Evaluating The Protective Effect of Calcium Carbonate Coating On Sandstone Cultural Heritage

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Research Article

Keywords: Sandstone, depositing, Vaterite, Aragonite

Posted Date: October 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-956354/v1>

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Version of Record: A version of this preprint was published at Coatings on December 14th, 2021. See the published version at <https://doi.org/10.3390/coatings11121534>.

Abstract

The purpose of this work is to use different surfactants to deposit different crystal forms of calcium carbonate film on the surface of sandstone through a simple double replacement reaction. The protective effect of calcium carbonate coatings was evaluated through water absorption, water vapor permeability and weather resistance tests. The results show that the stone treated with vaterite calcium carbonate has excellent water absorption and permeability. Compared with untreated stone, the water absorption rate is reduced by 0.5 times, and the weather resistance is increased by 4 times, effectively hindering the erosion of water and soluble salts. These findings are expected to provide useful suggestions for the protection of stone cultural heritage.

1. Introduction

Sandstone is an ordinary sedimentary rock, frequently encountered in heritage buildings [1]. However, the outdoor macroporous sandstone is vulnerable to severe damage by soluble salt. If the internal structure of the stone is destroyed, we will have great difficulty with its preservation in the future [2]. Coating materials can effectively protect sandstone buildings and have received extensive attention from researchers. However, most of the coating materials currently used are organic materials. organic protective materials tend to have a short performance life, poor chemical compatibility, and due to limited protectant permeability, a hydrophilic hydrophobic interface is formed within the stone, which can cause aggravated stress damage and acceleration of the stone weathering rate [3].

In the past few years, researchers have discovered an environmentally friendly consolidation strategy based on the ability of bacteria to induce the formation of calcium carbonate in the porous system of the material [4]. The metabolic activity of bacteria changes the external environment of minerals, and their cell structure, fragments and secreted exosomes (EPS) can serve as the nucleus of heterogeneous calcium carbonate crystals [5]. Fadwa Jroundi et al. used the bacteria to mineralize and consolidate the gypsum materials in situ, the bacteria produce newly formed calcium carbonate formed by the vaterite, embedded in an organic matrix, which enhances the mechanical resistance of gypsum, and it does not change the appearance of the processed material [6]. Willem De Muynck et al. studied the effect of bacterial carbonate precipitation (biological deposition) on the durability of the mortar samples with different porosities, and durability was evaluated from the permeability and the degradation resistance. The results show that the biological deposition treatment can be regarded to form the coating protection on the surface of the mortar, which increases the resistance of the mortar samples to carbonization, chloride penetration, freezing and thawing [7].

Bacterial mineralization can produce calcium carbonate, which is an environmentally friendly technology that operates under mild conditions and can be used to reinforce and consolidate the soil/sand, protect and repair the stone and concrete structures. The application of bacterial mineralized calcium carbonate as a protective coating on stone cultural relics is feasible, but the bacterial mineralization method is

complicated to operate, and the cost is high and it is difficult to apply outdoors. Therefore, we consider a simple synthesis method of calcium carbonate coating and apply it to the surface of the sandstone.

Recent studies have shown that the reaction process can be controlled by adding a surfactant to synthesize different crystal forms of calcium carbonate. For example, Chen Zhiying et al. studied the effect of sodium dodecyl sulfate (SDS), an anionic surfactant on the crystallization of calcium carbonate. The results show that when the SDS concentration is controlled at 0.5 mM, agglomerated rod-shaped aragonite can be obtained; when the SDS concentration is 1 mM, pure vaterite with a novel flower-like morphology can be obtained; when the SDS concentration is increased to 2.5 mM, it is formed a mixture of vaterite and calcite [8]. Li et al. synthesized a three-dimensional vaterite self-supporting film by a simple gas diffusion method, Under the action of polyvinyl alcohol (PVA) [9]. Guo et al. synthesized aragonite calcium carbonate with complex morphology by homogeneous precipitation method under the action of polyvinylpyrrolidone (PVP). The morphology and structure of calcium carbonate particles were characterized by SEM, XRD and FT-IR. The results show that the calcium carbonate particles are mainly aragonite, with rod-like, bouquet-like and dumbbell-like shapes [10]. Naoyuki Kubo et al. used the polyvinyl alcohol (PVA) as a template, the calcite calcium carbonate was biomimetically synthesized at room temperature [11]. Il Won Kim et al. studied the effects of different degrees of hydrolysis and different contents of polyvinyl alcohol on the crystal form and morphology of the calcium carbonate. The results show that by adjusting the degree of hydrolysis of polyvinyl alcohol, the content can produce vaterite with different crystal forms. When the content of polyvinyl alcohol is higher, more vaterite can be formed, less PVA can be used to form the aragonite, and the vaterite still exists [12]. Therefore, we can choose different surfactant templates to control calcium carbonate crystallization to prepare different crystal forms of calcium carbonate.

