Study on the weathering mechanism and protection technology of stone archives

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Abstract. The mechanism of weathering damage on stone archives by several factors was analysed, such as human, physical, chemical and biological factors. It was also put forward the surface decontamination, reinforcement, restoration and sealing technology to provide the stone archives. Furthermore, the advantages and disadvantages of each technology were also compared in detail. It was provided a new way for restoration and protection of stone archives.

1. Introduction

China is rich in cultural relic resources, they are the witness of the Chinese nation's 5000 years of history. It is very important in the world cultural heritage, of which the more valuable one is the stone archives. Stone archives usually record the ancient merits and virtues, promulgation of the Constitution, oath of alliance and other major events, which exhibit important historical value. However, as a precious cultural carrier, stone archives show some weathering symptoms such as flaky peeling, powder peeling, surface pan-salt, empty space cracking, and discoloration and shedding in addition to being artificially destroyed. While with the development of industry, environmental pollution, acid rain aggravated the damage to the stone archives, which greatly affects the real expression of historical materials and artistic effects of cultural relics [1]. Therefore, it is urgent to protect stone archives. In this paper, it is systematically analyzed the weathering erosion mechanism of stone archives and its surface cleaning, decontamination, reinforcement, restoration and sealing technology, which will be the guiding for more comprehensive protection and restoration of stone archives.

2. The factors affecting the weathering of stone archives

Before we start to solve the weathering of stone artifacts, it is necessary to understand the weathering mechanism. Because most of stone archives are in the outdoor environment, weathering and corrosion is complex such as man-made factors and physical, chemical, biological and other factors of the comprehensive role [2]. In recent years, environmental pollution is increasingly serious, which accelerated the process of weathering and alteration of stone cultural relics, thus, it is very urgent to put forward new requirements for the protection of stone archives.

2.1. Human factors

In the long-term preservation process of stone archives, the influence of human factors is an important reason for the destruction of stone archives [3]. For example, historical wars led to great damage to a large number of stone archives and stone tablets, tourists touch, portrayal, knocking, the impact of worship activities and so on. Especially the action of theft, resulting in many precious
cultural relics were sold and a large number of cultural relics been destroyed and lost. In addition, in recent decades, the vigorous development of tourism also caused a lot of damage to the stone archives, such as dust, sweat, breathing gas, hand touch, foot stepping and camera flashes. The bad habit of archives and painting on the monuments by some tourists seriously destroyed the artistic value of stone archives. At the same time, some unintentional or ignorant behavior will also cause damage to stone cultural relics, such as the vibration caused by tourists, vehicles and traffic, improper protection and treatment. Therefore, large-scale construction such as roads and railways should be as far away from cultural relics as possible. In the restoration and protection of stone cultural relics, there are some problems, such as unreasonable protective materials [4], unsatisfactory treatment methods, unskilled operation and imperfect technical facilities, which may lead to the damage of cultural relics, i.e. "protective damage", which requires us to improve the ability of restoration and protection.

2.2. Physical factors

Physical weathering mainly refers to the destruction of stone archives caused by wind-blown and rainwater, changes in the physical state of soluble salts, temperature and water. Physical weathering shows great influence on open-air stone cultural relics, and its destructiveness cannot be ignored. Usually, wind, sand and rain will abrade the scaling, loose particles, weathering products of the old rock surface, and then increase its weathering rate, accelerate the damage of stone archives. The change of soluble salt physical state is also easy to make rock mass instability and image weathering because under low temperature and high humidity conditions the salt compounds absorb water and dissolve and seep into the rock fracture. While under high temperature and low humidity, the salt solution crystallized and leads to the high expansion pressure [5]. Dry and wet alternation, salt recrystallization and dissolution process make sandstone crisp and fall off. The difference in temperature and humidity caused by periodic changes also leads to the destruction of stone artifacts. Furthermore, the surface temperature of stone archives is too high after exposure to sunlight. When the temperature drops quickly at night, the extrusion force produced by high temperature expansion and the tensile force produced by low temperature will cause great damage to stone archives. Under sunshine conditions, the coefficients of heat absorption and expansion of different rocks are different [6]. For example, the volume expansion coefficient of quartz is about 4 times of that of feldspar. Because the thermal expansion and cold shrinkage of rock are not uniform, the links between the surface layer and the particles of rock wall are destroyed, the internal structure is gradually decomposed, and then micro-cracks are also gradually formed.

