leaving a space for water to evaporate (hydrorepellent*- inhibit the transfer of water in the liquid phase but allow the passage of water in the form of vapor).
A penetration depth of 2-10 cm has been reported.

Alkoxysilanes have been developed and mostly used for the consolidation of sandstones, but there have been attempts at using them on marble and limestone as well, even though there is no clear evidence of any consolidation effect on those calcareous materials. Some damage on certain kinds of limestone has been reported as well.

Organosilanes in contact with water form a rigid polymer network that is brittle. A brittle film formed by some products (THEOS) can cause a problem with soluble salts on limestone. Recent studies with tetra ethyl silicate (THEOS) - confirm these experiences.

The evaluation of the method based on ethyl silicate was performed on lime stone monuments in South Korea and Egypt because of the fact that conservation treatment in stone monuments is difficult to remove even if it shows a negative effect on the durability of stone. It was shown that the consolidation with product Wacker OH 100 /THEOS is effective in filling up the pore space in lime stone, but it hardly improves the strength of limestone. After a consolidation a color change in the surface of limestone appears, but it disappears with time. (Shin G. H. 2004, p. 471-477)

The difficulty of bonding a silicate material to calcite has been discussed for a long period of time. Elastified silanes, have been developed to improve bonding processes, which leads to better hydrophobic properties and longer crystallization cycles of salts.

Some conservators do not consider the lack of bonding as a failure, meaning that even an unbounded network of the consolidant could still provide strength. According to A.E.Charola et al., the lack of chemical interaction with the substrate may be an advantage. Because of the bond with limestone, alkoxysilanes can form micro cracks caused by shrinkage in polymeric film, which as previous mentioned, will eventually lead to crystallization of soluble salts and exfoliation of the surface.

The majority of alkoxysilanes do not provide any water repellency except for those with methyl groups (CH_3) MTMOS, which are still not compatible with the limestone. A test that has been performed in this thesis shows that same result; water absorption is the same before and after consolidations with THEOS.
Aloxysilanes do not prevent the passage of water vapor which also makes them permeable to harmful gases. (Price (1996) p. 21*)* It does not make stone more resistant against air pollution, more then it creates a consolidating effect which is excellent on sand stone but performs completely different on limestone. Studies show that a damaging effect of THEOS on limestone is not possible to remove. (Shin G. H. 2004, p. 471-477)

In this thesis the tetraethoxisysilane THEOS was tested for water porosity, comparing treated and untreated sample. The test is performed with total immersion as previously explained in chapter 6. The result of this test will be discussed later on.

7.2. Barium hydroxide

With this method, harmful salts, sulfate in gypsum transforms into more stable and not deleterious barium sulfate (barite) and calcium dihydroxide (lime) which further carbonize into barium carbonate and calcium carbonate. This process can be controlled by keeping the stone humid, which slows down the formation of barium carbonate and calcium carbonate, probably allowing for more time for deeper penetration into the stone pores. It is not known enough how this process proceeds and there are varied opinions about the end results. It is known that barium sulfates make stone more resistant to sulfides, which might protect the stone from polluted air and acid rain. Barium sulfate probably acts as filler in the stone's pores which can be negative and should certainly be a subject for further investigation.

It is doubtful if barium could penetrate deeper into the stone. The molecular size and mobility has not been sufficiently investigated. One should examine the penetration potential of barium in different situations, temperature etc. It might be investigated whether the large crystals of barium created in second phase of carbonization prevent further penetration of barium and eventually cause an exfoliation. Lewin, (1974) has suggested that this approach ensures a formation of well formed carbonate crystals, still advocating for this even 15 years after his proposal.

This method includes a range of chemical processes which have to happen in suggested time. A particular subject and an important part in this treatment is the one of soluble salts,

especially since several salts are involved in the processes.
The immersion in water or application of water to salt-laden materials can mobilize the salts and cause further damage. Liberated in the water, ions will combine in new ways which will also increase the ionic strength in the solution and affect the individual solubility of the salts involved. That makes the problem of desalination much more demanding or sometimes even impossible in cases were certain salts are involved.
In the case when the salts do not have any ions in common, as is in the case of sulfate gypsum and sodium chloride, the solubility of both salts will increase. In general, the salt with the lower solubility (in this case calcium sulfate dihydrate -gypsum), will increase in solubility much more than the more soluble sodium chloride. Immersion in water only, would increase solubility of the sulfates, which thereafter would crystallize.