In this work, We use the surfactant to control the crystallization process of calcium carbonate, directly deposit different crystal types of calcium carbonate on the surface of the sandstone as a protective layer. XRD, IR, SEM and other methods are used to characterize the structure and performance of calcium carbonate powder samples, with special attention to the influence of calcium carbonate protective film on the permeability, water absorption and weather resistance of sandstone surface.

2. Materials And Methods

2.1. Materials

In this study, we choose the following analytical reagents (purity over 99.7%): the calcium chloride (CaCl_2 ; Aladdin, Waukesha, WI, USA), the sodium carbonate (Na_2CO_3 ; Aladdin, Waukesha, WI, USA). Anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$; Aladdin), the Deionized water (H_2O ; laboratory-made), the anhydrous sodium sulfate (Na_2SO_4 ; Aladdin, Waukesha, WI, USA), polyvinyl alcohol (PVA; Aladdin, Waukesha, WI, USA). polyvinylpyrrolidone (PVP; Aladdin, Waukesha, WI, USA).

We used the sandstone, purchased from Guizhou province of China, to evaluate the protective effect of materials. Its main component is 98.5% silica. All samples were sliced into 5 cm in length and width, and 3 cm in height.

2.2. Materials Preparation

The sandstone surface is washed with running water to remove the dust. Then we dry it in a vacuum drying box to remove the water until its mass change is less than 0.1 g and then soaked in alcohol for a few hours. The samples were taken out and then dried in the air. At room temperature, the stock solution of the CaCl_2 and Na_2CO_3 reactants was prepared to a concentration of 0.05 mol/l, and all solvents were water.

Figure 1 is the flow chart of stone treatment experiment. Stone processing: Add a certain amount of PVP to saturated calcium chloride, stir to dissolve the surfactant concentration to 4 g/l, after 6 h of action, add the saturated calcium chloride containing the surfactant PVP dropwise to the washed stone, and it will naturally appear on the surface of the stone, and then add saturated sodium carbonate solution dropwise at a rate of 1 ml/min. A protective film of aragonite calcium carbonate is formed, and the film gradually thickens after repeated operations 5 times; Add a certain amount of PVA to saturated calcium chloride, stir and dissolve the surfactant at a concentration of 4 g/l, after 6 h of action, add saturated calcium chloride containing the surfactant PVA to the washed stone, flow naturally on the surface of the stone, and then add saturated sodium carbonate solution dropwise at a speed of 5 ml/min. A protective film of vaterite calcium carbonate is formed, and the film gradually thickens after repeated operations 5 times. All samples were dried under the same conditions for 24 hours. The untreated blank sandstone sample is denoted as B, the treatment of aragonite crystalline calcium carbonate is denoted as A, and the treatment of vaterite crystalline calcium carbonate is denoted as V.

2.3. Characterization of Stone Samples

Use the X-ray diffraction (XRD) (Rigaku, D/Max-3B, Tokyo, Japan) and Fourier Transform Infrared Absorption Spectroscopy (FTIR) to analyze the structure of power samples, and choose the Scanning Electron Microscope (SEM) (FEI), Nova Nano SEM 450, Hillsboro, OR, USA) to observe the surface microtopography. Use the contact angle measuring instrument (SDC-100, Dongguan City, Guangdong Province) to test the static contact angle of the sandstone surface.

2.4. Protection Performance of materials

In order to analyze the protective performance of the protection materials, according to the requirements of JC/T973-2005 [13], we have tested the water vapour permeability, the weather resistance, the water absorption of the sandstone surface before and after the treatment.