The texture of stone materials also determines the weathering rate of stone archives, and the texture of stone is closely related to rock types and porosity. For example, The Grottoes in Northwest China are made of sandstone and have been seriously weathered, while the Longmen Grottoes in Luoyang are made of limestone, which are well preserved. Furthermore, as the porous material, rock can absorb a large amount of water and lose water quickly in the dry state. Thus, the rapid transformation of water absorption and loss of water state caused repeated expansion of stone cells, which will accelerate the weathering of rocks.

2.3. Chemical factors

The weathering damage of stone archives is also closely related to the degree of air pollution. The harmful gases such as carbon oxides, sulphur oxides, nitrogen oxides, hydrogen sulphide and hydrogen chloride in the atmosphere bring obvious corrosion to the rocks. Especially in the process of modern industrial development, environmental pollution is particularly serious which greatly aggravates the rate of weathering and destruction of stone archives. Chemical weathering and physical weathering generally exist at the same time, the destructive effect of these factors on stone archives can be expressed as [7]:

\[(\text{Atmosphere} + \text{biosphere} + \text{water vapour circle}) + \text{Porous stone archives} = \text{weathering material} + \text{residual matter} + \text{dissolved matter}\]

Sulfur oxides, nitrogen oxides and other harmful acidic gases in the air [8] will cause corrosion damage to the stone, such as SO$_2$ dissolved in the atmosphere in water, the acidic H$_2$SO$_3$ is formed, then oxidized by O$_2$ in air, the formation of strong acidic H$_2$SO$_4$ which is serious to stone archives.
Some soluble salt ions such as Na\(^+\), Ca\(^{2+}\), SO\(_4\)^{2-}\) formed by hydrolysis can make hard limestone loose and powdered. Atmospheric CO\(_2\) cause carbonation on stone archives, for example, the Hongshixia rock mass in Yulin is mainly calcareous cementation, and its carbonation is more obvious. Calcite, plagioclase (Formula 1, 2) and orthoclase (Formula 3) all exhibit chemical reactions in carbonated water[8], as follows:

\[ 2\text{Na}[\text{AlSi}_3\text{O}_8] + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{SiO}_2 + \text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4 \]  
\[ \text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8] + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4 + \text{Ca}^{2+} + 2\text{HCO}_3^- \]  
\[ 2\text{K}[\text{AlSi}_3\text{O}_8] + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4 + \text{SiO}_2 + \text{K}_2\text{CO}_3 \]

\textbf{Biological factors}

In recent years, the problem of biological erosion of stone archives has attracted more and more attention. It is generally accepted that biological erosion processes are biophysical erosion and biochemical erosion. Biophysical erosion mainly includes the destructive effect of plant roots and mycelia. The growth of plant roots around the stone archives produce splitting action, which can lead to the enlargement of rock fissures, thus accelerating biological weathering. The moss, lichens, and fungus microbes cover the surface of the rock and contaminate the stone archives.

Biochemical erosion includes the decomposition of stones by various chemicals released from bacteria, algae and lichens. Biophysical erosion and biochemical erosion usually coexist and cause serious damage to stone cultural relics. In addition, sulfur bacteria and iron bacteria can directly transform the important components of stone materials through oxidation and reduction [9]. Moreover, due to the production of metabolites (such as water, oxalic acid) in the life process of microorganisms, it may lead to the formation of color spots and black contaminated layers on the surface of lithologic relics, which will change the chemical composition of rocks[10]. In addition, microbial secretions can change the pH value of the stone, which also corrode the stone archives.

\textbf{3. Protection technology for historical archives of stone archives}

The stone archives are mostly scattered in mountains, rocks and wilderness, and have been eroded by wind and rain for a long time. Many stone archives have long been vague and need to be repaired. Specific protection techniques are needed. As for the restoration and protection of stone archives, appropriate technical measures should be taken according to the principle of minimal intervention and no influence on the original appearance of cultural relics, therefore, it can greatly reduce the possibility of natural weathering. At present, the main protection and restoration technologies of stone archives are surface cleaning and decontamination technology, reinforcement technology and restoration and protection technology.

