



Technical note

Protection of the surface weathering stone artworks by a chemical conversion method

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ABSTRACT

A chemical conversion method for the protection of the surface weathering stone artworks was explored. By this method, the harmful calcium sulfate weathering layer on the stone relics was converted into a protective calcium oxalate layer *in situ*. The calcium oxalate conversion layer was characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD) and polarizing microscope (PLM). The conversion layer was also estimated by chromatic aberration, capillary suction, adhesive force and dissolution stability tests. The calcium oxalate conversion layer with good weatherability, adherence and compatibility will be promising as a solution for the protection of the surface weathering rock relics.

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1. Introduction

Calcium sulfate is the principal component of the weathering crust [1] on the surface of the limestone artworks. Because of its high solubility in water, calcium sulfate can be washed away by rain and cause surface recession of the historic stones [2]. More seriously, calcium sulfate can lead to serious structure damage of the rock relics. When calcium sulfate crystallizes continuously inside the small fissures and pores of the stones, a tremendous and destructive crystallization pressure builds. Generally, this crystallization pressure is blamed for the spalling and flaking of the rock relics [3].

In the past, a variety of precautions were used to protect these surface gypsification stone relics. Ever since 1950s, synthetic polymer coatings have been extensively adopted [4] in the conservation field. However, organic polymer materials were found to be less compatible with the inorganic rock heritages recently [5]. In some cases, the application of the organic polymer materials even led to the accelerated deterioration of the stone relics. In contrast, the inorganic protective materials have better compatibility with the same quality of rock relics. The preservation method using alkaline earth metal hydroxides [6] as coating precursors was thus explored. In this method, the metal hydroxide materials exist in the form of carbonate coating eventually. However, little success

was achieved yet. This was mainly attributed to the weak adhesion and weatherability of the carbonate coating [7]. For the past few years, SRB (sulfate reducing bacteria) method [8] was studied to transform calcium sulfate crust into calcium carbonate layer under laboratory conditions. However, calcium carbonate layer itself is also easily weathered and the SRB method cannot be used for the protection of the stone relics in outdoor settings.

Maybe, we can get inspiration from the natural calcium oxalate film, which is common on the surface of the carbonate stone in the field [9–11]. This kind of calcium oxalate film is protective and the carbonate stone under it is often well preserved [12,13]. It is due to the low solubility, good weatherability and adhesion of calcium oxalate film [14,15].

In this paper, an artificial calcium oxalate film was prepared *in situ* on the surface weathering stone substrate by a chemical conversion method (see Fig. 1). After treatment by the chemical conversion method, a compact calcium oxalate film with good adhesion, weatherability and compatibility was prepared, which can provide enough and durable protection for the surface weathering stone relics.

2. Experimental

2.1. Sample preparation

Analytical reagents were used throughout the experiment. Absorbent cotton, ammonium oxalate, sulfur dioxide and potas-

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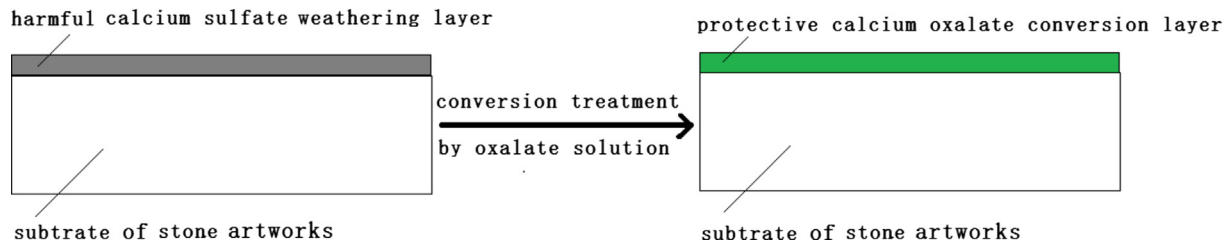


Fig. 1. Strategy scheme of chemical conversion method for the protection of surface weathering stone artworks.

sium sulfate were purchased from Sinopharm Group Co., Ltd. Five specimens were prepared for each kind of stone sample.

Surface sulphation of the limestone specimens (4.0 cm × 4.0 cm × 2.0 cm, Table 1) was carried out in a homemade climatic chamber. The concentration of sulfur dioxide, air flow and relative humidity was 60 μg/m³, 0.1 L/s and 80%, respectively [16]. After sulphation treatment for 3 days, the limestone specimens were taken out, washed with deionized water and dried naturally for 24 h.

Conversion treatment: the specimens were packed with absorbent cotton pad (impregnated with solution of 5% ammonium oxalate and 10% potassium sulfate) and plastic wrap successively. 12 h later, the specimens were taken out, rinsed and dried naturally for 24 h before further investigations.

