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Application of chemical consolidants into the conservation of limestone monuments

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Abstract: There are many stone monuments which are weathered by natural or artificial factors in Korea. The partly weathering in stone could accelerate the rate of weathering, so it is demanded to keep them from the further weathering. Consolidation is evaluated as one of the efficient treatments which have a good effectiveness in stone monuments. But following the former researches, the effectiveness of consolidation could be different, related to the kinds of stone or consolidants. Therefore, in this study, the change of properties was monitored in the long term for the exact evaluation of the stability of the consolidated stone. It is estimated that the pore structure of consolidated stone was filled by consolidant, according to the measurements of ultrasonic velocity, and the digital image analysis of the sample was shown that the color property of stone surface has varied during the curing.

1. Introduction

In Korea, there are many valuable stone monuments over 1,400 pieces, which are registered as a nation treasure. But many of them are weathered by natural and artificial factors and some such as the stone Pagoda in Iksan Mireuksaji are highly damaged by war, fire and human activities. The rate of weathering in a weathered stone monument gets accelerated more and more as time goes by, even if it is partly weathered. Thus it is important to decrease the velocity of weathering in stone monuments in order to preserve them from the serious damage which is caused by weathering.

Consolidation using chemical consolidants is considered as one of the best ways to reduce the rate of weathering and to prevent the monuments from the further weathering without serious side effects. There have been many researches on the effectiveness of consolidation up to now, but the conclusions on the effects of consolidation were different from each other (Table 1). It is because the effectiveness of consolidation relates to the kinds of chemical consolidants and stone which are used in experiments. Therefore it is necessary to examine the stability of the consolidated stone in the scientific, engineering way and in the long-term, in order to evaluate the effectiveness of consolidation. In the present research, the effectiveness of application of chemical consolidants is evaluated through the measurements of the physical properties, using the Mokkatam limestone.

Table 1. The summary of the former researches (Won, 2001; A. Caselli et al., 1995; J. W. Lukaszewicz et al, 1995; Lise Leroux et al., 2000, N. Garcia Pascua et al., 1995).

Consolidant	Sample	Application	Measurement
Wacker OH 100 (Wacker-Chemie)	Granite	Immersion for 3 days	The properties of pore structure Strength
Stone strengthener OH (Wacker-Chemie) Funcosil OH (Remmers)	Gotland sandstone	Capillary suction for 10 minutes	Color property Monitoring through the artificia ageing
Stone strengthener OH & Stone strengthener H (Wacker OH 100) Brethane (Colebrand Pty. Ltd.)	Bacchus Marsh sandstone	Flooding using squeeze bottle	Monitoring through the artificia ageing The properties of pore structures
Mowilith 35/73 (Hoecht) Minersil SH&Minerxan(Prolab) H-224 (Rhone Poulenc)	Sandstone Limestone	No description	The properties of pore structure
Silicic acid ester solution	Marble Sandstone Chalk Limestone	Capillary absorption	The properties of pore structure

2. Experimental methods and materials

Materials

Mokkatam limestone was selected as a sample for consolidation. It was taken from Mokkatam Quarry which is located in the southeast part of the Cairo. Mokkatam quarry is close to Giza Pyramids and its layer has interbedded by Marl and limestone (Aboushook et al, 1999). Through the X-Ray Diffraction and X-Ray Florescence analysis, it has shown that calcite and a small amount of magnesium, iron, silicate and aluminium compose to the Mokkatam limestone (Table 2).

Mokkatam limestone was shaped as a core which has the diameter of 1.5 inch for the convenience of measurements. In order to guarantee the objective reliability, the samples of total 27 were used in this study.

Table 2. The results of XRF (weight %).

CaO	MgO	Fe_2O_3	Al_2O_3	TiO_2	P_2O_5	K_2O	Na_2O	MnO	L.O.I	Total
50.63	0.88	0.24	0.73	0.35	0.03	0.19	-	-	41.51	99.13

For this study, 'Wacker OH 100' which is produced by Wacker Chemie was used as a consolidant. It mainly consists of ethyl silicate and it reacts with the moisture by the chemical mechanism of ethyl silicate. As a result of reaction, it leaves the silica gel binder on the surface of the stone and produces ethanol which is evaporated.

'Wacker OH 100' is one of the consolidants which have a good performance in stone (Eddy de witte, 1981; N. Garcia Pascua, 1995). 'Wacker OH 100' has low viscosity and density relatively in comparison with the other consolidants (Table 3), so it could penetrate to the inner structure of stone better.

Table 3. The comparison of property between the consolidants.

Consolidant	Density at 25°C (g/cm^3)	Viscosity at 25°C (mPa·s)
Wacker OH 100	1.0	Approximately 1.08~1.18
Epoxy Resin (Araldite AY 103/ Hardener HY 956)	1.6	Approximately 850~140

Methods

The samples which got shaped as a core were treated with consolidant after having dried inner chamber of 60℃ during 48 hours. The drying procedure is necessary to remove the moisture and bubbles inside of pore, so it helps to get the good penetration of consolidant.

The consolidant was penetrated to the sample by the capillary rise method, considering of the performance in-situ. After the samples were immersed in the consolidant during 72 hours except one of faces, they were cured as the following condition during 4 weeks (Fig. 1).

