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Experimental study of sulfate crystallization damage to glutenite rock in the Maijishan Grottoes

Yumeng Sheng[1,2], Ping Liu[1], Wentao Shi[1], Bo Sun[1,2,3,6*], Ningbo Peng[3,4], Dading Jiao[5] and Changqing Li[6]

Abstract

Salt crystallization is one of the most important factors causing weathering in grottoes. Cumulative crystallization of salts causes damage such as flaking and peeling of the rocks and accelerates the weathering processes of the grottoes. The accumulated crystalline salts cause spalling, skinning and other damage and accelerate the weathering process of the grotto rock body. It is necessary to study the existing glutenite rock grottoes. This paper took the glutenite rock of the Maijishan Grottoes as a case study, and Na_2SO_4 or $MgSO_4$ solutions were applied to glutenite rock specimens subjected to different deterioration cycles. The crystallization patterns of the two different salts and their damage to the glutenite rock were analyzed and studied, the mechanism for salt crystallization damage to the glutenite rock was explored, and the crystallization pressures of the two salts in the glutenite rock were derived with theoretical calculations. The results showed that both Na_2SO_4 and $MgSO_4$ crystallization damaged the glutenite rock, and the former different sulfate solutions changed at different rates, and the changes in the wave caused faster damage than the latter. The physical indices of the rock samples in the velocities and tensile strengths were consistent. Na_2SO_4 was mainly accumulated on the surface of the specimen and damaged the glutenite rock centripetally via pulverization and exfoliation. $MgSO_4$ mainly crystallized inside the glutenite rock, which created internal fissures and reduced the strength of the rock. The theoretical maximum crystallization pressures of Na_2SO_4 and $MgSO_4$ in the glutenite rock specimens reached 33.00 MPa and 9.94 MPa, respectively. This study provides a theoretical basis for studies of salt crystallization in glutenite rock grottoes and provides a method for protecting the stones in cultural heritage sites against weathering.

Keywords Glutenite rock grottoes, Maijishan Grottoes, Sulfate solutions, Salt crystallization, Crystallization pressure, Pore damage

*Correspondence:
Bo Sun
1343354131@qq.com
[1] College of Civil Engineering and Mechanics, Lanzhou University, Lanzhou 730000, China
[2] Heritage Protection Science and Innovation Center, Northwest Research Institute Co. Ltd. of C.R.E.C, Lanzhou 730000, China
[3] Faculty of Architecture and Civil Engineering, Huaiyin Institute of Technology, Huaian 223001, China
[4] Institute for Conservation of Cultural Heritage, Shanghai University, Shanghai 200444, China
[5] Power China Northwest Engineering Corporation Limited, Xi'an 710065, China
[6] School of Civil Engineering, Lanzhou University of Technology, Lanzhou 730050, Gansu, China

Introduction

The opening of the Silk Road greatly facilitated cultural exchanges between China and other regions. Grotto temples, as carriers of religious and cultural dissemination, were distributed in large numbers along the Silk Road. The construction of different raw materials can slightly differentiate the grottoes. With the passage of time, many grottoes have experienced deterioration, including rock collapse, weathering, unloading fissures and salt damage. Therefore, studies of grotto damage are necessary. Currently, most of the studies on salt crystallization diseases in grottoes are focused on the apparent characteristics

of rock damage, with less research on micromechanisms and quantitative studies. Due to the complexity of the composition and structure of glutenite rock, most of the studies on salt crystallization damage to rocks have focused on more homogeneous rocks, while studies on glutenite rock are rare. Most of the grottoes in Northwest China are excavated on top of glutenite rock grottoes and the Maijishan Grottoes is a classic representative of the glutenite rock grottoes. Due to the excellent artistic value and unique geological environment, the Maijishan Grottoes have become the hotspot of research for scholars at home and abroad. In fact, there are many other cultural heritages excavated in glutenite rocks around the world, which are also facing the double challenges of natural weathering and man-made damages, and it is urgent to carry out in-depth research in related fields and formulate practical protection measures. Therefore, this study used the glutenite rock of the Maijishan Grottoes as the research object and investigated the mechanism for salt crystallization damage with cyclic damage tests involving sulfate salt crystallization to provide references and bases for the protection of cultural heritage sites constructed from glutenite rock grottoes worldwide.

The Maijishan Grottoes are among the "Four Great Grottoes of China" and are important world cultural heritage sites on the "Silk Road" in China. These sites reflect the spread and development of Buddhism along the Silk Road from the 5th to the thirteenth centuries A.D. and have important cultural and artistic value. The name Maijishan is derived from the fact that its peaks bear a striking resemblance to the stacks of wheat piled up in a farmer's house. The Maijishan Grottoes, the first batch of key national cultural relic protection units announced by the State Council in 1961, are located on Xiaolong Mountain on the north side of the western extension of the Qinling Mountains. The lithology of the cliff body of the Maijishan Grottoes is a set of Tertiary purplish-red and brick-red glutenite rocks, which are mainly cemented with mud, iron and calcium cements. The development of fractures in grottoes is obvious, and the shallow surface part of the weathering phenomenon is more significant [1]. Investigations and studies have shown that continuous or intermittent seepage of water from inside to outside the cave rock body, as well as the accumulation and crystallization of soluble salts migrating with the water in the shallow surface part of the rock [2–4], are the main factors contributing to the weathering of the surface part of the rock, in addition to biological weathering, fissure cutting, and other damages. On the one hand, moisture interaction with the rock mass reduces the degree of cementation of the grotto glutenite rock, which in turn reduces the strength of the rock mass. Furthermore, moisture serves as an important carrier for the migration of soluble salts and facilitates the continuous accumulation and crystallization of salts to the surface. After several large-scale seepage control projects in the Maijishan Grottoes were implemented, the seepage damage was somewhat controlled. However, seepage still occurs around some cave niches, either continuously or only intermittently during the wet seasons. In these areas, the accumulated salts on the surface of the rock are particularly obvious, resulting in the development of damage such as chalking, skinning and even flaking of the surface of the grotto rock. This further exacerbates the weathering and destruction of the grotto rock body. After the field investigation, it was found that there are four main types of weathering damage in the Maiji Mountain grottoes, including: (1) the middle and upper part of the cliff body and the periphery of the grotto niches had relatively concentrated crusting and flaking (Fig. 1a); (2) the mural paintings inside the grotto niches appeared to be crispy, detached from the rock body and

Fig. 1 Weathering damage to the Maijishan Grottoes: **a** exfoliation; **b** detachment; **c** fissures and **d** salt crystallization

perhaps hollowed out, and even whole pieces were falling off, resulting in serious damage to the mural paintings (Fig. 1b); (3) Some of the niches had internal or external fissures, which were wide, extended, and in some cases ran through the entire niche (Fig. 1c); (4) There was salt crystallization and chalking of the rock around the drainage outlets and seepage points (Fig. 1d). The presence of the drainage outlets allowed water to continuously drain out of the rock, causing the surrounding old layers to begin flaking. As the water evaporated, the salts began to accumulate around the drainage outlet, causing chalking of the rock mass. Although the water flow at the seepage was transient, but due to rapid evaporation of the water, salt accumulated rapidly, and large areas of the rock body appeared to be damaged. Therefore, it was necessary to study weathering by the salt crystals in the Maijishan Grottoes.

