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Study on Weathering Mechanism and Protection Method of Masonry in Humid Environment

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In order to better protect brick and stone cultural relics, this paper studies the present situation of brick and stone cultural relics in the open environment in humid areas with Xi'an city wall as an example. With various textures of brick and stone culture relics and complex and changeable natural environment, it determines that the protection methods of brick and stone cultural relics should be adapted to local conditions. For example, the protection methods should be different, as the outdoor environment is different from the indoor environment or in cases when there is big difference between a humid and warm environment and a dry and cold environment. This paper attempts to analyze and study the weathering status and disease mechanism of brick and stone cultural relics in humid areas. The study shows that humid environment is the most important factor causing damage to the weathering of brick and stone relics, and all kinds of diseases are generated or aggravated by the participation of water. A high efficiency and low toxicity compound antiseptic and mildew proof agent is made up by scientific proportion, whose bactericidal and bacteriostatic effect is verified with inhibition zone, the most commonly used method in biological control experiment. Moreover, the prevention and protection methods of biological weathering of brick and stone relics are put forward. It is concluded that the study of brick and stone cultural relics in humid environment can help to better carry out management and restoration of cultural relics.

1. Introduction

The science of cultural relics conservation is a discipline in the natural sciences that studies the laws of qualitative change of non-renewable cultural relics with precious historical and scientific values under the influence of their own and external factors (Phillipson et al., 2016). At the same time, it is also a marginal, comprehensive basic applied discipline and emerging technology discipline based on muti-disciplinary comprehensive science and engineering (Schnepfleitner et al., 2016). Principles for the Conservation of Heritage Sites in China points out that the task of protection is to repair the damage caused by natural forces and human beings through technical and managerial measures and to prevent new destruction (Lee, et al., 2015). All protective measures must comply with the principle of not changing the original form of cultural relics (Guo and Jiang, 2015). One of the most important tasks in preserving cultural relics is the removal of cultural relic's diseases (Silva-León, et al., 2014). In order to remove the disease and prevent the damage to the cultural relics, it is necessary to investigate the diseases of cultural relics and analyze the harmful factors causing the diseases first (Brueckner and Lambert, 2014), so as to take effective measures to eliminate the causes of damage and destruction of cultural relics, such as the mold stains on paper and textile artifacts, powdery rust on bronze (Abdellah et al., 2017), the soluble salt on murals, pottery and brick artifacts (Přikryl et al., 2017). All causes of diseases, such as pests on lacquer ware, should be completely removed so as to ensure that the cultural relics can be preserved in a healthy and safe state as long as possible (Al-Omari et al., 2015).

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2. Study on the Protective Materials of Brick and Stone Cultural Relics in Humid Environment

Normally, humidity is used to refer to the conditions in which the air is damp without raining (Verganelaki et al., 2015). For the quantitative characterization of humid environment, there are two parameters, rainfall and relative humidity (Toe and Kubota, 2015). In the field of cultural relics conservation, the wording, humid environment is commonly used (Daly, 2016), but so far there is no uniform definition for it. The object of this study is brick and stone relics preserved in the open-air which are greatly influenced by the external environment. Therefore, the location will belong to the scope of humid environment discussed in this paper, if its average humidity in atmospheric environment is above 70%.

2.1 Classification and performance requirements of masonry protective materials in humid environments

For brick and stone cultural relics that weather in humid environments, the currently widely accepted chemical protection method is to use a material with a certain penetration depth and reinforcement strength for consolidation and necessary surface protection treatment of the weathered and endangered cultural relics (Franzoni et al., 2014). Therefore, to enable the brick and stone artifacts to acquire good waterproof performance is not only an important method to prevent weathering, but also the primary requirements for chemical protective materials (Godts et al., 2017).