The Barium method includes both sulfides and chlorides in the process of desalination. The sulfates convert into more stable compounds, while the chlorides migrate to the surface, where they can be easily removed. With this process of desalination, even an effect of consolidation is achieved. The only question is if the consolidation effect is satisfying enough.

There are some other problems which appear under different circumstances.
Adding 10% urea and glycerol in the hot barium hydroxide solution; this method performs completely different than the previous barium method , but some claim that it is still not effective enough when applied by capillarity, in “in situ” conservation (Schnabel 1992). (Price 1996, p.18)

Barium hydroxide must retain moisture during the consolidation process, which can be problematic in an outdoor environment, “in situ” work. Lewin solved this problem by the addition of urea and glycerol. This procedure was proposed for the use by immersion but there may still be problems with in situ restorations. According to literature, Schnabel suggests that there is no consolidation effect at all. Price (1996) has questioned this method because of barium carbonates anisotropic crystals growth, where crystals have larger molecular volume than calcite. (Athuman, M. K. Ngoma 2009, p. 24)

Despite of many advantages of this method and its use in large projects in both the industrial and conservation field, it is still experimental. Apparently the alkaline/caustic nature of barium hydroxide (pH 13) can cause damage to other building materials like glass, aluminum, and zinc. In addition, this method also involves hazards to human health, if proper protection is not used.

My short experience of the method has been the reason for the research. It is obvious that this method has advantages on deteriorated stone, and it is most likely useful for the purpose of preventive consolidation. If any penetration on well preserved stone surface was possible, it would have shown that barium penetration can be very satisfying on degraded stones. SEM shows that barium has entered the stone sample to a depth of 1.5 mm. On the depth of 3 mm no barium compounds were found. The earlier measurement of water absorption of the Gotland limestone was extremely low, and these results were anticipated.

7.3 Ammonium carbonate

The method with ammonium carbonate proposed reduction of sulfides and chlorides which is often the main reason for the degradation of ancient monuments. Unfortunately, these chemical conversions cannot eliminate the nitrates, and if chemical analyses have been established in the stone, they can be removed only by immersion in a water bath, rinsing with water or with wet compresses. (Malinar H. 2003, p.79) According to the C.A. Price (1996) it is still experimental, and the results of application of this procedure on stone are yet to be reported. (Price 1996, p.18) Since then, experience on this has increased and treatment has proved very satisfactory in the presence of sulfates and neutral to some pigments and dyes. ((Malinar H. 2003, p. 79; Svahn Garreau 2010, p. 16)

In this thesis the ammonium carbonate tests include application tests with different percentages of medium to see how this influences the penetration rate. It was not possible to determine the penetration depth of ammonium carbonate due to the same nature of the compounds and the original substrate.

7.4 Calcium hydroxide (limewater)

A reason why development of this technique was of importance is the belief that limestone retains its original properties and behavior after chemical treatment with this method. Precipitated calcium carbonate is supposed to bind degraded but chemically identical limestone compounds together. The critique of this method is based on the fact that calcium hydroxide solubility and penetration ability is low, which can cause the formation of hard surface or soluble salt as a byproduct of this method. A precipitation of consolidant happens too rapidly before any deeper penetration is possible.

Some conservators claim that there is no proof that calcium carbonate has the ability of binding detached particles with a substrate, coarser opposite (Price). (Price (1996), p. 18-22) The limited solubility of calcium oxide is due to multiplied application of limewater in the wet state of the stone. A huge amount of water includes a certain risk and danger to the substrate, either mechanically, by mobilization of soluble salts, or by dissolution and recrystallization of carbonates.
The high pH level of the solution may affect pigments sensitive to an alkaline medium. The technique is improved by adding crystallization inhibitors or carbamides, or by the use of alcohol instead of the aqueous solution. The use of alcohol shows that the rate of agglomeration is much slower and therefore slows down the sedimentation rate of lime particles. (Hansen, Doehne et.al 2000, p.1-10)

It was not possible to determine how much calcium hydroxide penetrated the stone sample due to the same nature of the compounds as the original substrate. The SEM cannot distinguish consolidation agent from the substrate.

7.5 Colloidal calcium hydroxide sols -“Nano-lime”

This technology, which suspends the nano-scale calcium hydroxide particles in alcohol, permits deep penetration of the stone and at the same time limits carbonation by CO_2, before the particles are deposited in the porous stone. The lime with a high concentration of calcium hydroxide particles in nano size is much more reactive then a lime slaked in water. Some new products have been tested and can be combined, or are compatible with silicic acid ethers (SAE). *“Nano Lime”* with different percentage of nano- lime particles, is in use, as a good material to fill micro cracks. (Piaszczynski & Wolf 2010, p. 2)

The nano lime particles fulfilled the requirement that the consolidation materials should be compatible with the substrate.

