

STONE IN ARCHITECTURE AND SCULPTURE, DETERIORATION AND CONSERVATION

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Abstract:

The conservation of stone monuments in the scientific aspect became the subject of research in the nineteenth century, when the foundations of the theory of conservation of monuments, today more widely understood as the protection of cultural heritage, were laid. Since then, in spite of many projects, publications and even patents, the issue of stone monuments conservation is still open and the research continues. The significance of the issue is evidenced by rich volumes of conference materials from The International Congresses on Deterioration and Conservation of Stone, held every 4 years. The materials from these conferences are available on the ICS-ICOMOS website (<http://iscs.icomos.org>). The aim of this work is to familiarize the readers with many years of experience of the so-called "Polish school of conservation of monuments" in the field of conservation of stone monuments. The causes of deterioration, the basic principles of conservation and the methods used in individual stages of conservation and restoration work on stone sculpture and architectural detail will be discussed.

1. Introduction

Stones have accompanied man since the dawn of their history, as tools, weapons, building material and the material of works of art. Ancient buildings, but also sculptures, including, among others, stone images of the ancient philosophers Plato or Aristotle have survived to our times, thanks to the high durability characteristic of stones. Stone, rock is a material considered to be exceptionally durable in all cultural circles, which is mentioned not only in the "sacred books" of Judaism, Christianity, Islam or the youngest Buddhism, but also in the folk art and proverbs. Stones have been used to build or support objects of worship and important secular objects to ensure their durability. For this purpose, local stones

were chosen or individually selected, taking into account the properties of the rock. Therefore, for the construction of foundations, bases on which wooden or later ceramic constructions were built, durable granite of very low porosity was chosen, fig. (1). It ensured high strength, durability and stability of the structure and protected it against capillary movement of ground water in higher parts of the structure to materials of higher porosity, such as wood or brick. Unfortunately, with time and under the influence of many factors, all stones are eroded and corroded. The speed of these processes depends on the type of stone and the conditions of its exposure [1].



Figure (1) Shows Iwięcín, branch church of our lady the queen of Poland in Iwięcín (Poland, Zachodnio-Pomorskie Province)

2. Erosion and Corrosion of Stone Monuments

When discussing the state of preservation of stone monuments, we analyze the resistance of the material to destruction, i.e. the ability of the rock to permanently maintain its properties and functions. Even the most durable, most resistant rocks undergo natural processes of weathering, i.e. *erosion*, which takes place under the influence of typical components of the climate, such as: precipitation, sunshine, winds. We encounter this phenomenon in areas where the environmental pollution is small, e.g. in rural areas. In cities, highly industrialized areas with a high level of atmospheric contamination, *corrosion* processes mainly occur. Both of these processes are compounded by the *aging of stone*, which takes place as a result of chemical, physical and biological transformations [2]. These processes can lead to the partial or complete decomposition of some of the rock-forming minerals in the stone and the migration of the products of these transformations to the surface. They are very complex and in practice it is often difficult to distinguish the influence of individual destructive factors, most often they act synergistically. The speed and extent of the stone's aging transformation depends on many factors, the number of which increases due to the fact that the rock is given a sculptural form. The specific surface area increases, cavities or thin-walled elements are formed, which has a decisive influence on aging. The fac-

tors influencing the state of preservation of the stone sculpture or architectural detail are most often divided into two basic groups: *Internal factors*; resulting from the construction of the object, its type, form and age, as well as the structure of the matter from which it is made, i.e. mineralogical, chemical, structure and texture, and physical and mechanical properties of the rock.

