

Effect of Sulfate Crystallization on Sandstone in the Yungang Grottoes

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Abstract

Subjected to various weathering in nature over long time, sandstone has been deteriorated in the Yungang Grottoes. The repeated dissolution and crystallization of soluble salts are important factors that cause the deterioration of the grotto sandstone. In order to study the action mechanism of sulfate crystallization in the Yungang Grottoes sandstone, deterioration tests were carried out by the "soaking-evaporation" cycle of saturated magnesium sulfate (MgSO_4) and saturated sodium sulfate (Na_2SO_4) solutions in laboratory. The test results show that the participation of sulfate greatly accelerated the weathering speed of sandstone. The ultrasonic velocity of the specimens circulated in both Na_2SO_4 and MgSO_4 solutions show a trend of first increasing and then decreasing, and changes more obviously in Na_2SO_4 solution. In the evaporation stage of the circulation, the peeling mass of the specimens circulated in Na_2SO_4 solution is significantly greater than that in MgSO_4 solution. From the evaporation tests on saturated Na_2SO_4 and MgSO_4 solutions and observation with optical microscope and scanning electron microscope, it is found that a dense crystal layer was formed on the surface during the evaporation of saturated MgSO_4 solution, and it gradually seals the internal solution, slowing down the further evaporation. During the solution evaporation, Na_2SO_4 crystallizes into powdery crystals in a flocculent and soft state, and there are pores between the crystal grains. The change in the ultrasonic velocity of specimens in the "soaking-evaporation" cycle tests can be explained by the evaporation test results.

1. Introduction

Located in the western suburbs of Datong City, Shanxi Province (Fig. 1A), the Yungang Grottoes (Fig. 1B) is a masterpiece of early Chinese grotto art and a cultural heritage that is well-known in the world. The main sculpture stratum at the Yungang Grottoes is sandstone lens [1]. The Yungang Grottoes were excavated in the 5th century and have a history of more than 1,500 years. Subjected to various weathering in nature over long time, the sandstone has been deteriorated (Fig. 1C), and the number of existing Buddha statues is only half of the original. The modern industrial development in Datong City has been increasing in the SO_2 content in air, which causes the rain to be acidic. Rain falls on the top of the grottoes and infiltrates downwards along the cracks in rock. During the infiltration process, the acidic rainfall reacts with carbonate minerals in the rock to form soluble salts, which enters the grottoes with the seepage. Salts containing crystal water accumulate in the pores and micro-cracks on the sandstone surface (Fig. 1D). When in low temperature and/or high humidity, the salts absorb water and expand to produce crystallization pressure, which accelerates the destruction of the connection between the mineral particles and the expansion of the fissures, causing irreparable damage to the sandstone cultural relics [2]. Therefore, to study the weathering of Yungang Grottoes, it is necessary to have a good understanding of how water and salts affect the grotto sandstone.

Scholars in the world have done a lot of study on the weathering effect of salts on the grotto cultural relics. Correns et al. first concluded that the maximum stress of salt crystallization is a function of solution supersaturation [3]. Scherer et al. found that salt crystallization not only requires sufficient

supersaturation to cause the material damage, but also requires crystals to grow in a relatively closed environment [4]. Huang and Yuan found that salts containing crystal water accumulated in the pores and micro-cracks on the sandstone surface, when the crystal water is lost (or reduced) in a dry environment, the volume decrease; when in low temperature or high humidity, it will absorb water and expand to produce crystallization pressure, which accelerates the destruction of the connection between the mineral particles and the expansion of the fissures [1]. Steiger used thermodynamic equations to calculate the crystallization pressure of various salts, which are generally greater than the tensile strength of sandstone, confirming that the crystallization pressure generated by the salt crystallization is sufficient to cause the sandstone deterioration [5–7]. Al-Naddaf et al. found that the salt crystallization in sandstone reduces the water absorption rate of sandstone. It is mainly due to the blockage of pores by salt crystals, which reduces the porosity and pore sizes of sandstone. After removing the internal salt, the water absorption rate exceeds the original level. It may be attributed to the increase of pores under the action of crystallization pressure [8]. Lee et al. used high-concentration salt solution to simulate the chemical weathering of rocks by seawater, and found that the circulation of salt solutions reduces the elastic wave velocity and increases the porosity [9]. Ozsen et al. found that under the action of salt crystallization, the ultrasonic velocity, uniaxial compressive strength and tensile strength of the rock decreased [10]. Menendez and Petranova found that single salt brines, especially sodium sulphate, produce more weathering than complex brine compositions during wetting and drying cycles [11].

Previous researches have greatly improved the protection level of the grotto cultural heritage. However, the crystallization and dehydration process of salt in sandstone, the mechanical action mechanism of salt on sandstone, and the expansion of fissures have not been studied clearly. And the current research results are mainly concentrated on the sodium salt [12–14], and the dominant salt on the rock wall in the Yungang Grottoes is sulfate deposits, and the main components are epsomite and mirabilite, which are crystalline hydrates of magnesium sulfate (MgSO_4) and sodium sulfate (Na_2SO_4), respectively [15]. Therefore, studying the action mechanism of magnesium salt on the grotto sandstone, together with comparing the mechanism of sodium salts, is of great significance to the protection of the Yungang grottoes.

In order to simulate the weathering of sandstone caused by the crystallization of sulfate in the Yungang Grottoes, a series of deterioration tests was carried out by the “soaking-evaporation” cycle of saturated magnesium sulfate (MgSO_4) and saturated sodium sulfate (Na_2SO_4) solutions in laboratory. The mass, ultrasonic velocity, surface morphology and mineral composition of the sandstone specimen were measured during the cycle, and the evaporation tests on two saturated salt solutions were carried out, to study the crystallization and dehydration process of salts in sandstone and analyze the mechanical action mechanism of salt on sandstone. The findings should make an important contribution to the field of the protection of the Yungang Grottoes.

2. Testing Program

2.1 Specimen preparation

The fresh sandstone samples used for the tests were taken from the mountains near the Yungang Grottoes. According to the laboratory measurement standard of rock ultrasonic elastic constant of the American Society for Testing and Materials (ASTM D2845-2008), the Yungang sandstone was processed into standard specimens with a size of 50 mm×50 mm×100 mm. The mineral composition, natural density, moisture content, and ultrasonic velocity of fresh samples were measured. X-ray diffractometer was used for the mineral analysis and the results of fresh sandstone are shown in Table 1. The main component of sandstone is quartz, and the main cement is calcite. It also contains minerals such as feldspar, kaolinite and mica. The GJT-U200 ultrasonic rebound hammer (50000 Hz) was adopted for measuring the ultrasonic velocity in the direction of rock deposition. At the same time, nine specimens were chosen with similar physical parameters to ensure that the initial states of all specimens are close to the same. The natural mass, density, moisture content and ultrasonic velocity of fresh specimens are about 585g, 2.3 g/cm³, 0.48%, and 2800 m/s, respectively. The specific parameters of all specimens are listed in Table 2.

