INVESTIGATIONS ON SANDSTONE DETERIORATION

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ABSTRACT

In this study the main decay mechanisms of the sandstones from Nemrut Dağı Monument were analysed to be able to diagnose the most important factors that affect their long term alteration that was important for the development of their conservation methods.

Analyses of non-weathered, weathered and artificially weathered sandstones by salt crystallization were done to determine their physical and physico-mechanical properties such as bulk density, total porosity, color, and ultrasonic velocity values. Pore size distribution was studied by Mercury Intrusion Porosimetry. Their microstructural properties were examined by the analyses of cross and thin sections using optical microscopy, XRD, as well as Raman spectroscopy.

The sandstones of Nemrut Dağı Monument had good physico-mechanical properties, high bulk density and low porosity, the non-weathered coarse grained sandstones having lower porosity (~0.8%–1.5%) than the non-weathered fine grained ones (~5.2%). In naturally weathered sandstones samples from the site, representing the weathering form as separation by layering, total porosity (~6%) have increased, pore diameter of the finest pores have increased about twice. Sandstones were mainly composed of quartz, feldspars and clay minerals such as chlorite, illite and kaolinite as well as iron oxides. Clay and iron oxide accumulation on the surfaces of the microcracks and cracks that resulted in separation by layering parallel to each other and bedding planes were observed in naturally weathered sandstones. Considerable intracrystalline swelling characteristics were observed in chlorites of naturally weathered sandstones that played major role in their deterioration.

INTRODUCTION

Sandstone is a widely used stone in historic buildings and artifacts. Despite its wide use, its deterioration and conservation problems are not well understood. Weathering can be the result of many processes; those processes may act together; successively or separately. Thus the relationships between the processes resulting in the weathering should be investigated together with the rock's properties, environmental conditions and their relations. Sandstone weathering system and each mechanism in the process of deterioration are thought to be a function with multivariate character from microscopic scale to the macroscopic scale (Turkington, et al., 2005, Jimenez-Gonzalez, et al., 2008).

Sandstones are sedimentary rocks composed of different rock fragments and minerals. Their durability characteristics are affected by their intrinsic characteristics i.e. mineralogical composition, porosity, cement-matrix properties, grain size distribution, packing density etc. They are clay containing stones, which is one of the reasons for them to be suspected of alteration because of the swelling-shrinkage characteristics of clays during wetting-drying cycles (Jimenez-Gonzalez and Scherer, 2004, Jimenez-Gonzalez et al., 2008, Wangler and Scherer, 2008). The clay containing stones also have a considerable amount of small pores which affects their durability.
during freezing – thawing cycles and make them vulnerable to salt crystallization to a great extent (Wendler et al., 2006, Jimenez-Gonzalez and Scherer, 2004). It is also stated that sandstones having silica or calcareous cement have better mechanical strength than the ones with clay minerals; Hsieh, et al., 2008).

Mobilization and transformation of iron in building sandstones under different conditions such as atmospheric pollution and chemical cleaning are reported that may lead to discoloration and in some cases surface crusts (McAlister et al., 2003). It is important to have a knowledge of the circumstances under which the iron is mobilised and/or transformed to different iron oxides, since those may affect negatively the durability and aesthetics of the sandstones.

The Nemrut Dağ Monument is an archaeological site in Adıyaman - Turkey, famous for its monumental tumulus of Antioch 1(c.69–c. 34 BC), a ruler of Commagene and its statues and stellas. The statues and stellas are made of limestone and sandstone which show some signs of deterioration. Those sandstones look similar to the sandstone formations nearby the site identified as sedimentary formations of lower Miocene (Tuna, 1973, Perincek and Kozlu, 1983). The main visual weathering forms of the sandstones at the site were separation by layering (flaking/scaling), back weathering, cracking, granular disintegration, rounding/notching, depositions and biological growth.

The aim of this study is to investigate the main decay mechanisms of Nemrut Dagi Monument’s sandstones for developing its conservation treatments.