Studies of rock damage caused by salt weathering began earlier in other countries, particularly among scientists studying geomorphology. In their study of erosional weathering characteristics in coastal as well as arid regions, Wellman et al. [5] reported that the erosional characteristics caused by salt weathering, though highly similar to other types of weathering, differ mostly in that they act on the superficial part of the rock rather than on the surface alone. Subsequently, through salt weathering tests on ancient building stones, López-Acevedo et al. [6] discovered that salt enrichment in the internal pores of the rock and changes in the crystallization pattern, which ultimately led to the destruction of the rock, did not reveal how the salts were crystallized. Salt crystallization is associated with specific temperature and humidity values as well as evapotranspiration effects. These factors led to an increase in the concentration of salt solution inside the stone. Moreover, the higher the concentration of salt solution is, the greater the degree of crystallization and, consequently, the greater the intensity of damage [7]. The degree of salt weathering is related to the rock pore characteristics and mechanical properties in addition to the water absorption rate [8]. Glutenite rocks are highly sensitive to the damage caused by salt crystallization [9]. There is a significant correlation between freeze–thaw cycles and salt crystallization tests and between effective porosity and rock durability indices [10]. Zhang et al. [11] conducted a detailed investigation and study of salt weathering on the surface of the Mogao Grottoes cliff body and determined that the main salt types responsible for salt weathering are Na_2SO_4 and NaCl. On this basis, Yang et al. [12] analyzed the salt damage threshold of porous materials by preparing Na_2SO_4 and NaCl solutions with different ratios. Heidari et al. [13] suggested that salt crystallization cycles are more damaging to stone than freeze–thaw cycles by conducting freeze–thaw and salt crystallization experiments on Anahita Temple building stone. The physical and mechanical properties of Persepolis historical complex limestone under weathering factors such as freeze–thaw cycles, thermal shock and salt crystallization were studied by Torabi-Kaveh et al. [14]. Çelik et al. [15] assessed the impact of the durability of Döğer tuff used as a building stone for cultural heritage by means of salt crystallization tests. With the continuous deepening of related research, researchers have shown [16, 17] that the damage mechanism of salt weathering is also related to the cohesion between particles within the rock, the more cohesion between particles decreases, the greater the degree of salt weathering. Research on salt weathering has begun to progress toward microscopic as well as quantitative studies. It was found that salt crystallization stress had the greatest effect on the deterioration of feldspathic sandstone [18], while acidic solutions and wet/dry cycles also accelerated sandstone destruction [19]. These findings provide a reference for evaluating and protecting the stability of grotto rocks. By analyzing the mechanical properties, microstructures, and response mechanisms of sandstone and limestone during wet and dry cycling, the researchers provided a reference for quantitatively evaluating the fracture tendencies and microstructural characteristics of the rocks [20], and they emphasized the importance of salt crystallization and its effect on the durability of limestone [21, 22]. The studies pointed out that red sandstone and Ahlat igneous rocks experienced degradation of the physical, mechanical and microstructural properties during the freeze–thaw cycles of salt solutions, which led to deterioration of the physical and mechanical properties. These studies also proposed predictive models for evaluating the long-term degradation patterns of rock mechanical properties [23–26]. Through water chemistry and freeze–thaw cycling with Longshan Grotto sandstones, the researchers found that the freeze–thaw cycles and salt were the main causes of sandstone pulverization and stripping. They also compared the effects of different salt solutions on the sandstone samples via water chemistry, temperature and humidity cycling tests [27, 28]. In addition, the researchers analyzed the changes in the physical properties of the red sandstone and the hydrochemistry of the soaking solution with accelerated simulation experiments, and they found that dry and wet cycling significantly reduced the physical strength of the sandstone, while acidic or salt compounds accelerated deterioration of the sandstone [29]. Protective coatings prevented the penetration of water and salt solutions and maintained the high quality of the stone. Studies showed that coatings remained hydrophobic after salting tests [30]. Another study showed that the clay/sand ratio had a significant effect on the hygrothermal properties of the

soil mortar in the Maijishan Grottoes and that changes in the relative humidity led to differences in the water contents of different types of mortar, which is important for conservation of the frescoes and restoration of the multilayered fresco structures [31]. These conclusions are extremely important for protection of the stone cultural relics, but most of them are focused on sandstone, and there is still a lack of research on the effects of salt crystallization on glutenite rock. Therefore, it is necessary to carry out research on the destruction mechanism for gravel salt crystallization, especially for existing glutenite rock artifacts, for which targeted research and protection measures are needed.

This paper discusses the glutenite rock of the Maijishan Grottoes as the research object. Cyclic deterioration tests were conducted on the specimens to simulate the salt transport and crystallization damage process in the rock body of the Maijishan Grottoes. To study the crystallization patterns, damage characteristics and differences of different salts in glutenite rocks, the changes in specimen mass, elastic wave velocity and strength during cyclic tests were examined. The theoretical values of crystallization of different salts in glutenite rock specimens were quantified by crystallization theory and verified via comparison with experimental phenomena. This approach provides valuable experience and entry points for subsequent glutenite rock cultural heritage conservation.

Sample preparation and test methods

Sample preparation

The Maijishan Grottoes are located approximately 40 km southeast of Tianshui city, Gansu Province, China, at coordinates 106°00′10″E and 34°21′03″N (Fig. 2). The Maijishan area has a humid mountainous climate with relatively developed vegetation. The average annual precipitation is 800 mm, the evaporation is 980 mm, and the relative humidity is 70.8%. The average annual temperature is 11.5 °C, the maximum recorded temperature is 34 °C, and the minimum temperature is − 7.81 °C. Observations from the meteorological station of the Maijishan Grottoes east of the Maijishan Botanical Garden are shown in Table 1. The rock body of Maijishan grottoes is mainly glutenite rock, and physical and mechanical tests identified the basic properties of the glutenite rock (Table 2). From the densities of glutenite rock particles and the bulk density, it can be seen that the internal

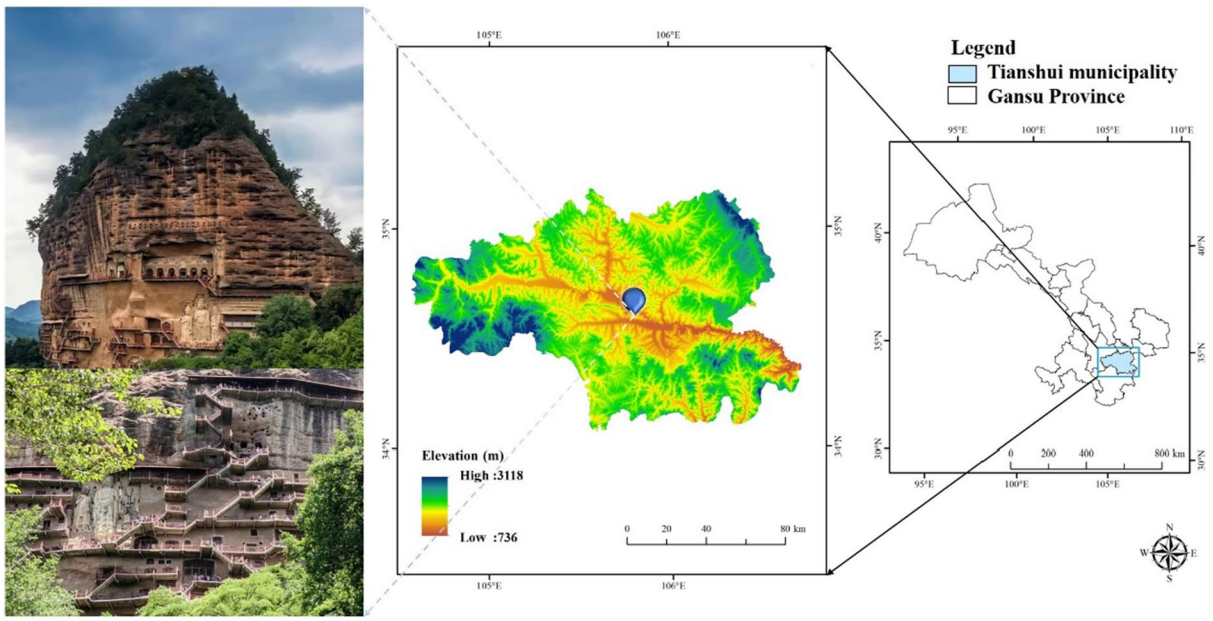

Fig. 2 Map of the Maijishan Grottoes

Table 1 Climatic data of the Maijishan Grottoes

Maijishan	Temperature *(°C)*			Relative humidity *(%)*		
	Maximum	Average	Minimum	Maximum	Average	Minimum
	34	11.5	− 7.8	100	70.8	13.4

