

RESEARCH

Open Access



A comparative study between aqueous and methanol solutions of barium hydroxide: implications for applying barium protectants in gypsification calcareous relics

Jingchen Yan¹, Guang Huang², Xiangnan Li¹, Qing Liu¹, Yan Liu¹, Fuwei Yang^{1*}, Kun Zhang¹ and Yichen Sun¹

Abstract

Gypsification is a common problem in weathered calcareous relics. In previous studies, the solutions of barium hydroxide in water and methanol were used as protectants for gypsification calcareous relics and showed significant differences in permeability. In this study, the underlying reasons for permeability differences between these two solutions were investigated using optical microscopy, ultraviolet–visible spectrophotometry, X-ray diffractometry, Fourier transform infrared spectroscopy, the phenolphthalein test and physical property characterizations. The results indicated that the permeability differences were primarily caused by the solutions' reactivity. Specifically, owing to the high reactivity of barium hydroxide in water, it reacted rapidly with atmospheric CO₂ and gypsum (the weathering product) to generate barium carbonate, barium sulfate and calcium hydroxide precipitates. These precipitates hindered the penetration of solution into weathered relics. In contrast, barium hydroxide in methanol did not react with atmospheric CO₂ or weathered relics, which also kept the solution in a liquid state during the infiltration process. Therefore, the solution of barium hydroxide in methanol exhibited high permeability. Based on the above findings, this study is meaningful for applying barium protectants in the conservation of gypsification calcareous relics.

Keywords Barium hydroxide, Methanol, Gypsification, Relic, Permeability

Introduction

Gypsification is a common problem observed in calcareous relics, such as murals, stone carvings and ancient architectural mortar [1–3]. Essentially, it is a process of forming gypsum (CaSO₄·2H₂O) through the interaction between calcium carbonate and sulfur-containing

pollutants [1]. The gypsum in calcareous relics is more susceptible to erosion by rainwater due to its porous mineral structure and higher solubility ($K_{sp} = 3.14 \times 10^{-5}$) [1, 4, 5]. Additionally, the dissolution, migration and recrystallization of gypsum create crystalline pressure within relics, which also accelerates the deterioration process [6–8]. Consequently, the conservation of gypsification calcareous relics has been a research focus and a global challenge.

Theoretically, the transformation of soluble gypsum into insoluble barium sulfate in situ, facilitated by the reaction between barium hydroxide and calcium sulfate, is considered as an effective protective measure. This method not only prevents the erosion of gypsification calcareous relics but also preserves their surface patterns and information. Therefore, since the nineteenth century,

*Correspondence:

Fuwei Yang
yangfuwei@nww.edu.cn

¹ China-Central Asia “the Belt and Road” Joint Laboratory on Human and Environment Research, Key Laboratory of Cultural Heritage Research and Conservation, School of Cultural Heritage, Northwest University, Xi'an 710127, People's Republic of China

² Sino-Portugal Belt and Road Joint Laboratory on Science of Cultural Heritage Conservation, City University of Macau, Macau 999078, People's Republic of China



© The Author(s) 2024. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>. The Creative Commons Public Domain Dedication waiver (<http://creativecommons.org/publicdomain/zero/1.0/>) applies to the data made available in this article, unless otherwise stated in a credit line to the data.

the solution of barium hydroxide in water (BW) has been used in reinforcement experiments, yet its effectiveness remains controversial [9]. In 1960s, the barium hydroxide method was developed for the protection of gypsification murals [1, 10]. This method involved two successive steps: desulfurization and reinforcement. Specifically, ammonium carbonate solution was applied to convert gypsum into calcium carbonate and ammonium sulfate at first. The highly soluble ammonium sulfate could be removed by paper pulp method. Subsequently, the BW solution was applied as the consolidant, and meanwhile, it could consume the remanent ammonium carbonate and ammonium sulfate. The results indicated that the barium hydroxide method not only exhibited excellent reinforcement effects but also transformed the weathered gypsum layer in situ, concurrently preserving historical and cultural information on the surface of relics. Afterward, Toniolo et al. employed the BW solution to reinforce Italy's renowned Arch of Peace, but the barium element primarily existed as barium sulfate on the weathered limestone surface [11]. It implied that, in weathered limestone, the BW solution had low permeability and could not achieve internal reinforcement. Rodrigues et al. used the BW solution to protect limestone and lime mortar with varying porosities [12, 13]. They observed that the penetration depth of BW solution in limestone was less than 1 mm, while in lime mortar, it reached 5 mm. The aforementioned studies confirmed that the permeability of BW solution was significant in murals with thin gypsum layers and loose-textured lime mortar, but less effective in dense-textured limestone with thick gypsum layers. To tackle this challenge, Lu et al. from our group firstly utilized the solution of barium hydroxide in methanol (BM) to reinforce gypsification limestone [1]. Their findings demonstrated that the BM solution achieved a penetration depth of 3 mm in weathered limestone, in contrast to the BW solution whose penetration depth reached only 0.3 mm. To expedite carbonation and enhance reinforcement efficacy, Lu et al. introduced urea as a carbon source into the BM solution [2]. This modification resulted in a reduction of the carbonation time to 1 week, a 7.2-fold increase in erosion resistance, and the maintenance of a 3mm penetration depth. Lu et al.'s studies showed that the BM solution, using methanol as a solvent, exhibited exceptional permeability in gypsification limestone and met the protective requirements of limestone relics.

The above studies highlighted significant permeability differences between BW and BM solutions as protectants, especially for protecting dense-textured limestone with thick gypsum layers. In conservation practices, both BW and BM solutions inevitably contact with air and weathered limestone mainly composed of gypsum

and marble. Therefore, it's highly possible that the permeability may be closely related to the kinetic stability of the solutions in the air and the reaction characteristics between the solutions and weathered limestone, yet the underlying reasons remain unclear. To explore these issues, this study comparatively investigated the kinetic stability of BW and BM solutions in the air, as well as their reaction characteristics and penetration effects in gypsum and marble. To some extent, the results offered guidance for applying barium protectants of gypsification calcareous relics.

Materials and methods

Materials

Methanol, barium hydroxide, phenolphthalein and calcium sulfate were purchased from Sinopharm Group Co., Ltd., Shanghai, China. All chemicals were of analytical grade and used without further purification. Marble composed of CaCO_3 (Fig. 10a) was obtained from the local stone market.

The kinetic stability of solutions during air exposure

The BW and BM solutions (37.00 g/L) were poured into separate open culture dishes, each with a diameter of 5.00 cm and marked with a blue numeric label (1 or 3) at the bottom, ensuring that the solutions could completely cover the bottoms of culture dishes. Then, the culture dishes were positioned directly under the optical microscope (30 \times , 4800, Xinlun Technology Co., Ltd., China) to enable the solutions to undergo natural carbonation in the ambient air (25 °C, relative humidity: 56%), while capturing images of the solution's surface film at different times (0, 1, 3 and 120 min). The film-forming speed of the solutions in the air was compared by observing the states of the solutions' surface films and the clarity of the numeric labels.

The BW and BM solutions (60 mL) with different concentrations (12.30, 24.70 and 37.00 g/L) were separately placed in cylindrical open plastic cups with a diameter of 9.00 cm, allowing the solutions to naturally carbonate in the ambient air (25 °C, relative humidity: 56%). Subsequently, the absorbance of the solutions at 600 nm was measured at fixed time intervals using a ultraviolet–visible spectrophotometer (UV-1700, Shimadzu, Japan) [14–17]. Right before analysis, the solutions were subjected to 5 min ultrasonic bath (200 W, KQ5200E, Kunshan Ultrasonic Instrument Co., Ltd., China). The ABS values of the solutions were then calculated according to Eq. (1):

$$\text{ABS} = \frac{A_t - A_0}{A_0} \quad (1)$$

where A_t represented the absorbance of the solution at time t , and A_0 was the initial absorbance of the solution.