7.6 Ammonium oxalate

The hope is that a simple conversion of calcium sulfates and carbonates to calcium oxalates may provide a safe and effective way to protect limestone from the destructive effects of acid deposition, while still retaining the porous and hydrophilic properties of calcareous stones due to the fact that calcium oxalate itself is hydrophilic. Without inhibiting the natural mechanism of the stone, a free diffusion of soluble salts is possible. It has been proven that the ammonium oxalate more readily converts sulfates than carbonates into calcium oxalate. (Cezar, Tody M. (2006). p 1-25)

The porosity tests might show difference in water absorption of treated and untreated samples. The SEM could not distinguish calcium oxalate from carbonate (CaC_2O_4 due $CaCO_3$), since the layer is extremely thin. No other test is performed on sample with an ammonium oxalate due to the time limit of this thesis.

7.7 Comments on the results of experiment

In the experimental part of this bachelor thesis (Chapter 6), the following tests were performed on limestone from Gotland: water absorption by total immersion, penetration depth of barium hydroxide measured by SEM and consolidating effects judged visually (ocular) or by microscopy.
The SEM results show that the penetration of barium hydroxide is in direct proportion to low porosity of the material and that the penetration is possible even on limestone which is not deteriorated, although it is very limited. This result probably indicates the similar result for the ammonium carbonate.

Due to the same nature of consolidant and substrate, the SEM cannot distinguish between compounds and give any result compared to methods with carbonates and oxalates. The slight difference in luminance is observed on a sample treated with ammonium oxalate (Table 1-2) by visual observation.
No other tests were performed on the sample with the ammonium oxalate or calcium hydroxide due to the time limit of this thesis.

It was also not possible to convert the unstable calcium sulfates to more stable compounds with the samples chosen in this experiment. And even if it were possible, the analysis and evaluation of the methods should require much more knowledge of investigative techniques than the framework of this thesis allows.

Additionally is very difficult to observe any change in surface reinforcement by consolidant THEOS or by any other method for that matter, mostly due to samples' good condition.

SUMMARY AND CONCLUSION

In the last 30 years the organic polymers, silicone and acrylic consolidants, have mostly been used and tested in the consolidation of stone, some of them more due to their availability than their predetermined qualities. Many were developed for use on sandstone but have even been applied on marble and limestone, without consideration of compatibility (Price, 1996). Compatibility in this matter should ensure that no moisture barrier prevents soluble salts from freely migrating to the surface.

A lot of research in the Seventies and Eighties was directed at finding a single treatment that would both consolidate a stone, maintaining the hydrophilic features, and protect the stone surface from environmental damage. The major problem in this regard is to find the materials which are compatible with the components of substrate. Some other problems are the depth of penetration and the long term stability. Another challenging problem is a lack of bonding to the substrate. Conservators have different opinions regarding the importance of bonding abilities of the consolidant. According to A.E. Charola who tested her thesis on acrylic agents, a lack of molecular bond can even be an advantage.

In the past, the development of inorganic consolidates has also been dominated by the organosilicon consolidants. Those mostly used are alkoxysilanes, epoxy resin and acrylic polymers. The siliceous consolidants have been used to consolidate limestone and sandstone based on the process in which insoluble silicates occur within the pores of the stone. They can cause a formation of soluble salts, which cause exfoliating of the surface.

Alkoxysilanes have been developed as a combination of organic and inorganic compounds. For some reason the treatment with alkoxysilanes is often recommended as a surface protector (water-repellent coating) after the treatment with inorganic methods. On the other hand there were reports of damage to certain stones following treatment with tetraethoxysilane (THEOS), unless the stones were also given a water-repellent coating. (Price 1996, p. 21). That is why it is important to take those into consideration as well.

Several inorganic treatments/consolidants deserve attention as they operate quite differently: barium hydroxide, ammonium carbonate, ammonium oxalate and the new research on calcium hydroxide -”nano-lime” method. In the past most of these methods were tested. The inorganic materials, such as barium hydroxide and limewater have been known for a long period of time and have been used for consolidation of stone with different results.