Table 1
Mineral compositions of fresh Yungang sandstone

| Mineral | Quartz | Microcline | Plagioclase | Mica | Calcite | Kaolinite |
|--|---------------|-------------------|--------------------|-------------|----------------|------------------|
| | (%) | (%) | (%) | (%) | (%) | (%) |
| Content | 55 | 5 | 4 | 9 | 16 | 11 |
| Note: Data is measured by the X-ray diffractometer of Micro Structure Analytical Laboratory. | | | | | | |

Table 2
Parameters of fresh sandstone specimens

| Specimen | Natural density (g/cm ³) | Natural moisture content (%) | Ultrasonic velocity (m/s) |
|----------|---|------------------------------|------------------------------|
| YG-1 | 2.29 | 0.47 | 2819.6 |
| YG-2 | 2.30 | 0.48 | 2853.1 |
| YG-3 | 2.34 | 0.46 | 2830.3 |
| YG-4 | 2.35 | 0.45 | 2863.0 |
| YG-5 | 2.33 | 0.47 | 2838.2 |
| YG-6 | 2.34 | 0.48 | 2879.0 |
| YG-7 | 2.33 | 0.48 | 2862.4 |
| YG-8 | 2.34 | 0.50 | 2772.7 |
| YG-9 | 2.28 | 0.51 | 2775.4 |

2.2 Testing method

In the tests, the controls of temperature and humidity, the choices of salt and test methods need to be considered. According to measured temperature and humidity at the Yungang Grottoes, the high temperature in summer is accompanied by high humidity, and the low temperature in winter is accompanied by low humidity. The changes in temperature and humidity variables were not considered in this study, only temperature of 15°C and the relative humidity of 60% are adopted for tests, which are similar to the average temperature and humidity in spring and autumn. The dominant salt on the rock wall in the Yungang Grottoes is sulfate deposits, and the main components are epsomite and mirabilite [15]. Therefore, MgSO₄ and Na₂SO₄ were selected as the salts for tests. In order to make the test phenomenon more obvious, saturated salt solution was used. About the test method, the ultrasonic technology of non-destructive measurements was adopted. The ultrasonic wave passes through the rock, and it will be reflected or diffracted when it encounters the pores or cracks, which causes the ultrasonic velocity to drop [16]. Therefore, the mechanical properties and structural characteristics of the rock can be reflected indirectly by the ultrasonic velocity.

The test plan is as follows:

(1) Nine specimens with basically the same initial state were divided into three groups, each with three specimens. Another fresh specimen is cut into three parts with similar size, and a part to each group was added for the mineral analysis after the cycles. Hence each group has four specimens.

(2) The specimens were dried in an oven (105°C) for 24h, and were taken out for measuring the weights. After being cooled in a desiccator, three groups of specimens were soaked in saturated Na₂SO₄ solution,

saturated MgSO₄ solution, and deionized water, respectively, at temperature of 20°C. The specific process of immersion is shown in Fig. 2, porous stones were put under the specimens at the beginning of soaking, and the upper quarter of specimens was exposed to air, which facilitates the discharge of pore air in specimens and accelerates the saturation. After being soaked for 12h, the specimens were completely soaked, and the specimens were weighed regularly during the soaking process (After taken out of the solution, the specimen was wrapped with a wet tissue for 5 seconds and then was weighed). After the mass changes no longer, the specimens were put in a temperature and humidity chamber, the temperature and the relative humidity were controlled at 15°C and 60%, respectively. The specimen was taken out and weighed regularly until the specimen mass is basically unchanged in the evaporation process. The above process is a complete “soaking-evaporation” cycle.

(3) The specimen was soaked in the solution and then evaporated again. The soaking and evaporation cycle process was repeated for 8 cycles. The peeled rock was collected and weighed during the soaking and evaporation process.

(4) After each cycle, the mass and the ultrasonic velocity were measured, and the specimen surfaces were photographed. And additional specimen of each group was taken for XRD test to analyze the mineral change during the cycles.

3. Test Results

3.1 Ultrasonic velocity during cycles

Although the sandstone was taken from the same area of the mountain, the ultrasonic velocities of the fresh sandstone specimens are slightly different, thus the ultrasonic velocity is normalized by a parameter B , which is defined as:

$$B = \frac{V}{V_0} \quad (1)$$

where V_0 and V are the ultrasonic velocities of fresh sandstone and specimens after the cycles. The changes in the ultrasonic velocities of the specimens circulated in saturated Na₂SO₄ and MgSO₄ solutions during the cycles are shown in Fig. 3A and B, respectively. The comparison of the ultrasonic velocity changes of the three groups is shown in Fig. 3C, here \bar{B} is the average of the B values of 3 specimens in each group.

From Fig. 3A and B, it can be seen that the ultrasonic velocity changes of 3 specimens circulated in Na₂SO₄ solution are similar but relatively dispersed, and those in MgSO₄ solution are almost the same. From Fig. 3C, we can see that: (1) As the cycle progresses, the ultrasonic velocity of the specimens circulated in both Na₂SO₄ and MgSO₄ solutions show a trend of first increasing and then decreasing, and that in deionized water is almost unchanged. (2) In first 3 cycles, the ultrasonic velocity of the specimens circulated in Na₂SO₄ solution is faster than that in MgSO₄ solution. (3) As the cycle progresses, the

ultrasonic velocity of the specimens circulated in Na_2SO_4 solution shows a downward trend faster than that in MgSO_4 solution, and the ultrasonic velocity of the specimens circulated in Na_2SO_4 solution decreases faster than that in MgSO_4 solution. At the same time, the downtrend of the ultrasonic velocity of the specimens circulated in Na_2SO_4 solution is gradually obvious as the number of cycles increases, and that in MgSO_4 solution almost unchanged.