Table 2 Basic properties of the glutenite rocks in the Maijishan Grottoes

Particle density *(g/cm³)*	Bulk density *(g/cm³)*	Saturated water absorption rate *(%)*	Compressive strength *(MPa)*	Tensile strength *(MPa)*
2.66	2.40	3.23	11.67	0.8

porosity of the gravel rock is high, and the overall structure is relatively loose. The compressive and tensile strengths of the rock show that the overall strength of the glutenite rock is poor, and cohesion between the internal particles is weak and easily affected by external influences that jeopardize the overall stability of the rock body. And mineral composition analyses (Table 3) showed that the mineral composition of the glutenite rock mainly quartz, feldspar, calcite, in addition to many clay minerals. It also contains small amounts of minerals such as black mica and white mica. The presence of the many clay minerals makes the whole glutenite rock appear as muddy cement, which also limits the overall strength of the rock and the weathering resistance. The results of the ion concentration test (ICS-2500 ion chromatograph) on the rock samples from the salt crystallization weathering area of the Maijishan Grottoes are shown in Table 4.

Twelve cylindrical sandstone core samples with 5.5 cm diameters were extracted from the Maijishan Grottoes test area for this study (Fig. 3). Specimens with height-to-diameter ratios of 1:1 were made in accordance with engineering rock testing standards. Therefore, this test was conducted in a Thermoline L+M plant growth chamber (model: TPG-1260-TH), with the internal temperature of the growth chamber controlled at 11.5 °C and humidity controlled at 70 ± 1%.

Fig. 3 Raw Samples: **a** tests with the Na_2SO_4 solution; **b** tests with the $MgSO_4$ solution

Test methods

1. Soaking solution: According to the identification results of the ion concentration test, a 5% solution composed of two sodium salts ($MgSO_4$ and Na_2SO_4) was chosen as the soaking solution. The prepared specimens were divided into two groups, numbered M and N, which represent the specimens in the presence of two salt solutions, $MgSO_4$ and Na_2SO_4, respectively. It should be noted that for the concentration, a salt solution with a mass fraction of 5% was selected to accelerate the process of salt crystallization in the glutenite rock.
2. Cyclic test: The prepared cylindrical specimens were numbered as M11, M12, M21, M22, M31, M32, N11, N12, N21 and N22. The groups were placed in closed containers containing $MgSO_4$ or Na_2SO_4 solution, with the height of the specimen below the liquid level being 1 cm (Fig. 4). Once the sample was immersed in the solution, it was withdrawn, and put in an oven at 105 °C for 24 h. Three types of tests were conducted and included a three cycle deterioration tests on the samples M11, M12 and N11, N12; b six deterioration cycles of the samples M21, M22 and N21, N22; and c nine deterioration cycles on the samples M31 and M32. At the end of the tests, the average crystallization pressure resulting from internal salt crystallization during each cycle was calculated, and

Table 3 Mineral compositions and contents of the glutenite rocks of the Maijishan Grottoes

Mineral types	Quartz	Feldspar	Calcite	Black mica	White mica	Clay minerals
Mineral contents *(%)*	30%	23%	15%	9%	5%	18%

Table 4 Ion types and concentrations in the Maijishan Grottoes

Ion Types	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Concentration *(mg/l)*	18.39	71.70	927.62	237.30	26.37	131.36	172.51

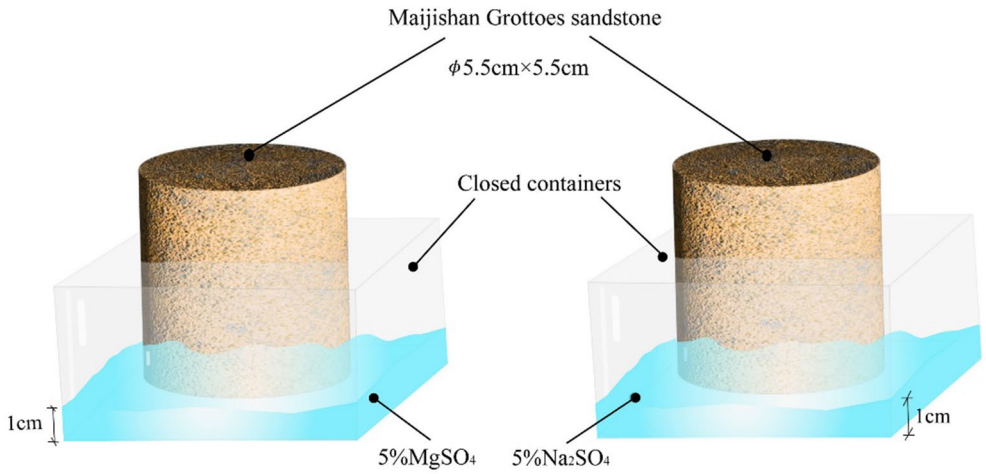

Fig. 4 Schematic diagram of test device

the average tensile strength of each specimen was tested.

3. Results: At the end of the cycle, the mass of each group of specimens was tested, and longitudinal wave speed (sonic wave meter test model: RSM-SY5N, frequency: 50 Hz), tensile strength (electrohydraulic universal testing machine model: CSS-WAW1000DL) and SEM (scanning electron microscope model: SU-1500) were used to test the edge surface. On this basis, the crystallization pressures generated by the $MgSO_4$ and Na_2SO_4 salts were calculated.

Damage characteristics

Mass change

After the cyclic deterioration test, the rate of specimen mass loss (in %, (mass of original rock—mass of specimen after cyclic test)/mass of original rock) under the effect of different salts varied, as shown in Fig. 5. As shown in the figure, for specimens M11 and M21 in the M series (in the $MgSO_4$ solution), the mass loss rates were lower than 0.6% for the first category (three cycles tests), and they progressively increased with further increases in the number of cycles. The maximum mass loss rate of each specimen throughout the test ranged from 0.5% to 1.5%. Excluding sample M31, when the number of cycles reached 6, the mass unexpectedly decreased, and I also increased. This might have occurred because of mass imbalance between the mass lost due to salt crystallization damage and the salts that were crystallized in the pore spaces of the sample. The degree of mass change during the first 2 cycles of specimens N11 and N21 in the N series (Na_2SO_4 solution) was slightly greater than that of the M series specimens. However, from the 3rd cycle