2.2. Characterization

Microstructure of samples was observed by SEM (FEI SIRION-100, 5.0 kV of accelerating voltage and 8.0 mm of working distance) with EDX for composition analysis. Phase constituent of the samples was examined by XRD (AXS D8 ADVANCE, Cu Kα radiation, scan range 2θ = 10–80°). Stratification structure of the conversion film was determined by PLM (Olympus Co. Ltd, Tokyo, Japan).

Chromatic aberration of the samples was investigated through a reflectance spectrophotometer (Concise Apparatus Co. Ltd, Shanghai, China) using D65 illuminant, 8°/d optical geometry and CIE standard. The formula for the calculation of chromatic aberration (ΔE):

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

Capillary suction of the samples was measured in accordance with GB/T 9966.3-2001 [17]. The formula for the calculation of capillary suction (W_a):

$$W_a = \frac{m_1 - m_0}{m_0} \times 100\% \quad (2)$$

m_0 and m_1 are the mass of the dry and water-saturation test specimens.

Surface adherence of the specimens was measured by Scotch Tape Test (STT) [18].

The dissolution stability of samples was evaluated by dynamic erosive experiments [19]: in an airtight glass container, water was sprayed just from the top of the stone samples. To simulate the natural rainfall, the concentration of CO₂ gas and the amount

of the spraying water in the container were set to 1000 ppm and 10 ml cm⁻² d⁻¹, respectively. The stone samples were taken out, dried to constant weight at 50 °C and weighed every 24 h.

3. Results and discussion

Fig. 2a shows a dense microstructure of the limestone sample. After sulphation treatment, it becomes some kind of loose and porous. Fissures, holes and weathering sediments [20] are visible on it (Fig. 2b). The XRD spectrum (d = 7.70, 4.31, 3.08, 2.88 and 2.69 Å in Fig. 3a) analysis shows the calcium sulfate dihydrate constitution of the surface weathering layer. After conversion treatment, the surface of the calcium sulfate weathering layer and limestone are both converted into some kind of structure with grainy texture (Fig. 2b, c, e and f) by the proposed method. EDX and XRD were employed to verify the composition of the conversion layer. EDX results (Fig. 2b and e) show that the constituent elements of the grainy texture are carbon, oxygen and calcium. Its calcium oxalate composition is affirmed finally by the XRD results in Figs. 3 and 4 (d = 5.93 Å, 3.65 Å, 2.97 Å and 2.35 Å). Calcium oxalate comes from the conversion reaction between oxalate ion and the calcium sulfate layer or limestone substrate.

The conversion reaction stops about 9 h later in the proposed experimental conditions (Figs. 3 and 4). However, the conversion reaction is not complete, which is revealed by the characteristic diffraction peaks of calcium sulfate dihydrate in Fig. 3 and calcite in Fig. 4. It is further proved by the results of the PLM in Fig. 5a.

The results show that the sample from the surface sulphation specimens has a “sandwich” structure consisting of calcium oxalate layer (outermost layer, green), calcium sulfate layer (middle layer, orange) and limestone (substrate, violet). Similarly, the sample from the limestone has a double layer structure: the calcium oxalate conversion layer and limestone substrate. This indicates that the conversion reaction is self-limiting and it stops completely when calcium oxalate film is compact and thick enough.

Performances of the calcium oxalate conversion layer were estimated by capillary suction, chromatic aberration, adhesive force and dynamic erosive experiments.

Capillary suction of the samples is almost not changed after the conversion treatment (Table 2). This suggests that the porous structure [21] of the samples are not affected by the calcium oxalate conversion coating and the “breathing function” [22] of them was maintained.

Chromatic aberration among limestone, calcium oxalate conversion layer and the calcium sulfate layer is less than 1.4 (Table 2). Thus, the surface difference of the samples before and after treatment is hardly detected by visual observation and the “original state” [23] of the samples are not altered.

Thickness of the calcium oxalate conversion layer is about 3 μm, which is much smaller than that of the calcium sulfate layer (about 5 μm) or the limestone substrate. This is the result of the incomplete conversion. When calcium oxalate coating is compact and thick enough, the conversion reaction stops gradually. In fact, gyp-

Table 1
Properties of the limestone specimens.

Trade name	Pc	Wt (%)	OP (%)	TP (%)
Guangxi White	Calcite	99.3(±0.3)	0.25(±0.12)	0.38(±0.15)

Pc: phase composition, Wt (%): content of calcium carbonate, OP (%): open porosity, TP (%): total porosity.

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