The experiment was conducted with an average of 3 measurements under different concentrations. A higher ABS value indicated a less stable solution.

After 120 min, the remaining BW solution underwent centrifugation. The resulting precipitate was washed with distilled water, dried at 80 °C for 6h and weighed in sequence. The precipitate concentration was confirmed based on an average of 3 repeated experiments, and the carbonation rate of BW solution was then calculated using this average. Afterward, the crystalline characteristics of the precipitate were determined using X-ray diffractometry (XRD). XRD measurements were carried out on the sample on a Rigaku Smartlab rotating target X-ray diffractometer (scanning range $5^\circ < 2\theta < 90^\circ$, step length 0.01°), using Cu K α radiation (40 kV, 150 mA), a high resolution graphite monochromator, a rotating sample holder and a proportional detector. The crystal composition of the sample was confirmed by comparing it with the standard map.

Reaction characteristics between solutions and weathered limestone

Reaction characteristics between solutions and gypsum

Calcium sulfate and distilled water were mixed in a 5:3 ratio, subsequently dried and molded, which produced gypsum blocks composed of CaSO₄·2H₂O (Fig. 5a). Following that, BW and BM solutions (37.00 g/L) were separately applied to the surfaces of the gypsum blocks, with real-time analyses of their crystalline characteristics and infrared spectra (FTIR) being performed. FTIR in transmission mode was performed using a TENSOR 27 Spectrometer (Bruker, Germany). The samples were ground into fine powder and subsequently analyzed as KBr pellets (wavenumber 4000–500 cm⁻¹, resolution 4 cm⁻¹, 40 scans). For XRD and FTIR analyses, the gypsum block was vertically fractured along the middle of the dripping surface. The entire cross-section was then sanded using sandpaper to obtain the powder sample for testing.

Reaction characteristics between solutions and marble

The BW and BM solutions (37.00 g/L) were separately dropped onto the surfaces of the marble blocks. After that, the crystallization characteristics and infrared spectra of the treated blocks were measured in real-time. The sampling and analysis methods for marble blocks were consistent with Section “Reaction characteristics between solutions and gypsum”.

Permeability experiments of solutions [1]

The BW and BM solutions with varying concentrations (12.30, 24.70 and 37.00 g/L) were respectively infiltrated into gypsum and marble blocks, until they could no longer be absorbed. To avoid the carbonation of

barium hydroxide in the air, phenolphthalein solution was brushed on the cross sections of the treated blocks immediately after the blocks were cut open. The penetration depth was calculated as the mean of 3 tests per treatment.

Physical property characterizations

The BW and BM solutions (37.00 g/L) were respectively infiltrated into gypsum and marble blocks, until they could no longer be absorbed. Then, the sufficient water was provided to the blocks treated with BM solution by surface drip-permeance. All blocks were further cured in the ambient air (25 °C, relative humidity: 56%) for 1 month prior to various tests. Capillary water absorption and open porosity of the blocks before and after treatment were determined by an electronic density tester (MZ-C300, Mayzun, Shenzhen, China). Surface hardness of the blocks before and after treatment was measured using a shore D durometer (LX-D-1, Dongguan SanLiang measuring tools Co., Ltd., Dongguan, China). Average values were based on at least 3 repeated experiments per testing condition.

Results and discussion

The kinetic stability of solutions during air exposure

As shown in Fig. 1, initially, BW and BM solutions were colorless and transparent, and the numbers (1 and 3) at the bottoms of culture dishes were clearly visible. A film formed on the surface of BW solution after 1 min, causing the blurring of the number 3. At the same time, the surface of BM solution remained unaltered, with numeral 1 preserving its clarity. The surface film of BW solution thickened after 3 min, which further exacerbated the blurring of the number 3. Following a 120 min duration, the surface film of BW solution fully covered the number 3, while the surface of BM solution remained film-free and the clarity of the number 1 persisted. This film-forming experiment showed a significant difference

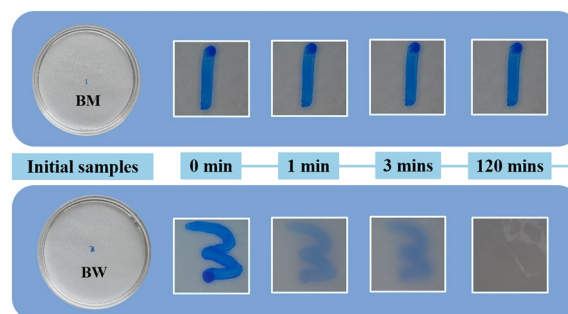


Fig. 1 Images depicting the surface films of BM (1) and BW (3) solutions during air exposure

in reactivity between BW and BM solutions during air exposure. The BW solution exhibited high reactivity and a rapid film-forming speed (1 min), whereas the BM solution remained stable even after prolonged exposure to air (120 min).

Figure 2 illustrated the varying ABS values of BW and BM solutions with different concentrations during air exposure. The ABS values of BW solutions showed a continuous increase in relation to exposure time, with the increase being particularly pronounced at higher concentrations. After 120 min, the ABS values of BW solutions were 4.91, 5.08 and 5.25, respectively. This phenomenon arose from the fact that extended exposure times coupled with increased solution concentrations led to the formation of more precipitates within the solution, which contributed to heightened absorbance. As depicted in Fig. 3, the XRD pattern indicated that the precipitate in BW solution was identified as BaCO₃ (PDF-99-0108, 2θ=19.57, 24.02, 27.79, 29.83, 33.24, 34.23, 39.32, 42.17, 44.83, 46.92). This implied that the BW solution rapidly reacted with atmospheric CO₂ to form barium carbonate which in turn increased the solution’s turbidity and absorbance, thereby leading to its instability in the air. The reaction process was shown in Eq. (2).



In conservation practices, the preparation, storage and utilization of BW solution inevitably expose it to air. As a result, barium carbonate generated in these processes can block the surface and internal pores of weathered samples, which reduces the solution’s permeability. 120 min later, the ABS values of BM solutions were 0.30,

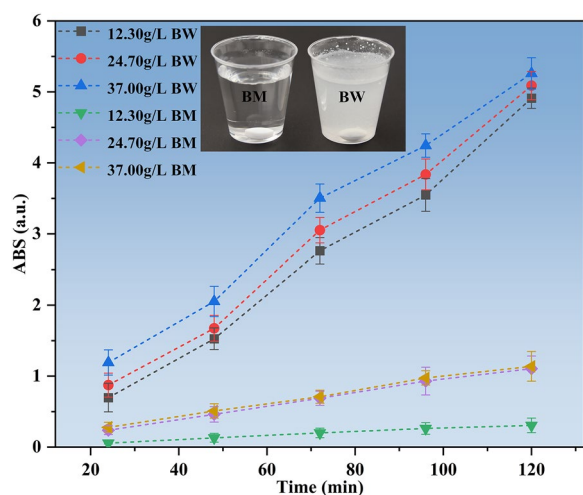


Fig. 2 ABS values for BW and BM solutions at different times. The inset: a photograph of the solutions after 120 min of air exposure