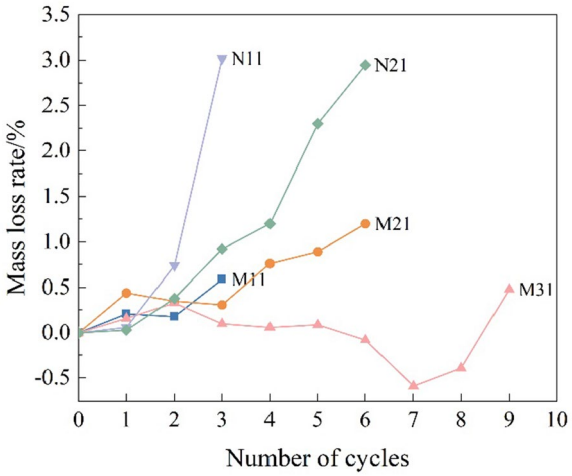

Fig. 5 Mass loss rate change curve of each specimen after 3, 6 and 9 cycles of degradation

onwards, the amount of mass loss began to increase significantly and substantially, with a maximum loss rate of 2.95% for the N series throughout the test. In conclusion, the curves in Fig. 5 reflect dynamic changes in the mass loss rates of the glutenite rock specimens during the salt crystallization cycles. The differences in the curves reflect the different effects of the salt solutions on the specimens.

Wave velocity changes

As shown in Fig. 6, specimens M11, M21, and M31 exhibited insignificant changes in wave speed during the first three cyclic degradation tests. Starting from the 4th cycle, the wave speeds of specimens M21 and M31 began

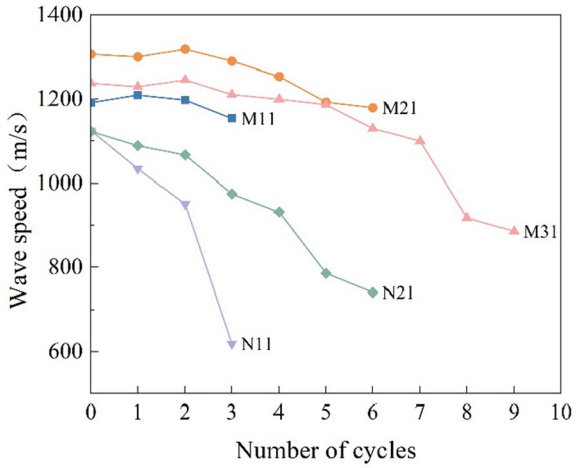

Fig. 6 Wave speed curves of specimens with the number of cycles

to decrease more significantly. By the end of the 6th cycle, the wave velocities of the two samples decreased by 9.62% and 8.72%, respectively. After the 7th cycle, the wave velocity for sample M31 decreased significantly, and by the end of the cycles, the wave velocity decreased by 28.43%. The wave speeds of specimens N11 and N21 decreased more significantly than did those of the M series ($MgSO_4$ solution) throughout the test, and the wave speeds measured at the end of the 3rd cycle were more significant than were those of the last 2 cycles (the slope of the line segment increased significantly between the 2nd and 3rd cycles). At the end of the cycling tests, the wave speeds of both decreased by 34.01% and 44.98%, respectively. The experimental data show that the increased crystallization pressure and the wave velocity attenuation had a positive relationship. Higher crystallization pressures generated more significant decreases in the wave velocity. Since the Na_2SO_4 solution showed more rapid crystallization, the crystallization pressure is greater, which directly led to a faster rate of decline for the N series specimens and the amplitude was greater. This phenomenon confirmed the positive correlation between the crystallization pressure and the extent of wave velocity decay, and it provides experimental evidence for the effect of salt crystallization on the properties of the glutenite rock.

The above data show that both salts, Na_2SO_4 and $MgSO_4$, can cause damage to the specimens, which leads to a significant decrease in the wave speed. As the number of cycles increases, the wave speed of the specimen gradually decreases, which indicates that the degree of damage occurring in the specimen gradually increases with the increase in the number of cyclic deterioration tests. After the first 2 cycles, the wave speed of each specimen did not decrease significantly, mainly because not much salt was accumulated in the internal pores of the specimens. The crystals were not in contact with the pore walls due to their small sizes and quantities and thus did not generate any crystallization pressure on the pore walls. According to the wave speed test results, for the specimens in the 1st and 2nd cycles, the measured wave speed slightly decreased or increased, respectively, due to the dissolution of water causing collodion damage and a small portion of the salt crystallization affecting the mechanical properties of the collodion enhancement effect. As the number of cycles increases, the salt accumulation in the internal pores of the specimen gradually increases, the volume of salt crystals continues to increase, and when in contact with the pore walls, the crystals that continue to crystallize exert crystallization pressure on the pore walls. When this pressure exceeds a critical value, pore destruction occurs (Fig. 7). Thereby, the porosity increases, and the wave speed decreases rapidly in the damaged specimen. On the other hand,

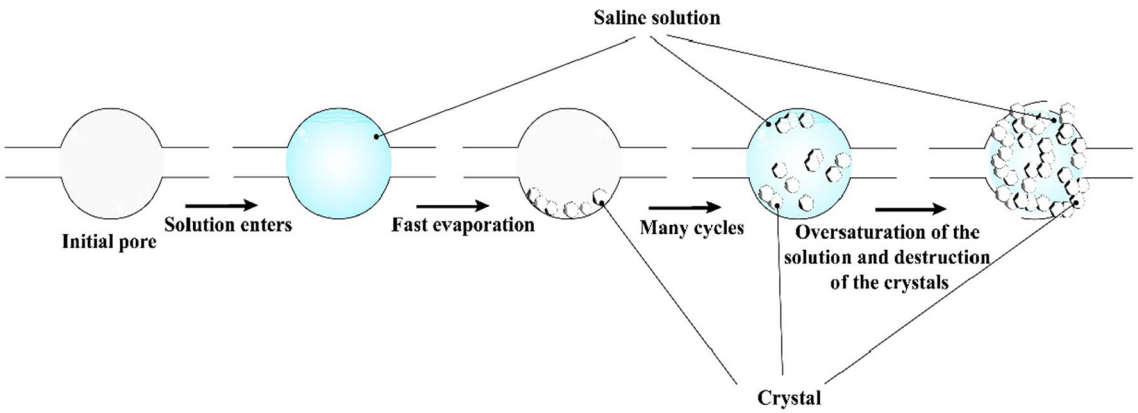

Fig. 7 Schematic diagram of pore destruction process

destruction of the glutenite rock porosity by Na_2SO_4 was more rapid and obvious than that by $MgSO_4$. The wave speed test data show that after the end of the 3rd cycle, the wave speed of the N series (Na_2SO_4 solution treated) specimen begins to significantly decrease, which indicates that after the 3rd cycle, the crystallization of Na_2SO_4 in the pores has already produced a large crystallization pressure on the pore walls within the specimen and caused its destruction. In contrast, the wave speed of the M series (treated with the $MgSO_4$ solution) specimens began to decrease significantly after the 7th cycle, indicating that the crystallization damage caused by the $MgSO_4$ crystallites on the pore walls developed on a large scale inside the specimens after 7 cycles, resulting in the generation of a significant decrease in the wave speed.

