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Mechanical Properties of Tonalite Subjected to Combined Effects of Chemical Corrosion and Freeze-Thaw Cycles

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Abstract: This paper presents an investigation into the coupled effects of chemical corrosion (by Nitric acid solution) and freeze-thaw cycles on the physical and mechanical properties and damage deterioration of tonalite specimens. The experiments included the uniaxial compression test, three-point bending test, the Young's modulus test, the X-ray diffraction test and the scanning electron microscope test. The damage condition of tonalite specimens was analyzed using scanning electron microscope (SEM). The experimental results reveal that chemical erosion has a significant influence on the propagation of micro cracks and accelerates the development of damage in the tonalite samples under monotonic loading. Due to cementation, no noticeable difference in uniaxial compressive strength was observed between the specimens subjected to combined effects of chemical corrosion and freeze-thaw cycles and those subjected to freeze-thaw cycles only. The amount of cementing materials in the chemically treated samples was found using SEM, which shows that chemical reactions promoted mechanical properties to some extent.

Keywords: tonalite; chemical corrosion; freeze-thaw; coupling effect; mechanical properties

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1. Introduction

Granitic rock is widely distributed on the earth's mantle and is extensively used in engineering projects. In the complex natural environment, granitic rock may be affected by several factors, which lead to degradation of physical and mechanical properties. In cold regions, rocks are subject to frost weathering that arises from the diurnal cycle or seasonal variation. This weathering can lead to significant changes in the state of water in the rock voids, inducing the dissolution of materials in the rock mass and associated chemical changes. Therefore, the mechanism of the damage that occurs under freeze-thaw cycles is widely concerning and has a vital significance for environmental geotechnical engineering projects. Parts of the cold region in China is subjected to acid rain for a long time. The building stones in the area of Longmen caves, Luoyang city, easily crack or break. The rock materials have suffered from the combined effects of freeze-thaw cycles and acid rain for centuries. The pH of acid rain is around 4.38, and the temperature always changes in the range of 6 to −10 °C. With the development of the western regions in China, the issue of rocks subjected to freeze-thaw cycles and chemical corrosion becomes more frequent. The rock slope of an iron mine in Qinghai province, western China, is subjected to a freeze-thaw cycle from −20 to 10 °C. The rock of the slope also suffers from long-time chemical corrosion.

In recent times, weathering induced by the action of freeze-thaw cycles with different temperatures and numbers of cycles has been extensively studied. Several studies have indicated that there is 7–9% volume expansion during water-ice transformation, which is the main reason for freeze-thaw damage [1–4]. The engineering properties of granitic rock have been shown to be affected by the influence of freeze-thaw cycles. These properties include strength [5], thermodynamic properties [6] and permeability [7,8]. However, the most significant changes have been found to occur in the mechanical properties [9–15] (including quality, density, longitudinal wave velocity, porosity and Young's modulus) of various rocks that have been subjected to freeze-thaw cycles. The results of these studies revealed that most physical characteristics and mechanical properties decline with greater numbers of freeze-thaw cycles. Moreover, uniaxial compressive strength, triaxial compressive strength, tensile strength and deformation characteristics of various rocks have been measured [16–19]. It is believed that the low porosity and high strength of granitic rock plays a significant role in the low levels of damage that arise during freeze-thaw cycles, and that elastic modulus and uniaxial compressive strength (UCS) are suitable mechanical parameters to reveal freeze-thaw damage.

In addition, the interaction between water and rock is of great importance to engineers worldwide. Acidic environments can also have a positive or negative effect on the physical characteristics and mechanical properties of buildings and rock masses [20]. Under the influence of temperature, dissolution of chemical matter in water will also affect rocks, especially when it coincides with freeze-thaw weathering. Some research has focused on the changes in physical characteristics and micro-mechanical properties of rock subjected to chemical corrosion. The mechanical properties have been investigated using the uniaxial compression test, tri-axial compression test and direct shear test [21–27].

