Environmental control for mitigating salt deterioration by sodium sulfate on Motomachi Stone Buddha in Oita prefecture, Japan

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Abstract

This study aimed to develop an appropriate interior environment to mitigate the deterioration by sodium sulfate crystallization on Motomachi Stone Buddha in Oita prefecture of Japan. This Stone Buddha is carved on the fragile welded tuff and has been covered by a shelter for the preservation. On this site, salt crystallization, especially in winter, is a major deterioration factor of this Buddha. In previous studies, the crystallization of sodium sulfate and calcium sulfate were identified by XRD. The temperature and relative humidity were measured both indoor and outdoor. Water quantity analysis of the groundwater near the Stone Buddha has been conducted revealing a higher solute content near the Buddha than in the general groundwater in Japan. According to the temperature and humidity measured inside the shelter in winter, it was suggested that the solubility of sodium sulfate decreased greatly with dropping in interior temperature and phase change from mirabilite to thenardite (sodium sulfate anhydrate) caused the deterioration of the statue. Hence, the shelter was improved to reduce ventilation frequency and block the direct solar radiation in order to reduce evaporation and decreasing interior temperature in winter. In this study, we have conducted environmental research and salt crystallization experiments under controlled temperature and relative humidity to assess the improvements of the shelter. After improvements of the shelter, the indoor temperature and relative humidity increased in winter. According to our experimental results, the deterioration of the Stone Buddha is reduced highlighting the efficiency of the improvements.

Keywords: salt deterioration, sodium sulfate, shelter

1. Introduction

Salt crystallisation is one of the most common cause of stone deterioration.[1] In the field of conservation , it is well known that repeated cycles of dissolution and recrystallization of salts inside a stone can provoke serious damage. Especially for sodium sulfate, with both hydrated and anhydrous phases, is one of the most dangerous salts for stone.[2-5] The solubility depends on temperature and decreases as the temperature falls. The effects of temperature and relative humidity on in-situ salt weathering have been investigated in literature.[6,7] However, the mechanism of in-situ salt weathering remains controversial.

At the Motomachi stone-cliff Buddha to prevent collapse of the stone, polymers have been used. But they have strengthen the stone surface causing more degradation. A tunnel has been dug to lower the groundwater levels and limits the salt crystallization. However, the issue of an ideal environment to restrain salt deterioration awaits further investigation. Many recent studies focus on mixed salt behaviour. However, it is too complicated and controversial to discuss the matter in this paper. Therefore, this paper attempts to investigate the effects of the improvements of the shelter at the Motomachi stone-cliff Buddha and aims to consider methods to mitigate salt deterioration, especially in sodium sulfate.

2. Background of the Motomachi stone-cliff Buddha

The Motomachi stone-cliff Buddha is located in Oita prefecture, Japan. It was engraved onto a cliff of soft welded tuff around the 11th to 12th centuries and was covered by a shelter which was built during in the 20th century *(Figure 1 and Figure 2)*. The entrance of the shelter faces east. Salt crystallisation especially in winter is the most important cause of deterioration. Powdering and scaling occur at the surface of the stone. A previous investigation identified thenardite, mirabilite and gypsum by X-ray diffractometry (XRD).[8,9] Furthermore, a past study showed that sulphate, calcium and sodium ions, that are the origins of thenardite, mirabilite and gypsum, are detected in the groundwater near the site. And the content is higher than in the general groundwater in Japan.[9] Although a drainage tunnel and well were built in order to lower the groundwater levels *(Figure 3)*, an increase in the amount of salt was reported after this construction. A past study also suggested that drop in inside temperature in winter due to door-opening of the shelter and water leaking into the high-water-content stone could be causes of salt crystallisation at the Motomachi stone-cliff Buddha.[9] Therefore, the shelter was improved by setting door closer, double glass windows and boards to reduce ventilation frequency and to block the direct solar radiation to the Buddha in November 2015 by the Oita-city board of education.