2.4.1. Test of Stone surface color change

After the cultural relics are processed, the surface cannot show obvious chromatic aberration changes destroying the integrity. In many cases, some color changes on the surface cannot be observed with the

naked eye, which need to be tested with the aid of an instrument. In this paper, WBD-1b digital whiteness meter is used to measure the total color difference to evaluate the color change. Compare the total color difference of stone samples before and after treatment, the calculation formula was as followed [14]:

$$\Delta E^* = \frac{\Delta E_1^* - \Delta E_0^*}{\Delta E_0^*} \times 100\% \quad (1)$$

The total color difference of the stone sample after treatment was, the total colour difference of the stone sample before treatment was, each sample shall be tested at least 5 times.

2.4.2. Test of Water Absorption

The water absorption means the changes of sandstone samples that have been immersed in the distilled water. On the detailed procedure of the experiment, first, weigh the stone samples as M_0 (g), and then immerse these samples in distilled water for 48 h; lastly, take out the samples and record their weight as M_1 (g). The calculation of the water absorption ΔM (%) is shown below:

$$\Delta M = \frac{M_1 - M_0}{M_0} \times 100\% \quad (2)$$

Counting every calculation of the samples data as a cycle, this experiment is repeated until the mass change rate is less than 0.1 %.

2.4.3. Test of Water Vapor Permeability

At first, pour a little water into a glass, put the sandstone samples at the top of the glass and seal the seam with glass glue. Then, record the initial weight as M_0 (g) and keep the system at room temperature for 24 h. Finally, record the final weight as M_1 (g). The calculation of the water vapor permeability of the samples is supported by the formula below:

$$\Delta M = M_0 - M_1 \quad (3)$$

Counting every calculation of the samples data as a cycle, this experiment is repeated until the mass change is less than 0.1 g.

2.4.4. Test of Weather Resistance

Figure 2 shows the weather resistance cycle steps. First record the initial weight of the sandstone sample as M_0 (g), soak the sample in 0.5 M Na_2SO_4 solution for 24 h, then wipe off the surface moisture, freeze it at -30°C for 6 h, take it out and place it at room temperature, and finally, put it in a vacuum drying oven, dry it at 60°C for 6 h, record the final weight as M_1 (g), use formula (2) to calculate the quality change of weather-resistant stone [15]. From the first cycle to the last cycle, the weathered appearance and quality loss of the aged sandstone samples are recorded until its surface begins to fall off.

2.4.5. Contact angle test

To test the contact angle of the sandstone surface, we use the contact angle meter (SDC-100) to test the static contact angle of the sandstone sample and select a water droplet with a volume of 5 μL to

measure it. The test result is obtained by taking an average of 5 measurements. According to the national standard [13], the wettability can be divided into the following grades, as shown in Table 1 [16]:

Table 1
Relationship between wettability and contact angle.

Grade	Static contact angle $\theta/^\circ$	Wetting effect
I	$\theta \leq 30^\circ$	Complete wetting
II	$30^\circ < \theta \leq 90^\circ$	Obvious wetting
III	$90^\circ < \theta \leq 110^\circ$	Slight wetting
IV	$110^\circ < \theta \leq 130^\circ$	Poor wetting
V	$\theta > 130^\circ$	Extreme wetting

3. Results

3.1. Chromatic aberration analysis

According to the protection principle of stone cultural relics, the surface of the stone before and after treatment shall not produce obvious color differences [17]. Therefore, we need to consider the influence of the reactant concentration and the number of coatings on the color difference of the sandstone surface. Figure 3 Variation curve of sandstone surface chromatic aberration with the concentration of reactants and the number of coatings. As the concentration of reactants increases, the rate of change of sandstone surface chromatic aberration is greater even if the number of coatings is the same, and as the number of coatings increases, the overall color difference change rate shows an upward trend. Due to the limited number of nanoparticles adsorbed on the surface of sandstone, the chromatic aberration will not change significantly with the increase of the number of layers and tends to be stable. Considering that the surface protection material of the stone sample must not only play a protective role, but also reduce the color difference, the concentration of precipitated calcium carbonate is selected as 0.05 mol/l in this work, and the number of coatings is 5 times.

3.2. Characterization and analysis of powder samples

In order to easily analyze the structure of materials, the structure of calcium carbonate powders, which were directly precipitated by the same precursor solutions instead of the film on the stone, was determined using XRD, IR and SEM.