Changes in the tensile strength

As shown in Fig. 8, the tensile strengths of the glutenite rock specimens gradually decreased during sulfate cycling. The tensile strength of the N series (Na_2SO_4 solution) specimens decreased rapidly and to a large extent, with decreases of 68.79% and 88.75%, respectively, after the 3rd and 6th cycles. However, the tensile strength of the M-series ($MgSO_4$ solution) specimens decreased by 10% and 21.25% for the same number of cycles. Since the average tensile strength of the specimens after 6 cycles of Na_2SO_4 treatment was nearly 88.75%, the specimens were considered to have been completely destroyed; therefore, the 7th, 8th, and 9th cycles were not carried out for these specimens. The tensile strength of the specimens treated with $MgSO_4$ decreased by a maximum of 21.25% after 6 cycles; thus, these tests were continued for the 7th, 8th, and 9th cycles, and the tensile strength of the specimens after the 9th cycle was tested. As shown in Fig. 6, the average tensile strength of the specimens treated with $MgSO_4$ decreased by 71.25% after 9 cyclic deterioration tests. The strength changes in all the specimens are basically consistent with the characteristics of the changes in wave speed during the previous period. The wave speed and tensile strength data showed that with increasing cycles, both Na_2SO_4 and $MgSO_4$ damaged the glutenite rock specimens, but the type of damage and the timing of the two cycles were different. The tensile strength decay rates during the crystallization cycles of different salt solutions were different: the M series ($MgSO_4$ solution) showed a relatively stable strength in the initial cycles, but showed an obvious accelerated decline after 6 cycles, while the N series (Na_2SO_4 solution) showed faster strength decay at the beginning, especially in the early cycling stage. This difference stemmed from the different effects of the different salt solutions on the glutenite rock specimens, and the N series (Na_2SO_4 solution) had stronger damage, so its tensile strength decayed faster.

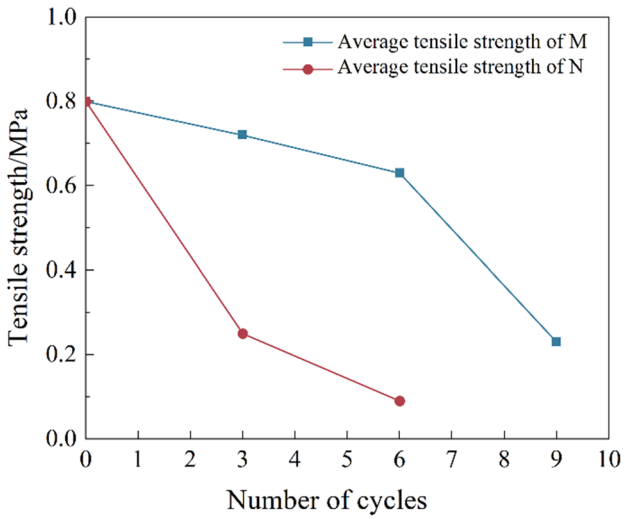

Fig. 8 Tensile strength curves of specimens with cyclic deterioration numbers

Epigenetic characterization

The above data indicate that after 3 cycles, the degree of glutenite rock mass loss caused by Na_2SO_4 is much greater than that caused by $MgSO_4$. As the crystallization volume change during the crystallization of the Na_2SO_4 solution is greater than that of $MgSO_4$, its volume expansion after crystallization is more obvious. This is because at temperatures lower than 32.4 °C, the Na_2SO_4 crystals are in the form of Na_2SO_4-$10H_2O$, which is 4.6 times of the volume of anhydrous Na_2SO_4 crystals. When the Na_2SO_4 solution in the pores reaches supersaturation, the material begins to crystallize, and the resulting crystals are $Na_2SO_4{\cdot}10H_2O$. This is when the physical state of Na_2SO_4 undergoes a rapid transformation, causing a change in volume. With an increase in the number of cycles, the crystallites accumulate and expand in the pores of the specimen surface, destroying the pore structure and causing the glutenite rock surface to begin to crust, pulverize or even flake (as shown in Fig. 9c and d).

From the test results, the damage caused by $MgSO_4$ crystallization on glutenite rock occurs mainly inside the specimen, which is obviously different from the form of Na_2SO_4 crystallization damage (as shown in Fig. 10c and d).

The reason is mainly because the two salts have different crystallization rates under the same external environment, resulting in different locations of their respective crystallization enrichment, so the degree of destruction varies. Under the test conditions, approximately 10 g of Na_2SO_4 and 29 g of $MgSO_4$ were dissolved in 100 g of distilled water. The difference in solubility leads to

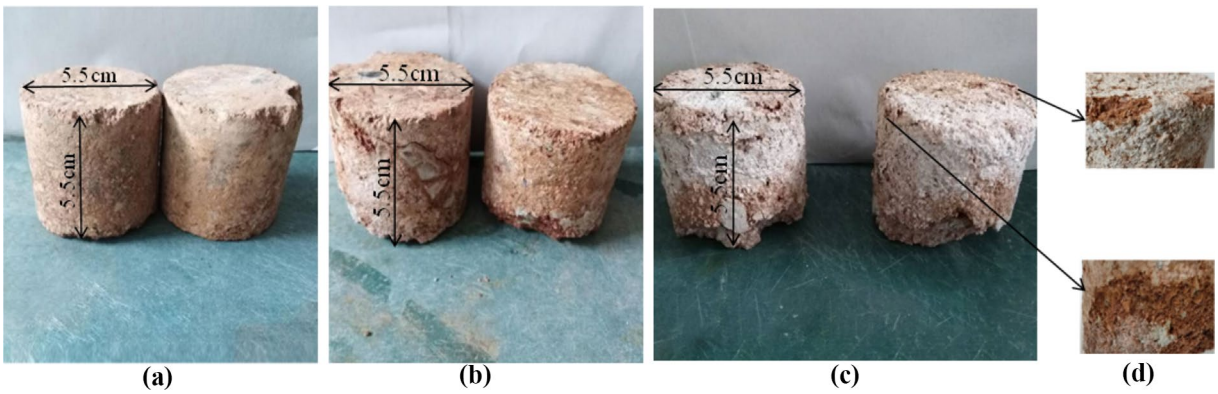

Fig. 9 Appearance of specimen N11 and N12 cyclic deterioration test (**a**, **b**, **c** are photos of the 1st, 3rd, and 6th cycles, respectively, and **d** is a close-up showing some damage)

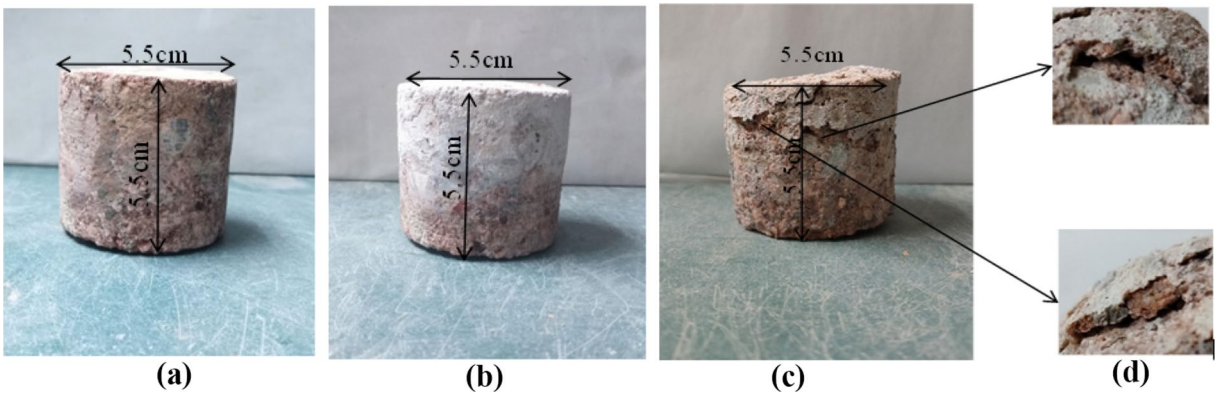

Fig. 10 Appearance of specimen M31 cyclic deterioration test (**a**, **b**, **c** are photos of the 1st, 3rd, and 6th cycles, respectively, and **d** is a photo of partial damage)