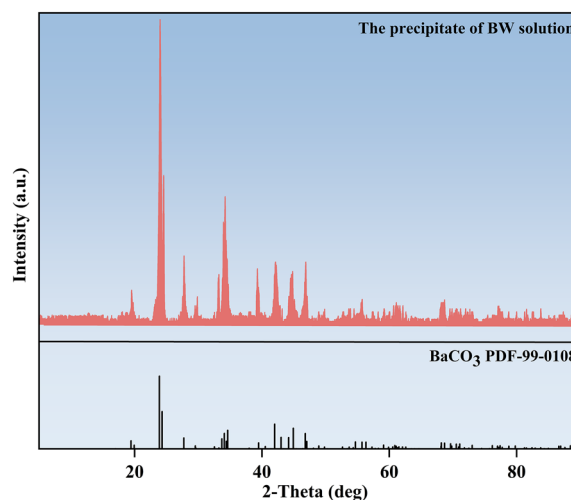


Fig. 3 The XRD pattern of the precipitate from BW solution

1.10 and 1.13, respectively. The increase in absorbance was much lower than that of BW solution, and no precipitate was observed in BM solution. The smaller increase in absorbance might be attributed to the higher concentration caused by solvent evaporation. This phenomenon also indicated that the BM solution did not react with atmospheric CO₂ and was relatively stable in the air. The inset in Fig. 2 depicted the actual appearance of BW and BM solutions exposed to air for 120 min. It was evident that after prolonged exposure, the BM solution remained clear and transparent, while the BW solution transformed into a cloudy suspension. In summary, the BM solution exhibited higher kinetic stability in the air compared to the BW solution, and the stability period of 120 min fully met the preservation requirements [14].

Figure 4 revealed that the barium carbonate yield of BW solution increased from 0.0011 to 0.0022 g/mL with the increase of concentration from 12.30 to 37.00 g/L

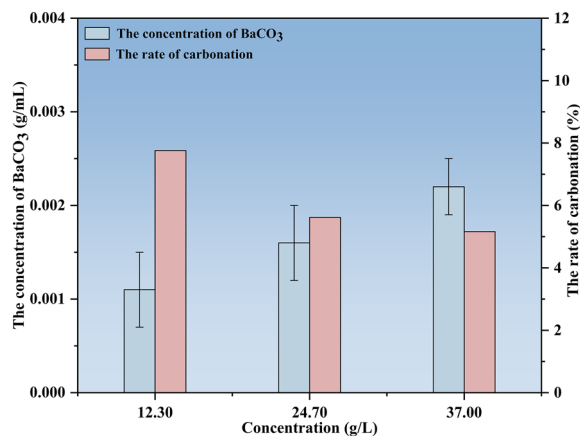


Fig. 4 Barium carbonate yield and carbonation rate of BW solution

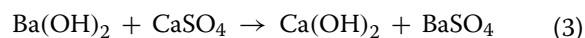
after 120 min of air exposure. The reason was that, under a constant gas–liquid interface, an increase in concentration led to more participation of Ba^{2+} in the reaction, thereby generating more barium carbonate. Conversely, the carbonation rates (7.76%, 5.62% and 5.16%) decreased as the concentration increased. This was attributed to the fact that the carbonation reaction of Ba^{2+} primarily occurred at the gas–liquid interface where the precipitated barium carbonate impeded the carbonation of the remaining Ba^{2+} . More barium carbonate was generated at the gas–liquid interface as the concentration rose, which further hindered the carbonation. Therefore, the higher concentration meant the lower carbonation rate. In practical applications, a larger surface area and higher permeability of weathered samples facilitate greater exposure of solutions to air, which results in higher carbonation rates and degrees than those observed in the current experiment.

Reaction characteristics between solutions and weathered limestone

Reaction characteristics between solutions and gypsum

According to Fig. 5, barium sulfate (PDF-76-0213, $2\theta=23.10, 25.13, 26.11, 27.15, 31.82, 33.08$) and calcium hydroxide (PDF-76-0570, $2\theta=18.34, 29.10, 34.35$) were detected just 5 min after dripping the BW solution onto the gypsum block (PDF-70-0982, $2\theta=11.82, 20.89, 23.57, 28.28, 29.28, 31.27, 32.26, 33.54, 34.74, 36.14, 36.81$). As the reaction time was extended to 10 min, the peak area changes were tiny for calcium hydroxide and barium sulfate. The integrated peak areas for calcium hydroxide were 41.49 and 40.84 at different reaction times, with a difference ratio of 1.59%. For barium sulfate, the integrated peak areas were 80.65 and 79.16, with a difference

ratio of 1.88%. The difference ratios for both substances were within 2%, indicating that the reaction between barium hydroxide and calcium sulfate was essentially finished within 5 min. Based on the findings in Section "The kinetic stability of solutions during air exposure", the BW solution reacted with atmospheric CO_2 to generate barium carbonate within 1 min. However, barium carbonate was not detected in the reaction system. This is because barium ions in water preferentially react with sulfate ions, and only trace amounts of barium ions at the gas–liquid interface can be carbonated. As a result, the resulting barium carbonate cannot reach the detection limit of the instrument. These results indicated that the reaction mechanism among BW solution, atmospheric CO_2 and gypsum conformed to Eqs. (2) and (3).



It is well known that the solubilities of barium carbonate ($K_{\text{sp}}=2.58 \times 10^{-9}$), barium sulfate ($K_{\text{sp}}=1.08 \times 10^{-10}$) and calcium carbonate ($K_{\text{sp}}=3.36 \times 10^{-9}$) are much lower than that of gypsum ($K_{\text{sp}}=3.14 \times 10^{-5}$) [1, 2]. Barium carbonate, barium sulfate and calcium carbonate generated after the carbonation of calcium hydroxide can reinforce and protect gypsification calcareous relics. Nevertheless, these precipitates formed prematurely hinder the permeation of BW solution, as shown in Fig. 6. Once the BW solution, carbon dioxide and gypsum come into contact, precipitates of barium carbonate, barium sulfate and calcium hydroxide are rapidly generated at the contact surface. These precipitates aggregate into a film at the contact surface, which blocks both surface and internal micropores and cracks of the gypsum block, thereby impeding the penetration of BW solution into gypsum. Additionally, the hindrance effect of precipitates causes a significant accumulation of BW solution on the superficial surface of gypsification relics. After solvent evaporation, a large amount of white powder deposits on the relic surface (a phenomenon known as "back migration"), severely destroying the appearance of relics [18]. Hence, the BW solution is only suitable for the conservation of relics such as wall paintings with thin gypsum layers and lime mortar with loose and porous texture. Its penetration effect is not ideal for dense-textured limestone relics with thick gypsum layers.

XRD results of the gypsum blocks before and after treatment with BM solution were shown in Fig. 7. It was observed that after 40 min of dropping BM solution onto the gypsum surface, only the peaks of gypsum were detected. This phenomenon arises from the incapacity of reactants to dissociate within organic systems employing methanol as the solvent, thereby precluding ion reactions. Consequently, compounds such as barium sulfate,

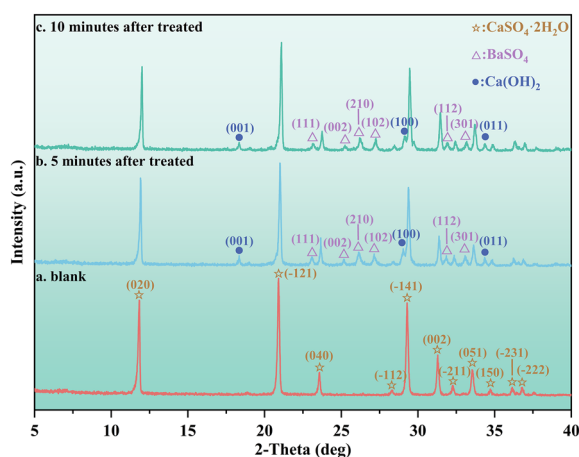


Fig. 5 XRD results of the gypsum blocks before and after treatment with BW solution