The protective materials for masonry must have the following characteristics. First, the materials must be colourless and transparent, and does not react with the stone body. They must have strong penetration ability with a depth of penetration that can guarantee they will not flake off with the surface weathering layer together (Bai et al., 2016). The materials must form a layer with strong weathering resistance, prominent strong waterproof and harmful gas prevention abilities. The layer must be breathable and permeable, so that the water on the surface cannot easily penetrate the stone, while the water inside stone can escape from the inside (Suling et al., 2016). Here is a list of centralized protective materials: reinforced protective materials including silicone, acrylic acid, ethyl silicate system vinegar; inorganic reinforcement protective materials including lime water, strontium hydroxide and barium hydroxide; and organic reinforcement protective materials including paraffin wax, silicone and acrylic resin etc.

2.2 Composition and ratio of alternative protective materials for brick and stone cultural relics in humid environment

The material used in the experiment is a new kind of silicone materials made of WD-10 organic solvent (ethanol) and WD-10 water agent developed by Wuhan University, which is long-chain alkyl trimethoxysilane with dodecyltrimethoxysilane as the main gradient. Its chemical formula is C12H25Si (OCH3) 3, and it is homologous to methyl trimethoxysilane. It is a colorless transparent neutral liquid, soluble in ethanol, ethyl ether, butyl acetate and other organic solvents, and also soluble in water. With good penetration effect, this kind of material can effectively resist the erosion of acid rain, while not affecting the original appearance of cultural relics.

The transmittance of quartz glass specimen coated with this material in the range of 340-740A was measured by Nissan MPS-50000 spectrometer in Northwest Optical Instrument Factory. There was no adverse effect compared with blankness. The results show that the WD-10 film is almost transparent and will not change the appearance of cultural relics. The acid resistance of WD-10 film can be seen by inspecting the contact angle before and after immersion in 0.1% acetic acid solution. It is found that WD-10 has good acid resistance.

Table 1: Test results of acid resistance of WD-10 and other material films

Materials		Contact angle		Film surface change	
Code	Blocking group	Original	Second acid-resistance cycles	Unchanged numbers	Corroded number
WD-10	$C_{12}H_{25}$-	97.5	99.1	9	0
3204	$C_{12}H_{25}$-	93.6	76.9	6	3

3. Study on the Mechanism and Prevention of Disease in Xi'an City Wall of Ming Dynasty

Located in the downtown area of Xi'an, Shaanxi province, Xi'an Ming City Wall of Ming Dynasty is a rectangular wall with a height of 12 meters, a bottom width of 18 meters, and a top width of 15 meters. Its western wall is 2,590 meters long, western wall 2,631.2 meters long, southern wall 3,441.6 meters long, the northern wall 3,241 meters long, with a total circumference of 11.9 km. There are a total of 17 gates, of which the four largest are, Eastern Changle Gate, Western Anding Gate, Southern Yongning Gate, and Northern Anyuan Gate, each composed of a watchtower and a gate tower. The whole city walls constitute an intact medieval ancient castle with their moat, the suspension bridge, the gate, the towers, the main building, the turret, the enemy building, the daughter wall, the crenel and other facilities.

3.1 Geological and climatic conditions of Xi'an city wall

As the capital of Shaanxi Province, Xi'an is located in the central part of Guanzhong Plain, bordered by Weihe River to the north, Qinling Mountains to the south. The atmosphere in the urban area of Xi'an is greatly influenced by the natural position of Shaanxi province, where it is a continental monsoon climate. The significant difference in wind direction there between the north and the south is mainly the Northeast wind. Xi'an belongs to warm temperate semi-humid continental monsoon climate, with distinctive warm-cold and dry-wet changes and four distinct seasons. The average annual precipitation in the urban area of Xi'an is concentrated in the summer and autumn seasons, accounting for 78.7% of the total annual precipitation. The annual average relative humidity is 70%, the minimum 63%, and the highest 79%. With the rainfall concentrated in spring and summer, and the brick is washed more violently, adding that the relative humidity is higher, causing repeated expansion and contraction of the brick body, which is unfavorable to the overall preservation of the wall.

The monitoring results of atmospheric environmental quality in recent eight years and the limit of harmful gas concentration stipulated by People's Republic of China air quality standard GB3095-3096 are illustrated in Table 2. Besides, the environmental air quality function is divided into three categories. Compared to Figure 1, it is found that the content of SO2 and NOx in Xi'an is in line with the national secondary standard. However, the pollution level has been deepened after 2007, and the total particulate suspended matter has basically exceeded the national level standard since 2005.