To achieve consolidation with those alkaline earth hydroxides, as well as with ammonium carbonates, the right understanding of this methods is important, and it includes several treatments and chemical processes. The interesting part is a reduction of sulfides and chlorides, which are often the main reason for the degradation of ancient monuments. Some of the treatments result in a stone with much higher resistance to polluted atmosphere. But the methods are still experimental and, according to some conservators, should not be used on monuments of higher importance.

In this bachelor thesis, which is divided in seven chapters, discusses the factors of deterioration and methods for consolidation of salt laden limestone.

The main questions and problems discussed here are: Which methods are the most compatible with the limestone and which are the reasons why we use silicic acid ether with a Si-O- Si structure (siloxane bonds) even on the limestone?

This bachelor includes experimental part which attempt to analyze penetration depth and consolidation quality of methods in focus.

There are many parameters to be considered for the right performance of consolidant: porosity, water absorption, water repellence as a pore size distribution. It seems that universal consolidant does not exist since every situation and stone is different.

In this thesis the criticism of using THEOS for treatments on limestone is based on the fact, that THEOS is not compatible with a limestone. Judging from the fact that THEOS do not influence hygroscopicity of the limestone, which is actually positive quality of a consolidant, one can also conclude that the limestone treated with THEOS is still exposed to negative intrusions of water, frost and gaseous pollutants, such as sulfuric dioxide, by water vapor. In the case of limestone where bonding between minerals and consolidant is not established, this could lead to serious damage.

The literature consulted acknowledges that THEOS is not a possible treatment for consolidation of salt laden limestone or in any other case of deterioration of limestone. Not only due to its instability in presence of salts, but also because any consolidation effect on un-desalinated limestone would only increase the problem.

My own opinion about the methods in focus: ammonium carbonate and barium hydroxide methods, except for the threat to human health, are positive.

The visual estimate of consolidation effect considering reinforcement of surface and depredated carbonates is very clear on deteriorated limestone, which I have introduced in my case studies.

The methods are very useful in the process of desalination, due to the fact that both chlorides and sulfides are stabilized.

The long term stability is taken as a possible problem, at least considering some literature.

It seems that a new technology can improve the inorganic methods described in this bachelor by using a nano size particles of different compounds. Further investigations and reports are required.

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FIGURE 1-13
Figure 1,6,7 – Barium hydroxide method “Case study” , Project of Croatian Conservation Institute, Photos: Vinka Marinkovic
Figure 2,3,4,5,8, 9,10,11- Barium hydroxide method “Case Study”, Project of Croatian Conservation Institute, Photos: Doris Bengtsson
Figure 12-13: SEM results

ANNEX 1- Gothenburg University, SEM result1
ANNEX 2- Gothenburg University, SEM result2

DICTIONARY

Compatibility* state that; “the introduced treatments or materials will not have negative consequences” Teutonico et al. (1997).

“the new materials should be as durable as possible without (directly or indirectly) causing damage to the original material”. Van Hees (2000)

Hydrorepellent/transpiring protective coatings* - inhibit the transfer of water in the liquid phase but allow the passage of water in the form of vapor.

Water permeability*- that allows water to permeate through its structure

Porosity* - the ratio of the volume of pore space to the bulk volume

Transpire* - to escape through pores, as vapor.

Weathering* - all changes that occur.

Sulfide*- A chemical compound of sulfur and another element or radical, such as hydrogen sulfide.

Sulphate/sulfate -*Chemistry / Elements & Compounds) any salt or ester of sulphuric acid, such as sodium sulphate, $Na2SO4$, sodium hydrogen sulphate, or diethyl sulphate, $(C2H5)2SO4$

Weddellite* - calcium oxalate ($CaC2O4 \bullet 2H2O$)