The variation in mechanical properties of granitic rock subjected to the combined effect of chemical corrosion and different freeze-thaw cycles has been experimentally studied. It is believed that the deterioration of tonalite is much more obvious at earlier stages and becomes slower in later periods [28]. The phenomenon of freezing-thawing has also been extensively studied in limestone and sandstone, which share many common features. The physical and mechanical properties of white sandstone subjected to different chemical corrosion and freeze-thaw weathering under uniaxial and tri-axial compression tests have been investigated [29,30]. A stereoscopic microscope was used to observe the fracture surface of white sandstone. Consequently, it was summarized that the elastic modulus and peak stress of white sandstone decrease after the combined effect of chemical corrosion and freeze-thaw cycles. The experiments on limestone under several different chemical solutions and freeze-thaw cycles have been carried out to study the physical damage characteristics [31–35]. The results revealed that the abundance of condensation nuclei and the pH value of water solution are the most important factors affecting the degree of damage to limestone under coupled chemical corrosion and freeze-thaw processes. The uniaxial compression tests have been to investigate the behaviour of yellow sandstone subjected to the combined effects of chemical corrosion and freeze-thaw cycles [29]. It was concluded that rocks exhibiting higher porosities are more prone to damage. Moreover, intercrystalline cracks can be more easily generated in yellow sandstone that has been subjected to chemical corrosion. Most of the studies on the combined effect of chemical corrosion and freeze-thaw weathering have focused on the physical and mechanical changes with different numbers of freeze-thaw cycles, however, the effect of minimum freezing and thawing temperatures has been ignored. It is possible that chemical reactions are affected by different low temperatures. In addition, no uniform method has been suggested to study the combined effects of rock type, chemical solution, number of freeze-thaw cycles and freezing time. This paper presents a study on the relationship between macro and micro mechanical properties of rocks and minerals subjected to the combined effect of chemical corrosion and freeze-thaw weathering.

Biotite tonalite from He'nan province, China, has been selected for this study. The tonalite specimens were soaked in nitric acid solutions. Cyclic freeze-thaw experiments were then carried out, followed by uniaxial compression. SEM was used to observe the failure plane, and to investigate the deterioration mechanism for tonalite that had been subjected to the combined effect of chemical corrosion and freeze-thaw weathering. The results of this study would play an important role in decision-making for engineers in a practical engineering setting.

2. Experimental Setup

2.1. Specimen Preparation

Tonalite was collected from an outcrop at a depth of 2 m in Luoyang City, He'nan Province, China. The diameter and height of the specimens used for uniaxial compression tests were 50 mm and 100 mm, respectively. This is in line with the recommendations of the International Society for Rock Mechanics (ISRM). The three-point bending test piece is made into a rectangle with a length of 250 mm, a height of 50 mm, and a thickness of 50 mm. The pre-fabrication width of the specimen is 3 mm crack, the depth is 26.5 mm, and the bottom end of the crack is tapered. The specific dimensions are shown in Figure 1.

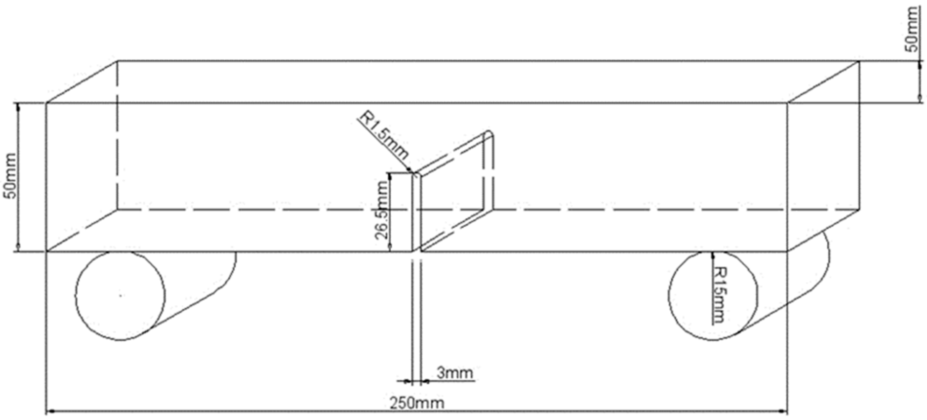


Figure 1. Three-point bending test specimen.

2.2. Physical Properties

The physical properties were determined by standard methods. The recommended procedures of ISRM for the sample preparation and the measurements were used for the following:

(1) Dry weight, dry density and saturated density determined by saturation and caliper method.
(2) The pore volume values and the porosity were obtained by the water saturation procedure.

The results are listed in Table 1.

Table 1. Original properties of tonalite.

Dry Weight (g)	Dry Density (g/cm^3)	Saturated Density (g/cm^3)	Saturation Moisture Content (%)	Porosity (%)
538.13	2.74	2.744	0.083	0.23

2.3. Equipment

A WGD-501 air-cooling freeze-thaw testing machine was used to carry out the cyclic freeze-thaw tests. Uniaxial compression test and three-point bending test were carried out using an electro-hydraulic servo triaxial compression test machine with a maximum load capacity of 2000 kN. The P-wave velocity and Young's modulus of tonalite specimens were measured using a V-MTER III ultrasonic pulse velocity tester, which has an accuracy of 0.1 μs. The mineral content of the samples was determined using an X-ray diffractometer (Bruker/D8 Advance, BRUKER Company, Beijing, China). The microstructure of the tonalite was examined using a VEGA-SBH scanning electron microscope.