**EXPERIMENTAL STUDIES AND RESULTS**

Experimental studies included examination of non-weathered and weathered sandstones from Nemrut Dağ Monument, and examination of artificially decayed sandstone cubes from near sandstone formations after subjecting them to salt crystallization cycles. Analyses were done to determine physical and physico-mechanical properties such as bulk density, porosity, color, and ultrasonic velocity of sandstones as well as their microstructure. Microstructural characteristics were studied by the analyses of cross and thin sections using optical microscopy, XRD, as well as Raman spectroscopy.
Physical and Physico-Mechanical Properties of Sandstones

Since sandstones of the site were found to have the similar characteristics with the sandstone formations at the near environs of the site, samples from the sandstone formations were studied in detail for their weathering behavior by subjecting them salt crystallization cycles using saturated sodium sulfate solution (RILEM, 1980).

Bulk density, effective porosity and ultrasonic velocity values of the sandstones from Nemrut Dağ Monument were found according RILEM standards. Besides, the porosity values and pore size distribution of the representative samples of deteriorated and non-deteriorated sandstones were studied with the help of Mercury Intrusion Porosimetry.

Changes in Bulk density and Porosity:

The average bulk density values of sandstones from nearby formations were found to be 2.58 ± 0.01 g/cm³. Bulk densities changed in the range of 2.48 g/cm³ - 2.66 g/cm³. The average total porosity was 3.57 ± 0.01% and porosity change was in the range of 0.43% - 6.05% (Figure 2). The porosity values have increased with artificial weathering by salt crystallization. The average porosity increased at 15th cycle of salt crystallization was about 16% (Figure 3). The greater change in the porosity values through the cycles of salt crystallization was observed for the stones having lower density and higher porosity (Sample 28 & 29, Figure 3).

Ultrasonic Velocity Measurements of the Sandstones

Ultrasonic Velocity values (USV) of sandstone samples taken from the sandstone formations near the site were measured from three different directions a, b, c of the cubes cut independent of bedding direction (Figure 4) since the bedding direction was not clear for the sandstone cubes.

The USV values have shown that there were directional differences in the sandstone cubes. Generally one of the USV values of three directions was smaller than the others that probably indicated the bedding direction of the sandstone formations. The USV values were around 2500-3500 m/s.
**Color Measurements**

The color measurements were done on the sandstone cubes of the nearby sandstone formations and on sandstones at the site. Color values were determined by using a spectrocolorimeter KonicaMinolta 2600Cmd and according to the CIELAB coordinates (CIELAB, 1973). The L*a*b* values measured in the laboratory under the same relative humidity conditions (40%) fell into the same groups for all sandstone samples (Figure 5). The change in color by artificial weathering with salt crystallization was evaluated by \( \Delta E \) value of each sample at the end of the 5th, 10th and 15th cycles. The color change at the end of the 5th cycle was evident to the eye. Average \( \Delta E \) values for each 5 cycles were graphed in Figure 6. The color change in the sandstones for the first 5 cycles was slight (\( \Delta E = 4 \)), however after the 10th cycle the color change was more noticeable and that could be expressed by the greater \( \Delta E \) values \( \Delta E(10) = 8 \) and \( \Delta E(15) = 7 \). Color change was also planned to be used as a criteria for the evaluation of future conservation treatments. Conservation treatments were expected not to cause considerable color change, e.g. \( \Delta E \leq 5 \) before and after the treatments.

**Pore Size Distribution by Mercury Intrusion Porosimetry**

The pore size distribution of several sandstone samples, including the ones from the sandstone formations nearby the monument as well as the samples representing the main weathering forms on the monument and artificially weathered sandstones, were studied e.g., non-weathered fine grained and non-weathered coarse grained sandstones from the formations near the site, naturally weathered sandstones showing layering and showing granular disintegration and artificially weathered sandstones subjected to different cycles of salt crystallization.
Non-weathered sandstones had considerably low porosity in comparison to the weathered ones. In addition, the non-weathered coarse grained sandstones had lower porosity (~0.8%-1.5%) than the non-weathered fine grained ones (~5.2%). The total porosity of the naturally weathered sandstones at the site, those exhibiting granular disintegration, were about 6% and those showing separation by layering were about 4.6%. Majority of the pores in non-weathered coarse grained sandstones were large having diameters greater than 10 microns, whereas non-weathered fine to coarse grained sandstones had smaller amounts of large pores (samples 94-1 and 94-2 in Figure 7). On the other hand, non-weathered fine grained sandstones had considerable amounts of fine pores smaller than 1 micron and a small portion of large pores having diameters around 100 microns (sample 91, Figure 8). It was clearly seen that non-weathered fine grained sandstones had higher total porosity and higher amount of fine pores that were smaller than 1 micron.

