The Effect of Chemical Treatments on Biodeterioration of Stone Cultural Properties

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Abstract - The biodeterioration with blue-green algae has been studied since 1997 up to 2000 in the tomb of King Mooryong in Kongju, Korea. Biodeterioration in the tomb initially started from the formation of micro-organismic biofilm that had been suggested to make minor changes on the stone surface. This study revealed that the biofilm formed by microorganisms could result in permanent damages on stone cultural properties. The application of a chemical, 'K201', developed by the author successfully removed fouling of biofilm on the surfaces of stone cultural properties. When small pieces of granite stone were embedded in the solution to study the side effects of the chemicals for a period of three months, the mechanical stability was 0.97 compared to control and there was no change in color. Biodeterioration is one of the most harmful factors that decrease the value of stone cultural properties but it may be treated with a development of proper chemicals.

Key words : biodeterioration, biofilm, blue-green algae, stone cultural properties, treatment

Introduction

The biodeterioration is considered to be one of the most destructive events that affect cultural properties (Lee 1991). Because the construction of stone cultural properties often requires relatively large space, this may also deteriorate the surrounding environments. As a response to this process, formerly destroyed micro-ecosystems begin to reestablish their initial state, therefore increasing the risk of contamination (Eckhart 1978; Dhawan 1988).

The biological processes which progress deterioration of the stone objects are subdivided into 3 groups: (1) changes of the surface environment due to attachment of microorganisms and lower plants; (2) cracking of stones due to the growth of plants in the surface environment; (3) direct damages by animals. Among these, the attachment of microorganisms and lower plants initiates the process of deterioration and is actually the most harmful. Direct damages by animals, such as mice and birds, are referred to biological deterioration, however, these kinds of damages are very rare and can easily be prevented. Attachment of microorganisms and lower plants is often regarded as a minor change until deterioration becomes obvious. The biofilms formed by blue-green algae on the stone surface enhance the moisture-keeping ability, thereby resulting in successive attachment and growth of plants (Graham and Wilcox 2000). The roots of plants erode surface and foundation of a stone, which is sometimes irreversible (Everett 1961). For example, in Angkor Wat, the biodeterioration had progressed for a long period of time, and plant roots made thousands of totally irretrievable cracks and cavities on the surfaces of buildings (Pochon and Jaton 1967; Sze 1995).

Due to the recent urbanization, air pollution becomes especially severe (Torraca 1979; Jokiel and York 1997). Various pollutants and acid rains cause destruction of the surfaces of stones, which resulted in formation of

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microscopic soils and accelerated biodeterioration. Stone cultural monuments have been maintained in nature for hundreds and thousands of years, but are being deteriorated rapidly during these days. Thus, it is absolutely necessary to develop methods for their preservation before more severe damages will occur.

This paper is based on our investigations and subsequent chemical treatment of biodeterioration in the tomb of King Mooryong in Kongju, Korea. The analysis of stages of biodeterioration and succession of vegetation on the surface of stone cultural properties is also given. The effect of chemical treatment was studied from the continuous observations of the investigated object and comparative analysis of data obtained before and after the treatment.

Materials and Methods

The tomb of King Mooryong (Kongju, Korea) was constructed in A.D. 525 and re-opened in 1971. At first, the tomb was maintained in a good condition, however it became covered with some microorganisms over time course.

Collection of the dominant species from the tomb was repeated 10 times. The plants were transported to the laboratory, separated into single strains and put in a culture medium. The culture medium was adjusted to various pH conditions to observe the effects of pH on algal growth. DIC micrographs were input to CAAR (Computer Assisted Algae Recognition) programs. To examine the growth of cryptoendolithic algae, sliced piece of samples were analyzed utilizing scanning electron microscope. The chemicals used for the prevention of primary succession of vegetation were as follows; EDTA 25 g, $(NH_4)_2CO_2$ 30 g, Na_2CO_3 50 g, $CuSO_4$ 10 g, NaClO 10% in 1 liter of tap water.

Results

In April 1997, the time we started our investigations, all inner surfaces of the tomb were completely covered with mostly blue-green algae (Figs 1A-C). The major aim of this chemical treatment lies in prevention of successive growth of lower plants, which may occur on an algal biofilm. Easiest method for controlling the concentration of the hydrogen ions includes pH control. As known, alkaline soils with a pH of 8 support growth of most soil algae, and in contrast, their number greatly decreases at a pH of less than 6 (Sze 1995).