Figure 1: Motomachi stone-cliff Buddha

Figure 2: Exterior of the shelter

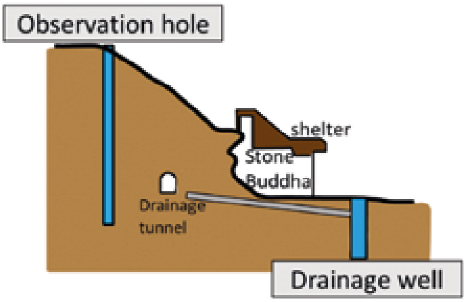


Figure 3: Cross sectional view

3. Methods

3.1. Environmental research

In order to assess the effects on the shelter improvements, the indoor temperature, relative humidity, ventilation frequency and local meteorological data have been measured before and

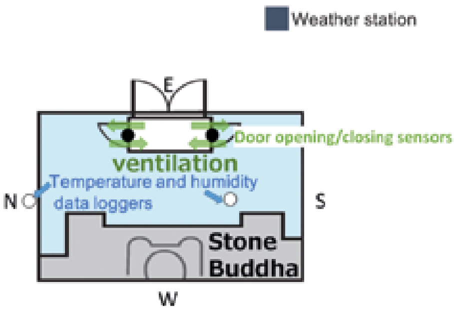


Figure 4: Schematic representation of the inside with location of data loggers

after the shelter improvements. Temperature and relative humidity have been measured inside and outside the shelter with data loggers (HOBO Prov2) from November 2014 *(Figure 4)*. The counts of door-opening/closing have been measured with door-opening/closing sensors (HOBO UX90 State Data Logger) from February 2015 *(Figure 4)*. A weather station was installed in February 2015 which measured local meteorological data (temperature, relative humidity, wind direction, wind speed, solar radiation and pressure). All measurements have been done at 10 minutes intervals and the data were collected roughly once in three months.

3.2. Experiments

First, Aso soft welded tuff, which is thesame stone of the Motomachi stone-cliff Buddha, was selected for the experiment. The stone with the porosity of 30.4% and the density of 1.64(g/cm^3) was cut into cylinders (50 mm x 20 mm). Second, to saturate the samples in order to have less effect on the depth of salt distribution at different relative humidity, all samples were immersed in distilled water for 3 days. Finally, the bottom face of the water-saturated samples were put into a 20ml/10w%Na_2SO_4 solution under controlled temperature and relative humidity (Table 1).

The conditions of 20°C, 10°C, 75% RH and low RH were chosen to reproduce field conditions in summer and winter in order to assess the effects of temperature and humidity conditions on crystallization of mirabilite and thenardite *(Table 1)*.

To prepare for samples A and B, an incubater was programmed to 20°C and 75% humidity. Sample A was enclosed in a desiccator containing silica gel, used to create a low humidity environment. Sample B was placed in an open desiccator. Both desiccators were placed into

	A	B	C	D
Temperature (°C)	21.7 ± 1.0	21.0 ± 1.1	10.4 ± 0.2	10.8 ± 0.2
Relative Humidity	59.8 ± 14.5	77.2 ± 5.0	27.8 ± 29.8	73.1 ± 1.4

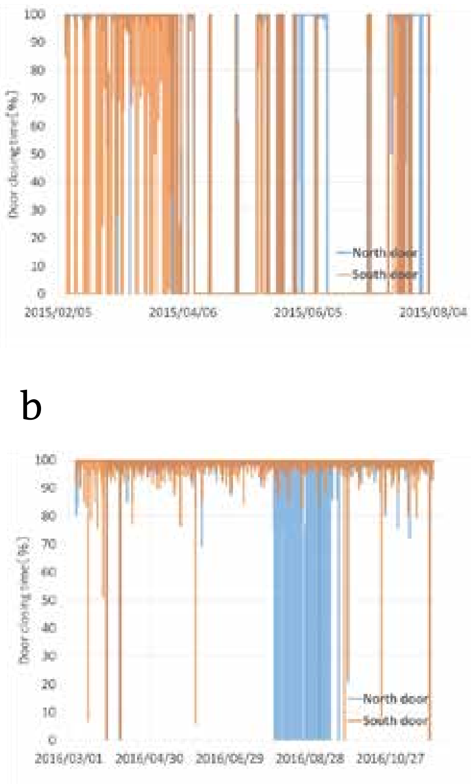
Table 1: Experimental conditions

	Average temperature (°C)
Nov. 2014 - Feb. 2015	9.9 ± 2.8
Nov. 2015 - Feb. 2016	13.3 ± 3.2