2.4. Test Procedure

Uniaxial compression tests and three-point bending test were conducted on 32 tonalite specimens respectively, which were divided into 8 groups based on different experimental objectives. Uniaxial compression tests had 5 samples and three-point bending test had 4 samples for each group. The Young's modulus and longitudinal wave velocity for several tonalite specimens were measured before treatment. The specimens were then treated by different experimental methods as indicated in Table 2. The variation of temperature in the freeze-thaw cycles is shown in Figure 2. The changing time for the freeze-thaw cycles was 30 min, and holding time was maintained for 4 h. Following treatment, the Young's moduli were determined. The specimens were then subjected to the uniaxial compression test and three-point bending test. Following the test, sample fragments were collected and analysed using the X-ray diffractometer (XRD) and scanning electron microscope (SEM).

Table 2. Groups of specimens treated by different methods.

Group	Method
G1	No treatment (1 group)
G2	Immersed in HNO_3 (pH = 1) for 60 days (1 group)
G3	Subjected to 30 freeze-thaw cycles at −30 °C, −40 °C and −50 °C (3 groups)
G4	Immersed in HNO_3 (pH = 1) for 60 days, then subjected to 30 freeze-thaw cycles at −30 °C, −40 °C and −50 °C (3 groups)

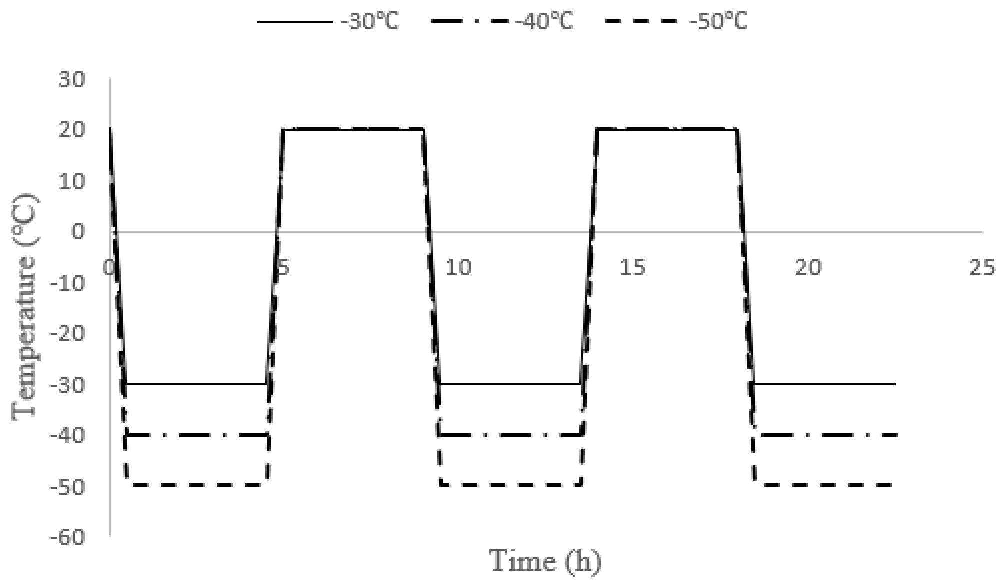


Figure 2. Temperature variation of freeze-thaw cycles for tonalite specimens.

3. Results and Analysis

3.1. Young's Modulus

The values of Young's moduli for the groups with different treatment methods are presented in Figure 3. The average Young's modulus for the control group (G1) is 40.23 GPa. The average Young's modulus for G2 is 40.65 GPa, which is similar to the original value. The Young's moduli of G3 tonalite specimens are reduced relative to the G1 group but they show no significant difference at different freezing temperatures. The average values of Young's moduli are 66.6%, 72.1% and 73.1% of original value following freeze-thaw treatment at −30 °C, −40 °C and −50 °C. The results show that freeze-thaw weathering at different freezing temperatures does not significantly influence the Young's modulus of tonalite. This can be attributed to the low porosity of the tonalite specimens.