However, *Gloeocapsa* and *Lyngbya* collected from the tombs had a high pH tolerance, thereby a pH control alone would not be effective. The low pH (~5.4) could suppress their growth, but the pH of soil inside the tombs was close to neutral (~8.3), thus making pH control impossible. Furthermore, it might have caused discoloration of the stone surfaces and contribute to structural instability of the tomb. In order to inhibit the algal growth, specially developed chemical mixture was required. Previously developed chemical mixtures were found to be ineffective in removal of the blue-green algae (Yamamoto & Kurumazuka 1986).

We have developed two solutions for direct application onto the stones with a minimum damage on their structure and natural color. The chemical mixture, K201, used for the prevention of primary succession of vegetation was as follows; EDTA 25 g, $(NH_4)_2CO_2$ 30 g, Na_2CO_3 50 g, $CuSO_4$ 10 g, NaClO 10% in 1 liter of water.

The effectiveness of the solutions was tested by adding them to the strains into the culture media at lower concentrations. As was found, the growth of algae suppressed, and lichens and mosses became extinct. To study the side effects, small pieces of stone were embedded in the solutions for a period of three months and thereafter their mechanical stability was examined. The mechanical stability was 0.97 compared to the control, and no changes in color occurred. Therefore, if chemical mixture is treated for a short time (1~2 days), this mak-

Table 1. The soil properties and the remaining amount of nutritional salts before and after chemical treatment in the tomb of king Mooryong (mean ± SD)

Soil properties	Before treatment	After treatment
Soil pH	8.5±0.0**	5.6±0.21**
Organic matter	8.6±0.4***	2.6±0.16***
Total Nitrogen (mg/g)	2.4±0.1**	0.5±0.12***
Phosphorus (ppm)	48.2±3.75***	4.6±1.13***
Sodium (mg/g)	1.7±0.12***	0.1±0.01***
Calcium (ppm)	18.7±0.93***	5.8±0.16***
Magnecium (ppm)	325.9±2.87***	85.7±0.56***
Total sulfur (ppm)	262.2±28.02**	160.4±13.5**

t-test, n = 20, ** $p<0.01$, *** $p<0.001$

Fig. 1. Biodeterioration in the tomb of king Mooryong before (A–C) and after (D–F) the conservation treatment. The surfaces were completely covered with blue-green algae in April 1997, but currently the surfaces are clean after the treatment with K201 in May 1997 (the pictures were taken in April 2000).

es no changes in the structural intensity and characteristics of the stone, so does even their sufficient application.

The chemical treatment inside the tomb was performed in April 1997. Sealing the floor of the tomb with a waterproof blocked income of the underground waters. Our later investigations showed that the biodeterioration was successfully removed from all the surfaces, and no further fouling occurred (Figs. 1D–F). Moreover, the total amount of organic compounds and the income of nitrogen and phosphorus reduced visibly (Table 1). These results suggest that when the biofilm is removed from