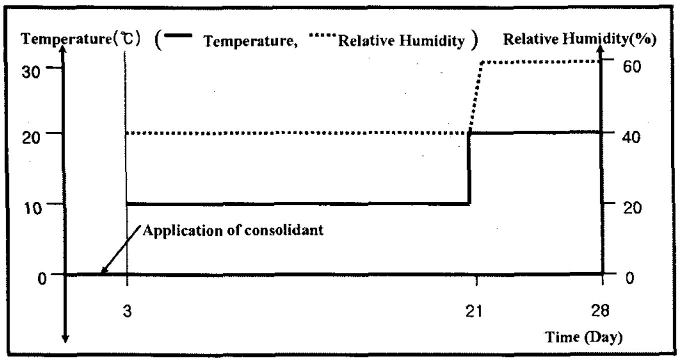

Fig. 1. Curing conditions of the sample.

In order to evaluate the effect of consolidation effectively, two categories of the measurements were carried out. First, the change of the pore structure in a sample after consolidation was examined through the measurements of porosity, permeability and ultrasonic velocity. These measurements have the advantage in common, which is that they give the information on the inner space of the sample without any destruction. The results taken before and after consolidation were compared.

Secondly, the measurement of the color property in the sample was performed by digital image analysis. The digital image of the sample was analyzed by the software 'ImageCraft (Chang, 2001)' and Colorcheker® which was made by KODAK was used as a reference for this analysis.

3. Results and Discussions

Curing procedure

After the application of consolidant, the consolidated sample was cured in a chamber which has kept its condition at 20℃, 40% RH. It was found that the several properties had been changed during the curing procedure.

First, the consolidant absorption rate was decreased during the curing process, as a result of the evaporation of ethanol. The consolidant absorption rates of the consolidated sample were measured in the range of 4.56~10.35 %, so it was shown that consolidant in Mokkatam limestone could not be absorbed more than 10.35% of its dry weight.

The decrease of weight has been observed until about 28 days since the application of consolidant (Fig. 2). Following this results, it is demanded to leave the consolidated sample for at least 28 days after the application of consolidant, for the effective consolidation. It is because the reduction of weight in the consolidated sample means that the reaction between ethyl silicate and moisture is not finished.

Secondly, the color properties got lightened more and more in curing. It is because of the silica which is a by-product and the remained silica on the surface of the stone was estimated to make the sample surface light.

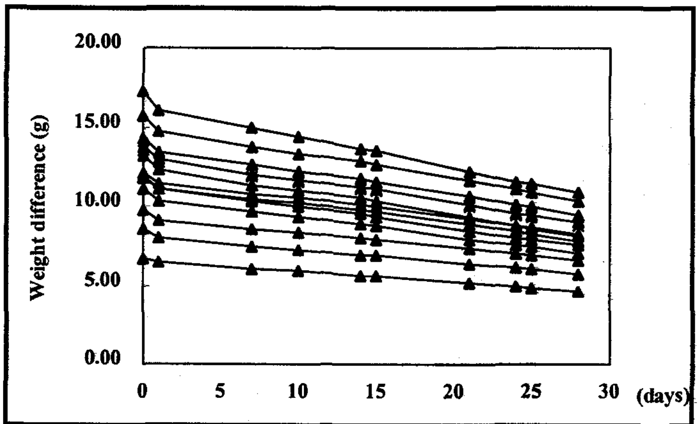

Fig. 2. Variation of the weight difference during curing process.

Comparison with the results before and after consolidation

It was shown that the ultrasonic velocity was increased after consolidation (Fig. 3). Before the application of consolidant, the ultrasonic velocity of the samples was in the range of 1.45~2.02 km/s (S-wave) and 2.96~4.05 km/s (P-wave), but it was increased by approximately 7~10%. So the ultrasonic velocity after consolidation was measured in the range of 1.62~2.15 km/s (S-wave) and 3.21~4.43 km/s (P-wave). The increasing of the ultrasonic velocity is caused by the filling of the inner space of the sample with consolidant.

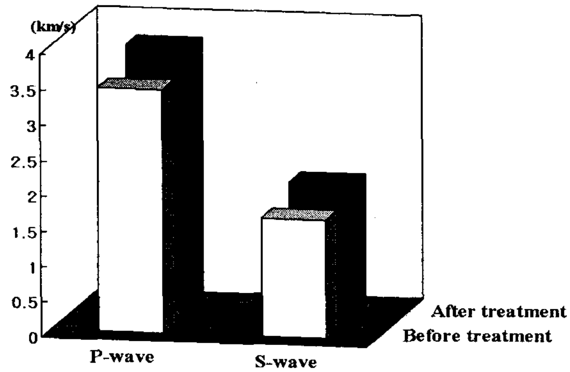

Fig. 3. Average ultrasonic velocity before and after consolidation.

4. Conclusions

The evaluation on the effectiveness of consolidation has been made, using total 27 samples of Mokkatam limestone. For the effective assessment, the two kinds of properties were selected and performed. One is to measure the properties which show the pore structure of the sample and the other is to verify the variation of color property quantitatively.

As a result of this study, it was shown that the ultrasonic velocity was increased by 7~10 % after consolidation, compared with the data taken before consolidation. And in curing process, the consolidant absorption rate was continued decreasing for 28 days after the application of consolidant, so it is demanded to cure the applied sample with consolidant during at least 28 days in order to get a good performance.

If the change of properties was monitored in the long term through the artificial ageing, it is estimated to get the data which show the entire stability. Through the results of the limestone samples, it is expected to assess the effectiveness of consolidation in the limestone monuments.

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