Table 2: Average indoor temperature before and after improvements in winter ns

the incubator. To prepare for samples C and D, the other incubator was programmed to 10°C and 75% humidity. Sample C was placed in the desiccator containing silica gel and sample D was placed in the open desiccator. Both of these desiccators were placed in the second incubator. The experiments consisted of 5 dissolution/recrystallization cycles at intervals of at least 4 days. At the beginning of the cycles, 20 ml distilled water was added to saturate the samples. After 5 cycles, stone powder was gently removed from the samples with a brush and collected. The residue was filtrated with 1 µm pore size quantitative filter papers to remove the salt. The filter papers and the residue were immersed in 50 ml of distilled water, which was replaced twice at an 1 hour interval. The filter papers were dried at 60°C until they reached constant weight. The percentage of damage was calculated by using equation (1).

a



b

Figure 5: Door closing time a) before the improvements b)after the improvements

Percentage of damage =

$$(M_{amount} \text{ of residue}/M_{drystone\ initial}) \quad (1)$$

4. Results and Discussion

4.1. Effects on the improvements of the shelter

The doors closing periods are given in *Figures 4a, b. Figure 4a* shows the door closing periods before improvements, on the other hand, *Figure 4b* indicates the state after the improvements. Before setting the door closers, the doors could stay open for a few days because visitors could keep opening and closing the doors freely. After the improvements, the doors became usually closed except during an operation periods of inside the shelter. Therefore, the results indicate that the ventilation frequency was reduced by the improvements.

Figure 5 illustrates a phase diagram for sodium sulfate and temperature and relative humidity of daily average inside the shelter. The continuous lines indicate the boundaries of the stable phases.[4] This diagram suggests that the interior environment before the improvements (November 2014-October 2015) mainly varied in both thenardite and mirabilite stable conditions. Previous studies showed the damage by sodium sulfate occurs because thenardite dissolution can produce solutions highly supersaturated with respect to mirabilite, so that precipitation of this phase can lead to large crystallization pressures.[5,10] Thus, it is important for the conservation of the Buddha that crystallization of sodium sulfate should be reduced, cycles of crys-

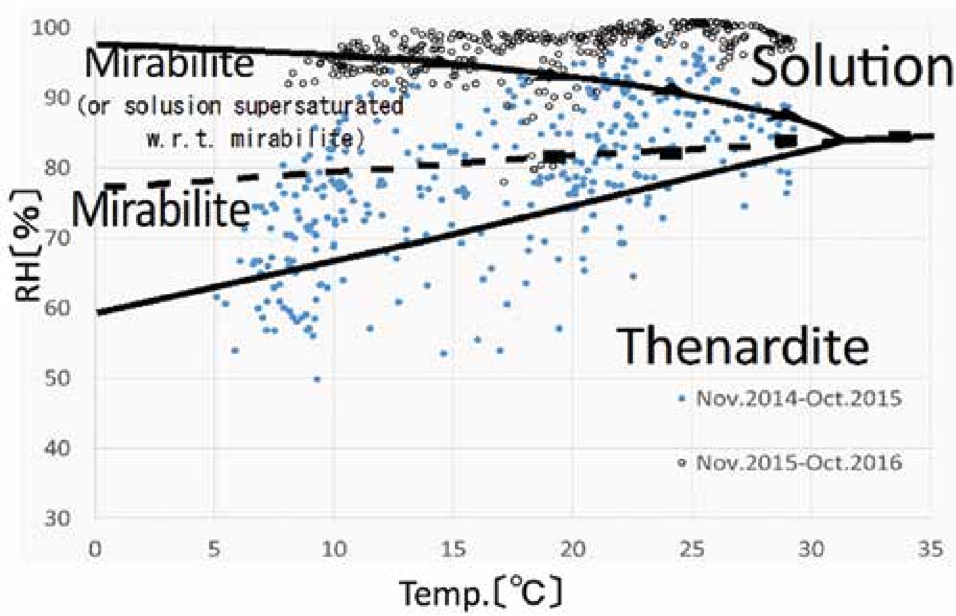


Figure 6: Phase diagram for sodium sulfate and temperature and relative humidity of daily average inside the shelter (based upon data from[4]) Blue dots are before improvements Temp. and RH, on the other hand white dots are after improvements.