3.2.1. X-ray Analysis

Figure 4 shows the XRD diffraction spectrum of calcium carbonate powder samples, as shown in the figure, $2\theta = 26.3^\circ, 27.3^\circ, 33.1^\circ, 36.3^\circ, 37.9^\circ, 38.5^\circ, 42.9^\circ, 45.9^\circ$ and 48.4° [18], which correspond to (111), (021), (012), (102), (112), (130), (122), (221) and (202) crystal planes of aragonite respectively. The sharp

peak shape and no miscellaneous peaks in the figure indicate the high crystallinity and the high crystal purity. The peak's shape corresponds with the PDF 76-0606. The characteristic peak of vaterite is located at $2\theta = 21.0^\circ, 25.0^\circ, 27.1^\circ, 32.8^\circ, 43.8^\circ, 49.1^\circ, 49.9^\circ$ and 55.7° [19], which correspond to (002), (100), (101), (102), (110), (112), (104) and (202) crystal planes of vaterite respectively. According to the Scherrer formula, it is shown that the half-height width of the diffraction peak is narrow, the average crystal grain size is small, the crystal purity is high, and there is no impurity peak. The peak shape corresponds to PDF 72-0506.

3.2.2. Fourier transform infrared absorption spectrum analysis

Figure 5 shows the infrared absorption spectrum of the calcium carbonate powder samples. We can observe that the characteristic absorption peaks belonging to the aragonite have strong absorption bands at 1082 cm^{-1} , 872 cm^{-1} , and 736 cm^{-1} , due to the stretching of carbonate (ν_1 model), the bending vibration out of the plane (ν_2 model) and the bending vibration in-plane bending vibration (ν_4 model) [20]. The infrared absorption spectra of three crystal forms of calcium carbonate contain the plane bending vibration (ν_2 mode), but their positions are different. The characteristic absorption peak of vaterite appears near 855 cm^{-1} , the plane bending vibration positions of aragonite and calcite are very close, and appear near 875 cm^{-1} [21]. The characteristic absorption peaks of vaterite are located at 1082 cm^{-1} , 854 cm^{-1} and 708 cm^{-1} respectively, they are caused by the bending vibration out of the plane, the symmetrical carbonate stretching and the bending of the aragonite in-plane, and the two curves have carbonate anti-symmetric stretching and shrinking vibration at 1492 cm^{-1} peak, which is consistent with XRD test results. There is no functional group related to the surfactant in the infrared absorption spectrum because it is taken away by deionized water during the washing process.

3.2.3. Scanning Electron Microscopic Analysis

Figure 6 shows the morphology of the calcium carbonate powder sample. According to Figure 6 (1), we can know that the aragonite crystal type calcium carbonate is rod-shaped and has a large aspect ratio, which is consistent with the literature [10]. We use the software Nano Measurer to calculate the particle size distribution in Figure 6 (1), according to the particle size distribution diagram, we can see that the average particle size of the aragonite crystal form is about 4 microns. The morphology of vaterite calcium carbonate in Figures 6 (2), and the small particle size leads to serious agglomeration. According to the particle size distribution diagram, the average particle size of the vaterite crystal form is about 46 nano. Irregular morphology may be caused by the rapid growth of a certain crystal plane or the influence of controlled formulations, which is consistent with literature records that the stretching of the surfactant PVA affects the nucleation rate and the crystal growth direction of calcium carbonate [12]. The average particle size of vaterite is smaller than that of aragonite.

3.3. X-ray diffraction analyses

Figure 7 shows the XRD pattern of the stone sample treated with calcium carbonate deposition. As shown in figure (1), $2\theta = 26.3^\circ, 27.3^\circ, 33.1^\circ, 45.9^\circ, 48.4^\circ$, which correspond to (111), (021), (012), (221)

and (202), crystal planes of aragonite respectively, and the peak shape corresponds to the card PDF 76-0606. As shown in figure (2), there are characteristic peaks of vaterite at $2\theta = 21.1^\circ, 24.9^\circ, 27.1^\circ, 32.8^\circ, 43.9^\circ$, and 50.2° , corresponding to (002), (100), (101), (102), (110), (104) crystal planes, and the peak shape corresponds to the card PDF 72-0506. There are characteristic peaks of silica at $2\theta = 20.9^\circ, 26.7^\circ, 36.6^\circ, 42.5^\circ, 60.1^\circ, 68.2^\circ$, corresponding to (100), (011), (110), (200), (21-1), (21-2) crystal planes, the peak-shaped card corresponds to PDF 85-1054. In the stone samples, the peak content of calcium carbonate is less, and the peak of the stone substrate is stronger, indicating that the protective film of calcium carbonate formed may be weak.

