INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 2, Issue 4, October-December 2011: 229-234 www.ijcs.uaic.ro

MODIFICATION OF THE PHYSICAL PROPERTIES OF DETERIORATED STONE BY CHEMICAL CONSOLIDATION TREATMENT

Sanjay Prasad GUPTA*

Archaeological Survey of India, Raipur Circle, Govind Sarang Comm. Complex, Ist Floor, New Rajendra Nager, Raipur, India-492006

Abstract

Consolidation treatments on cultural heritage assets have been performed for more than 20 years. However, very few studies on the employed products and methods have been done. The main purpose of the present study was to analyze the changes of physical properties in freshly quarried and in deteriorated stone, after a consolidation treatment with tetraethoxysilane. For this purpose we performed measurements of sorption (absorption of water and adsorption of solid particles on the stone surface), gas adsorption and ultrasonic velocity. The study implies that a consolidation treatment will improve the physical properties of deteriorated stone and have a satisfactory effect, if that treatment is performed in a correct way and the stone is allowed to absorb consolidation liquid until saturation. For badly deteriorated stone two consolidation treatments seem to be sufficient; a third application probably does not improve the physical properties of the stone. It was observed that treatments carried out 10 to 15 years ago still have the intended strengthening effect on the stone. In most cases, if stone remains exposed to water, the consolidating treatment ensures only a 5 to 10 years protecting effect; after that the treatment needs to be repeated. However, the long-term effects and efficacy of periodically repeated consolidation treatments of stone need to be studied further, before such a procedure can be recommended as standard procedure. We also present a suggestion for a preventive consolidation of freshly quarried stone used to replace damaged parts.

Keywords: *consolidation; tetraethoxysilane; sorption; gas adsorption; ultrasonic velocity.*

Introduction

In India, consolidation treatments of cultural heritage sandstone have been preformed for more than 20 years. However, very few studies of the employed products and methods have been done. Experts in the field of stone conservation have different opinions in regard to the effectiveness of consolidating treatments and the long-term effects thereof. These circumstances also apply to questions concerning the suitability of different consolidation products and treatments. Other controversial issues are the number of treatments needed to ensure a good result and the risk of over-treating the stone [1].

The main purpose of this study is to analyze physical property changes in freshly quarried and in deteriorated stone, after consolidation treatment with an ethyl silicate based compound. The study is based on data recorded during practical conservation works, in

* Corresponding author: guptasanjayprasad@gmail.com, +919406349684

combination with newly conducted laboratory tests aimed to establish the physical properties of stone [2]. Two samples located in the Budh Vihar, Sirpur were chosen to illustrate the effects of previous consolidation treatments before being applied on a monument.

Budh Vihar, Sirpur, 83 kms northeast of Raipur, was the capital of the kingdom of Mahakosala, between the 5^{th} and 10^{th} century AD. Located on the banks of river Mahanadi, and bordering the Barnawapara Wildlife Sanctuary, Sirpur, or ‘the City of Wealth’, is one of the most significant archaeological sites in Central India. Today it is a small, idyllic village in the Mahasamund district of Chhatisgarh, a historical site strewn with innumerable monuments and unexcavated mounds. Hindu temples, Buddhist Viharas, palaces and residential complexes are found all over Sirpur. Excavations carried out here since the 1950s, revealed the presence of extremely significant Buddhist, Shiva, Vaishnava and Jaina architecture. Extensive excavations in Sirpur continue to this date and each year exciting new finds are brought to light [3].

The stone of Budh Vihar is a very soft, highly porous material, with a fairly high degree of homogeneity, which makes it particularly easy to work with. Therefore, became a popular material for sculptures and ornaments. Sandstone is one of the most commonly used materials in buildings and objects of historic importance [1]. However, due to its matrix, rich in calcium and clay and to its high porosity, the stone is extremely sensitive to outdoor conditions. Inventory records compiled by the Swedish National Heritage Board show that the stone material that suffered most damage due to anthropogenic factors [4]. Stone weathering is visible primarily as sanding and exfoliation.