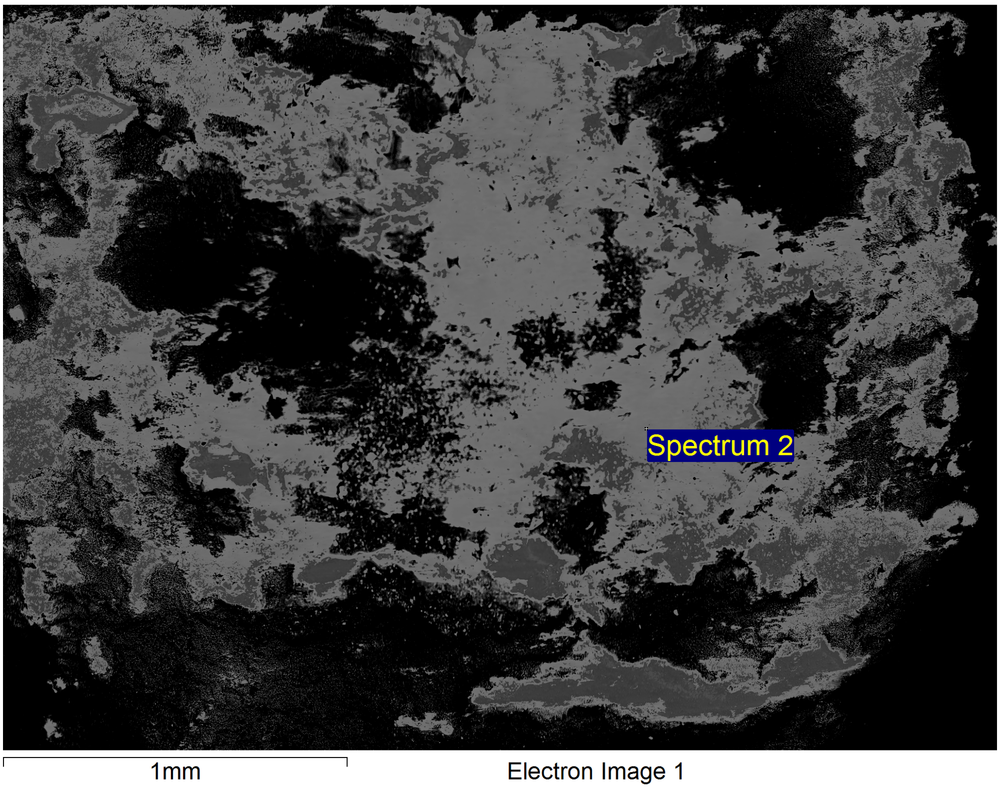
Whewellite* - calcium oxalate ($CaC2O4 \bullet H2O$)

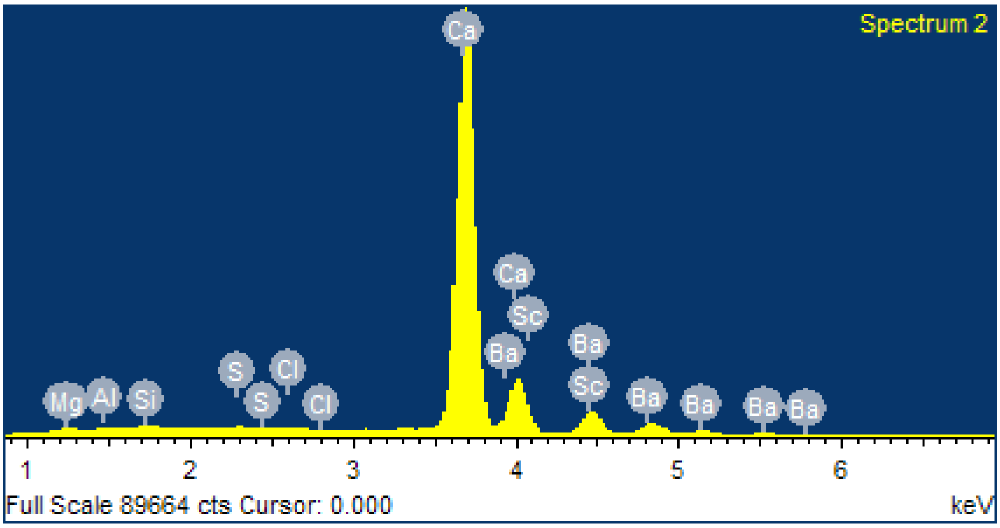
Alkoxysilanes* are a family of monomeric molecules which react with water to form either silica or an alkylpolysiloxane

Paraloid B-72 * - Chemically an ethyl methacrylate co-polymer, Paraloid B-72 is a durable and non-yellowing acrylic polymer used for consolidating wall paintings (1-5%), fragile wood (5-20%), etc. It may be used as a fixative when diluted with a solvent to secure markings on artifacts and as an adhesive (50%+) for a variety of substrates. Paraloid B-72 is soluble in acetone, toluene and isopranol. All the acrylic copolymers are dissolved in organic solvents and then applied to stone.