Naturally weathered sandstone samples from the site, representing the weathering form as separation by layering, had increased total porosity (~6%), pore diameter of the fine pores have increased about twice and large pores have also formed (sample A, Figure 8).

Pore size distribution was also studied by intrusion of mercury from a selected surface and the covering the other surfaces with a resin to have better idea on pore size distribution of that selected surface. The pore size distribution of the naturally weathered sandstone samples from the site, representing the weathering form as granular disintegration was studied by intrusion of mercury from its weathered surface and covering the other surfaces with resin. It was seen that fine pores at the surface have been enlarged and the larger pores have disappeared most likely due to weathering by granular disintegration (Sample B, Figure 8).

The pore size distribution of the naturally weathered sandstone samples from the site representing the weathering form as separation by layering was studied by intrusion of mercury from its exposed exterior and interior surfaces separately. Pore size distribution followed by the intrusion of mercury from the exterior surface has shown that majority of the pores smaller than 1 micron with a certain amount of large pores (Figure 9). On the other hand, pore size distribution followed by the intrusion of mercury from the interior surface has shown a great number of pores with diameter smaller than 0.01 micron, the pores with diameter about 0.1 micron and the absence of...
large pores (Figure 10). Considerable increase of the fine pores smaller than 0.01 micron at the interior surface, most likely corresponding to the bedding plane of the sandstone and representing its one of the surfaces, may be due to the increased amount of clay minerals in that region (Figures 9 and 10).

Pore size distributions of the artificially weathered sandstones from 10th and 18th cycles were shown in Figures 11 and 12. It was seen that, as the salt crystallization cycles were repeated the total porosity has doubled, large pores greater than 1 micron were formed and the average pore size increase from 0.9-5µm to 10-50µm, moreover, there was no change in the percentage of finest pores.

Petrographical and Mineralogical Properties of Sandstones

Petrographical and mineralogical properties of sandstones in Nemrut Dağı Monument were studied by optical microscopy observations of thin sections and XRD analyses of powdered samples.

Thin Section Observations: Sandstones of Nemrut Dağı Monument had heterogeneous grain size ranging from very coarse grains to fine ones. Majority of the grains were quartz. In addition, plagioclase feldspars, orthose, alkaline feldspars, igneous rock fragments such as granite, limestone,
biotite, calcedon, quartzite, calcite, particles together with opaque minerals (iron oxides) were observed (Figures 13). Cementing material of the grains was usually chlorite and clay minerals, micritic calcite, in some parts calcite supported the grains as granulated matrix (Figure 13).

**Figure 13.** Thin section view of a fresh sandstone sample (cross Nicoles). Quartz, Plagioclase Feldspar, Granite, Igneous rock fragments, Alkaline feldspar, Biotite, Orthose, Calcedon, Quartzite, Calcite, Limestone particles can be seen.

Amorphous ferric oxides as opaque minerals were also observed in the thin sections of fresh sandstone samples (Figures 14, 15).

**Figure 14.** Thin section views from the fresh sandstone samples, cross Nicoles X10 (left) and parallel nicoles X40(right), showing opaque minerals as iron oxides and some amorphous phases around them observed as spheres.

In thin sections of naturally weathered samples, parallel cracks were observed which were also parallel to the bedding planes (Figures 15, 16). Microstructural analyses have shown that intergranular detachment of the grains along the bedding planes of sandstones were preferred (Figure 15). In the cracks, the accumulations of micritic calcite and clay minerals on the crack surfaces were also observed (Figure 18).