3.4. Scanning Electron Microscopic Analysis

Figure 8 shows the surface morphology of the stone samples. As it is shown in Figures (a), the blank stone samples have a rough surface and high porosity. By observing Figure (b), it can be seen that the surface porosity of the stone sample treated with aragonite calcium carbonate is reduced, but a large number of cracks are generated. This is due to the large particle size of aragonite calcium carbonate, uneven distribution during the reaction process, the large pores on the surface of the stone cannot be filled, and a uniform and dense film cannot be formed. The surface of the stone sample treated with vaterite is uniform and dense without cracks as shown in Figure (c). According to the particle size distribution results, it can be proved that it is because the vaterite has a small particle size that it can fill up the pores on the stone surface during the reaction process and reduce the porosity, so the formed film is relatively uniform and dense.

3.5. Wettability

The wettability of the stone sample surface is evaluated by the static contact angle, the water absorption and the air permeability. The surface contact angle of the stone sample is shown in Figure 9. The static contact angle of sample B is 28° , the static contact angle of sample A is 18° , and the static contact angle of sample V is 13° . According to Table 1, the surfaces of the samples are all of the easily wettable types. After our treatment, the contact angle of the sandstone sample surface decreased, and the hydrophilicity increased. There are two reasons for the decrease in the contact angle of the sandstone surface: the first is that the calcium carbonate particles are on the sandstone surface, increasing the surface roughness of the hydrophilic stone and improving the surface hydrophilicity; the second is that calcium carbonate deposited on the surface of sandstone produces a large number of hydrophilic hydroxyl groups in the aqueous solution, which is easy to attract water molecules [22].

3.6. Water absorption analysis

According to the change of the water absorption rate shown in Figure 10, the water absorption rate of the stone sample changes very quickly within 48 hours of soaking in the first stage. The water absorption rate of the blank stone sample is as high as 3.6%, the water absorption rate of the sample treated with aragonite calcium carbonate is 3.4%, which is close to that of the blank stone sample, while the water absorption rate of the stone sample treated with vaterite is only 1.6%, which is lower than the half of the blank stone sample. The second stage of the change in water absorption is from 48 hours to 336 hours.

In this stage, the rate of change in water absorption slows down. The third stage is to soak for 336 hours to 432 hours, the water absorption rate gradually tends to be constant at this stage, and the water absorption reaches saturation.

It can be seen that the water absorption rate changes very slightly until the water absorption reaches saturation in the second stage. The water absorption rate of the blank stone sample only increases by 0.9%, the water absorption rate of the sample treated with aragonite increases by 0.7%, and the water absorption rate of the stone sample treated with vaterite increases by 0.4%. It shows that the water absorption rate of stone samples can reach the maximum after soaking for 48 hours. According to the water absorption test results, both materials have a protective effect, effectively reducing water absorption. However, sample V has the lowest water absorption rate. According to the analysis of the average particle size in Figure 6 (2) and the surface morphology Figure 8 (c), it can be seen that the small average particle size effectively reduces the porosity, and the formed film is dense and uniform, which hinders the water molecules enter the interior of the stone. Therefore, the water absorption is the lowest.

3.7. Water vapour permeability analysis

Figure 11 shows the change in water vapour permeability. Generally speaking, the Blank sample has the best air permeability, followed by sample A, and sample V has the worst air permeability, indicating that the larger the pores are, the better the air permeability is [14]. This confirms that vaterite calcium carbonate greatly reduces the porosity of the stone sample, resulting in poor air permeability. However, observing the entire change process, it is found that the difference of the three curves is not very large, with the increase of the number of cycles, the changes of the three curves are the same, and the mass change is less than 0.1 g, and the overall fluctuation is very small, indicating that two materials will not affect the water vapour in and out of the stone and do not affect the respiration of the stone.

3.8. Weather Resistance

The sandstone is outdoors for a long time, and its surface has large pores, so it is easily corroded by the soluble salt. To explore the feasibility of protecting materials, it is necessary to conduct weather resistance tests on the treated stone samples. Sodium sulfate is one of the most destructive and ubiquitous salts insoluble salts. We choose it as the soluble salt in this experiment for the weather resistance test [23]. The results of the weathering resistance test are shown in Figure 12 and figure 13.