3.2 Peeling mass during cycles

During the cycles of sulfate solution, the specimens had weathered peeling on the surface, and the peeled rock was collected and weighed during the soaking and evaporation process. Due to the inhomogeneity of the sandstone, the mass of the fresh specimens at the same size (50*50*100 mm) are slightly different, thus the peeling mass of the specimens is normalized by a spalling rate C , which is defined as:

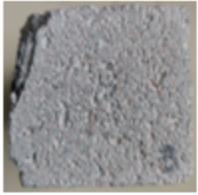
$$C = \frac{M}{M_0} \quad (2)$$

where M and M_0 are the masses of the peeling rock during each cycle and of the fresh sandstone specimen. The peeling rates of the specimens circulated in saturated Na_2SO_4 and MgSO_4 solutions are shown in Fig. 4A and B, respectively. Here C is the average value of C value of 3 specimens in each group. The peeling masses of the specimens during the soaking and the evaporation are respectively recorded. The comparison of the spalling mass of the three groups during the whole process is shown in Fig. 4C. The results show that the spalling of specimens circulated in Na_2SO_4 solution is mainly concentrated in the evaporation process, and increases significantly after 6 cycles, as shown in Fig. 4A. In contrast, the spalling of specimens circulated in MgSO_4 solution is mainly concentrated in the soaking process, as shown in Fig. 4B. And the peeling mass of specimens circulated in Na_2SO_4 solution is obviously greater than that in MgSO_4 solution, as shown in Fig. 4C. The peeling mass of the two groups is almost the same in the soaking process, and the difference in the evaporation process is great. No peeling was observed within specimens circulated in deionized water.

3.3 Surface change during cycles

After the evaporation process of each cycle, the specimen surface was photographed by camera (Canon 80D, 30 million pixels). The surface morphology change of the three groups during the cycles is shown in Table 3. 3nh spectrophotometer was used to measure the color value change of the specimen surface, the values of L , a , b represent the brightness, the color of red and green, the color of yellow and blue, respectively. Then the average value of all indexes of 3 specimens in each group was calculated. Figure 5A, B and C respectively show the relationship between the averages of L -value, a -value, b -value and the number of cycles.

Table 3 Surface morphology changes of specimens during cycles

| Number of cycles (Times) | 2 | 4 | 6 | 8 |
|---------------------------------------|---|---|---|---|
| Na ₂ SO ₄ group |  |  |  |  |
| MgSO ₄ group |  |  |  |  |
| Deionized water group |  |  |  |  |

It can be seen from Table 3 that as the soaking-evaporation cycle progresses, the specimens circulated in sulfate solution appeared salty on the surface, and the specimen had surface weathering peeling and surface dissolution, which results in the rough and uneven surface. The specimens circulated in Na₂SO₄ solution had higher unevenness than that in MgSO₄ solution, and the edge peeling of specimens was also more obvious. In contrast, the specimens circulated in deionized water had a high degree of integrity and almost no peeling on the surface. According to the results in Fig. 5, the surface color of specimens changed significantly under the circulation of sulfate solution. Compared with fresh sandstone, the *L*-value of specimens circulated in Na₂SO₄ solution increases as the cycle progresses, and the *a*-value and *b*-value gradually decrease. The *L*-value of specimens circulated in MgSO₄ solution shows a decreasing trend, and the *a*-value gradually increases but the *b*-value does not change much, while the *L*, *a*, and *b*-values of specimens circulated in deionized water are almost unchanged.

3.4 Mineral analysis results

Table 4 shows the comparison of the mineral composition content between fresh sandstone and specimens after six cycles of sulfate solutions. It can be seen that the calcite content decreases and the kaolinite content increases with circulating sulfate solutions. The circulation of the sulfate solution leads to the dissolution of calcite, and the crystallization of sulfate leads to the destruction of the connection between the mineral particles, which results in the shedding of calcite. Huang et al. found that detrital feldspar in sandstone would be hydrolyzed into clay minerals such as kaolinite in water [17], while the feldspar content of the specimens in this study did not decrease significantly.

Table 4
Changes in mineral composition content of sandstone specimens during the cycle

| Mineral | Quartz (%) | Microcline (%) | Plagioclase (%) | Mica (%) | Calcite (%) | Kaolinite (%) |
|--|------------|----------------|-----------------|----------|-------------|---------------|
| Fresh sandstone | 55 | 5 | 4 | 9 | 16 | 11 |
| Specimens circulated in Na ₂ SO ₄ solution (6 times) | 52 | 6 | 4 | 9 | 14 | 15 |
| Specimens circulated in MgSO ₄ solution (6 times) | 54 | 6 | 3 | 10 | 14 | 13 |

Note: The data is measured by the X-ray diffractometer of Micro Structure Analytical Laboratory.

4. Discussion

4.1 Evaporation tests on saturated salt solutions

To study the crystallization and dehydration process of salts in sandstone, the evaporation tests on two saturated salt solutions were carried out. The same molar masses of MgSO₄ and Na₂SO₄ were configured into saturated solution respectively, the molarities of saturated Na₂SO₄ and MgSO₄ solution are 1.20 and 1.77 mol/L, respectively. Two saturated solutions were dropped into petri dishes, and the temperature and the relative humidity were controlled at 15°C and 60%, respectively. The petri dishes were put on electronic balances to measure the mass change of the solution in the evaporation process. Optical microscope and scanning electron microscope were used to photograph the surface microscopic morphology of the salt crystallization. Figure 6 shows the result of the mass changes of the two saturated sulfate solutions during the evaporation process. The result shows that the initial slopes in the mass change of two saturated sulfate solutions are similar, which means that the initial crystallization rates of two salts are similar. The mass decreasing rate of Na₂SO₄ solution remains the same up to 5 hours, gradually decreases later and the mass was kept constant after 10 hours. But, the decreasing rate of MgSO₄ solution mass gradually decreases from the beginning of the test, and the mass remains the same after 6 hours. Finally, the mass decrease of Na₂SO₄ solution is significantly greater than that of MgSO₄ solution.

After the solution mass is stable, optical microscope and scanning electron microscope were used to photograph the surface microscopic morphology of the solution, and the result is shown in Fig. 7. During the evaporation test, Na₂SO₄ solution first evaporated into mirabilite and dehydrated to thenardite together with the volume being decreased slightly. After the evaporation reaches stable, there was no liquid left, only Na₂SO₄ crystals remained, which were in a flocculent and soft state, and there were pores between crystal grains (Fig. 7A and B). The volume of saturated MgSO₄ solution did not change much during the evaporation process, and a dense crystalline layer was formed on the surface (Fig. 7C). The

layer gradually sealed the internal solution, slowing down the further evaporation of the internal solution and reduced the amount of crystallization. If the surface crystalline layer is destroyed, the internal solution would continue to evaporate.