**Figure 15.** Thin section views from naturally weathered sample (DS1) cross nicol (left) and parallel nics (right). Cracks in the microstructure were observed in thin sections.
Figure 16. Thin section views from naturally weathered sample NS1 (left) and DS3 (right). Microcracks are observed in the microstructure.

Figure 17. Thin section views from naturally weathered sample (NS1) cross nicols (left) and parallel nicols (right). A crack of ~300micron size, accumulation of micritic calcite and clay minerals on one of its surfaces.

Those microcracks were suitable sites for further clay accumulation and iron oxides or recrystallization of calcite. They also are the entrance sites for water towards the interior of the stone.

XRD Analyses

Mineralogical composition of sandstones were examined by the XRD analyses of powdered sandstone. The results have supported the thin section observations. Quartz, feldspars and calcite were the main minerals observed in XRD traces (Figure 18). The opaque minerals, iron oxides and clay minerals that were observed in thin sections were not seen in XRD traces of the powdered stone. Magnetic separation was used for separation of iron oxides in the powder. Clay minerals were extracted from the powdered stone (Moore, and Reynolds, 1997). They were studied separately by XRD (CoKα, 1,79nm) (Figure 19).

Figure 18. XRD trace of sample GS1. P: Plagioclase Feldspar, Q: Quartz, C: Calcite.
The XRD analyses of the extracted clay minerals in oriented samples revealed the types of clay minerals as chlorite, illite and kaolinite that were present in sandstones (Figure 19), (Moore et al., 1997). In those clay minerals, only the distribution of chlorite was easily observed in thin sections of the sandstones by their greenish colour. Swelling characteristics of the clays in non weathered and naturally weathered sandstones were examined by following the XRD traces of oriented clay extracts before and after ethylene glycol treatment (Figures 19-20) (Moore et al., 1997).

![XRD traces](image)

**Figure 19.** XRD trace of the extracted part of the non-weathered sandstone, clay minerals before and after the ethylene glycol treatment. (left) XRD trace of the extracted part of a weathered sandstone: clay minerals before and after the ethylene glycol treatment (right) Ch: Chlorite, I: Illite and Ka: Kaolinite.

The shift in the position of the chlorite peak with the ethylene glycol treatment of the clay minerals separated from naturally weathered sandstones showed that swelling layers have developed among the chlorite sheets through weathering, since that type of a shift was not observed in the clays of non-weathered sandstones (Figure 20). That phenomenon for chlorites was reported by Wangler et al (2008).

**Identification of Iron oxides in the composition of sandstones by XRD and Raman Spectroscopy**

The presence of iron oxides as opaque minerals were observed in thin sections. There were also other evidences for the presence of iron oxides such as color change during the artificial weathering experiments by salt crystallization. Development of browning on the surfaces of the sandstone cubes indicated their presence as well their movement in the stone. The browning of sandstones surfaces exposed to atmospheric conditions was also observed at the site. Therefore, the presence of different phases of iron oxides were analysed by the XRD traces taken after their magnetic separation from the powdered stone and by Raman Spectroscopy of stone sections. The XRD traces showed the presence of the iron oxide phases such as magnetite/maghemite, haematite and goethite (Figure 20) (Clark et al., 1998).

In order to investigate the different phases of iron oxides with Raman spectroscopy one should pay a special attention to laser power in order not to change the phase of the iron oxide which is inevitable when they are subjected to a strong laser beam metals (Hanesch, 2009, Colomban et al. 2008; Froment et al. 2008; de Faria, et al., 2007; Ospitali, et al. 2006; Clark, et al., Ambers and Freestone, 2005, 1998 de Faria, et al.1997). Thus, in this study the INFINITY system was used with He-Ne laser (633 nm) and D2 filter to have a suitable laser power, the scattered light was collected through a X100 Olympus objective during a counting period of 60 s. The haematite was the only iron oxide mineral identified with Raman Spectroscopy so far (Figure 21). However spot analyses continue for the detection of the other iron oxide phases that were found by XRD.
DISCUSSION AND CONCLUSIONS

The site of Nemrut Dağı Monument poses the main weathering forms mainly as separation by layering especially along the bedding planes, back weathering, cracking, granular disintegration, and rounding/notching.