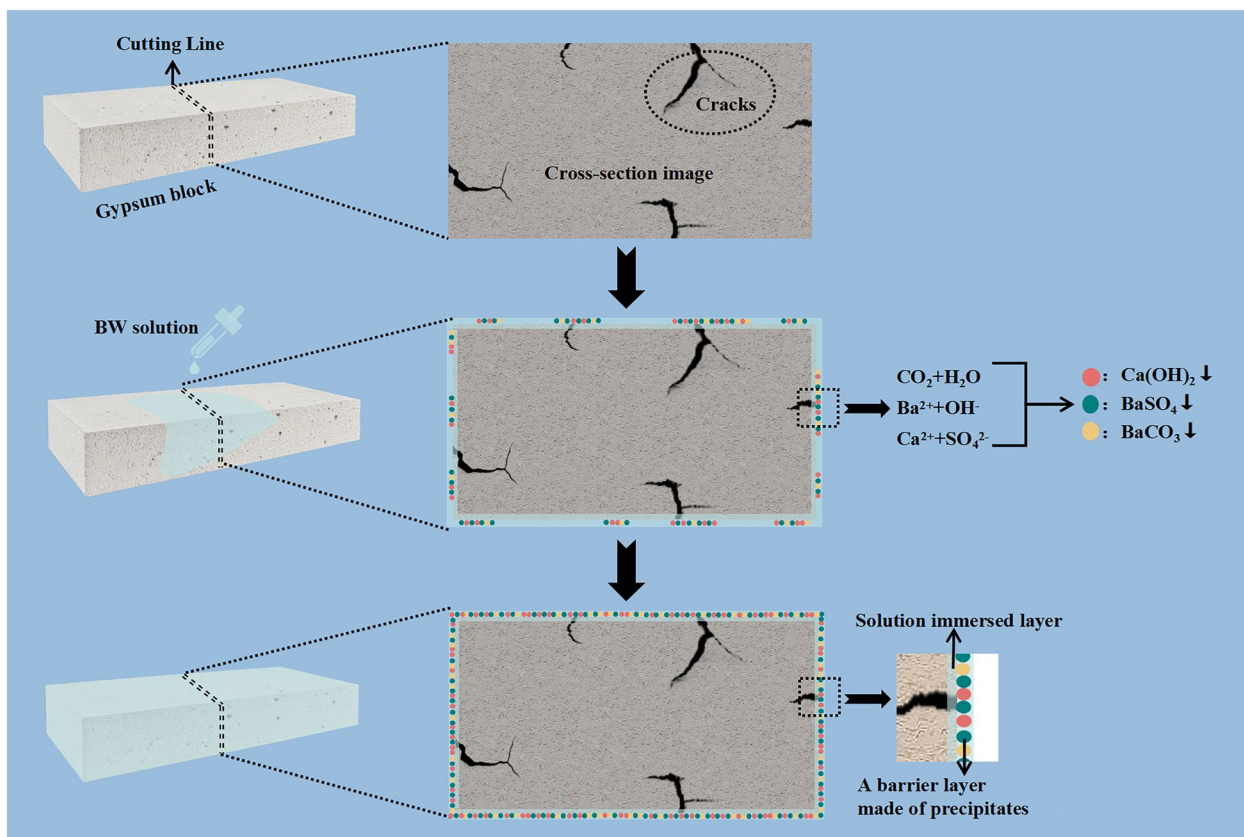


Fig. 6 The reaction and infiltration processes of BW solution in gypsum

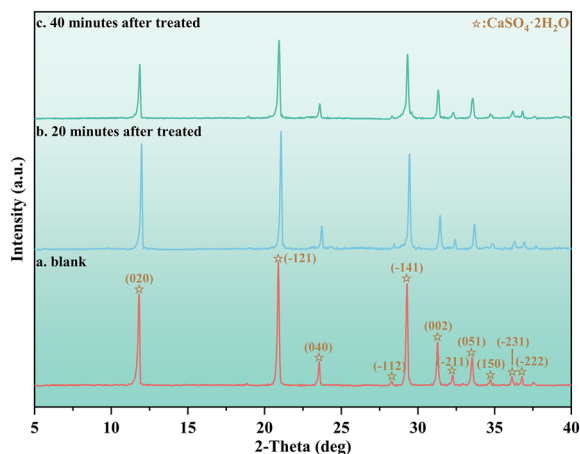


Fig. 7 XRD results of the gypsum blocks before and after treatment with BM solution

calcium hydroxide and barium carbonate were absent within the system. Furthermore, Starikova et al. found that barium hydroxide transformed into a complex in methanol, $[\text{Ba(OH)}_2(\text{MeOH})_2](\text{MeOH})$, where Me represented a methyl group [19]. The coordination effect made

barium hydroxide an amorphous compound. Therefore, the characteristic peaks of barium hydroxide were not detected. As shown in Fig. 8, when the BM solution drips onto the gypsum block, it does not react with gypsum or atmospheric CO_2 and remains in a liquid state. Without the hindrance effect of precipitates, the BM solution is able to effectively penetrate the interior of gypsum. As methanol evaporates, barium hydroxide physically adsorbs inside the gypsum block (confirmed later in FTIR results), and only reacts with calcium sulfate and atmospheric CO_2 when a sufficient amount of water is provided. In summary, this stepwise reaction enables the BM solution to penetrate the interior of gypsum and eliminates the phenomenon of "back migration".

Figure 9 showed FTIR spectra of gypsum (a), the dried sample of BM solution (b) and gypsum treated with BM solution (c). In Fig. 9b, the peaks at 3390 and 3580 cm^{-1} represented the characteristic peaks of OH [19, 20]. The broad peak at 2860 cm^{-1} corresponded to the C–H stretching vibration in CH_3 , and 1420 cm^{-1} was attributed to the deformation vibration of CH_3 [21]. The peaks at 1120 , 990 , 860 and 746 cm^{-1} resulted from C–O stretching vibrations [20]. The signal at 590 cm^{-1} was assigned to the Ba–O bond [20]. The FTIR results that

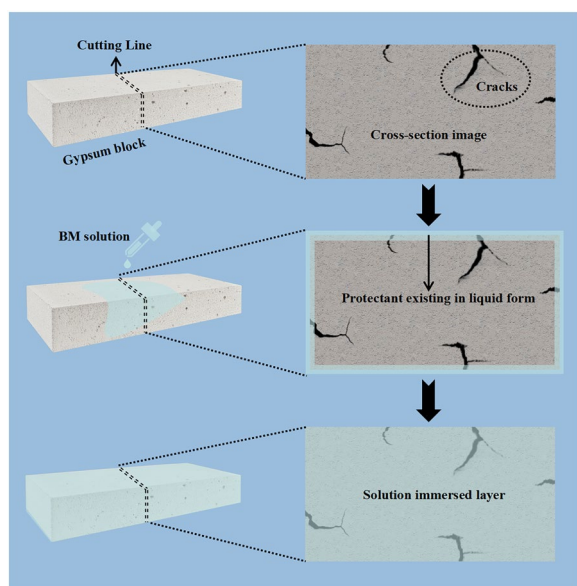


Fig. 8 The infiltration process of BM solution in gypsum

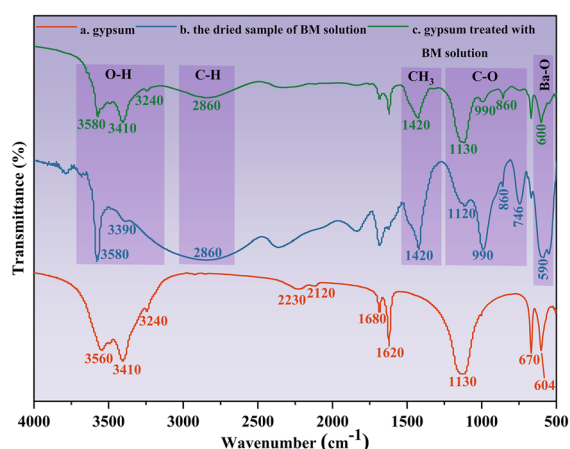


Fig. 9 FTIR results of gypsum (a), the dried sample of BM solution (b) and gypsum treated with BM solution (c)