4.2 Explanation of the cycle tests on sandstone

By analyzing the evaporation tests on saturated sulfate solutions, the results of the soaking-evaporation cycle tests on sandstone can be explained as follows:

(1) As the soaking-evaporation cycle progresses, the ultrasonic velocity of the sandstone specimens circulated in both Na_2SO_4 and MgSO_4 solutions show a trend of first increasing and then decreasing, and that in deionized water is almost unchanged, as shown in Fig. 3C. This is probably because the sulfate crystals fill the pores in the sandstone during the evaporation process in the first 3 cycles. The tensile strength of sandstone is generally less than 3MPa [5]. The crystals grow freely in the pores before the crystallization force reaches 3MPa, which makes the sandstone more dense and solid, and results in the ultrasonic velocity increase [18]. As the soaking-evaporation cycle continues, repeated salt swelling and dissolution of calcite cause the destruction of the connections between mineral particles and the expansion of superficial fissures [1], which results in the ultrasonic velocity decrease. Al-Naddaf et al. found that salt crystals in sandstone can reduce the water absorption rate. This is mainly due to the blockage of pores by salt crystals, which reduces the porosity and pore size. After the introduced salt is removed, the water absorption rate exceeds the original level, which may be attributed to the increase of pores under the action of crystallization pressure [8]. His finding is similar to the conclusion of this article. And Theoulakis and Tang also found similar test phenomenon [19, 20]. Lee et al. found that the circulation of salt solutions would reduce the elastic wave velocity of a rock [9]. Ozsen et al. also found that the ultrasonic velocity of a rock decreased with the cycle of salt crystallization [10]. Their findings are somewhat different from the law of ultrasonic velocity in this article. The average initial porosity of the rock specimen used by Lee is 1.11% [9], and the porosity of Yungang Grottoes sandstone is about 3.5%. It is speculated that the rock porosity used by Lee is so small that the salt expansion occurred during the evaporation process in the first few cycles, which causes the ultrasonic velocity to decrease.

(2) As shown in Fig. 3C, in the first 3 cycles, the ultrasonic velocity of the sandstone specimens circulated in Na_2SO_4 and MgSO_4 solutions increases up to 3 and 4 cycles respectively. The velocity of former increases with the cycles faster than that of latter. Combined with the evaporation test results, a dense crystalline layer will be formed on the surface of MgSO_4 solution, slowing down the further evaporation of the internal solution and reduces the amount of crystallization. Thus, the amount of crystals filling the pores in the specimens circulated in Na_2SO_4 solution is less than that in MgSO_4 solution, so the specimens circulated in Na_2SO_4 solution is denser than that in MgSO_4 solution. Therefore the ultrasonic velocity of the specimens circulated in Na_2SO_4 solution increases faster with the cycle [18].

(3) The ultrasonic velocity of the specimens circulated in Na_2SO_4 and MgSO_4 solutions began to decrease after 3 and 4 cycles respectively. The downtrend of the ultrasonic velocity of the specimens

circulated in Na_2SO_4 solution is gradually obvious as the number of cycles increases, and that in MgSO_4 solution almost unchanged.

Steiger provided an equation for the crystallization pressure based on the chemical potentials of the loaded and the unloaded faces of a growing crystal [5], and obtained the law that the crystallization pressure of different crystals (thenardite and epsomite) increases with increasing supersaturation, as shown in Fig. 8. The supersaturation required for the Na_2SO_4 solution to reach the crystallization pressure of 3MPa is less than that for the MgSO_4 solution, as shown by the dotted line in Fig. 8. When the crystallization pressure exceeds the tensile strength of the sandstone, the sandstone began to produce microcracks, which causes the ultrasonic velocity to drop [18]. The ultrasonic velocity of the specimens circulated in Na_2SO_4 solution shows a downward trend earlier. Under the same supersaturation, the crystallization pressure of thenardite is greater than that of epsomite, thus the Na_2SO_4 crystallization will produce greater crystallization pressure in the specimen than the MgSO_4 . Combined with the evaporation test results, during the evaporation of saturated MgSO_4 solution, a dense crystalline layer will be formed on the surface to slow down the further evaporation of the internal solution, which decreases the generation of pores and the expansion of surface cracks in specimens. Therefore, the ultrasonic velocity of specimens circulated in Na_2SO_4 solution decreases faster.

(4) During the cycles, the peeling mass of specimens circulated in Na_2SO_4 solution is obviously greater than that in MgSO_4 solution, as shown in Fig. 4C. According to the results of Steiger, the crystallization pressure due to Na_2SO_4 solution is greater than MgSO_4 solution under the same supersaturation [5], while the greater crystallization pressure results in more specimen peeling. At the same time, the MgSO_4 solution in the specimen forms a dense crystalline layer during the evaporation process, which has a protective effect on the specimen from peeling off. No peeling was observed within specimens circulated in deionized water, while several circulations of water have little impact on sandstone [21].

(5) Compared with fresh sandstone, the L -value of specimens circulated in Na_2SO_4 solution increases (Fig. 5A), and that in MgSO_4 solution shows a decreasing trend (Fig. 5B). After Na_2SO_4 crystallizes, white salt crystals are formed on the surface of the specimen, resulting in the increase in the brightness value L . The MgSO_4 solution forms a dense crystal layer on the surface of the specimen, in which the saturated solution evaporated incompletely. Part of the solution remains in the small pores, and the external light is refracted when the light goes through the solution in the small pores, which causes the brightness to decrease.

5. Conclusions

In order to study the crystallization process of MgSO_4 and Na_2SO_4 in sandstone, the mechanism of salt action on sandstone was analyzed, the “soaking-evaporation” cycle tests of MgSO_4 and Na_2SO_4 solutions on the Yungang Grottoes sandstone and the evaporation tests on two saturated salt solutions were carried out in laboratory. The main conclusions are as follows:

- (1) The specimens circulated in sulfate solution appear surface weathering peeling and surface dissolution, and the ultrasonic velocity changes obviously. In contrast, the specimens circulated in deionized water have no peeling on the surface, and the ultrasonic velocity does not change much. It shows that the participation of sulfate can greatly accelerate the weathering speed of sandstone.
- (2) As the cycle progresses, the ultrasonic velocity of specimens circulated in saturated sulfate solution shows a trend of first increasing and then decreasing, and changes more obviously in Na_2SO_4 solution, and that in deionized water is almost unchanged.
- (3) During the soaking-evaporation cycles, the peeling mass of specimens circulated in Na_2SO_4 solution is obviously greater than that of specimens circulated in MgSO_4 solution. The peeling mass of the two groups is almost the same in the soaking process, and the difference in the evaporation process is large. And no peeling was observed in the specimens circulated in deionized water.
- (4) From the evaporation tests on saturated MgSO_4 and Na_2SO_4 solutions, it was found that a dense crystalline layer will be formed on the surface of MgSO_4 solution, and the layer gradually seals the internal solution to slow down the further evaporation and reduce the amount of crystallization. Na_2SO_4 solution first evaporated into mirabilite, then dehydrated to thenardite, with the volume being decreased slightly. After the evaporation stops, only Na_2SO_4 crystals remain, which are in a flocculent and soft state, and there are pores between crystal grains.
- (5) The results of mineral analysis tests show that the content of calcite in sandstone decreases and the content of kaolinite increases with the circulation of saturated sulfate solution.