Materials and procedure of consolidation

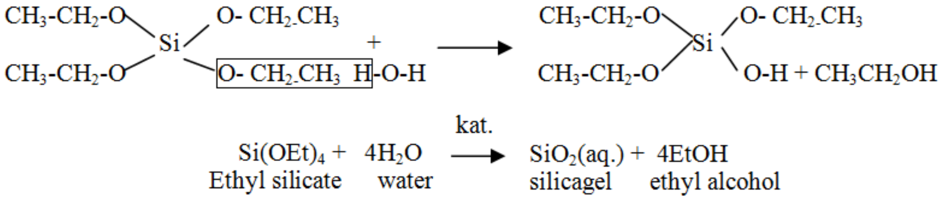
Stone of doorjamb[1] of Budh Vihar is a fine-grained sedimentary rock. It contains mainly quarts and feldspars, but also small amounts calcite and mica. The clay mineral glauconite gives the stone its slightly greenish colour. The stone has a mixed binder of calcium carbonate, clay minerals and silica. Its compressive strength is low (4-5 Mpa), its porosity high (5-20 %), resulting in a very high absorption capacity. Due to the composition of this lithotype and to its high, open porosity, objects deteriorate quickly when exposed to rain, snow and frost. The weak binder used for the stone is not resistant to the physical and chemical actions of water and it can easily be destroyed by frost and/or salt crystallization. Deterioration is also caused by the swelling of clay minerals and the dissolution of calcium carbonate [5].

In stone conservation, the micro structure of the deteriorated stone is stabilized by the introduction of a binder. This strengthening measure is generally combined with a waterproof impregnation to protect against further deterioration. The products used to conserve stone are impregnating agents which are applied freely, so as to saturate the building material. Once applied, the impregnating agent reacts with the water in the capillary pores to form a silica-gel-based mineral binder (SiO_2 aq.) [6].The silica-acid-esters are compounds of quartz (SiO_2) and ethyl alcohol (C_2H_5OH). The objects under study were consolidated and treated by employing the same conservation procedure, wet on wet application until saturation was reached. The ethyl silicate based consolidation compound, tetraethoxysilane (Wacker BS OH-100) was used for our object.

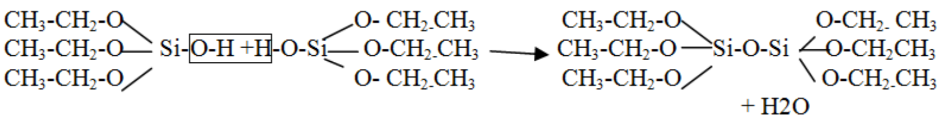
The impregnating agent (ethyl silicate) reacts with the water in the capillary pores by hydrolysis reaction to form a silica-gel-based mineral binder ($SiO_{2\ aq}$). The binding stabilizes the building material by way of covalent Si-O-Si bonds by condensation reaction.

[1] A **doorjamb** is the vertical portion of the frame onto which a door is secured

The hydrolysis reaction is the following:



The condensation reaction is the following:



The binding mechanism is related to the evaporation process. While the alcohol evaporates silica-dioxide is formed in the presence of water vapor. The reaction product is a silica gel that is formed in the pores, providing additional bond between the particles. The consolidation was performed in an open environment, to obtain a full saturation of pores. The doorjamb of Budh Vihar was in a poor condition, therefore, the treatment needed to be repeated after 15 days. Treatments used the “permanent flow” method, as shown in figure 2. Permanent flow means that the fluid is administered to the object without interruption, replacing the air in the stone capillaries, until they are saturated [7]. The quantity of fluid needed depends on the degree of deterioration and the porosity of the fabric; damaged parts absorb more and the undamaged less. The liquids can easily reach a depth of up to 0.5 to 10 mm in a relatively short time. That is considered sufficient to ensure a good consolidation. Due to the high absorption capacity of sandstone, the consolidation liquid penetrates deep into the stone and a strengthening gel develops over time [1].

Experimental

In order to analyze the physical properties changes in the stone caused by the consolidation treatment, measurements of porosity, compressive strength and ultrasonic velocity were performed. Samples of deteriorated stone were studied before the application of a consolidator (Fig. 1, 2 and 3). For capillary water adsorption and ultrasonic tests, we used small cubes of freshly quarried sandstone (50 x 50 x 50 mm) and irregularly shaped, deteriorated samples [8].

The measurement of porosity was based on the water absorption by total immersion method (the quantity of water absorbed by a sample is related to the total open porosity), the overall porosity of the sample being calculated according the following equation:

$$\% \text{ Total Porosity} = Vp/Va \times 100 \qquad (1)$$

where: Vp: Total volume of a solid occupied by pores, Va: Volume of a solid including space occupied by pores.