External factors; are related to the conditions of exposure, use of a monument or a work of art, atmospheric phenomena and environmental pollution, but also human activity. Considering internal factors, one should pay attention to the influence of mineralogical structure, rock and resistance to erosion and corrosion of individual rock-forming minerals. The second important factor influencing the destruction of stones is their texture, which is also connected with their porosity. Among the most durable and resistant to aging are magma rocks, especially deep rocks, formed as a result of a slow and even cooling of magma in deeper parts of the earth's crust. As a result, the rock was formed with a crystalline structure (crystals up to 5 mm) and a rough, compact texture with very low porosity. These are granites, syenites, diorites, gabbro. They include: silica and silicates (olivines, feldspars, micas). They are among the most resistant rock-forming minerals. Volcanic rocks, among them volcanic tuffs, have a similar mineralogical composition, but they

differ in structure and texture, as they are formed by the rapid and uneven solidification of lava, so that the degree of crystallinity of the minerals is low and their porosity is high and their resistance to aging is much lower, since the destructive factors act not only on the surface of the rock, but in its entire volume. The influence of texture is also observed when comparing the aging resistance of porous limestones with marbles and compacted limestones (sometimes called common marbles-among Polish rocks of this type, one can mention: Zyguntówka, Dębnik, Bolechowice, Morawica) and marbles. In all three cases, the basic rock-forming mineral is calcite (CaCO_3), a substance with very low resistance to all acidic substances, including carbon dioxide. The rate of corrosion is proportional to the porosity, so marbles, i.e. rocks with the highest degree of crystallinity and the lowest porosity, are the slowest to corrode, then the compact limestones, and, finally, porous limestones, which are the quickest to undergo corrosion processes. Among the sedimentary rocks, in addition to the limestones mentioned above, the materials often found in sculpture and architectural detail are sandstones and alabasters, the latter most often used indoors, as they exhibit low resistance to water caused by a relatively high solubility of 2.1g/dm^3 at 293K (20°C). Sandstones, although consisting of approximately 95-98% silica (SiO_2), a substance resistant to acid and alkaline agents, which is only metabolized under the influence of hydrofluoric and orthophosphoric acid, show relatively low resistance to corrosive agents. This is due to their high porosity and often low stability of the binder that bonds quartz grains. Among them, we distinguish silica, clay and carbonate binders and most often mixed ones. The most durable are silica binders, while clay binders plasticize and sometimes swell under the influence of water, and carbonate binder (calcite) decomposes under the influence of acidic agents. The information presented above shows that due to different mineralogical structure and texture, the rocks will exhibit different resistance to destructive factors in places where details and sculptu-

res are exposed. That is why sculptors and bricklayers carefully selected appropriate materials for specific works. Granites were often used to make foundations, wall bases or steps, from sandstone, limestone, because of the much greater ease of processing to form architectural details and sculptures. However, unfortunately, they did not always follow this principle, an example can be the portals made of black limestone from Dębnik in the Church of the Holy Spirit in Toruń, which in the conditions of external exposure quickly deteriorate, especially in the surface layer, fig. (2-a, b). The mechanism and speed of destruction of stone monuments is influenced by external factors, among which all climate components and acidic oxides (CO_2 , SO_2 , NO_x) or dusts polluting the atmosphere play a dominant role. We should also not forget the biological factors: bacteria, fungi and lichens, as well as the human factor. The growing of microorganisms on the surface of the stone monuments increase the humidity of the substrate, act mechanically penetrating the surface pores and act chemically, because in metabolic processes they secrete small amounts of organic acids, which disintegrate the substrate. This is a dangerous phenomenon due to the length of the process [3], fig. (3). Stone monuments remaining in external exposure are exposed to water soluble salts (NaCl , Na_2SO_4 , KCl , K_2SO_4 , NaNO_3 , NH_4Cl and other types). Sources of water-soluble salts may be different, mainly penetrating with ground water pulled up by capillaries. They are formed as a result of the reaction of atmospheric pollutants and the ground, or when the objects are located near large sea basins, the saline water can form an aerosol carried by the wind towards the stone monument where it accumulates. The action of water-soluble salts is related to the presence of water and water vapour [4]. The salts present in the monuments significantly increase the hygroscopicity of materials (the content of 1.02% NaCl in limestone increases hygroscopicity by 1725%). Salt solutions formed in pores, where they hydrolyze and consequently change the pH of pore water will have a chemical effect on rock-forming minerals leading to their decomposition.