6. Declarations

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Availability of data and material

The authors wish to confirm that the contents of this manuscript have not been published previously and the manuscript is not under consideration for publication elsewhere. The authors wish to confirm that this manuscript does not involve plagiarism, forgery, deception, cheating, sabotage or academic fraud.

Competing interests

The authors wish to confirm that there are no known conflicts of interest associated with this publication.

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Authors' contributions

WJ SUN, DA SUN, and JZ HUANG developed the idea of the study, WJ SUN and QT ZHOU participated in its design and coordination and helped to draft the manuscript. QT ZHOU contributed to the acquisition and interpretation of data. WJ SUN, DA SUN and JZ HUANG provided critical review and substantially revised the manuscript. All authors read and approved the final manuscript.

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Figures

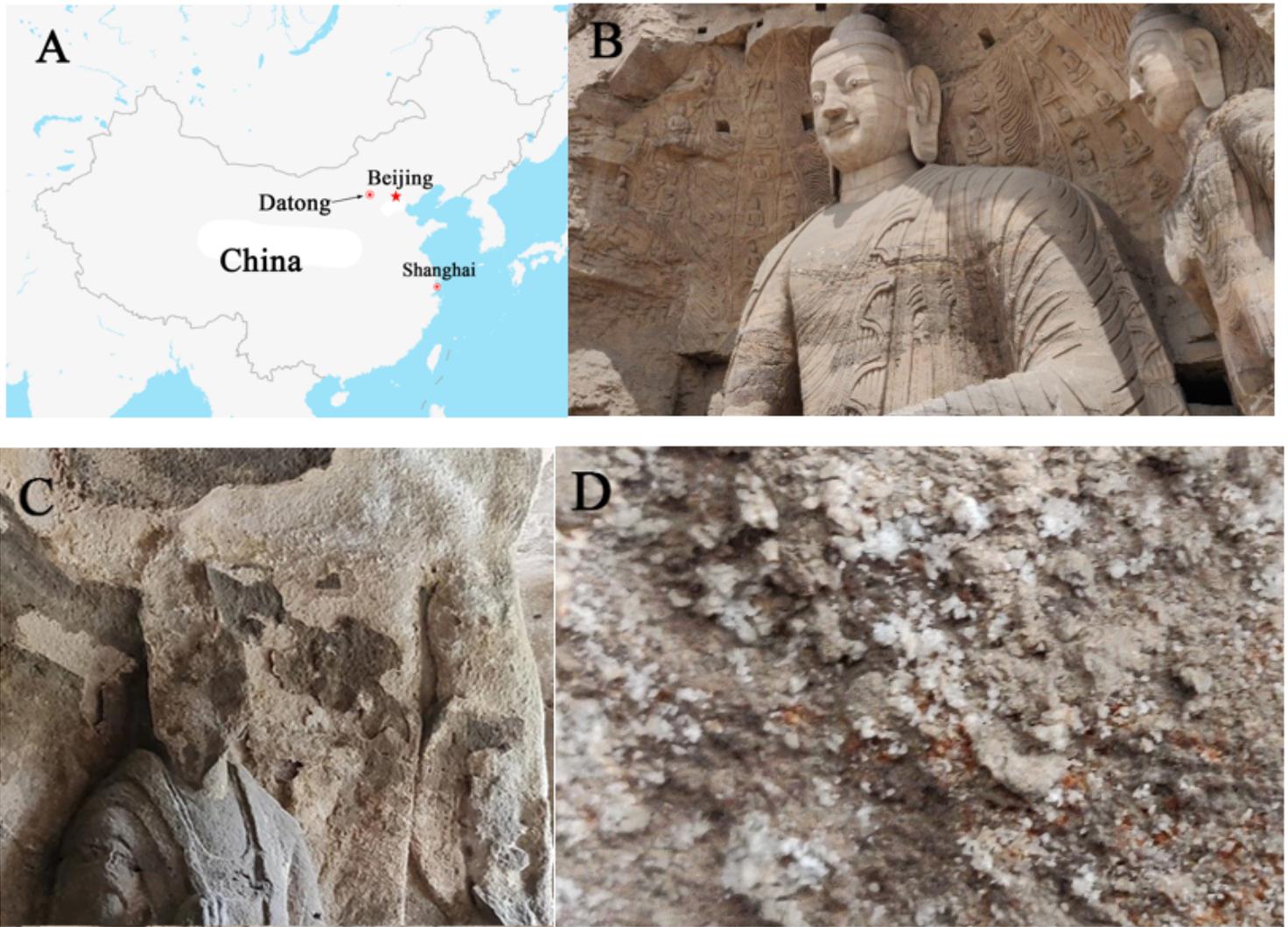


Figure 1

Weathering in the Yungang Grottoes: (A) Location of Yungang Grottoes. (B) Yungang Grottoes. (C) Weathered sandstone sculpture. (D) Salt on rock wall in the Yungang Grottoes. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