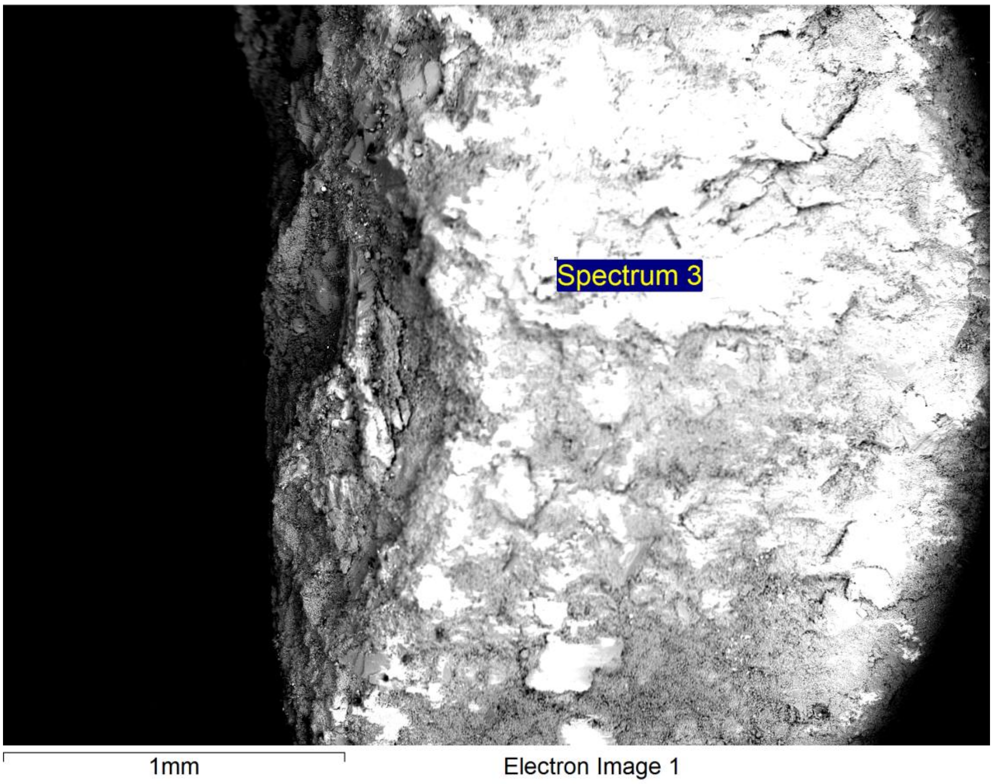
Silane-based materials* - organosilicon compounds which polymerized inside the stone

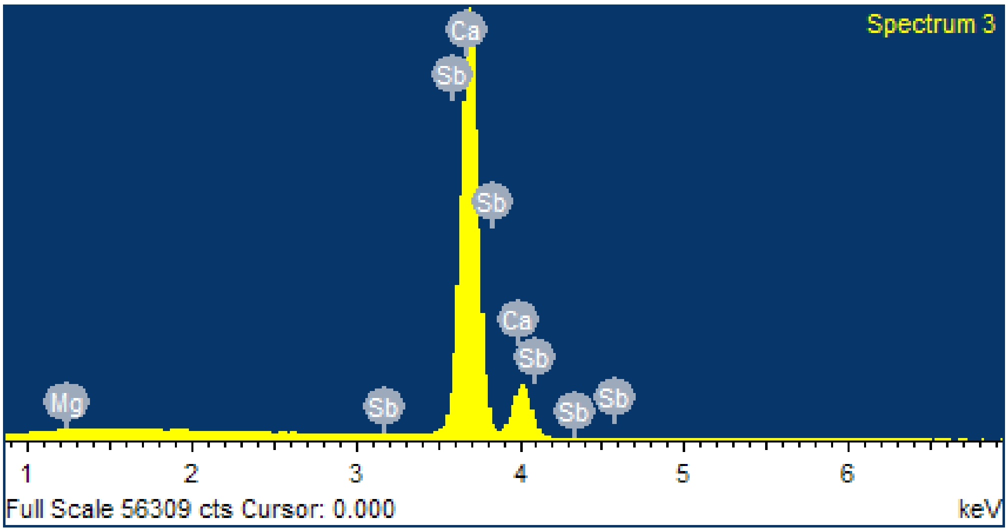
Cyclododecane* - is one of the so called volatile binding media. Volatile binders are non-polar organic compounds belonging to the class of saturated cyclic hydrocarbons. They can be used as hydrophobic protective coatings for water-sensitive objects as consolidants for fragile objects during excavation or transport, temporarily sealing or consolidating fragile objects. (http://cool.conservation-us.org/byform/)





Comment: Barium method, undefined position 90 c





Comment: Barium method, inner position 90 c

ANNEX III: LIST OF FIGURES 1-13