During the drying of the stones, the salt solutions will increase their concentration until they crystallize. The crystals that form as a result of the crystallization pressure will cause the surface of the stones to break down and disintegrate. One should not forget about human activity as well. In the past, the use of strengthening methods or horizontal insulation using water glass has caused strong salinity of the monuments, as well as the use of mortars with cement binder, fig. (4). All destructive factors, regardless of their nature, cause changes taking various forms. One of the first symptoms of these changes is the formation of gray and black *corrosive layers* (*black crusts*) on the surface, which are formed as a result of chemical and physical transformations between the substrate and the corrosive factors. Hence, the composition of layers is variable, depending on the chemical nature of the stone substrate and the environment in which the object is exposed, fig. (5). However, some properties of these layers are common and testify to their harmfulness towards the monument. These are: grayish color, compact texture and good adhesion to the ground. Due to the low porosity and dark color of the layers, they heat up easily, expand thermally, which leads to the formation of internal stresses and on the border of the layer and the substrate, which results in the formation of cracks, delamination of the stone and detachment of the crusts together with the substrate layer, the more so as the material underneath is very weakened, fig. (6-a, b). Disintegration of

stone, resulting in significant changes in mechanical strength may be the result of many factors, including dissolution and dispersion of rock-forming minerals in water, but also the appearance of internal stresses due to different thermal expansion rates of individual rock-forming minerals (e.g. in granite), thermal anisotropy of calcite in marble ($\alpha_x = \alpha_y = -6 \cdot 10^{-6}$, $\alpha_z = 26 \cdot 10^{-6}$), or crystallization pressure of water and water-soluble salts, etc. Cracks and mechanical damage are also a big conservation problem, they often occur in places where metal elements have been incorrectly installed or corroded, and the products of corrosive transformations produced have caused an increase in volume, which resulted in the bursting of the stone material, fig. (7). Unfortunately, it should also be mentioned that human activity may contribute to the deterioration of the object. Sometimes the damage or even falls of objects are accidental, fig. (5), but we also encounter cases of vandalism, where objects are destroyed on purpose, fig. (8). Often the mechanical action of water, wind or wind-blown sand, which acts as an abrasive, is underestimated. The best example of this is the destruction of the Great Sphinx in Giza, fig. (9). Thick layer of stone from the surface was removed mechanically by wind-blown sand. The extent of damage in this case is also due to the low mechanical strength of limestone, which is the building block of the monument. Additionally, sedimentation layers of limestone were visible, characterized by different strength and porosity.



Figure (2) Shows **a**. Toruń, church of the holy spirit, southern elevation, portal made of compacted limestone from Dębnik, **b**. Dębnik fragment (photos by the author)



Figure (3) Shows Gdańsk, lowland gate, capstone, Gotland sandstone, biological corrosion (*photo by the author*)



Figure (4) Shows horizontal insulation incorrectly made with water glass and cement (*photo by the author*)



Figure (5) Shows great armory in Gdańsk, relief covered with black, corrosive layers (*photo by the author*)



Figure (6) Shows **a.** architectural detail from Gotland sandstone, disintegration of stone under corrosive layers (*photo by the author*), **b.** fragment of the epitaph of Gottfried Mentzl and his wife Anna Rosina, disintegration of stone (sandstone with silica-loam sand binder) under the layers, action of salt and microorganisms (*photo by W. Domasłowski*)



Figure (7) Shows architectural detail destroyed as a result of material stress caused by corrosion of steel elements (photo by the author)



Figure (8) Shows sculpture of Christ from the tombstone of Prof. Mieczyslaw Limanowski at the St. George cemetery in Torun, after an act of vandalism on 26-06-2010. (photo by A. Gralińska-Grubecka)



Figure (9) Shows Giza, the Great Sphinx, the destruction caused by sand and wind (photo by the author)

3. Rules of Conservation Proceedings

We divide activities on monuments and works of art, including stone ones, into two groups:

Preventive conservation, whose main purpose of process is to provide ongoing care, consisting of monitoring the state of preservation, removing the accumulated layers in order to prevent corrosion changes occurring underneath them, or strengthening disintegrated places as soon as the process begins.