indicated the presence of $[\text{Ba}(\text{OH})_2(\text{MeOH})_2](\text{MeOH})$ were consistent with Starikova’s findings [19]. FTIR results of the treated gypsum were shown in Fig. 9c. The peaks at 3240, 3410 and 3580 cm^{-1} arose from the coincidence of OH peaks in $[\text{Ba}(\text{OH})_2(\text{MeOH})_2](\text{MeOH})$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The broad peak at 2860 cm^{-1} corresponded to the C–H stretching vibration of CH_3 , and 1420 cm^{-1} was attributed to the deformation vibration of CH_3 [21]. The peak at 1130 cm^{-1} resulted from the overlap between the C–O stretching vibration (1120 cm^{-1}) in methanol and the 1130 cm^{-1} peak of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the peaks at 990 and 860 cm^{-1} were also C–O stretching vibrations

[20]. The peak at 600 cm^{-1} represented the Ba–O stretching vibration [20]. Therefore, the treated gypsum also displayed the characteristic peaks of $[\text{Ba}(\text{OH})_2(\text{MeOH})_2](\text{MeOH})$. Combined with the XRD results in Fig. 7, it was found that the BM solution did not react with gypsum. Instead, it was physically adsorbed within the gypsum block as methanol evaporated.

Reaction characteristics between solutions and marble

As shown in Fig. 10, the peaks of barium carbonate (PDF-71-2394, $2\theta=24.37, 28.07, 34.66, 42.46, 45.28$) were detected just 5 min after dripping the BW solution onto the marble block (PDF-88-1807, $2\theta=23.19, 29.53, 31.71, 36.11, 39.53, 43.29, 47.26, 47.63, 48.63, 56.70, 57.53$), and the carbonation of BW solution continued thereafter. This phenomenon indicated that the BW solution did not react with marble. Instead, it rapidly reacted with atmospheric CO_2 , which was consistent with the kinetic stability results in Section "The kinetic stability of solutions during air exposure" (Eq. (2)). The reaction and penetration processes of BW solution in marble were depicted in Fig. 11. Although the BW solution does not react with marble, it can be rapidly carbonated by atmospheric CO_2 . The resulting barium carbonate aggregates into a film at the contact surface, which blocks both surface and internal micropores and cracks of marble, thereby impeding the penetration of BW solution into marble. In Fig. 12, the results showed that after 40 min of dropping BM solution onto the marble surface, only the peaks of calcium carbonate were detected. This suggested that the BM solution did not react with marble or atmospheric CO_2 . The reason is that reactants are unable to dissociate in organic systems that employ methanol as the solvent, leading to the fact that ion reactions are

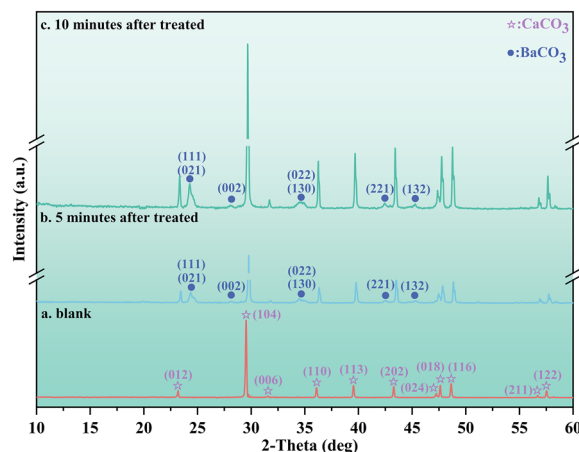


Fig. 10 XRD results of the marble blocks before and after treatment with BW solution

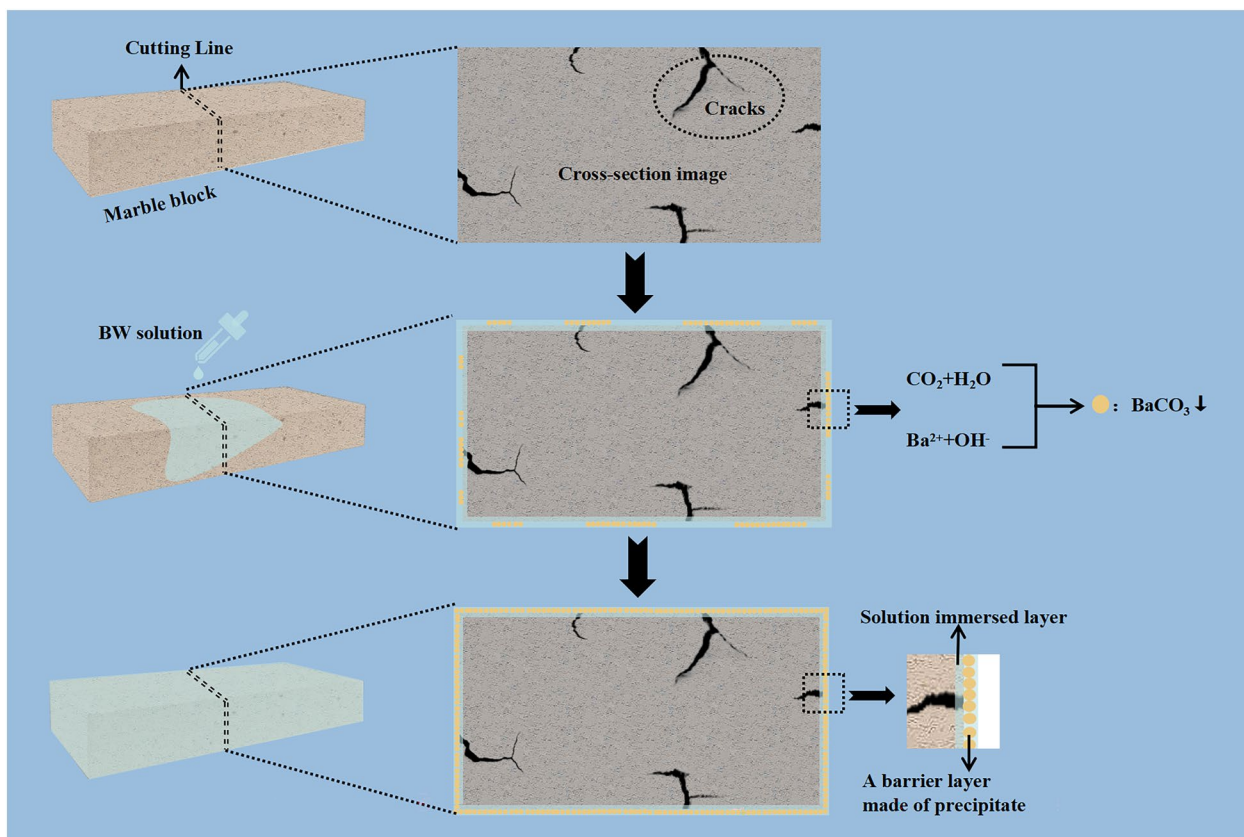


Fig. 11 The reaction and infiltration processes of BW solution in marble

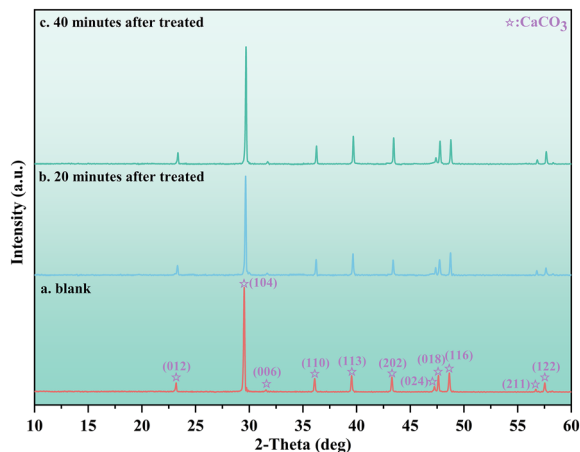


Fig. 12 XRD results of the marble blocks before and after treatment with BM solution