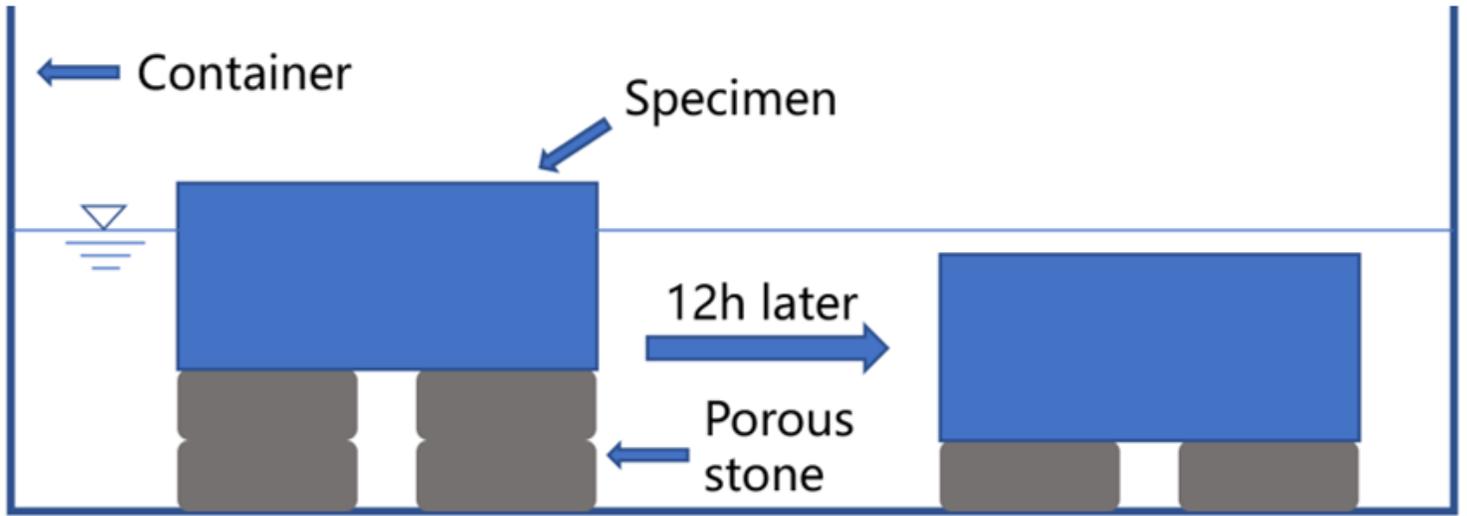


Figure 2

Schematic diagram of soaking process

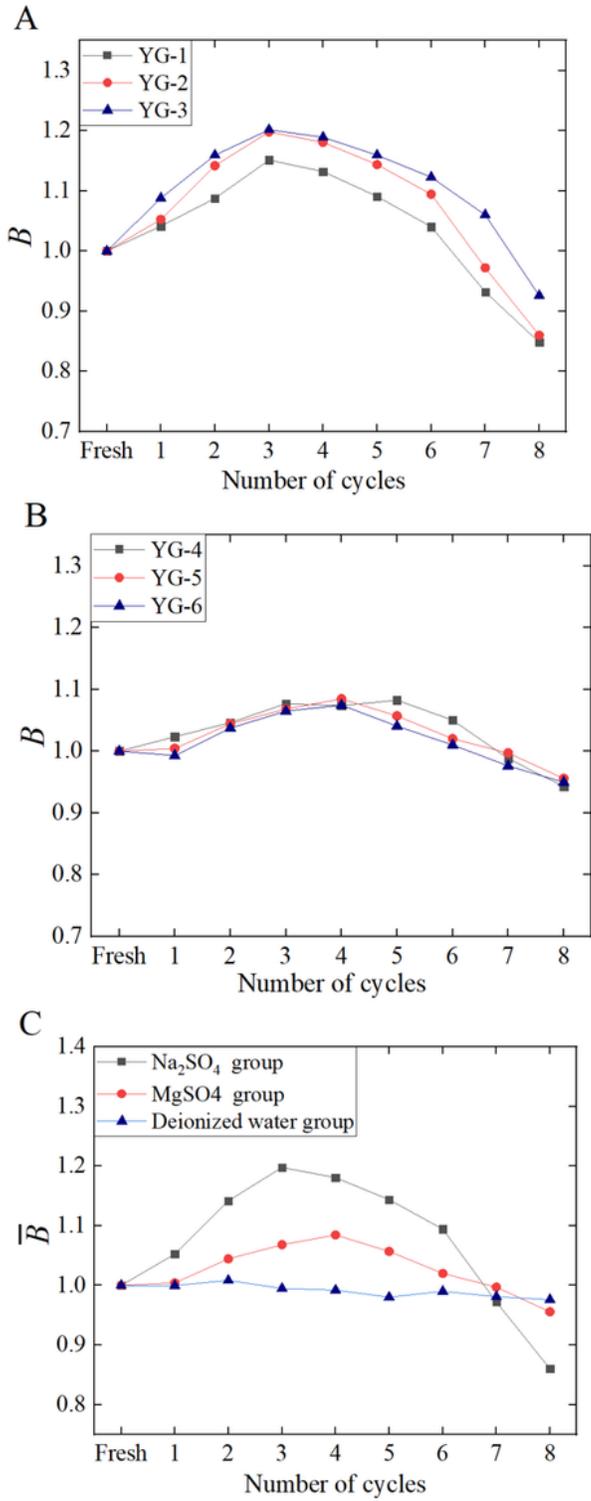


Figure 3

Normalization of ultrasonic velocity during circulation: (A) Na₂SO₄ group, (B) MgSO₄ group, and (C) Comparison of three groups

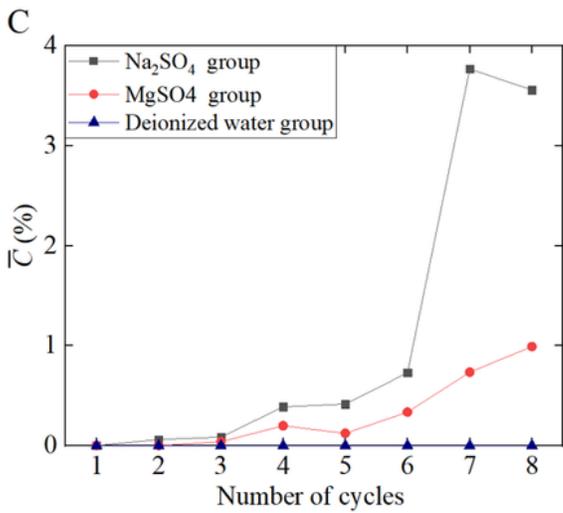
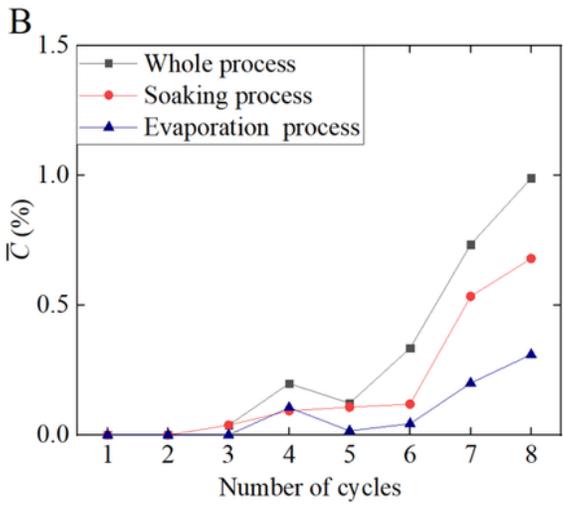
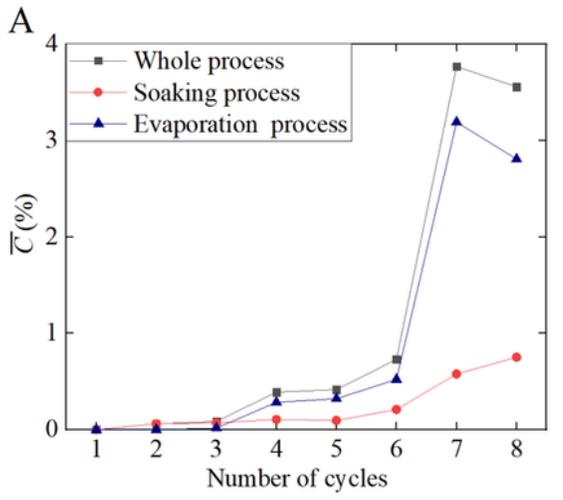