	A	B	C	D
Rate of deterioration (%)	0.0034 ± 0.0009	0.0009 ± 6E-05	0.0035 ± 0.0026	0.0003 ± 8E-05

Table 3: Percentage of damage from equation (1)

tallization and dissolution of sodium sulfate should be avoided and phase change to thenardite should be suppressed even if mirabilite crystallizes. *Figure 5* indicates that the interior environment after the development of the shelter (November 2015-October 2016) were mostly under solution of sodium sulfate stable phase, even though sometimes in mirabilite stable phase. This results shows that the improvements reduced the risk of precipitation of thenardite. Furthermore, the indoor temperature before and after improvements in winter is shown in *Table 2*. The temperature in winter increased 3.4°C after the renovation, which could lead to inhibit decreasing solubility of sodium sulfate. Consequently, the interior environment has changed to reduce crystallization of sodium sulfate.

The amount of salt crystallization could not be measured quantitatively because usual salt crystallized area in winter was covered with Japanese papers in order to remove salts. However, according to observations, the amount of salt crystallization in winter decreased obviously. Therefore, it is considered that deterioration by powdering on the stone surface was reduced. On the contrary, on the other part of the stone surface, new salt crystallization was confirmed after the improvement. The salt was identified as gypsum by XRD. Furthermore, molds were confirmed on wood parts of the shelter by observation after the improvement. The high water content caused by the rise in inside relative humidity may be considered as the causes of increasing gypsum and molds. These changes after the improvement were caused by suppressing the ventilation of the shelter throughout the year. Generally speaking, winter in Japan is cold and dry, on the other hand summer is hot and humid. Therefore, it is necessary to consider operation method of the shelter in each season in the future. This could lead to reducing molds or other microbiology attack caused by humid condition.

4.2. Deterioration comparison by sodium sulfate

The results of the experiments are provided in *Table 3*. The rate of deterioration of samples are calculated by using equation (1). The rate of deterioration of sample A and sample C were greater than sample B and sample D. It is inferred that phase change to Thenardite may have an effect on the rate of deterioration. It is also possible that Increasing in evaporation rate may promote further damage. As for the difference of temperature (sample B and sample D), significant difference did not be detected. These result indicate that to reduce lowering relative humidity is more important than to decrease drop in temperature. Furthermore, the depth of salt crystallization affected by evaporation rate did not be examined in this study. Hence, this is a subject for future analysis.

Conclusion

Salt crystallization, especially in winter, is a major deterioration factor of this Buddha. Although salt deterioration may have been caused by decreasing interior temperature and relative humidity in winter, environmental control could not have been carried out because of the poor airtight of the shelter. Then, the shelter was improved in order to reduce a drop in temperature and humidity in winter. To evaluate the shelter improvements' effect on the salt deterioration, environmental research and observation were carried out. After these shelter improvements which led to reduction of ventilation frequency, it is considered that deterioration by powdering on the stone surface was reduced. However, predictable problems by humid condition such as new crystallization of gypsum and mold were detected after the improvement. Furthermore, in order to set the target value of the environmental control, effects of temperature and humidity on salt deterioration were investigated by salt crystallization experiment. The results of the experiments indicate that to reduce lowering relative humidity is more important than to decrease a drop in temperature.

For future research, a target value of the interior environment in each season needs to be considered. Furthermore, by an appropriate operation of the shelter which increased the airtight and could control environment more easily, mitigating methods for not only salt crystallization in winter but also other deterioration problems of the Buddha should be considered continuously.

Acknowledgements

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