limited. Additionally, the coordination effect made barium hydroxide an amorphous compound [19]. Therefore, the characteristic peaks of barium hydroxide were not detected. The penetration process of BM solution in marble was illustrated in Fig. 13. The BM solution does not

react with marble or atmospheric CO₂ and remains in a liquid state. Without the hindrance effect of precipitates, the BM solution is able to effectively penetrate the interior of marble. As methanol evaporates, barium hydroxide physically adsorbs inside the marble block (confirmed later in FTIR results), and only reacts with atmospheric CO₂ when a sufficient amount of water is provided. Overall, this stepwise reaction enables the BM solution to penetrate the interior of marble and eliminates the phenomenon of "back migration".

Figure 14 showed FTIR spectra of marble (a), the dried sample of BM solution (b) and marble treated with BM solution (c). In Fig. 14c, the triple-peak pattern at 3380, 3490 and 3580 cm⁻¹ arose from the overlap of the OH peaks in [Ba(OH)₂(MeOH)₂](MeOH) and the double peaks at 3550 and 3410 m⁻¹ in marble [19, 20]. The double peaks of marble at 2870 and 2990 cm⁻¹ coincided with the C-H stretching vibration of CH₃ at 2860 cm⁻¹ to form the double peaks at 2870 and 2990 cm⁻¹ in the treated marble [21]. The strong and broad peak at 1420 cm⁻¹ was attributed to the antisymmetric stretching of CO₃²⁻ in marble. Due to its strong response signal, it masked the deformation vibration peak of CH₃ in [Ba(OH)₂(MeOH)₂](MeOH) [21]. The peak at 990 cm⁻¹

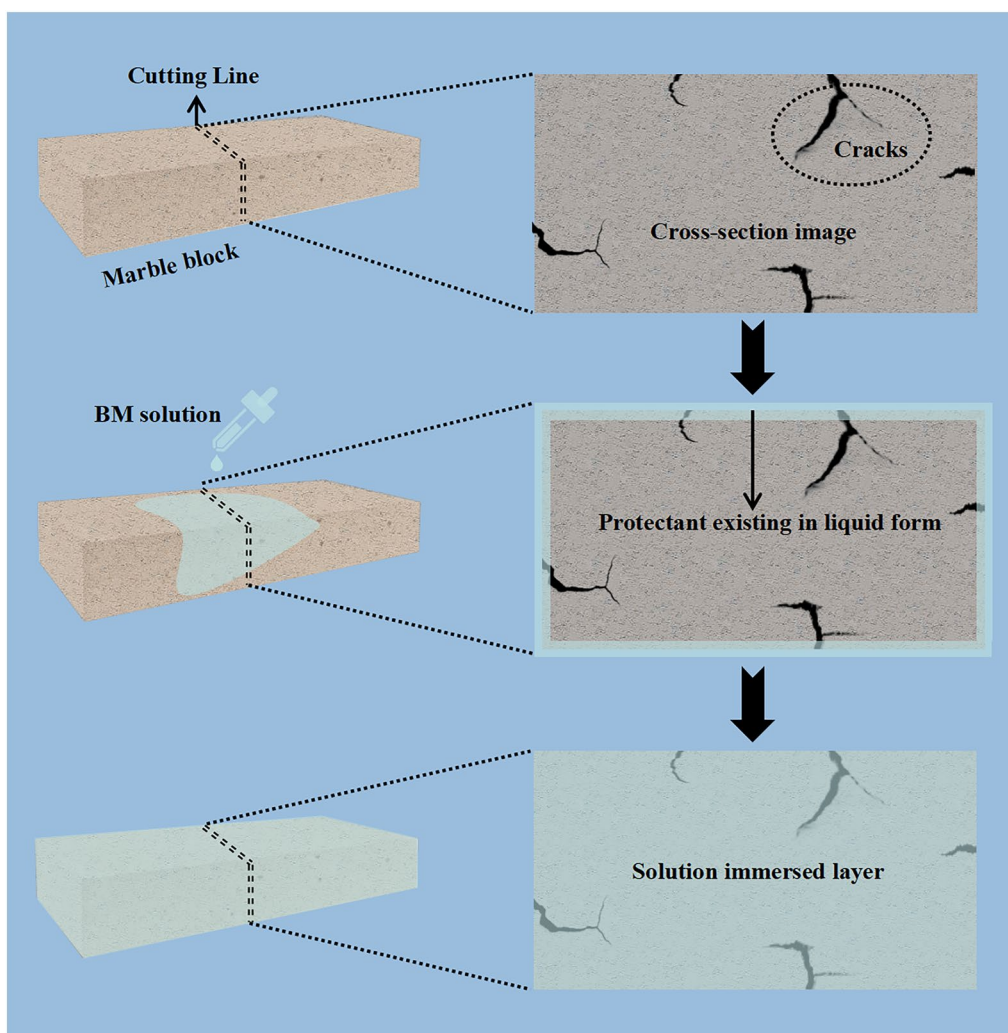


Fig. 13 The infiltration process of BM solution in marble

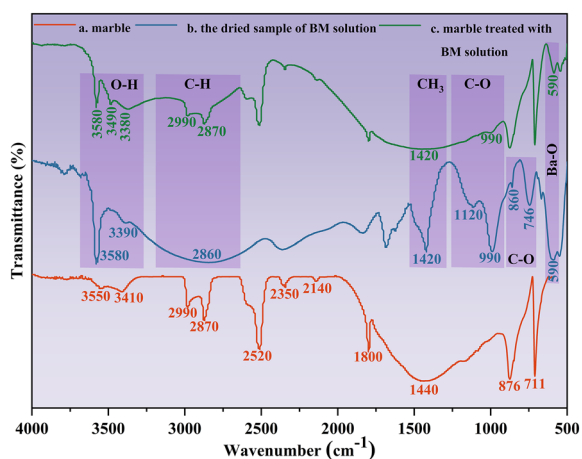


Fig. 14 FTIR results of marble (a), the dried sample of BM solution (b) and marble treated with BM solution (c)

corresponded to the C-O stretching vibration [20]. The peak at 590 cm^{-1} was assigned to the Ba-O stretching vibration [20]. The above results indicated that $[\text{Ba}(\text{OH})_2(\text{MeOH})_2](\text{MeOH})$ was present in the treated marble. Combined with the XRD results in Fig. 12, it was found that the BM solution did not react with marble. Instead, it was physically adsorbed within the marble block as methanol evaporated.