differences in the times and rates at which the respective solutions reached the saturation point. The lower the solubility is, the shorter the time required for the solution to reach oversaturation. Therefore, at the same evaporation rate, the Na_2SO_4 solution crystallized on the surface of the specimen before the $MgSO_4$ solution, which causes a large accumulation of crystals after many cycles, resulting in the destruction of the specimen from the surface to the interior through processes such as chalking and flaking (Fig. 11a). For the $MgSO_4$ solutions, the time required to reach saturation was relatively longer. As the saturation front within the specimen continues to shrink to the interior, the crystallization progresses to the interior, and correspondingly, fewer crystals remain on the surface. Therefore, the chalking and flaking phenomenon on the surface of the specimen was not obvious, and thus, the change in mass loss caused by these phenomena was not significant [32]. However, after many cycles, the crystalline expansion of $MgSO_4$ caused cracks inside the specimen, and during the subsequent cyclic deterioration process, the $MgSO_4$ crystals were continuously enriched in these fissures, causing further development of cracks, which resulted in severe damage to the specimen (Fig. 11b).

Microstructural changes

After analyzing the fresh rock samples of the original rock, it was found that there were more clay minerals inside the Maijishan Grottoes glutenite rocks, mainly two types of illite and montmorillonite (as shown in Fig. 12a, b); the internal pore sizes varied, the mineral particles were poorly sorted, and there were mostly more crushed clay minerals filling between quartz and calcite.

After 9 cycles of deterioration testing with $MgSO_4$ solution, the microscopic characteristics near the exterior of the rock samples are shown in Fig. 12c, d). As shown in the figure, the accumulation of salts close to the surface of the rock samples is low, and the salts exhibit a band-like distribution with respect to the mineral contacts. The mineral surface area has not changed

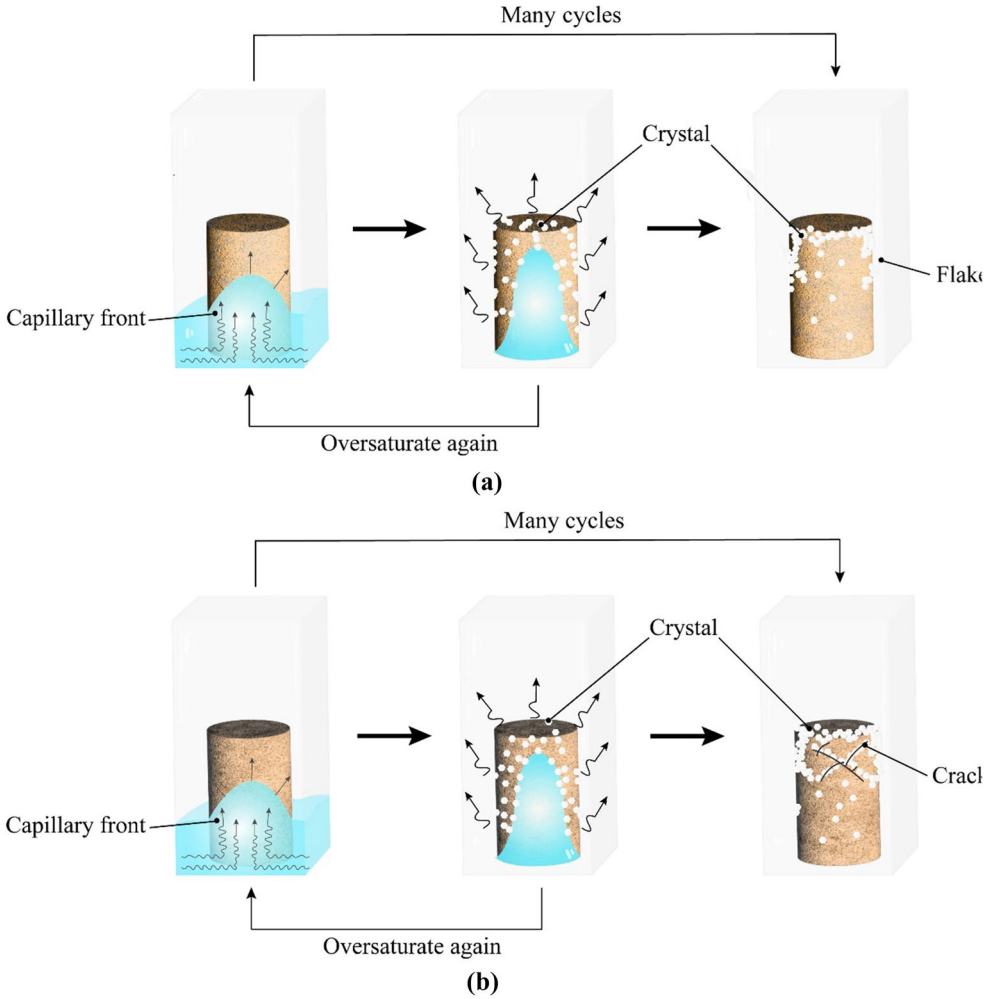

Fig. 11 Schematic diagram showing salt migration and crystallization damage: **a** Na_2SO_4 solution transport and crystallization destruction; **b** $MgSO_4$ solution transport and crystallization destruction

(See figure on next page.)

Fig. 12 Micromorphological characteristics of the glutenite rock samples before and after destruction (**a**, **b** are micrographs of the original rock samples; **c**, **d** are external micrographs of the M-series samples; **e**, **f** are internal micrographs of the M-series samples; **g**, **h** are internal micrographs of the N-series samples; **i**, **j** are external micrographs of the N-series samples; in the figure, Qz represents quartz, K represents kaolinite, Cal represents calcite, Ab denotes sodium feldspar, I/S denotes imbricated layer, and M and N are $MgSO_4$ and Na_2SO_4 crystals, respectively)

much, and the distribution characteristics have not changed significantly. The microscopic characteristics of the minerals near the interior of the rock samples are shown in Fig. 12e, f. There are many $MgSO_4$ crystals in the pores inside the rock samples, and it is obvious that the distribution is increasingly extensive than that near the surface of the rock samples. Additionally, the accumulation of many $MgSO_4$ crystals makes the mineral surface appear similar to the radial pattern of the fissures. The creation of cracks destroys the original morphology of the pores and increases their connectivity.