Figure 4

Spalling rate of specimens during cycling: (A) Na₂SO₄ group (B) MgSO₄ group (C) Comparison of three groups

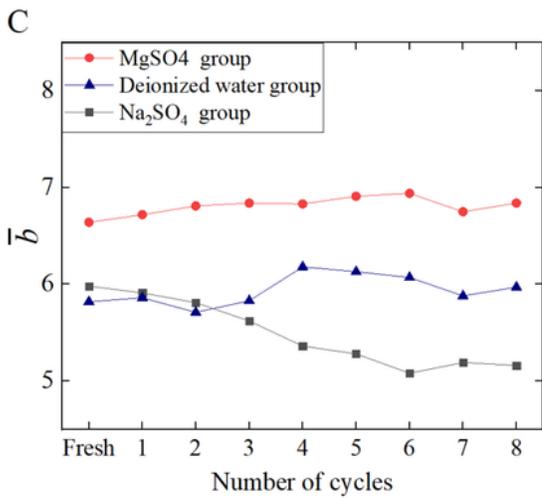
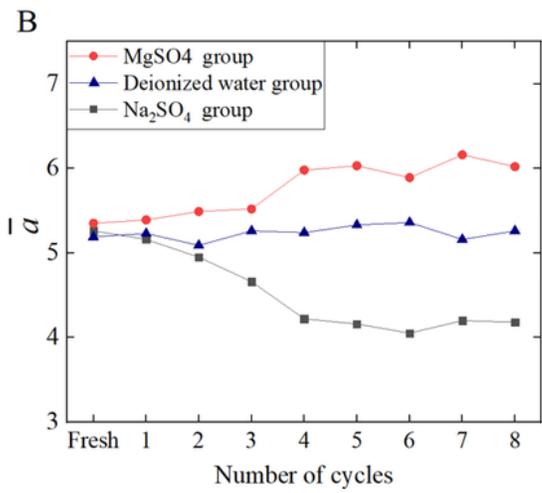
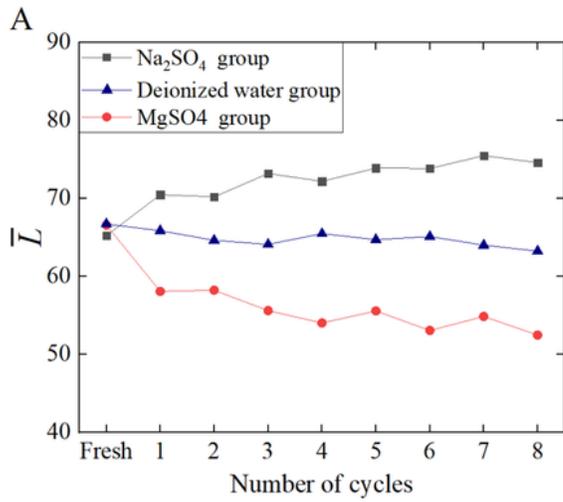


Figure 5

Changes in the brightness and color of the specimen surface during cycles: (A) L-value (B) a-value (C) b-value

