DETERIORATION MECHANISMS OF HISTORIC LIMESTONE AND DEVELOPMENT OF ITS CONSERVATION TREATMENTS WITH NANODISPERSIVE Ca(OH)$_2$ SOLUTIONS
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ABSTRACT

Deteriorated statues carved from karstic limestones in Nemrut Dağ Monument were studied to discover the decay mechanisms that had major roles in their present state of deterioration during 2000 years of exposure to atmospheric conditions as well as their treatments with nanodispersive Ca(OH)$_2$ solutions. Exposed surfaces of limestones having karstic veins, interior crack zones and their surfaces were examined and compared with relatively undeteriorated interior parts. Similar limestones from the geological formations nearby were artificially deteriorated by salt crystallization and were also examined. In addition, the surface soil around the monument was analyzed for its clay content. Standart physical and physicomechanical tests, petrographical analysis, XRD, SEM-EDX and FTIR were used during examinations.

The microstructure of limestones was observed to be composed of micritic calcite with karstic veins of sparitic calcite crystals. Some karstic zones were found to be preferred sites of decay for the start of surface dissolution and for the formation and widening of cracks. Presence of clay minerals in those decay zones, their swelling nature, iron oxides that move through those zones, as well as biological activity were found to be closely related to those phenomena. The treatments with nanodispersive Ca(OH)$_2$ solutions and their roles were discussed in the light of those decay factors.

INTRODUCTION

An exposed stone either in an archaeological site or on a monument is subjected to weathering by physical, chemical and biological processes. In time, those weathering processes cause considerable changes in microstructure of stone, such as increase in porosity, decrease in mechanical properties, quite a number of changes in chemical composition etc. starting from exterior surfaces towards interiors of the stone. Those changes are also visible by change in color, detachments as scales and flakes, crack formation material loss as powdering, granular disintegration, outbursts etc.

Importance of clay minerals and biological activity has been emphasized by a number of researchers on those decay processes accompanied by wetting and drying cycles of exposed stone environment [1][2].

In the past years, some organic fixatives, synthetic acrylic polymers, organosilicone compounds etc. were used for consolidation of limestone [3][4][5][6]. But the usage of those compounds had many disadvantages for the use as conservation treatments. The main problems with those treatments were

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their physicochemical incompatibility with the limestone [7]. In recent years, the ideas that the original constituent of limestone can also be its most effective consolidant that may have the great advantage of high compatibility with the limestone have gained importance.

Physical, mechanical and chemical compatibility with the original stone is a requirement for the conservation treatments of historic stones. During the consolidation treatments of the weak stone compatibility can best be achieved by producing a similar structure to the original stone. For that purpose nanodispersive solutions of calcium hydroxide have been studied [7][8][9].

The aim of this study was to examine the mechanisms involved in the decay of limestone statues in Nemrut Dag Monument and propose its conservation treatments. Limestones of Nemrut Dağ Monument belong to the large Midyat Formations of Eocene age, precipitated in marine environment. Abundance of decay forms as fragmental disintegration through some karstic veins of micritic limestone, colored biological depositions and pitting were observed at the site (Figure 1). In this study, development of conservation treatments that could control the process of fragmental disintegration and improvement of decayed microstructure of limestone by forming a calcite infill that was compatible with the original structure of limestone were tried to be achieved.

EXPERIMENTAL STUDIES AND RESULTS

Examinations were done on the deteriorated samples from Nemrut Dag Monument and on the samples taken from the geological formations nearby that showed similar deterioration forms with the Nemrut Dag Monument’s limestones. Samples from the geological formations were artificially deteriorated by cyclic salt crystallization tests. Both naturally and artificially decayed limestones were examined for their physical, physico-mechanical and microstructural properties. Physical and physico-mechanical properties were examined by bulk density, effective porosity, and ultrasonic velocity measurements [10]. Microstructural properties of deteriorated limestones were observed by examination of cross sections with SEM-EDX, by analyses of thin sections with optical microscopy and by examination of powdered samples scraped from exterior surfaces, crack surfaces and interiors of the stone using XRD and FTIR analyses. Distribution of biological activity was determined by qualitative and quantitative analyses with FDA [11].

Deteriorated limestones by fragmental disintegration were treated with nanodispersive Ca(OH)$_2$ solutions in ethyl alcohol for a range of concentrations. The depth of penetration was followed in thin sections using calcein indicator which was fluorescent under ultraviolet light. Morphology of newly formed calcite infill was examined by SEM-EDX analyses. The changes in physicomechanical properties were done in treated samples.