After 6 cycles of deterioration testing with Na_2SO_4 solution, the microscopic characteristics of the minerals near the rock surface are shown in Fig. 12g, h. As shown in the figure, many Na_2SO_4 crystals are distributed on the surface of the minerals, and multiple continuous damage phenomena occur. The surface layer of the mineral starts to pulverize and flake with a radial pattern. Local magnification of the damaged area revealed that many Na_2SO_4 crystals

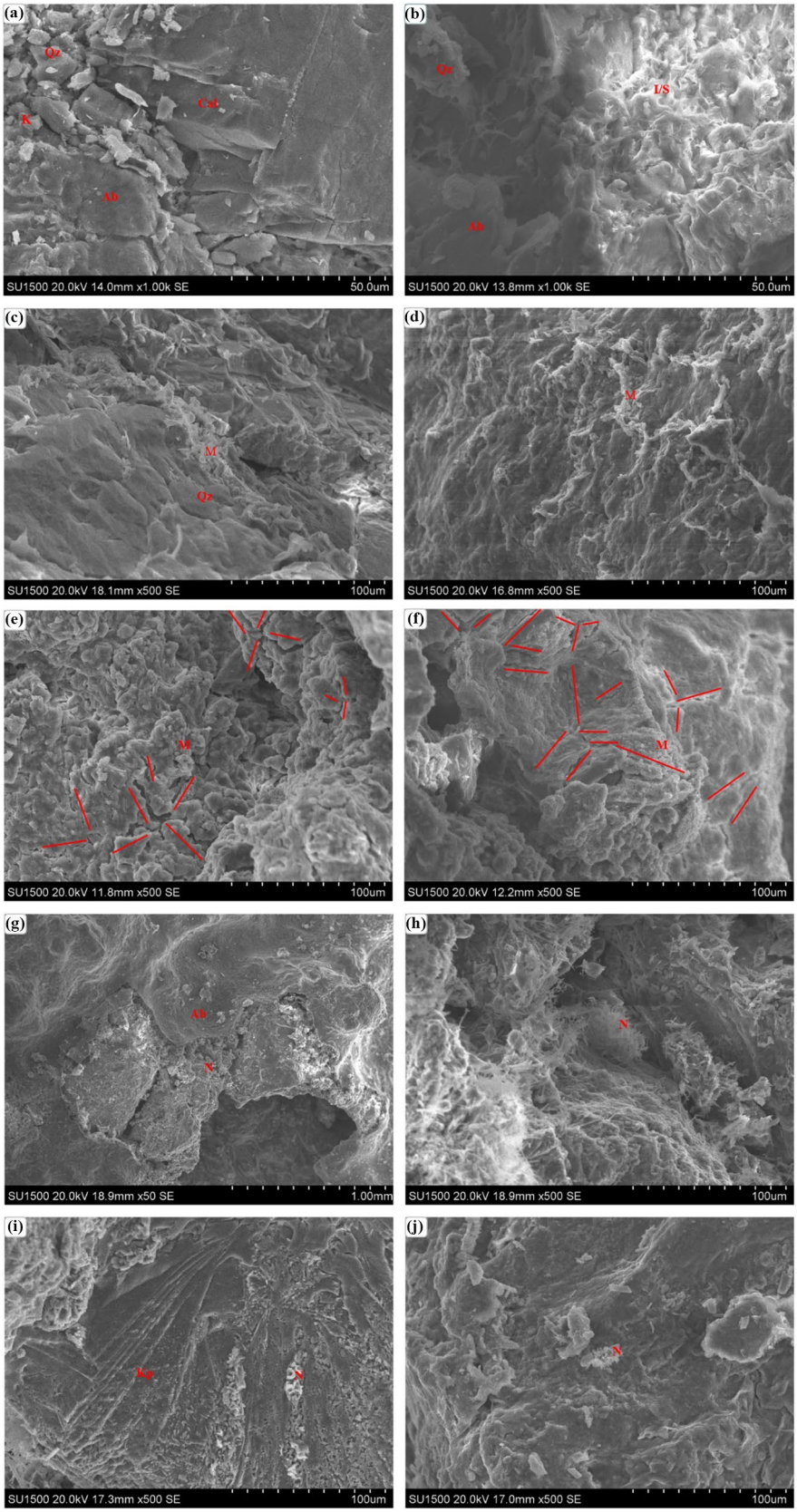

Fig. 12 (See legend on previous page.)

in the internal pore space formed needles and aggregated into clusters. The presence of the crystals causes the pore volume to increase; Fig. 12i, j shows the surface characteristics of the minerals close to the interior of the rock samples. The Na_2SO_4 crystals are sporadically distributed in the pores on the surface of potassium feldspar, the feldspar grains exhibit little alteration, and the overall damage is not obvious.

From the above analysis, it can be seen that from the microscopic point of view, both $MgSO_4$ and Na_2SO_4 can cause damage to glutenite rock, but the location and form of the damage are different: $MgSO_4$ crystals are mainly attached to the inside of the rock samples, and through the generation of fissures, the pore connectivity of the surface of the minerals increases, which damages the minerals in the surface pores of the rock samples. The damage effect is relatively small, indicating that the damage caused by $MgSO_4$ to the sandstone samples occurs centrifugally. $MgSO_4$ crystals are also present in the surface pores of glutenite rock, and the damage effect is relatively small, which indicates that the damage caused by $MgSO_4$ to the glutenite rock samples occurs from the centripetally. Na_2SO_4 crystals mainly adhere to the surface pores of the samples, and the large amount of salt aggregation enlarges the pore space to the surrounding areas, increases the volume, and pulverizes and exfoliates the minerals in the surrounding areas through damage. There are also a few Na_2SO_4 crystals in the pore space near the inner part of the glutenite rock, but the degree of pore destruction is lower, indicating that Na_2SO_4 mainly causes the destruction of glutenite rock from the outside to the inside through pulverization and exfoliation.

Crystallization pressure calculation

Theoretical analyses

The destruction of rocks results in the destruction of the pores within the rock. The main cause of pore destruction is the crystallization pressure exerted on the pore walls by salt crystallization. Throughout the cyclic degradation test, the salt solution concentration gradually increased with increasing evaporation of water. When the concentration exceeds the saturated concentration of the salt solution at the current temperature, the solution will begin to crystallize in the pore, and the crystals will continue to grow within the saturated solution before they come into contact with the pore walls.

Cahn [33] and Scherer [34]. Proposed that the magnitude of the pressure exerted by crystals on pore walls can be expressed by Eq. (1):

$$P = \frac{R_g T\, ln\left(\frac{C}{C_0}\right)}{v} \tag{1}$$

During this test, the calculated crystallization pressure of the crystals was mainly determined by the saturation of the solution within the pores. As the number of cycles increases, the concentration of the solution inside the specimen changes, so correction Eq. (2) is introduced:

$$P_N = \frac{R_g T\, ln\left(\frac{C_N}{C_0}\right)}{v} \tag{2}$$

where R_g is the gas constant, T is the absolute temperature, C is the concentration of the solution, C_0 is the saturation concentration of the solution, P_N is the crystallization pressure (corrected), C_N is the concentration of the solution inside the specimen during the N^{th} cycle and N is the number of cycles.

Calculated results

As shown in Fig. 13, for the specimens in the N series (Na_2SO_4 solution), 3 versus 6 cyclic deterioration tests started to generate crystallization pressure between the 2nd and 3rd cyclic deterioration tests, with crystallization pressure values of 5.90 MPa and 1.31 MPa, respectively. For the M series specimens in the presence of $MgSO_4$ solution, no crystallization pressure was generated during the first 6 cyclic deterioration tests. It was not until between the 7th and 8th cyclic deterioration tests that crystallization pressure started to be generated with a pressure value of 1.56 MPa. As seen from the foregoing, the average tensile strength of the original rock specimen is 0.80 MPa, so the N-series (Na_2SO_4 solution) and M-series ($MgSO_4$ solution) specimens in the 2nd to 3rd and 7th to 8th cycle degradation test processes will begin to obviously experience destruction, respectively. These