The sandstones of Nemrut Dağı Monument were sedimentary rocks containing quartz, feldspars and rock fragments in a calcite and clay containing matrix. They have low porosity with good physico-mechanical properties. According to the Mercury Porosimetry results the porosity of the sandstones were low and the micro cracks were the main part in the porous structure. The coarse grained sandstones had lower porosity (~0.8%-1.5%) than the fine grained ones (~ 5.2%).

The total porosity of the weathered sandstones those exhibiting granular disintegration and scaling were increased. This was accompanied by the increase in the number of the pores with greater diameter in the overall distribution of the pore diameter size, in other words, the number of the average pore diameter shifted to a greater value. This was in accordance with the findings of Heinrich & Fitzner (2007) although there were some differences between those values. Furthermore, the finest pore sizes at the surface of the flakes found by Mercury Posimetry, could be explained by the accumulation of clays on those surfaces Mertz, 1991). Pore size distributions of the artificially weathered sandstones from 10th and 18th showed that, as the salt crystallization cycles were repeated the total porosity has increased, large pores greater than 1 micron were formed and the pores of sizes 0.9 to 5 μm got larger to 10 to 50 μm. However, there was no change in the percentage of finest pores. This type of enlargement of the pores was attributed to the weathering by salt crystallization cycles and was not the case in the site.
Through the microscopic examinations of thin sections, the micro crack formations parallel to the bedding planes were observed which also resulted in increase in the porosity. Those micro cracks were suspected to be the regions for the accumulation of clay minerals together with the iron oxides. The water penetration from those cracks, which were generally in contact with the stones surfaces, was also an important decay factor for sandstones, since the water was an agent for the swelling of clays, mobility of irons and the transformation of iron oxides from one to another (Hanesch, 2009).

The XRD analyses showed the existence of clay minerals as chlorite, illite, and kaolinite. Kaolinites and illites have non-swelling characteristics (Moore, and Reynolds, 1997). The mechanism for weathering by nonswelling clays were explained in elsewhere (Mohan et al., 1993). It should also be mentioned that the chlorites has been shown to gain swelling layers within the nonswelling layers upon weathering (Wangler et al., 2008). The XRD analyses have shown that the chlorites developed intracrystalline swelling in weathered sandstones of the Nemrut Dağı Monument.

XRD analyses have also shown the existence of iron oxides in the sandstones. The color change of the sandstones with the deterioration was thought to be connected to the mobilization and oxidation of iron oxides on the surfaces of the sandstones. The iron oxides such as hematite are the well known accessory minerals in the sandstones. Under certain conditions they undergo various phase transformations in aqueous media or in solid state, thus the different phases of iron oxides can be used also to understand the weathering environment of the sandstone. The stability of the iron oxides under different conditions was studied by different authors (Monnier et al., 2008, Gotic, et al, 2007, Dromgoole and Walter, 1989, Barnes et al., 2009, Sun, et al., 2004). Although a certain consensus was not reached about the activity of different phases under different conditions; magnetite, maghemite and goethite were accepted as the non-reactive phases whereas lepidocrocite, ferrihydrite and feroxyhite considered as reactive phases (Monnier et al., 2008). Furthermore, different authors tried to define the ratio of stability by using the ratio of different phases of the iron oxides (Monnier et al., 2008). The iron oxides found in the XRD traces of the magnetically separated samples showed the existence of magnetite/maghemite, goethite and hematite, each of which were known to be the non reactive phases, however it should be kept in mind that the not well crystallized forms of iron oxides, e.g., goethite, were known to be reactive.

Raman Spectrometry studies continue for better understanding of the iron oxides. Haematite was detected by Raman Spectroscopy so far. The studies continue to establish a better understanding of iron oxides about which iron oxides were hosted by the sandstones and which were the result of weathering.

A better understanding of the weathering environment and mechanisms seems to be the most vital input for the development of conservation methods. The present study showed that the prior measures for the conservation of sandstones in Nemrut Dağı Monument could be stated as the control of the water penetration, the control of the clay damage and the movement of the iron oxides in the stone.

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