The penetration depths of BW and BM solutions in gypsum and marble

Figure 15 illustrated the penetration depths of BW and BM solutions with different concentrations in gypsum and marble blocks. The inset in Fig. 15a presented actual photographs from the phenolphthalein test on the cross-sections of gypsum and marble blocks. As depicted in Fig. 15a and b, the penetration depths of BW solution were lower than that of BM solution in both

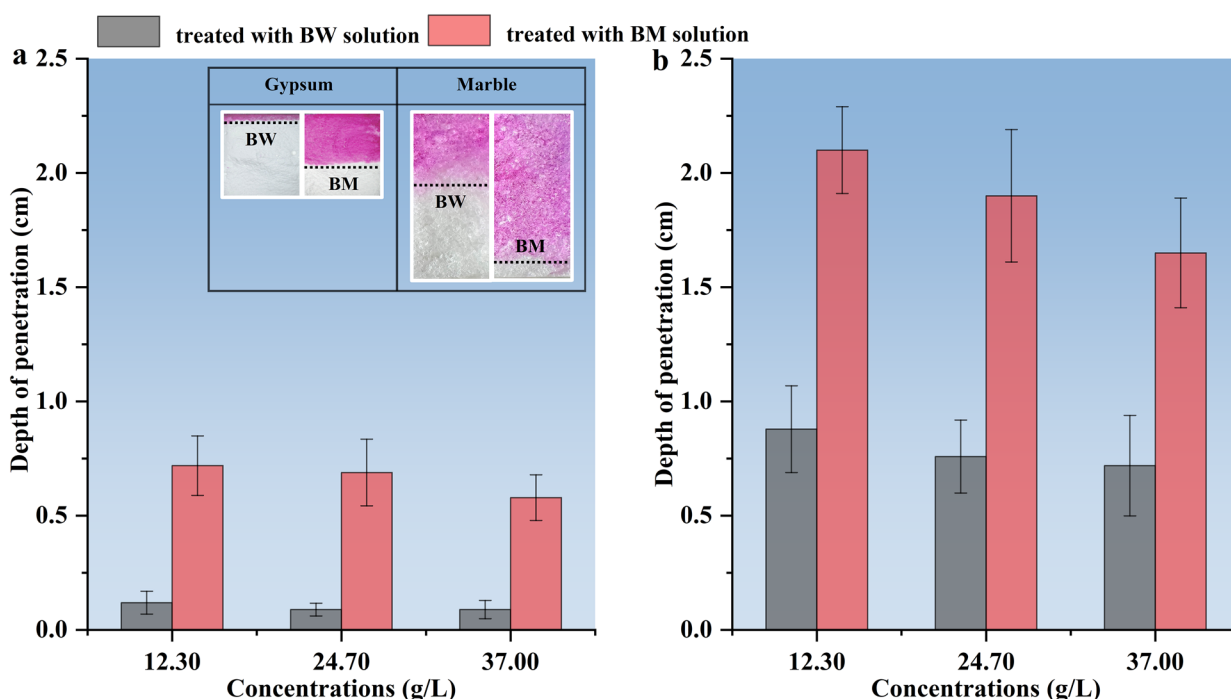


Fig. 15 The penetration depths of BW and BM solutions in gypsum (a) and marble (b). The inset: actual photographs from the phenolphthalein test

marble and gypsum blocks. To be specific, in the gypsum, the penetration depths of BM solutions were 0.72, 0.69 and 0.58 cm, whereas those of BW solutions were 0.12, 0.09 and 0.09 cm, which indicated that the maximum penetration depth of BM solution was 6 times greater than that of BW solution. As for the marble, the penetration depths of BM solutions reached 2.10, 1.90 and 1.65 cm, compared to BW solutions whose penetration depths were 0.88, 0.76 and 0.72 cm, suggesting that the maximum penetration depth achieved by BM solution exceeded that of BW solution by 2.3 times. These experimental phenomena corresponded to the reaction characteristics outlined in Section "Reaction characteristics between solutions and gypsum" (Eqs. (2) and (3)) and Section "Reaction characteristics between solutions and marble" (Eq. (2)). Due to the higher reactivity of BW solution, prematurely formed precipitate particles such as barium sulfate, calcium hydroxide and barium carbonate, blocked both surface and internal micropores and cracks of the treated samples, thus reducing the permeability of BW solution. On the contrary, the BM solution did not react with gypsum, marble and atmospheric CO_2 , and remained in a liquid state throughout the entire reinforcement process, which ensured the effective permeability of BM solution. Another point to note was that the penetration depths of both solutions decreased with increasing concentration. On one hand, an increased concentration of BW solution yielded a greater number

of precipitate particles, consequently reducing its penetration depth. On the other hand, the volatile nature of methanol led to solute deposition, hindering BM solution penetration as well, which ultimately resulted in a shallower penetration depth for BM solution at higher concentrations.

Physical property variations of gypsum and marble blocks

Figure 16 showed the open porosity, capillary water absorption and surface hardness of gypsum and marble blocks before and after treatment with BW and BM solutions. After treatment with BW and BM solutions, the open porosity and capillary water absorption of gypsum and marble blocks (Fig. 16a and b) decreased to varying degrees. The reductions were more pronounced in the blocks treated with BW solution than BM solution. In addition, the surface hardness of treated blocks increased to varying degrees (Fig. 16c). However, the blocks treated with BM solution showed a greater increase than BW solution. This was because the BW solution reacted rapidly with gypsum or atmospheric CO_2 to generate precipitates that blocked the micropores and cracks, thereby preventing the solution from penetrating inside the blocks. As a result, after treatment with BW solution, the open porosity and capillary water absorption were significantly reduced, but the reinforcement effect was not satisfactory. Conversely, the BM solution did not react with the treated samples or atmospheric CO_2 within

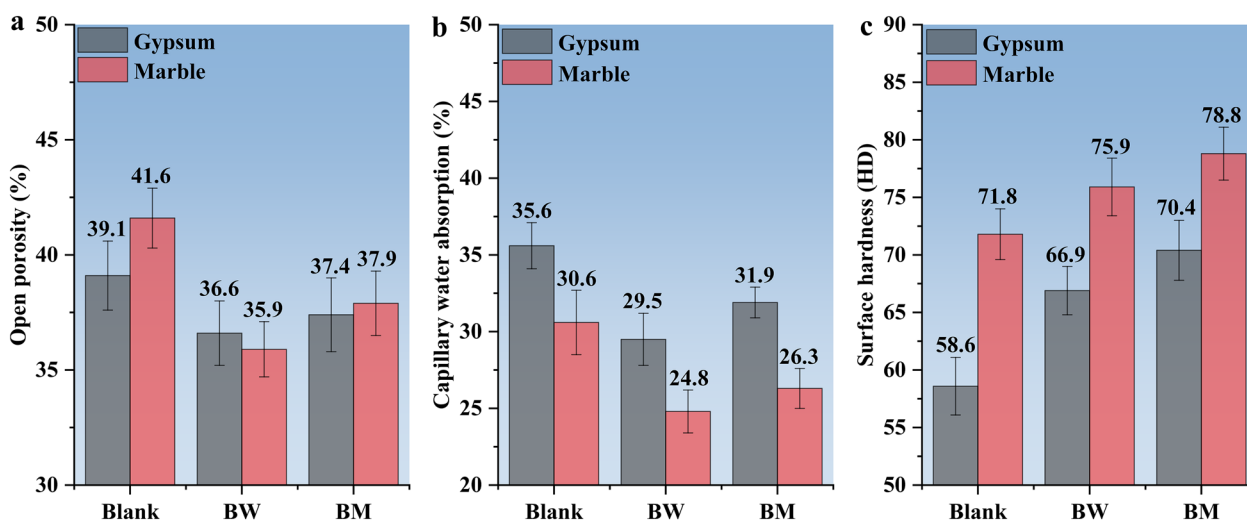


Fig. 16 Open porosity (a), capillary water absorption (b) and surface hardness (c) of gypsum and marble blocks before and after treatment with BW and BM solutions

a certain time, which ensured that the solution could penetrate into the interior of samples and formed an infiltrating protective layer [3]. Hence, the BM solution achieved better reinforcement effects, while maintaining the blocks' inherent breathability. Given that the aim of this study was to investigate the reasons of the solutions' permeability rather than to explore the optimal protective effect, the optimization of reinforcement conditions and the optimal reinforcement effect were not extensively discussed here. Details of the protection experiments can be found in references [1, 2].

