Selectional removal of the harmful gypsum weathering layer on the calcareous stone heritages

Yan Liu

Northwest University

Kun Zhang

Northwest University

Fuwei Yang (✉ zhuoyingyang@126.com)

Northwest University <https://orcid.org/0000-0003-3222-2209>

Research article

Keywords: removal, gypsum weathering layer, conservation, calcareous stone heritages

Posted Date: July 2nd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-39566/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

A novel method for the selectional removal of the harmful gypsum weathering layer on the calcareous stone heritages was studied. By this method, the gypsum weathering layer was cleared away and the carbonate substrate of the calcareous stone was left intact at the same time. The removal effect was evaluated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD), capillary suction and color difference measurement. This selectional removal method will be highly helpful for the conservation of the surface weathering calcareous stone relics.

1. Introduction

Gypsum layer is common on the surface of the calcareous stone relics^[1]. It is a weathering product of calcareous stone under the attack of sulfur oxide pollutants in the air^[2]. The formation of gypsum weathering layer is often accompanied with appearance alteration^[3], surface dissolution^[4] and structure disruption^[5] of the rock relics. The removal of this kind of harmful gypsum layer is thus believed to be necessary^[6, 7].

In the past, chemical, microblasting and laser methods were developed successively for the removal of the gypsum layer on stone heritages^[8]. Traditionally, basic carbonate, sodium citrate and exchange resin were common detergents in chemical cleaning^[9]. They can act as solvent, chelating agent and ion exchanger during the cleaning process, respectively. Chemical cleaning can eliminate almost all of the gypsum layer efficiently. However, the chemical cleaning agents are often harmful and they can even accelerate the weathering of the stone objects^[10]. In recent years, laser and microblasting were also studied as physical cleaning tools. Under the irradiation of the high energy laser, the gypsum layer and other stains on the stone artworks can be removed through gasification. Due to the good controllability, high accuracy and little impact on the environment, laser cleaning is extensively studied^[11]. However, laser cleaning is too costly and beyond the reach of the conservation practice of most stone heritages. Moreover, the ablation effect of laser often leads to the composition change and appearance alteration^[12] of the stone heritages. Microblasting was also considered in the cleaning of historical stones recently^[14]. In this cleaning technique, abrasives with energy are used to break the bonding between the gypsum layer and the stone substrate. It is effective in the removal of the surface deposits for building stones^[14]. However, as a mechanical method, the over cleaning of blasting is normally noticeable. The gypsum layer and the unweathered substrate of stone relics under it will be removed indiscriminately during the cleaning process. So, the selection of microblasting should be careful for the cleaning of the stone heritages^[15]. To sum up, the existing cleaning methods are all non-selective and the substrate of the stone heritages can be damaged during the removal process of the gypsum weathering layer.

In this paper, a novel method for the selective removal of the harmful gypsum weathering layer on the calcareous stone heritages was developed. By this method, the gypsum weathering layer is dissolved and swept away with the aid of the detergent of barium carbonate. The carbonate substrate of the calcareous

stone, however, cannot reaction with barium carbonate and remains intact. The removal effect was evaluated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD), capillary suction and color difference measurement. The removal mechanism of this method was also investigated.

2. Experimental

2.1. Sample preparation

Analytical reagents were used throughout the experiment. Absorbent cotton, barium carbonate and sulfur dioxide were purchased from Sinopharm Group Co., Ltd. The marble stone is mainly composed by calcite ($\geq 98.0\%$). The marble specimens ($4.0\text{ cm} \times 4.0\text{ cm} \times 2.0\text{ cm}$) with gypsum layer were prepared by sulphation method in a homemade climatic chamber. The concentration of sulfur dioxide, air flow and relative humidity in the chamber was set as $60\text{ }\mu\text{g/L}$, 0.1 L/s and 80% , respectively^[16]. After 60 days of sulphation, the specimens were taken out, rinsed with water and dried naturally. The gypsum layer prepared by above method is about $5\text{ }\mu\text{m}$ in thickness.

The removal of gypsum layer on marble specimen was carried out according to the procedures in Fig. 1. Firstly, the detergent of barium carbonate was imbedded in the absorbent cotton to make a cleaning pad with a sandwich structure. Then, enough water was introduced into the cleaning pad by soaking. Finally, the marble specimen with gypsum layer was coated with the water-saturated cleaning pad. 1–5 days later, the marble specimen was took out, washed with deionized water and dried naturally before further investigations.

2.2. Characterization

The microstructure of samples were observed by a scanning electron microscopy (SEM, FEI SIRION-100, 5.0 kV of accelerating voltage and 8.0 mm of working distance). The phase constituent of the samples were detected by an X-ray diffraction (XRD, AXS D8 ADVANCE, scan range $2\theta = 10\text{--}80^\circ$).

The color difference of samples was determined by a Chromatic meter (WSC-S, D65 illuminant, $8^\circ/\text{d}$ optical geometry and CIE standard).

The capillary suction of samples was tested according to the national standard of GB/T 9966.3–2001^[17].