Conservation, often combined with *restoration*, whose task is to save the monument when the corrosion processes have caused very large damage and the resulting cavities require reconstruction of the sculptural form. For the sake of the welfare of the objects, but also for economic reasons, we should firstly strive for a situation in which preventive actions will be carried out; unfortunately this is rarely the case. The conservator usually appears only when the stone sculpture, or architectural detail, has lost its original form, is cracked, the stone has disintegrated. In such a case, the actions at the monument are time-consuming and very expensive. The main goal of conservation activities is:

- *Removing the causes of damage.*
- *Restoring the matter to its original properties (assuming that it is the carrier of the sculptor's idea)*
- *Protecting the object against further corrosion.*

In order to achieve the indicated objectives, conservation work on a stone monument or a stone work of art requires the completion of many tasks, which can be divided into three main groups:

- *Conducting comprehensive conservation studies leading to the development of a work program, selection of working methods and materials.*
- *Realization of the program of work.*
- *Developing as-built documentation.*

An extremely important element of the work on the monument is conservation research, which is to lead us to a full recognition of the monument, its history, the scope and methods of previous conservation work, establishing the technique and exe-

cution technology of work. This research is carried out with the use of equipment, which is the result of the latest scientific achievements in the field of natural sciences. Parallel to these activities there is a need to conduct basic research on new materials and methods of conservation. This is necessary so that the selection of conservation materials can take place on the basis of chemical structure similarity and properties. In the era of computerization, we often talk about the compatibility of historical matter and conservation materials. The overriding conservation principle is to preserve the authenticity of the historical matter, while taking over from medicine the principle attributed to Hippocrates "Primum non nocere" - first of all, do no harm [5]. Just as every patient is an individual "case" for a doctor, every monument or work of art is unique and treated individually.

4. Methods and Materials Used in the Conservation of Stone Monuments

Among the works carried out on stone objects, the following treatment procedures are most often performed: disinfection, pre-reinforcement, protection of the polychrome, removal of corrosive layers, desalination, structural reinforcement (deep consolidation), filling of cavities, hydrophobization.

4.1. Disinfection

We start the conservation work with disinfection, which aims at destroying and removing bacteria, fungi and lichens from the surface of the stone. Most often commercial preparations with different names are used for this purpose, based on the following groups of active substances, classified according to their chemical structure. These are: alcohols and their derivatives: aliphatic alcohols, e.g. aromatic, phenols and ethanol, for example: phenol and its derivatives, aldehydes: formaldehyde and glutaldehyde, organic acids and their derivatives: mono- and multicarboxylic aromatic acids and there, derivatives, quaternary ammonium salts, heterocyclic compounds:

thiazole and triazole derivatives. They are used in water or organic solvents, usually ethyl alcohol. Disinfectants should be applied 2-3 weeks before starting the work. If the microorganisms are not destroyed by the use of biocides, the disinfection procedure should be repeated. After the death of the microorganisms, they should be removed by mechanical methods, brushes with artificial bristles, scalpels or small spatula.