\textbf{Table 1} Advantages and disadvantages of surface cleaning method

| Cleaning method         | Advantages                                              | Disadvantages                                      |
|-------------------------|---------------------------------------------------------|----------------------------------------------------|
| Water cleaning          | Simple, efficient, cheap and environmentally friendly.  | Potential hazards such as water shock damage.      |
| Chemical cleaning       | Good selectivity.                                       | May causing new damage to the stone archives.      |
| Particle injection      | Clean and environmental friendly.                      | Low efficiency and expensive.                      |
| Laser cleaning method   | Remove many impurities from the surface.                | Expensive.                                         |

\textit{3.1. Surface cleaning and decontamination technology}

Stone archives have been affected by various factors in the long historical process, a variety of dirt and imprints were left on the surface. These surface stains are evidence of the vicissitudes of archives history and should not be cleaned. At the same time, many pollutants or sediments are accelerating the
process of weathering archives, destroying the surface microstructure of cultural relics, if not timely maintenance and protection of many historical and cultural information will be lost. Thus, cleaning becomes the first process of protection and maintenance, and cleaning methods can generally be divided into [11]: water cleaning, chemical cleaning, particle injection, and laser cleaning (Table 1).

3.2. Reinforcement technology

Weathering leads to cracks and shedding in some stone archives, while the composition and structural properties of some stone archives are poor, with large porosity and easy weathering. Therefore, for these types of open-air stone archives, after effective cleaning treatment, reinforcement will delay the aging of cultural relics. This is currently the most commonly used open-air stone heritage preservation of an effective method.

Special attention should be paid to the fact that some weathered stone archives cannot be cleaned and reinforced first, only the surface of the archives can be strengthened immediately after a little cleaning. The reinforcement of this kind of stone archives must be carefully carried out. It is difficult to solve the problem by applying reinforcement materials only on the surface and crevices of stone archives. It is also necessary to use materials with certain fluidity, high strength after solidification, similar thermal expansion coefficient to the matrix of stone archives, and to reinforce rock archives slowly by grouting. For rock archives that break apart along the matrix or cracks, anchors are used to fasten them first, and then grouting is used to reinforce them [12]. The common reinforcements are acrylic resin [13], epoxy resin [14] and organic silicone resin [15]. However, organic reinforcing agents are susceptible to physical or chemical changes caused by oxidizing gases, water and light radiation in the environment, resulting in accelerated aging, and its permeability in stone is generally inferior to that of inorganic reinforcing agents. Commonly used reinforcement methods are brushing reinforcement method [16], slow flow reinforcement method [16], cyclic spraying method, and immersion reinforcement method [17].

3.3. Repair technology

Some of the stone archives have cracks, defects, and some even have been broken. It is urgent to carry out effective repair to avoid further damage and prolong their life. General Stone restoration mainly includes filling cracks, repair defects and fracture connections. First of all, crack filling is usually needed for stone archives with cracks. Secondly, for defective stone archives, it is necessary to repair defects. Mortar is also used for repairing defects, filling and repairing cracks and defects respectively. Epoxy resin with strong bonding force can be directly used to connect the fractured stone archives with small volume and light weight. As for the fractured stone archives with large volume and weight, in addition to epoxy resin and other strong resin adhesives to bond the fractured parts, also need to use metal clamps, anchor rods and other external reinforcement.

3.4. Sealing technology

After cleaning, strengthening and repairing the stone archives, in order to prevent further weathering, sealing treatment should be carried out to slow down the weathering erosion. Generally, polysiloxane is used as the sealing agent. This kind of polymer material is colorless, transparent, hydrophobic, and easy to form film, long aging period, acid and alkali resistance, sun exposure resistance. Thus, it is a very ideal stone protection material. Polysiloxane is diluted by ethanol in use, and then is stirred thoroughly. It is evenly smeared on the stone surface at a suitable viscosity. After drying, ethanol evaporates and polysiloxane remains on the stone archives surface to form a transparent and uniform protective film. For some small movable stone archives or particularly precious stone archives, epoxy resin, nylon and other thin film materials can be used for surface insulation protection to prevent harmful gases, wind and sun damage to the stones.

4. Conclusion

Stone archives are the brilliant treasure in human history. However, most of these historical relics are very dilapidated, but they can still reflect the glorious history of the Chinese nation. They are non-renewable precious resources. They have important practical significance in protecting national
cultural heritage. After decades of research, we have made great progress in researching the weathering mechanism of stone archives. It is found that the main factors of weathering of stone archives are derived from human factors, physical factors, chemical factors and biological factors. With the continuous development of industrialization, environmental pollution is becoming more and more serious, which will also accelerate the weathering of stone archives. Therefore, it is of great significance to clean, decontaminate, reinforce, repair and seal the stone archives, reduce their damage degree, improve their anti-weathering ability and prolong their life.

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