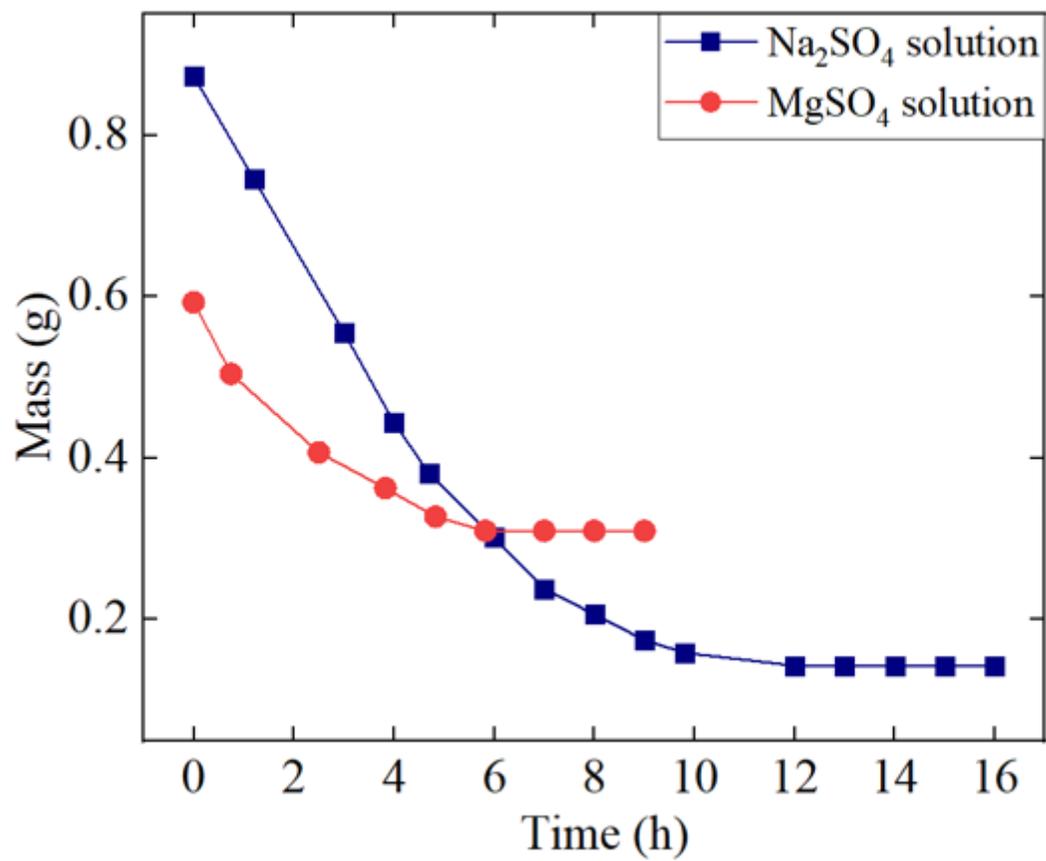


Figure 6

The mass changes of two kinds of sulfate saturated solutions during evaporation

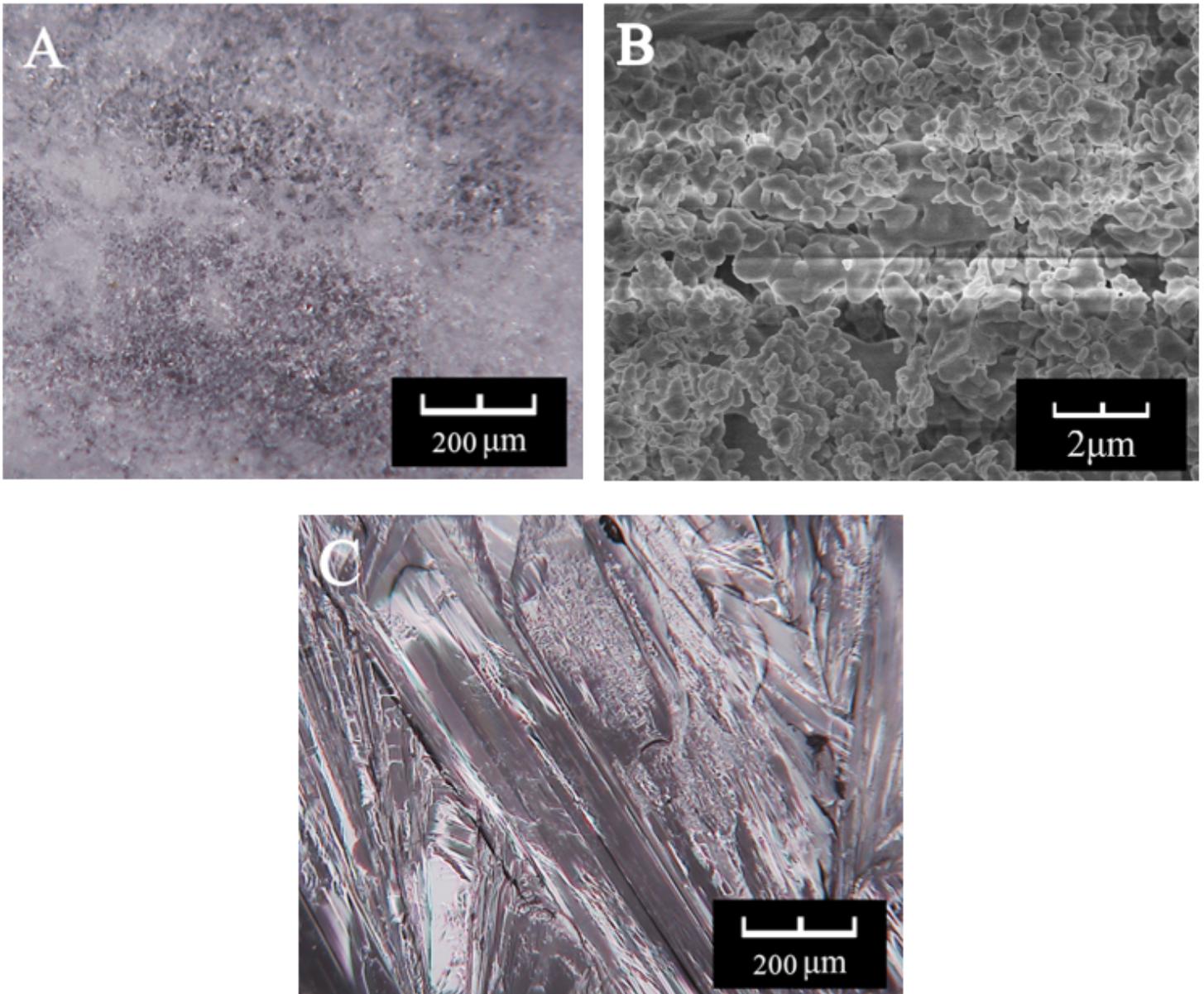


Figure 7

Microscopic morphology of sulfate crystals: (A) Optical microscope image of Na₂SO₄ (B) SEM image of Na₂SO₄ (C) Optical microscope image of MgSO₄ crystalline layer

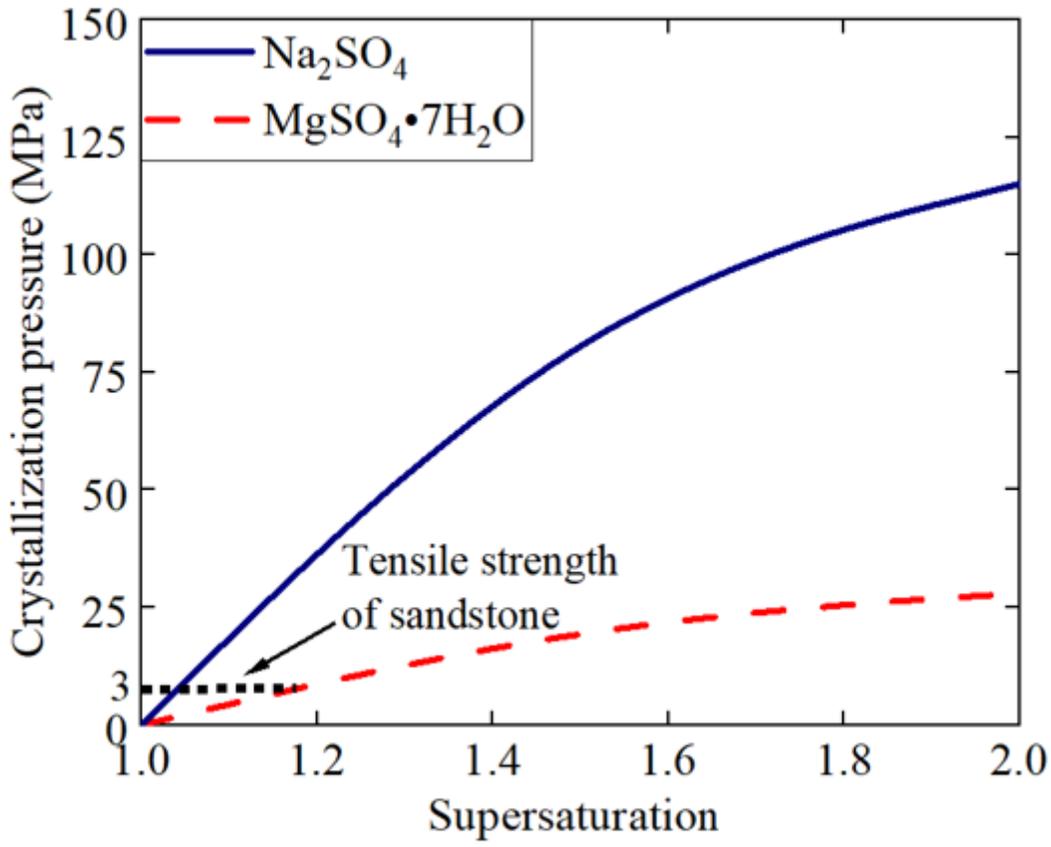


Figure 8

The crystallization pressure of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite) and Na_2SO_4 (thenardite)