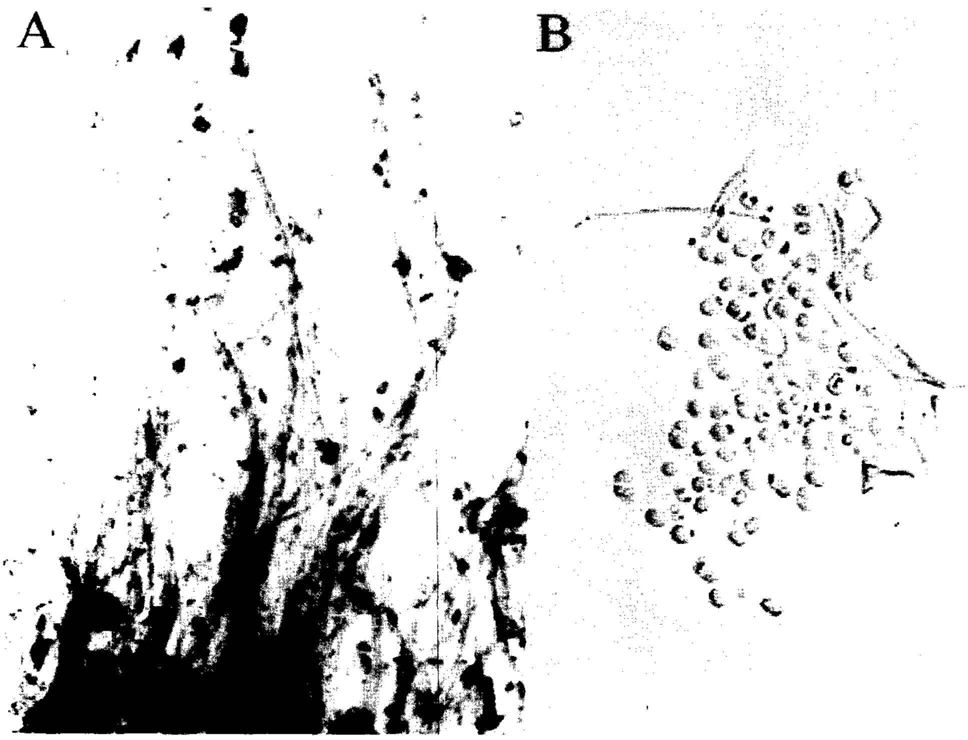

Fig. 2. Blue-green algae collected from the inner surfaces of the tomb of king Mooryong. A. *Lyngbya* spp.; B. *Gloeocapsa* spp.

the stone surfaces, the re-initiation of biodeterioration takes a long time.

Discussion

Algae occur in virtually all earth's environments. Some species are reported capable of growth in thermal waters at 80°C and below 0°C in the polar regions (Sze 1995). *Lyngbya* spp. have been reported to possess a high tolerance to different temperature spectrums. They are capable of growth even in the Antarctic lakes (Parker *et al.* 1981). *Lyngbya* can form resting spores that float in the air, but settle down and germinate under the favorable environmental conditions. Thus, the isolation of stone constructions in an attempt to reduce the algal attachment is impossible as long as they are not sealed up and closed to the public. Even when the airflow is blocked completely, an income of blue-green algae may occur with the underground waters. Alternatively, chemical treatment can remove algae from the stone surfaces, and may possibly prevent from the successive growth of the lower plants, lichens, mosses, and ferns.

The growth of plants on the surfaces of stone cultural properties alters organic compounds that are very nutritious to the microorganisms, and accumulate diverse environmental changes due to the differences in energy sources and inorganic substances required for each microorganism. For example, in photosynthesis of the blue-green algae that propagate in hot springs, the ions of sulfur or iron existing in the thermal waters are used as hydrogen donor instead of water (Parker *et al.* 1981; Parker 1947). This is a representative process, which oxidizes the sulfur and iron ions, and results in inevitable changes of the surrounding environments. A peculiar thing is that microorganisms such as algae can directly affect the granite or metal constructions (Eckhart 1978). This becomes obvious when the synthesis process is examined. The microorganisms change pH environment to maintain proper pH balance required in photosynthesis and chemical synthesis, and secrete adhesive materials outside the cell to complete efficient attachment (Graham and Wilcox 2000).

Korean stone cultural properties are mostly made from granites, limestone and tuffs. These stones are known to make surface bulges as temperature changes. The internal pores and cracks give rise to the scaling in microscopic layers. In these layers, crytoendolithic and nitrogen-fixative algae, and sulfur bacteria form micro-soils and microorganismic systems (Torraca 1979). Depending on a stone material, white or yellowish-white crusts termed as monolich, mainly composed of carbonic acid calcium, can be formed. These changes deteriorate the surface engravings and carved texts, thus making the secondary succession of the lower plants easier.

Microorganisms attached to the stone surface form thin biofilms from the secondary metabolic productions. These biofilms provide substrate for the attachment of various algae and spores of the lower plants (Mun *et al.* 1996). Subsequently, they form micro-soils, which increase moisture-keeping ability of the stone and provide aquatic environment for the growth of lower plants.

As a result, lichens begin to grow faster and roots of the mosses and plants begin to damage stone surface later. The degree of deterioration by mosses is relatively low, however they can keep moisture longer, which accelerate chemical deterioration and promote propagation of lichens. In some case, mosses enter hyphae deep into the stone material that is soft or seriously weathered. Considering these, mosses are regarded as regular soil-forming species. Following the succession of plants, small animals and insects inhabit the stone surface. Thus, it can be clearly seen that stone cultural properties begin to act as micro-ecosystems and become a part of nature, as normal rocks.

A real value of cultural properties can be determined from their style and fine artistic elements. Deterioration of the engravings and sculptural details causes the most serious problem, thus the major aim of the preservation treatment must lie in prevention from early stages of biodeterioration, rather than in treatment of the already deteriorated objects.

Since cultural properties act as a part of ecological environments, an active growth of biological organisms, which attach or live on their surfaces, results in their gradual deterioration. Succession of the lower plants on the surface of stone cultural properties turns rocks into soil, and therefore is associated with the formation of substrate and environmental circulation of nature. It is our duty to preserve the values of cultural properties for our descendants. Thus, proper preserving methods that prevent deterioration of their artistical values and structural stability, and are harmless to the surrounding ecosystems should be developed.

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