Examination of the physical and physicomechanical properties of limestones

Deteriorated limestone pieces from Nemrut Dağ Monument and samples taken from the limestone formations nearby the monument were analyzed for their physical and physicomechanical properties. Limestone samples from nearby formations were cut in 5 cm cubes and subjected to artificial salt crystallization cycles by saturated sodium sulphate solution [10].
Figure 1: Head of Antiochus in East Terrace of Nemrut Dağ Monument showing various decay forms

- Microkarstification
- Pitting
- Fragmental disintegration: through micro&macro karstic network of limestone
- Color change and microbiological deposition
- Material loss

Figure 2: Small pieces of fragmental disintegration collected in the vicinity of the statues and their basement blocks.
Artificial Weathering Tests by Salt Crystallization

Limestones from geological formations in the vicinity that looked quite similar to the ones used on the Nemrut Dağ Monument were collected, cut to 5 cm cubes and were used for artificial weathering by salt crystallization (Figure 3).

Progress of stone deterioration was examined in the laboratory by salt crystallization tests [10]. Unlike most other techniques the sodium sulphate crystallization test was a comparative test to obtain data for monitoring and discovering the weak zones of limestone. Good correlation between the results of the tests and the overall weathering behaviour of limestones [12].

![Image of limestone cubes](image)

**Figure 3:** Limestone cubes prepared by using the samples taken from formations in the vicinity that looked quite similar to the ones used on the Nemrut Dağ Monument.

The limestone cubes were soaked in 14% Na₂SO₄.10H₂O solution for 2 hours and dried at 60°C for at least 16 hours and that cycle was repeated. After each 5 cycles of salt crystallization, 8 limestone cubes were taken out of the test. Their weight loss, porosity, bulk density and ultrasonic velocity measurements were done.

**Table 1:** Average bulk density, porosity and ultrasonic velocity values of the samples before and after the artificial weathering tests

<table>
<thead>
<tr>
<th></th>
<th>Before salt crystallization cycles</th>
<th>After 50 salt crystallization cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.69</td>
<td>2.68</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>0.50</td>
<td>0.80</td>
</tr>
<tr>
<td>Ultrasonic Velocity (m/s)</td>
<td>3200-5000</td>
<td>1400-2600</td>
</tr>
</tbody>
</table>

The average bulk density of the samples after the salt crystallization tests has slightly changed. The porosity has increased from 0.50% to 0.80% at the end of the 50th test cycle. On the other hand, the notable decrease in average ultrasonic velocity values indicated the microstructural changes of the limestone samples (Table 1).
Physicomechanical properties of the samples taken from the monument:

Small pieces of fragmental disintegration collected in the vicinity of the statues and their basement blocks were taken to represent the weathered samples. The average bulk density of those samples were found to be 2.67 g/cm$^3$ and the average porosity were about 0.80%. Average ultrasonic velocity values of the samples were about 1870 m/s. Those results were quite similar with the results of geological samples that were artificially weathered with 50 cycles of salt crystallization.

Examination of Microstructure

The change in the microstructure of weathered limestone was examined through mineralogical and petrographical analyses by thin section examinations with an optical microscope, XRD, SEM-EDX and FTIR.

Thin section examination of the decayed limestones:

The thin section analysis of limestones by optical microscope indicated that the limestones had micritic and microsparitic particles and they bonded with sparitic calcite. Some opaque minerals were also observed. These opaque minerals were submicroscopic and included iron in their structure. The cracks were filled with limonite and micritic calcite minerals. Some fossils were also observed in the thin sections (Figures 4-7).

Figure 4: (a) (scale bar: 250 microns), (b) (scale bar: 250 microns). Thin section views of limestone showing cracks and opaque minerals.

Figure 5: Thin section view of Nemrut limestone(E2) crack zones (scale bar:500 microns)

Figure 6: View of a Karstic vein in Nemrut limestone (scale bar:100 microns)
Figure 7: View of a crack with karstic vein having iron oxides and calcite crystals (scale bar: 100 microns)

Limestone samples from geological formations in the vicinity of Nemrut monument that looked quite similar to the ones used on the Nemrut monument had some natural cracks and karstic veins (Figures 6-7). Those cracks were the weak parts of the limestones and they were first to open during the salt crystallization tests.