Table 2: Annual average concentration limit

Annual mean value of pollutants(mg/m^3)	Concentration limit		
	Standard I	Standard II	Standard III
SO_2	0.02	0.06	0.10
NO_2	0.04	0.04	0.08
Total suspended particulates	0.04	0.10	0.15

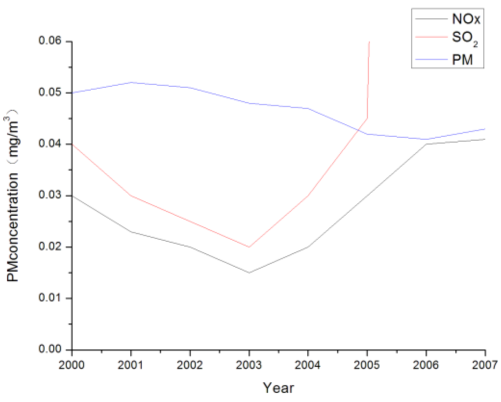

Figure 1: Annual average mass concentration of major pollutants in Xi'an

3.2 Field investigation and analysis of the disease of Xi'an city wall

The body of Xi'an wall is composed of rammed earth core within the brick body and the outer bricks made of solid clay. Most of the kilns in the north were located Linqing, Shandong province. According to different clay processing techniques, fine or rough, the bricks mainly fall into three categories, bricks made of cleaned mud, bricks made of fine mud, mud bricks with coarse sands on the surface. The inside of the brick adobe is made of lime, soil and glutinous rice juice. Below are the specific damages to city walls:

Settlement, cracking and bulging of city wall. Most city walls are built on the soil layer which contains many soluble salts. With the erosion of groundwater and rain erosion, the soluble salt will gather at the bottom of the wall, thus there are more salts at the bottom of the wall body than on the top. The dissolution and shrinkage of soluble salt destroys the original crystal structure of the wall, and reduces the mechanical properties of the wall. Therefore, the crystal structure of the brick wall soil becomes loose, with decreased cohesion and reduced strength.

Efflorescence and surface weathering of wall. It is common to see efflorescence on the surface of Xi'an city wall, mainly in the middle and upper part of the side of the city wall and near the drainage ditch. Serious surface weathering appears on the southern and western sides of the wall and on the slope for ups and downs. Due to the damage to the wall structure caused by constant dissolution and contraction of the wall salt, the mechanical properties of the wall are reduced, the cohesion decreased and the strength reduced.

Biological diseases of Xi'an city walls. Mole attachment is found in all four gates of the city walls, Eastern Gate, Southern Gate, Western and Northern Gate. This fungal microbial erosion is very common. The collected samples were cultured, isolated and purified until a single strain of purebred species was identified and a total of five kinds of bacteria were identified, all of which were common colonies.

3.3 Detection and analysis of weathering samples of Xi'an city walls

In order to understand the weathering conditions of bricks and the formation of efflorescence in Xi'an city walls, 4 salt samples at different heights and weathered brick samples were taken at each position out of the ten different locations sampled on the city wall. The collected samples were then analyzed by X-ray powder diffractometry with D / max-rA X-ray diffraction (XRD), in a scanning angle range of from 0 degrees to 80 degrees, with a voltage of 40KV, current of 100mA, and a range of 2000 counts/s. Microscopic elemental analysis was carried out by using environmental scanning electron microscopy (EDS) to determine the composition of dissolved salt and its distribution on masonry walls, and then the composition and structure of salt dissolution and crystallization and their impact on brick quality were analyzed.

According to the composition analysis of the efflorescence samples of Xi'an city wall, it is found that components mostly are NaCl, $NaNO_3$, anhydrous thenardite and $Na_2SO_4 \cdot 10H2O$. Figure 2 shows the solubility of NaCl and Na_2SO_4. Figure 3, Figure 4, Figure 5 and Figure 6 show the composition of Xi'an wall efflorescence with $Na_2SO_4 \cdot 10H_2O$, SiO_2, NaCl and $NaNO_3$ as examples.