3. Results And Discussion

The microstructure of the marble samples were investigated by SEM. The fresh marble sample is flat and compact in morphology (Fig. 2a). After sulphation treatment, the surface of the sample becomes coarse and porous (Fig. 2b), which is similar with the natural gypsum weathering layer^[18]. The surface composition of the marble sample is also converted from calcium carbonate (calcite, $d = 3.86, 2.29$ and

2.09 Å) to gypsum (calcium sulfate dihydrate, $d = 7.70, 4.31, 3.08, 2.88$ and 2.69 Å) (Fig. 3a). That means, a gypsum layer is formed during the sulphation process. In the wild, this kind of gypsum layer is from the weathering of calcareous stone such as marble and limestone in polluted air containing sulfur oxides^[19].

After the removal treatment by the proposed surface application method in Fig. 1,

the surface of the sample becomes flat and compact again (Fig. 2c). Meanwhile, the diffraction peaks of calcite become stronger and the ones of calcium sulfate become weaker in the XRD spectrum (Fig. 3b and 3c). Calcite is from the marble substrate. Calcium sulfate, however, is from the gypsum weathering layer. These results indicate that the gypsum layer is removed gradually. EDX results in Fig. 4 can provide further evidence. During the cleaning treatment, the strength of sulfur peak is reduced and the ones of carbon peak is enhanced progressively (Fig. 4a, 4b and 4c). About 72 hours later, the morphology of the treated marble sample is almost the same as the fresh marble (Fig. 2d). Accordingly, the diffraction peaks of calcium sulfate in Fig. 3d and the dispersive peak of sulfur in Fig. 4d are all absent, suggesting the total removal of the gypsum weathering layer.

The phase change of the detergent of barium carbonate in the absorbent cotton pad was also studied. In the XRD results of Fig. 5, the diffraction peaks of barium carbonate become weaker, while the ones of calcium carbonate and barium sulfate become stronger during the treatment process. It is a result of the reaction between calcium sulfate and the detergent of barium carbonate. In water solution, calcium sulfate from the gypsum weathering dissolves and dissociates into calcium and sulfate ions^[20]. These calcium and sulfate ions react with barium carbonate and produce less soluble calcium carbonate and barium sulfate in the cleaning pad of absorbent cotton subsequently^[21]. This reaction has an equilibrium constant of about 10^5 and can be carried out completely in room temperature^[22]. Owe to the continuous depletion of the

calcium and sulfate ions, the dissolution of the gypsum weathering layer will go on until it is cleared away thoroughly. According to above principle, this removal method is selective and safe for the calcareous stone heritages. The mineral composition of calcareous stone is insoluble carbonate and it cannot react with the detergent of barium carbonate. That means, only the gypsum weathering layer is removed and the carbonate substrate of the calcareous stone remains intact. Moreover, this removal method is of low residual. The detergent barium carbonate, its products calcium carbonate and barium sulfate are all insoluble substances. According the solubility products, their residues in the cleaning water are as low as about 10^{-5} mol/L.

The removal effect can also be seen from Fig. 6 and Table 1. The fresh marble is semitransparent and the crystal grains of calcite can be distinguished easily from it (Fig. 6a). After sulphation treatment, a white and opaque calcium sulfate weathering layer is produced. The crystal grains of calcite under it are covered and become unrecognizable (Fig. 6b). After cleaning treatment, the white calcium sulfate layer are eliminated and the original appearance of marble is recovered on the whole (Fig. 6c).

Table 1
Properties of test specimens

samples	surface composition	color difference (ΔE)	capillary suction (%)
marble	calcite	/	0.08($\pm$ 0.03)
marble with gypsum layer	calcium sulphate	3.6($\pm$ 0.02)	0.10($\pm$ 0.02)
marble after removal of gypsum layer	calcite	0.8($\pm$ 0.03)	0.09($\pm$ 0.02)

As shown in Table 1, the color difference between the fresh marble and the marble with gypsum layer is 3.6, which is higher than the noticeable detection limit of the human eye of 3.0. It indicates that an appreciable appearance change has taken place after the surface weathering of marble. The color difference between the fresh marble and the marble after removal of gypsum layer, however, is just 0.8. This suggests that gypsum layer on marble is completely removed and the original appearance of the marble sample is restored.

4. Conclusion

A safe cleaning method was explored for the removal of the harmful gypsum weathering layer on the calcareous stone relics in this study. By this method, only the gypsum layer is removed and the carbonate substrate of the calcareous stone is not affected. This method will be highly helpful for the conservation of the calcareous rock heritages suffering from surface weathering.

Declarations

Competing interests

We declare that there are no competing interests associated with this manuscript entitled “Selectional removal of the harmful gypsum weathering layer on the calcareous stone heritages”.

Funding

This work was supported by Natural Science Foundation of China (B0501 21975202), Collaborative Innovation Team Foundation of University in Gansu Province, China (2017C-20), Key R & D Program in Shaanxi Province, China (2019ZDLSF07-05, 2020SF-363).