**XRD analyses**

XRD pattern of the Nemrut limestone showed that calcite mineral was the main constituent of the limestone. No secondary minerals were detected in the XRD patterns probably due to very high percentage of calcite. However, there were some minor minerals in the structure of Nemrut limestone other than calcite. For the determination of minor components, some samples were treated with 5% HCl to dissolve the major component that was calcite mineral. The percentage of those minor minerals were calculated after 5% HCl acid treatment. It was found that limestones had ~4% acid insoluble part in weight. Those minor minerals were mostly located in the cracks and karstic veins. During the salt crystallization tests in the laboratory and visual observations at the site, detachments of limestones were from the cracks and karstic veins due to the existence of those minor minerals in them. Thus it was important to identify those minerals and study their behaviour in the stone. Those crack surfaces which were brown colored were scraped and the acid insoluble part of the powder was examined by XRD. XRD analysis of acid insoluble part of powder was done in the following way: the powder was dissolved in 2% HCl solution. The acid insoluble part was filtered through a filter paper, washed until free of chloride ions and air dried. XRD traces of those oriented samples were given in Figures 8 and 9.
The XRD patterns of crack surface material revealed that main component was quartz with kaolinite, illite, chlorite and albite (Fig. 8). For avoiding misidentification of clay minerals, ethylene glycol solvation method was used [13]. Oriented samples were exposed to the vapor of the reagent (ethylene glycol) for at least 8 hours at 60°C and analyzed by XRD (Figure 9).

In XRD traces of ethylene glycolated sample, clay minerals especially chlorite were seen more clearly.

The surface soil around the monument was also analyzed for its clay content. The surface soil was treated with 2% HCl, air dried and analyzed by XRD.
Quartz, kaolinite, illite and albite were detected by XRD analysis of surface soil around the monument. After the ethylene glycolization of the sample, chlorite mineral was also observed (Figure 11).

Figure 10: XRD patterns of surface soil around the monument (2% HCl treated, oriented)

Figure 11: XRD patterns of surface soil around the monument (2% HCl treated, glycolated and oriented)
SEM-EDX analyses

SEM analysis aimed to provide information about the microstructure and morphology of crack surfaces, the presence of clay minerals and their distribution in the stone. For those purposes crack surfaces and cross sections were analyzed by SEM-EDX. Opaque minerals were also detected by SEM analyses and EDX analyses revealed that opaque minerals had high iron content in their structure. (Figure 12).

Figure 12: A view from iron rich region of the limestone (scale:40 microns)

Figure 13. EDX analysis of the iron rich region of the limestone observed in Fig. 12. A crack zone of limestone was analyzed by SEM-EDX. The elemental distribution maps of Fe, Ca, Si and Al indicated that the clay minerals and iron oxides were mostly located in the crack zones (Figure 14 a, b).

(a)  
(b)  
Figure 14: A view of thick section in optical microscope (a) 2,5X cross nicol, (b) 10X cross nicol
**Figure 15:** View of a crack (a) and distribution of Fe, Ca, Si and Al in the same region (scale: 400 microns)

**Figure 16:** EDX spectrum of the whole area shown in Figure 15 (a).
FTIR analyses

Samples examined by XRD were also examined with FTIR. The FTIR spectra of the sample scraped from the surface of the crack (C) and the spectra after its 2% HCl treatment (D) have both shown kaolinite peaks at 3697 cm\(^{-1}\) and 3620 cm\(^{-1}\). FTIR analyses of surface soil around the monument before and after 2% HCl treatment have also shown presence of kaolinite in the samples. Although FTIR was good to reveal the kaolinite peaks clearly in samples before and after acid treatment, it was not so good to identify the other types of clay minerals.

**Figure 17:** Infrared spectra of the sample scraped from the surface of the crack (B) and surface soil around the monument (C) after 2% HCl treatment.
A: surface soil around the monument before acid treatment
B: surface soil around the monument after acid treatment
C: sample scraped from the surface of the crack before acid treatment
D: sample scraped from the surface of the crack after acid treatment
Preparation of nanodispersive solutions and treatments of decayed limestone

Preparation of nanodispersive solutions was an important step of the treatment. There were some different ways to the preparation of nanodispersive solutions in literature. Some authors have used soluble calcium salts such as calcium hydroxide and bicarbonate. Those methods allowed more calcium ions to be introduced in a single application, and many applications were needed [7] [14].