4.2. Preliminary protection, consolidation

Places where the stone has been severely damaged, delaminated, lost its cohesiveness and mechanical strength, as well as preserved mono- or polychrome, should be protected against possible damage during further work. For this purpose, the material is reinforced, glued and the gaps are filled. Conservation materials for the above mentioned treatments should have good hydrophilicity, be porous and resistant to solvents, which will be used in further works, i.e. removal of layers, desalination, deep consolidation or hydrophobization. For these reasons, it is best to use preparations containing tetraethoxysilane oligomers (e.g. Steinfestiger OH - Wacker Chemie, KSE 500, KSE 500E - Remmers, Sarsil OH 100, 300 and 500 - Polish Silicones, SW-100 Golden Age and SW-300 Golden Age, Atlas sp. z o.o.), which, when subjected to hydrolytic polycondensation, produce hydrophilic silica [6]. These preparations are used to reinforce the disintegrated stone and as a binder for protective mortars and injection masses. In some cases good results have been obtained using calcium hydroxide nanoparticles.

4.3. Black-crust removal

Removal of harmful, corrosive layers is one of the most difficult procedures during conservation of stone sculpture and architectural details. It is performed not for aesthetic reasons, but for conservation reasons, to remove sealing layers from the surface and preventing the stone from "breathing" freely. We know many methods of removing layers from the oldest ones,

which consisted in chiseling and abrading them with abrasive stones to the newest ones using laser radiation. The method that can be applied must be characterized by: high safety, full preservation of the original surface, without the slightest trace of its deterioration, no possibility of creating by-products, e.g. water-soluble salts, which could pose a threat to the matter of the monument preservation of the properties of the original material, high efficiency. The choice of method is determined by the state of preservation of the monument and the properties and chemical structure of the layers. All known methods can be divided according to the way they work: mechanical methods (forging, abrasion, sandblasting, rubbing, dry ice), physical methods (water spraying, steam, surfactants, solvents, lasers), chemical methods (treatment with alkali, acid and salt). The most recent research shows that the above criteria meet the physical methods to the greatest extent, and among them, unfortunately, still the most expensive laser ablation method, using neodymium lasers emitting radiation

of $\lambda = 1064, 532, 266$ and 213 nm). This method was developed and applied in Poland by Prof. Jan Marczak from Military Academy of Technology (WAT) in Warsaw, in cooperation with the Intercollegiate Institute of Conservation and Restoration of Works of Art, fig. (10) [7,8]. Modern methods include the "Le gommage" rubbing method developed by Thomann-Hanry, using very fine aggregates, even up to $50 \mu\text{m}$ administered at low pressure and the use of dry ice (solid CO_2). Although the first attempts to use dry ice were made as early as the 1950s, the method has not found a wider application. Nowadays it is also proposed; the advantages of dry ice are emphasized, which is odorless, non-poisonous, chemically inert, biostatic, with a low hardness on the Mohs scale equal to 2. The only problem is the very low temperature of dry ice (-78.9°C), which can cause thermal shock and turn out to be extremely harmful in case of damp objects, causing rapid freezing of water in pores, fig. (11).



Figure (10) Shows cleaning of a ceramic architectural detail by laser ablation using a laser developed in the Military Academy of Technology in Warsaw (WAT) by Prof. Jan Marczak (photo by the author)



Figure (11) Shows dry ice cleaning, freezing of a damp wall (photo by the author)

4.4. Desalination (removal of soluble salts)

After removing layers and opening the pores of stone, water-soluble salts should be removed from them, this is a necessary condition to protect the object from further destruction. In case of small sculptures or details that can be transferred to the studio, we use methods of migration to an extended environment in the form of a static or dynamic bath. When it is necessary to carry out this procedure "in situ" i.e. at the site of the object's exposition, the method of migration to the extended environment in the form of poultices remains the only option. In the past various materials were used for this purpose: toilet paper, cotton wool, lignin, cellulose pulp. Nowadays, the poultices are usually prepared from cellulose pulp with glass sand and a small amount of bentonite. The latter component is added in order to increase the plasticity of the poultice and the effectiveness of the treatment, as bentonite is characterized by high ion exchangeability. The poultice should have a high capacity to accumulate salt, pore distribution adapted to the substrate to allow good capillary movement of water with salts from the substrate to the poultice. Most often the poultice is left to dry freely, slowly and completely.