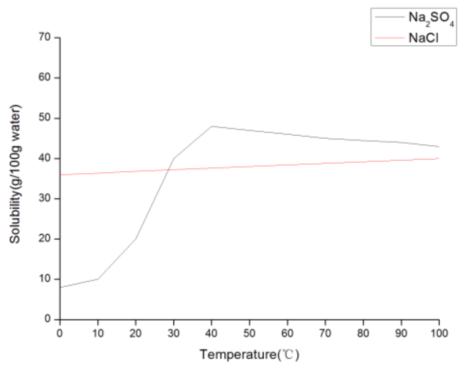

Figure 2: Solubility of NaCl and Na2SO4

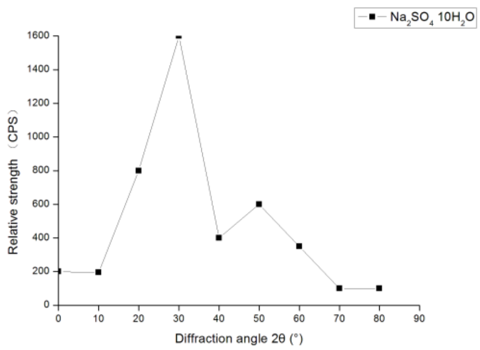

Figure 3: Analysis of the composition of Xi'an wall efflorescence with $Na_2SO_4 \cdot 10H_2O$

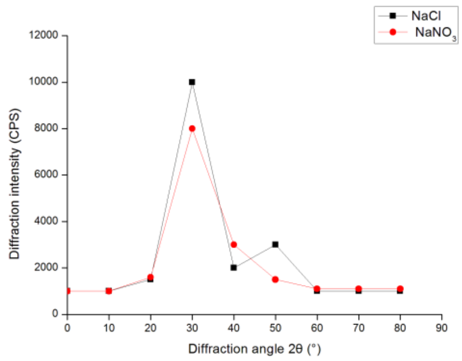

Figure 4: Analysis of the composition of Xi'an wall efflorescence with SiO_2

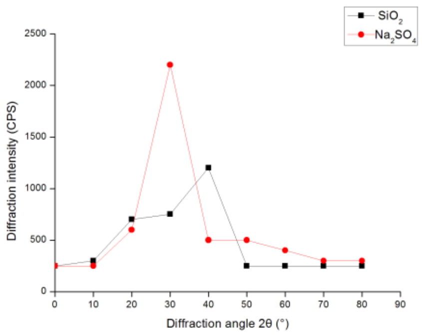

Figure 5: Analysis of the composition of Xi'an wall efflorescence with NaCl

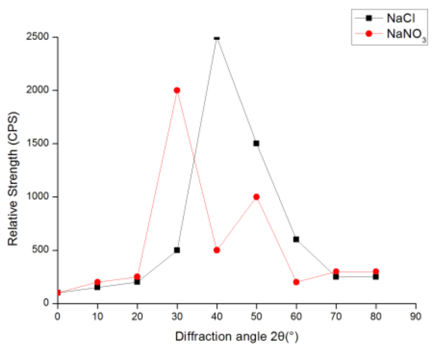

Figure 6: Analysis of the composition of Xi'an wall efflorescence with $NaNO_3$

4. Conclusions

Water is a major source of damage to the city walls of Xi'an, among the many contributing factors to its disease. Thus the erosion and penetration of water into the walls can lead to serious consequences. Owing to the effective drainage system built in its early stage, Xi'an ancient city walls can still be preserved intact so far. However, now many drainage facilities are damaged with some drainage outlets sealed and some blocked. As a result, a large amount of stagnant water causes cracks in the walls, which then lead to a further increase in riprap crack, thus a vicious circle is formed. Settlement, cracking and bulging of city wall pose a threat to safety of Xi'an city walls. The traditional deformation settlement observation is used to predict and prevent these threats, as long as they do not mutate.

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