Acknowledgments

This work was supported by Natural Science Foundation of China (B0501 21975202), Collaborative Innovation Team Foundation of University in Gansu Province, China (2017C-20), Key R & D Program in Shaanxi Province, China (2019ZDLSF07-05, 2020SF-363).

References

- [1] J.S. Pozo-Antonio, M.F.C. Pereira, C.S.A. Rocha, *Sci. Total Environ.* 584–585 (2017) 291.
- [2] A. Suzuki, S. Vettori, S. Giorgi, E. Carretti, F. Di Benedetto, L. Dei, M. Benvenuti, S. Moretti, E. Pecchioni, P. Costagliola, *J. Cult.Herit.* 32 (2018) 30.
- [3] S. Ordóñez, Á. La Iglesia, M. Louis, M.Á. García-del-Cura, *Constr. Build. Mater.* 112 (2016) 343.
- [4] Y. Liu, F.W. Yang, G. F. Zuo, R.X. Zhang, G.F. Wei, Q. Ma, *Constr. Build. Mater.* 182 (2018) 210.
- [5] H.D. Mooers, M.J. Carlson, R.M. Harrison, R.J. Inkpen, S. Loeffler, *Atmos. Environ.* 152 (2017) 156.
- [6] V. Comite, M. Álvarez de Buergo, D. Barca, C.M. Belfiore, A. Bonazza, M.F. La Russa, A. Pezzino, L. Randazzo, S.A. Ruffolo, *Constr. Build. Mater.* 152 (2017) 907.
- [7] M. Iqbal, *Int. J. Sus. Built Environ.* 2 (2013) 65.
- [8] J.S. Pozo-Antonio, A. Ramil, T. Rivas, A.J. López, M.P. Fiorucci, *Constr. Build. Mater.* 112 (2016) 682.
- [9] A. Moropoulou, S. Kefalonitou, *Build. Environ.* 37 (2002) 1181.
- [10] F. Cappitelli, L.Toniolo, A. Sansonetti, D. Gulotta, G. Ranalli, E. Zanardini, C. Sorlini, *App. Environ. Microb.* 73 (2007) 5671.
- [11] G.S. Senesi, I. Allegretta, C. Porfido, O. De Pascale, R. Terzano, *Talanta.* 178 (2018) 419.
- [12] C.M. Grossi, D. Benavente, *Appl. Surf. Sci.* 384 (2016) 525.
- [13] M. Godet, V. Vergès-Belmin, N. Gauquelin, M. Saheb, J. Monnier, E. Leroy, J. Bourgon, J.n Verbeeck, C. Andraud, *Micron.* 115 (2018) 25.
- [14] M. Carvalhão, A. Dionísio, *J. Cult. Herit.* 16 (2015) 579.
- [15] M.Á. Iglesias-Campos, J.L. Prada Pérez, S. García Fortes, *Constr. Build. Mater.* 132 (2017) 21.
- [16] Y. Liu, F.W Yang, G.F. Zuo, R.X. Zhang, G.F. Wei, Q. Ma, *Constr. Build. Mater.* 182 (2018) 210.
- [17] GB/T 9966.3-2001: "Test methods for natural facing stones. Part 3: Test methods for bulk density, true density, true porosity and water absorption".

- [18] T. De Kock, J. Van Stappen, G. Fronteau, M. Boone, W. De Boever, F. Dagrain, G. Silversmit, L. Vincze, V. Cnudde, *Talanta*. 162 (2017) 193.
- [19] T. Lamhasni, H. El-Marjaoui, A. El Bakkali, S. Ait Lyazidi, M. Haddad, A. Ben-Ncer, F. Benyaich, A. Bonazza, M. Tahri, *Chemosphere*, 225 (2019) 517.
- [20] A.L.Petrou, A. Terzidaki, *Chem. Geo.* 381 (2014) 144.
- [21] J.H. Tang, J.W. Bullard, L.N. Perry, P. Feng, J.P. Liu, *Chem. Geol.* 498 (2018) 96.
- [22] E. Torres, A. Lozano, F. Macías, A. Gomez-Arias, J. Castillo, C. Ayora, *J. Clean. Prod.* 182 (2018) 114-123.

Figures

Figure 1

Strategy scheme of the removal procedures of the surface weathering layer of gypsum on marble specimen

Figure 2

Micromorphology of samples. a. marble, b. gypsum layer, c. partly cleaning of gypsum layer(24h), d. totally cleaning of gypsum layer(72h)

Figure 3

XRD results of surface sulphation marble samples after different treat time. a. 0h, b. 24h, c. 36h, d. 72h

Figure 4

EDX results of the elemental composition change of the surface sulfation marble specimen after different treat time. a. 0h, b. 24h, c. 36h, d. 72h

Figure 5

The phase transformation of the detergent barium carbonate during the removal process. a. 0h, b. 24h, c. 36h, d. 72h

Figure 6

Photo pictures of the specimens. a. marble, b. marble with gypsum layer, c. marble after the cleaning of gypsum layer