4.5. Deep consolidation (structural reinforcement)

Another procedure, which is performed when the stone detail is strongly disintegrated, the natural binder has lost its binding capacity, is deep consolidation. Its aim is to introduce a new binder in the pores and improve mechanical properties. The first attempts to consolidate stones date back to the 19th century, when only materials such as drying oils, shellac, damara and water glass solutions were introduced into surface layers using a brush. The results obtained at that time already made it possible to state that the introduction of substances only into the surface layers of the stone failed, not only did it not protect against destruction, but it contributed to faster destruction of the

monument. In the twentieth century, when the synthesis of artificial polymers was developing, attempts were made to use vinyl, epoxy or acrylic resins for this purpose. At that time, however, these solutions were attempted to be introduced "structurally", as new methods of "deep" impregnation of up to a minimum of 10-15 cm were developed. Currently, solutions of organic silicon compounds with the above mentioned trade names are most commonly used. They are colorless, provide rapid capillary movement in the material and the possibility of full saturation of the element, they do not migrate to the surface during the bonding (they only require the object to be seasoned in an atmosphere of relative humidity raised to about 75-80%, at about 15-20 °C). They reinforce the stones by increasing their mechanical strength, depending on the type of preparation, by 60-120% and increase their resistance to corrosion.

4.6. Filling of cavities

Cavities resulting from the aging of stone are filled either with natural stone material by so called Dutchman repair (piecing-in in-kind materials), or with properly prepared mortars. We do this not only for aesthetic reasons, but above all to protect the object from damage, because the resulting cavities naturally accumulate water, which can freeze or snow. Regardless of the choice of the method, the material must exhibit properties similar to the original as regards: chemical/mineralogical nature, texture, color, thermal expansion, capillary properties, absorbability and porosity, resistance to soiling and aging. In the past, during the Dutchman repair process, the disintegrated material was chiseled off, giving the cavity a geometric form, and the original stone was removed irrevocably. In addition, the Dutchman (replacement piece) was mounted on metal pins or glue, which could contribute to the rapid destruction of the monument. More and more often mortars are used, which in the past were prepared with organic binders to maintain compatibility with the material that was used for deep consolidation, such as acrylic or epoxy resins. In recent years, the most common mortars used for restorative stone detailing

contain mineral binders, mainly limestone ones, with possible additives of hydraulic admixtures (pozzolana, trass).

4.7. Water repellent treatment

In order to protect stone monuments from water, hydrophobization is a popular treatment. As in the case of consolidation, this treatment can be carried out using the surface method by introducing hydrophobizing preparation to the depth of a few millimeters, or deep, structurally, to a few to several centimeters. The most popular preparations are solutions, emulsions, microemulsions or creams containing alkylpolysiloxanes. Their effectiveness is varied. By performing this treatment we change the natural hydrophilic properties of stones to hydrophobic, which prevents capillary movement of water in the pores of stone. However, it does not protect against penetration of water vapor and its condensation inside the material. The basic criterion for deciding on hydrophobization is the certainty that the object is fully protected against water penetration and does not contain water-soluble salts. Otherwise, hydrophobization may not only fail to protect the object against water, but also contribute to a very rapid destruction of the object, fig. (12).



Figure (10) Shows details of Gdańsk lintels, after hydrophobization, biological damage (photo by the author)

5. Conclusion

To sum up, conservation of stone monuments, sculptures or architectural details is a long and complicated process. It requires the conduct of complex multidisciplinary conservation stu-

dies, on the basis of which a programme of conservation works is prepared, and in special cases of restoration works. The effectiveness of the conservation work is determined by the professional preparation of the research and conservation team carrying out the project, in which the appropriate methods and materials have been selected.

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