Conclusion

The current study comparatively investigated the kinetic stability of BW and BM solutions in the air, as well as their reaction characteristics and penetration effects in gypsum and marble substrates. The findings elucidated the reasons of the solutions' permeability differences in gypsumification calcareous relics. Furthermore, the results offered guidance for applying barium protectants in the conservation of gypsumification calcareous relics.

This research demonstrated that the BW solution reacted rapidly with atmospheric CO₂ and gypsum to generate barium carbonate, barium sulfate and calcium hydroxide precipitates. These precipitates increased the turbidity and absorbance of BW solution, blocked both surface and internal micropores of the weathered relics, and hindered the penetration of BW solution into the weathered relics, thereby resulting in a decrease in the solution's kinetic stability and permeability. These reactions and phenomena are unfavorable for the storage and application of BW solution. Conversely, the BM solution consistently maintained a liquid state, as it did not react

with atmospheric CO₂ or gypsum and marble substrates. As a result, the BM solution exhibited higher kinetic stability and permeability. The penetration experiments indicated that the maximum penetration depth of BM solution in gypsum was 6 times greater than that of BW solution, and in marble, it was 2.3 times greater than that of BW solution. The physical property analyses revealed that the blocks treated with BM solution exhibited a smaller decrease in open porosity and capillary water absorption, as well as a higher increase in surface hardness, whereas the opposite phenomena were observed for the blocks treated with BW solution. These results aligned with the aforementioned mechanisms and highlighted the significant advantage of BM solution in terms of permeability.

It is well known that methanol is hazardous to human health, so conservators should be cautious during the protection process. When using the BM solution in an outdoor open environment where methanol easily evaporates, conservators can avoid hazards by wearing masks. In contrast, if the solution is used in an indoor enclosed environment, both protective equipment and ventilation measures are necessary. Consequently, more efforts should be made in seeking safe alternative solvents.

Author contributions

Conceptualization FY; methodology FY, JY; validation JY; formal analysis JY; investigation JY, YS, GH; resources GH, XL, QL, YL, KZ; data curation FY, GH; writing—original draft preparation JY; writing—review and editing FY, JY; supervision FY; project administration FY; funding acquisition FY. All authors have read and agreed to the published version of the manuscript.

Funding

The authors gratefully acknowledge the financial supports from the National Natural Science Foundation of China (B050121975202, 52108031)

and the Shaanxi Provincial Natural Science Foundation General Program (2023-JC-YB-097).

Availability of data and materials

All data generated or analysed during this study are included in this article, and no datasets were generated or analysed during the current study.

Declarations

Institutional review board statement

Not applicable.

Competing interests

The authors declare no competing interests.

Received: 11 March 2024 Accepted: 4 June 2024

Published online: 19 June 2024

References

1. Lu R, Wang L, Liu Y, et al. Conservation of surface gypsification stone relics using methanol solution of barium hydroxide as a novel treating agent. *Appl Phys A*. 2022;128(1):37.
2. Lu R, He L, Li T, et al. A novel protection method for carbonate stone artifacts with gypsum weathering crusts. *Coatings*. 2022;12(11):1793.
3. Wang L, Yang H, Chen W, et al. Preparation of infiltrating calcium carbonate layer in gypsum substrate using novel calcium precursor: the implication for the protection of the surface weathered carbonate heritages from water erosion damage. *Surf Interfaces*. 2024;44: 103685.
4. Sabbioni C, Bonazza A, Zappia G. Damage on hydraulic mortars: the Venice Arsenal. *J Cult Herit*. 2002;3(1):83–8.
5. Zhu C, Xu X, Liu W, et al. Softening damage analysis of gypsum rock with water immersion time based on laboratory experiment. *IEEE Access*. 2019;7:125575–85.
6. Scherer GW. Crystallization in pores. *Cem Concr Res*. 1999;29:1347–58.
7. Benavente D, García Del Cura MA, Fort R, et al. Thermodynamic modelling of changes induced by salt pressure crystallisation in porous media of stone. *J Cryst Growth*. 1999;204(1–2):168–78.
8. Schiro M, Ruiz-Agudo E, Rodríguez-Navarro C. Damage mechanisms of porous materials due to in-pore salt crystallization. *Phys Rev Lett*. 2012;109: 265503.
9. Tesser E, Conventi A, Majerle F. Characterization of barium hydroxide used as consolidating agent for monumental surfaces in Venice. *Heritage*. 2022;5(4):3280–97.
10. Giorgi R, Ambrosi M, Toccafondi N, et al. Nanoparticles for cultural heritage conservation: calcium and barium hydroxide nanoparticles for wall painting consolidation. *Chem-Eur J*. 2010;16(31):9374–82.
11. Toniolo L, Colombo C, Realini M, et al. Evaluation of barium hydroxide treatment efficacy on a dolomitic marble. *Anal Chim*. 2001;91(11–12):813–21.
12. Rodrigues JD, Pinto APF. Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. *J Cult Herit*. 2016;19:467–76.
13. Rodrigues JD, Pinto APF, Nogueira R, et al. Consolidation of lime mortars with ethyl silicate, nanolime and barium hydroxide effectiveness assessment with microdrilling data. *J Cult Herit*. 2018;29:43–53.
14. Rodríguez-Navarro C, Suzuki A, Ruiz-Agudo E. Alcohol dispersions of calcium hydroxide nanoparticles for stone conservation. *Langmuir*. 2013;29(36):11457–70.
15. Giorgi R, Baglioni M, Berti D, et al. New methodologies for the conservation of cultural heritage: micellar solutions, microemulsions, and hydroxide nanoparticles. *Acc Chem Res*. 2010;43:695–704.
16. Zhu J, Ding J, Zhang P, et al. In-situ growth synthesis of nanolime/kaolin nanocomposite for strongly consolidating highly porous dinosaur fossil. *Constr Build Mater*. 2021;300: 124312.
17. Rodríguez-Navarro C, Ruiz-Agudo E, Ortega-Huertas M, et al. Nanostructure and irreversible colloidal behavior of Ca(OH)₂: implications in cultural heritage conservation. *Langmuir*. 2005;21(24):10948–57.
18. Burgos-Ruiz M, Elert K, Ruiz-Agudo E, et al. Silica-functionalized nanolimes for the conservation of stone heritage. *Small*. 2023;19(33):2300596.
19. Starikova ZA, Kessler VG, Turova NY, et al. Interaction of barium oxide and hydroxide with methanol: X-ray single crystal study of Ba(OH)₂ methanol solvates. *Polyhedron*. 2006;25(12):2401–6.
20. Li XH, Jiang WH, Wei HY, et al. FTIR spectra analysis of metal chloroalkoxides. *Guangzhou Chem*. 2008;33:42–7.
21. Yang R, Liu JH, Li M. Preparation of rare earth alkoxides. *J Chin Ceram Soc*. 2004;08:982–7.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.