Compression test with a compression testing machinewas carried out to determine compressive strength[2] of building material. The formula describing the compressive strength is the following:

$$\text{Compressive strength} = \text{Load applied (N)} / \text{area of test sample (cm sq)} \quad (2)$$

The stones were washed and left to dry for 48 hours, at room temperature and afterwards were placed in tetraethoxysilane (Wacker BS OH 100) for slow absorption, by free capillary forces, until they reached saturation. Thereafter, all samples were left to air-dry, until they reached equilibrium (weight of immersed sample become constant after 14 to 16 days).

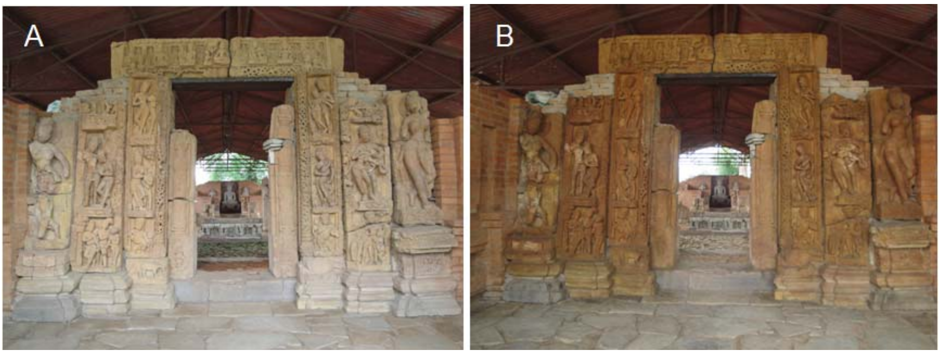


Fig. 1. Budh Vihar, Sirpur: A - before consolidation, B -after consolidation

Fig. 2. Budh Vihar, Sirpur: during Consolidation

Fig. 3. Budh Vihar, Sirpur (front view): A - before Conservation, B - during Conservation, C - after Conservation

Capillary water adsorption was performed according to EN 1925 for porous materials [7], being a parameter interconnected with the wettability of a sample. Absorption was

[2] "Maximum stress a material can sustain under crushing load" before getting failed.

determined by measuring weight gain, after placing one side of the samples in a water bath. The readings of weight gain were taken at precise intervals (in minutes): 0, 1, 3, 5, 10, 15, 30, 60, 480 and 1440.

In order to relate the results from capillary water adsorption to other measurements of porosity, ultrasonic velocity measurement techniques were applied. This is a non-destructive technique and it has the potential to detect deterioration and strengthening inside a stone.

Results and discussions

A direct comparison between the results for the fresh and those for the deteriorated samples is difficult to perform, due to the unknown origin of the deteriorated stone. After more than 300 years it is difficult to trace the original quarry for the stone of the treated objects. To date, no consolidation treatment is applied to fresh stones. Nevertheless, in some cases the replaced parts show a higher deterioration rate than the old ones. The clearly visible exfoliation on the porches, indicated that the original stone had a clear lamination (different grain size deposited in layers) and/or was previously treated with impregnating agents that created an external waterproof layer. The freshly quarried stone was characterized by a weak lamination, detectable by an analysis of the ultrasonic velocity propagation in two directions. In cases when a replacement of deteriorated parts is planned, the fresh stone should also be compatible with the old parts of the object. Moisture transport properties and porosity are probably the most important factors that should be investigated.

The compressive strength measured for both objects was low (4-5 MPa) and their porosity was high (5-20 %), which resulted in a high absorption capacity. Our experimental data showed that the porosity diminished after the consolidation treatment with 2-4% and compressive strength increased up to 35-40 Mpa. Which resulted in a low absorption capacity after treatment.