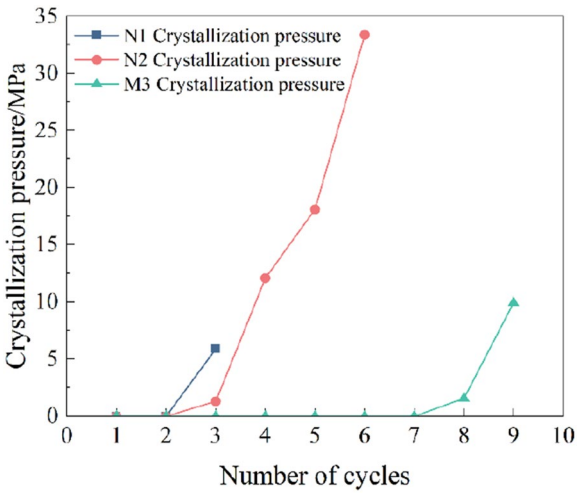

Fig. 13 Internal crystallization pressure of each specimen with different cycle numbers

data are basically consistent with the above change rules for wave speed and mass. It is also evident that Na_2SO_4 generates crystallization pressure in the specimen at a faster rate than $MgSO_4$, which is mainly due to the difference in the concentration of solution required to be achieved to generate crystallization pressure between the two. The crystallization pressure starts to increase when the concentrations of the Na_2SO_4 solution and $MgSO_4$ solution reach 0.95 mol/L and 2.48 mol/L, respectively. In the subsequent cyclic deterioration test, as the number of cycles increased, the crystallization pressures generated by the crystallization of the Na_2SO_4 solution and $MgSO_4$ solution in the specimen gradually increased. After calculation, it can be seen that the maximum crystallization pressure can reach 33.4 MPa and 9.94 MPa at the end of the test. However, these calculated values are only theoretical values, and the pressure in the actual test is lower. However, the theoretically calculated values can provide a quantitative reference for actual rock crystallization damage, especially as a metric of the damage to the Maijishan Grottoes glutenite rock caused by salt crystallization boundaries and reference values.

Discussion

In studies of sulfate crystallization and crystallization pressure, there are differences in research methods and conditions, so there are also discrepancies in the sulfate crystallization pressures obtained from tests or simulations by different researchers. Scherer et al. used a thermodynamic model to derive the maximum crystallization pressure of Na_2SO_4 as approximately 114 MPa [34], while Steiger deduced that it would reach 270 MPa in closed space [35]. Flatt et al. [36] described a simple but effective method for predicting the occurrence of salt damage and quantified the susceptibility to salt crystallization. In recent years, research methods have been constantly improved. Microfluidics has become an important tool for studying and controlling salt crystallization processes [37]. Derluyn et al. developed a computational model to reveal the coupled processes of heat, water and salt ion transport, and crystallization-induced damage in porous materials, and demonstrated the performance of the model through simulation experiments. The results of this study show that an accurate understanding of crystallization kinetics is essential for controlling salt damage [38]. The kinetics of recrystallization of sodium sulfate and sodium chloride during moisture cycling were found to have an effect on sandstone damage, with precipitation of sodium sulfate being preferred and crystal size being an important factor in explaining damage [39]. Espinosa-Marzal et al. explored the damage mechanism of salt crystallization on limestone, including the increase in crystallization pressure with increasing supersaturation, and the possibility that the crystallization pressure in small holes may arise from the curvature dependence of the solubility of salt crystals [40]. In addition to experiments, new techniques such as molecular simulation are widely used. Wu et al. recorded the crystal growth process using microscopy and image processing techniques and calculated the solution supersaturation and crystallization pressure [41]. By comparing the effects of different salt solutions on soil samples, Hu et al. found that sodium sulfate solution had the strongest salt-damaging effect on soil samples [42]. Some scholars have applied crystallization pressure studies to the protection of cultural relics. Ruiz-Agudo et al. chose the Monastery of San Geronimo as a case study to explore the effect of indoor environmental conditions on salt weathering and tested restoration methods using crystallization inhibitors. The results showed that magnesium sulfate was the main salt component and caused damaging events during seasonal changes. The experiments showed that an aqueous solution of organophosphates is an effective inhibitor. The Chapel of Muñoz in Cuenca, Spain, one of the most striking monuments in the World Heritage city, was severely damaged by stone weathering caused by salt mixtures. Martínez-Martínez et al. designed an adaptive preventive conservation plan to mitigate the salt damage by analyzing the crystallization dynamics of the salt and by environmental monitoring, and proposed precautionary measures to reduce the ingress of salt and moisture into the stone monument. Salt decay is a significant problem in modern and historic building materials, and the use of inhibiting chemicals that can control crystallization of porous materials is expected to mitigate this problem [45]. Salt accumulation in different types of sandstone increased over time, but with different gradients of increase, and the salt distribution further influenced the development of salt damage and evaporation rates [46]. Modifiers were used for sandstone desalination, and it was found that all three modifiers promoted the precipitation of sodium sulfate at the surface and could be used to protect sandstone artifacts from salt damage [47]. The crystallization pressures of 33 MPa for Na_2SO_4 and 9.94 MPa for $MgSO_4$ determined in the present study of glutenite rocks are within reasonable ranges compared to the above findings.

Conclusion

In this study, the mechanism of sulfate crystallization damage in glutenite rock grottoes was investigated by taking the Maijishan Grottoes as a case study. Salt crystallization tests were carried out on the glutenite rock samples by different salt solutions, and the following conclusions were obtained:

1. Both Na_2SO_4 and $MgSO_4$ can cause damage to the glutenite rock of the Maijishan Grottoes and accelerate the weathering and destruction of glutenite rock. Both of these salts caused damage to glutenite rocks by salt crystallization, but different salts accumulated at different locations.
2. The two salts showed different speeds and manifestations for destructive effects on the glutenite rock. In the same environment, the rate of glutenite rock crystallization damage by the Na_2SO_4 solution was greater than that of the $MgSO_4$ solution. Na_2SO_4 mainly caused skinning, flaking and other damage on the surface of the glutenite rock. $MgSO_4$ was mainly enriched in the internal pore spaces of the glutenite rock and reduced the overall strength of the rock by generating fissures and increasing the connectivities of the pore spaces.
3. The destruction of glutenite rock by sulfate was closely related to the concentration of the salt solution. When the concentrations of the Na_2SO_4 and $MgSO_4$ solutions inside the glutenite rock reached 0.95 mol/L and 2.48 mol/L, respectively, crystallization pressure was generated, and the theoretical crystallization pressures were 1.31 MPa and 1.56 MPa, respectively. These values are greater than the tensile strength of the original rock, and the maximum crystallization pressure can reach 33 MPa and 9.94 MPa, respectively.

Salt crystallization experiments were carried out with glutenite rocks from the Maijishan grottoes with two different salt solutions, and the crystallization pressures were calculated. Different salt solutions had different destructive effects on the glutenite rock, but they accelerated weathering of the rock body in the glutenite rock grottoes, and thus the weathering caused by different sulfate crystals should be considered for the grottoes. Therefore, prevention and control of salt crystallization damage to the glutenite rock grottoes should be different for different sulfate crystallization characteristics, and targeted measures should be taken. For sodium sulfate crystallization damage, the concentration of the sodium sulfate solution inside the glutenite rock should be controlled to reduce the damage done to the cultural heritage; magnesium sulfate crystallization damage should be controlled on the surface of the gravel rock. This study provides new insights into the prevention and restoration of salt crystallization damage in glutenite rock grottoes.

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Author contributions
Conceptualization, PL and BS; methodology, YS, NP and WS; validation, YS and WS; formal analysis, YS, WS and DJ; investigation, CL; writing—original draft preparation, YS and WS; writing—review and editing, PL, BS and NP; funding acquisition, PL and BS. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials
The data used to support the findings of this study are included within the article.

Declarations

Competing interests
The authors declare no competing interests.

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