Tiano et.al. [15] prepared supersaturated nanodispersive (20 nm) calcium carbonate solution by using ammonium carbonate and calcium chloride solution. For controlling the carbonation, bio macro molecules were also used. But they suggested that method for small objects.

Feng et al. [16] made calcium carbonate dispersion by CO$_2$ gas passing into the Ca(OH)$_2$ solution. They also tried some additives to control the particle size of calcium carbonate.

According to Ambrosi et.al [9] 0.25 gr Ca(OH)$_2$ in 40 ml of propan-1-ol by vigorous stirring at room temperature formed a stable dispersion and the dispersed particles were 300-600 nanometer.

Seo et al. [17] formed precipitated calcium carbonate in pure ethanol as main solvent. In this study many types of calcium hydroxide nanodispersive solutions were prepared and the concentrations of dispersed particles were detected by the EDTA titration. The most efficient nanodispersive solution was found by putting 66.25gr Ca(OH)$_2$ in 250ml water and 750ml ethanol by magneting stirring for 24 hours and 3 hours ultrasonic vibration of the solution. 19.52gr of Ca(OH)$_2$ particles in 1000 ml solution remained suspended.

The particle sizes of the nanodispersed particles were measured by Malvern Nano ZS90 instrument. The average particle size was found in the range of 350-600nm (Figure 15).

![Statistics Graph (1 measurements)](image)

**Figure 15:** The particle size distribution of nanodispersive Ca(OH)$_2$ solution.

**Preliminary consolidation treatments**

Nanodispersive solutions with 66.25 gr Ca(OH)$_2$ in 250 ml of distilled water and 750 ml ethanol were used for the preliminary consolidation treatments. For detection of newly formed calcite crystals, a small concentration of Calceine which made the calcite fluorescent under ultraviolet light was added to the nanodispersive solution before the application. In that way, it was possible to recognize the newly
formed calcite and the depth of impregnation of the nanodispersive solution. The application was carried out by dropping solution to the top of the sample. The prepared thin sections of samples were examined under the optical microscope with ultraviolet light. The thin section analyses revealed that nanodispersive solution went to the pores of the stone and formed calcite crystals. There was an increase in the Ultrasonic velocity of the samples after treatments.

CONCLUSIONS

Limestones of Nemrut Dağı Monument exhibit fragmental disintegration through some of its karstic zones together with some pitting, biological depositions and color change.

Before the conservation treatments, a study on the degree and the process of deterioration in the stone was required. It was expected to know the differences between the healthy and decayed zones of the limestone. After that, expected roles from the treatments could be defined and the success of the treatments procedures could be studied.

In this work the physical, physico-mechanical properties, microstructural properties and the weathering zones of the limestones of Nemrut Dağ Monument were studied. Physico-mechanical studies indicated that weathered limestone samples taken from the monument had bulk density $\sim 2.67\,\text{g/cm}^3$ and porosity $\sim 0.8\%$. Samples collected from geological formations in the vicinity were a bit denser and had slightly lower porosity. But after 50 cycles of salt crystallization, samples collected from geological formations had quite similar values with the weathered samples collected from the monument.

The petrographical analysis of limestones indicated that the limestones had micritic and microsparitic particles and they bonded with sparitic calcite crystals. Some submicroscopic opaque minerals as iron oxides and fossils were also observed in thin sections of limestones.

It was observed that micritic limestone decayed through some karstic veins and cracks in the form of fragmental disintegration where the veins were closely related to the presence of clay minerals, iron oxides and biological activity. XRD analyses revealed that those clay minerals were kaolinite, illite and chlorite. Quartz and albite were also found in the karstic veins together with those clay minerals. The presence of clay minerals in the karstic veins of limestone together with iron oxides were verified in this study by following their distribution in SEM images with EDX analyses (Figure 15). The swelling characteristics of kaolinite and illite were expected to be very small. However, they may take part in deterioration by several other mechanisms. The mobility of clay minerals in the aqueous media caused the transportation of the clay minerals to the fine capillaries of the stone [18]. The role of clay minerals in deterioration by other mechanisms such as ion exchange capacity, acting as reservoirs for nucleation of new crystals etc. may be important in the growth of cracks. Swelling of chlorites and increase in their swelling by weathering were mentioned by some studies [19].

Treatments of cracks with nanodispersive Ca(OH)$_2$ solutions proved to be a conservation method for deteriorated limestones of Nemrut Dağ Monument. However their role in the control of crack growth in the presence of clay minerals, iron oxides and biological activity need to be further studied.
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REFERENCES