The capillary water absorption of the fresh consolidated stone is similar to the deteriorated samples, which were consolidated two and three times. That means that the consolidation treatment significantly decreases the quantity of water passing through the pore system. This observation may be of value for conservators planning to replace deteriorated stone parts with freshly quarried pieces of the sandstone. As for the number of treatments, applicable here only for the deteriorated samples, it appears that the second treatment further decreases the capillary water absorption, after the first treatment, while the third treatment has no further effect on the analyzed properties. The treatment with tetraethoxysilane increases the ultrasonic velocities of the fresh samples by approximately 0.5 km/s and those of the deteriorated samples by 0.2-0.5 km/s. The basis for any interpretation of ultrasonic results should have a comprehensive knowledge of rock fabrics and their petro-physical properties, as well as the weather conditions. In order to quantify the strengthening effect of a consolidation treatment, the initial status of the treated object must be documented, due to the high heterogeneity of stone materials.

Conclusions

Sandstone is a material prone affected by weathering, which indisputably demands consolidation treatments, in order to maintain its intended shape. The porosity ensures a safe and successful consolidation treatment. Study shows that, the consolidation with tetraethoxysilane diminished the deterioration of the sandstone. However, the examples of ineffective consolidations imply that the application methods and/or the used consolidation products need further perfection. The advisable number of consolidation treatments depends on the condition of the object. The manufacturer recommends only one consolidation for stones in a relatively good condition and one or two additional treatments for stones in a poor condition.

The laboratory tests indicated that two consolidation treatments give a satisfactory result. A third application does not improve the physical properties of the stone any further [9]. Observations show that treatments preformed 10 to 15 years ago still have the intended strengthening effect on the stone. However, stone stays exposed to water and the consolidation treatment only ensures a 5 to 10 years protection period. It probably needs to be reapplied after that period. That fact should be taken into account when making conservation programs for objects chiseled in stone. In many cases the parts of a stone object replaced with freshly quarried and untreated stone, show a higher deterioration rate than the original stone parts.

Acknowledgements

The authors would like to thank Dr. P.K.Mishra, Superintending Archaeologist at the Archaeological Survey of India, Raipur Circle, Raipur, India and Dr. K. S. Rana, Director (Science) at the Archaeological Survey of India, Dehradun, India for their encouragement and guidance.

References

[1] E. Angelini, S. Grassini, G. Solorzano, G.D. Campos, G. Do Nascimento, T. De Caro, *Integrated approach to the characterization and conservation of artifacts of the Brazilian colonial period,* **Applied Physics A-Materials Science & Processing, 83**, 4, 2006, pp. 485-491.

[2] P. Maravelaki-Kalaitzaki, N. Kallithrakas-Kontos, Z. Agioutantis, S. Maurigiannakis, D. Korakaki, A *comparative study of porous limestones treated with silicon-based strengthening agents,* **Progress in Organic Coatings, 62**, 1, 2008, pp. 49-60.

[3] A. Ray, B.S. Roy, D. George, N. Dhingra, T. Mathew, *Sirpur Travel Guide,* **Chhattisgarh Tourism Board,** published by Good Earth Publications,eicher Goodearth Private Ltd., New Delhi, 2009.

[4] A. Nord, **Analysis of Deteriorated Sandstone at the Royal Palace**, Stockholm**.** GFF volume 117, 1995.

[5] J.W. Lukaszewicz , D. Kwiatkowski, M. Klingspor, *Consolidation of Gotland Stonein Monuments*, **Methods of Evaluating Products for the Conservation of Porous Building Materials in Monuments**, ICCROM, Rome 19-21 June, 1995.

[6] E.K. Kim, J. Won, J.Y. Do, S.D. Kim, Y.S. Kang, *Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants*, **Journal of Cultural Heritage, 10**, 2, 2009, pp. 214-221.

[7] S. Son, J. Won, J.J. Kim, Y.D. Jang, Y.S. Kang, S.D. Kim, *Organic-Inorganic Hybrid Compounds Containing Polyhedral Oligomeric Silsesquioxane for Conservation of Stone Heritage,* **ACS Applied Materials&Interfaces, 1**, 2, 2009, pp. 393-401.

[8] R.L. Coffman, N. Agnew, C. Selwitz, *Modification of the Physical Properties of Natural and Artificial Adobe by Chemical Consolidation,* in **Proceedings of Symposium G: Materials Issues in Art and Archaeology II. Materials Research Society Spring Meeting**, San Francisco, California, USA, April 16-21,1990.

[9] ***, *Silicon Division*, **Wacker Product Mnnual**, Wacker Chemie AG, Munchen, Germany, pp. 32-35.

Received: July, 30, 2011
Accepted: September, 30, 2011