For the blank sandstone in Figure 12 (a), the appearance of the three parallel samples began to weather after the 5th cycle, and a large area began to fall off after the 20th cycle, and the quality curve dropped significantly. For the sandstone treated with aragonite stone in Figure 12 (b), the surfaces of the three parallel specimens began to pulverize after the 10th cycle, and a large area fell off after the 20th cycle. Figure 12 (c) shows that after the vaterite treatment, the surface appearance and quality of the three parallel samples hardly changed significantly. The quality of the first few cycles of the quality change curve of all samples shows an upward trend, which is consistent with the viewpoint of the literature [15]. By comparing the mass change curve in Figure 13, it can be seen that the change of sample V is the smallest, indicating that the soluble salt content in sample V is the smallest. Combining the average

particle size of vaterite calcium carbonate as shown in Figure 6 (2) and the analysis of the deposition on the sandstone surface as shown in Figure 8 (c), due to its small average particle size, the thin film formed on the sandstone surface is dense and uniform. Not only can the porosity be reduced, but also the entry of water molecules and soluble salts can be prevented, thereby improving the protective effect.

4. Conclusion

We use different surfactants to control the crystallization process of calcium carbonate and deposit different crystals form calcium carbonate protective coating materials on the surface of the sandstone. The synthesis method of calcium carbonate deposition protection material is simple, easy to control, and low cost. The test results prove that when the concentration of the reactant is 0.05 mol/l and the number of coatings is 5, the appearance of the stone material will not be affected. The protective effect of the calcium carbonate film has passed the water absorption, air permeability and weather resistance tests. The results show that the performance of the vaterite calcium carbonate coating is the best, because its average particle size is smaller than other crystal types, and the film formed on the stone surface is more dense and uniform. Under the premise of little change in air permeability, the water absorption rate is reduced by 0.5 times, and the weather resistance is increased by 4 times. Effectively hinder the erosion of water and soluble salts. Therefore, the application of nanostructured coatings in the protection of stone cultural relics provides a new direction for development.

Declarations

Author Contributions: P.Y.W., L.H.Q., H.S. and Q.L. conceived and designed the experiment. P.Y.W. analyzed the experimental results and performance; P.Y.W. and wrote this paper. All authors have read and agreed to the published version of the manuscript.

Acknowledgements: This study was supported by the science and technology project of the national achieves administration of china (2021B03, 2021B04) and the construction project in the innovation team of philosophy and social sciences of Yunnan (No. 2021CX05), and the open project of Gansu Provincial Research Center for Conservation of Dun hang Cultural Heritage (GDW2021YB03). We would like to thank Hu Sha, School of Foreign Languages, Yunnan University, for his help in writing the thesis.

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Figures

Figure 1

Flow chart of stone treatment experiment.

Figure 2

Weather resistance cycle steps.

Figure 3

The color difference of the sandstone surface varies with the concentration of reactants and the number of coatings.

Figure 4

XRD diffraction spectrum of calcium carbonate powder samples, (1) is aragonite, and (2) is vaterite.

Figure 5

The infrared absorption spectrum of the calcium carbonate powder samples, (1) is aragonite, and (2) is vaterite.

Figure 6

Morphology of the calcium carbonate powder sample, (1) is aragonite, and (2) is vaterite.

Figure 7

The XRD pattern of the processed stone sample, (1) is an aragonite treated sample, and (2) is vaterite treated sample, ▲—Aragonite, ●—Vaterite, ◻—Silica.

Figure 8

The surface morphology of the stone samples, (a) is a blank stone sample, and (b) is an aragonite treated sample, and (c) is a vaterite treated sample.

Figure 9

The contact angle of a stone sample surface, B is a blank stone sample, and A is aragonite treated sample, and V is a vaterite treated sample.

Figure 10

Water absorption curve, B is a blank stone sample, and A is aragonite treated sample, and V is vaterite treated sample.

Figure 11

Water Vapor Permeability curve, B is a blank stone sample, and A is aragonite treated sample, and V is a vaterite treated sample.

Figure 12

The change of mass and surface morphology for the sandstones during Na₂SO₄ SLHA cycles, (a) Three parallel samples (B1-B3) are untreated blank sandstone samples, and (b) three parallel samples (A1-A3) are sandstone samples treated with aragonite calcium carbonate, and (c) three parallel samples (V1)-V3) are sandstone samples treated with vaterite calcium carbonate.

Figure 13

Mass change curve, B is a blank stone sample, and A is aragonite treated sample, and V is a vaterite treated sample.