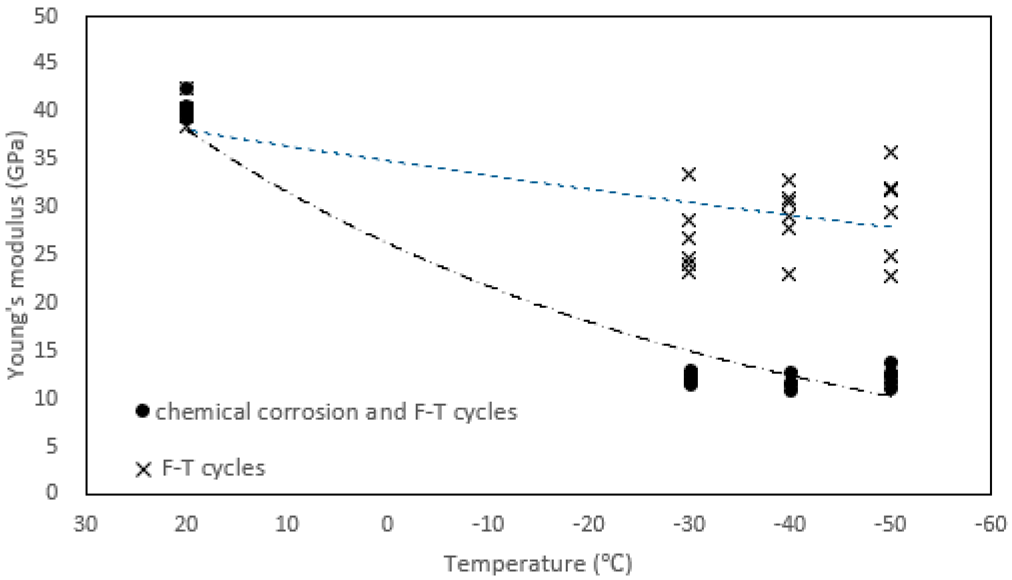


Figure 3. Young's moduli of tonalite specimens from different groups.

Again, the Young's moduli for G4 specimens are reduced relative to the G1 group but they do not show a distinct difference at different temperatures following the freeze-thaw treatment. The average values of Young's moduli are 30.6%, 29.4% and 30.3% of the original value after freeze-thaw treatment at −30 °C, −40 °C and −50 °C respectively. It can be concluded that the loss of Young's modulus of tonalite specimens subjected to the combined effects of chemical corrosion and cyclic freeze-thaw weathering is more significant than the result for each of the two treatments. The chemical effect amplifies the loss of the Young's modulus which results from freeze-thaw weathering. However, compared with the Young's modulus of samples after under the combined action of acid and freeze-thaw, the discreteness of the Young's modulus of the samples under freeze-thaw only is greater. This is because a large number of colloids were produced in the sample under the action of acid solution, making the internal structure of the sample more stable.

3.2. Uniaxial Compression Test

3.2.1. Uniaxial Compressive Strength

The values of UCS for tonalite specimens which were only subjected to freeze-thaw cycles are presented in Figure 4. The average UCS of tonalite specimens with freezing temperatures of −30 °C, −40 °C and −50 °C are 66.73%, 66.43% and 60.64% of the original value. The UCS of tonalite specimens subjected to the combined effect of chemical corrosion and freeze-thaw cycles is shown in Figure 5. The average UCS of tonalite specimens subjected to 60 days of chemical corrosion (G2) is 76.02% of that for the control group. The average UCS values for tonalite specimens subjected to combined effect (G4) with freezing temperatures of −30 °C, −40 °C and −50 °C are 65.69%, 74.45% and 59.20% of the original value. It can be seen that the UCS of tonalite specimens subjected to combined effect did not decrease distinctly with decreasing freezing temperature. The uniaxial compressive strength should have declined after freeze-thaw weathering. However, it did not decrease after chemical corrosion.

3.2.2. Peak Strain

The peak strains for the tonalite specimens are shown in Figure 6. The peak strain ε_f is the strain experienced by a tonalite specimen at peak stress σ_f. The average peak strain of tonalite specimens subjected to 60 days of chemical corrosion (G2) is lower compared with that of the control group (G1). This result, combined with the Young's modulus, indicates that the G2 specimens can be more easily destroyed. The average peak strain of tonalite specimens subjected to freeze-thaw cycles (G3) is shown to decrease with decreasing freezing temperature. In addition, the average peak strains of tonalite specimens subjected to combined effect (G4) are observed to be compared with those of G3 at −40 and −50 °C. Thus, strain softening that arises from chemical corrosion occurs in tonalite specimens subjected to the coupled effect after −40 °C freezing temperature. Although the UCS of G3 is found to be close to that of G4, the peak strain of G4 is higher than G3 and the deformation of G4 specimens is more prominent. This may imply that silica gel is created in the process of chemical corrosion, that has a cementing effect on the samples. After the specimens dry, the silica gel does not make the peak strain of G4 decrease too much. This also makes the UCS of G4, which has a lower Young's modulus, closer to the UCS of G3. (More evidences will be given in the next sections).

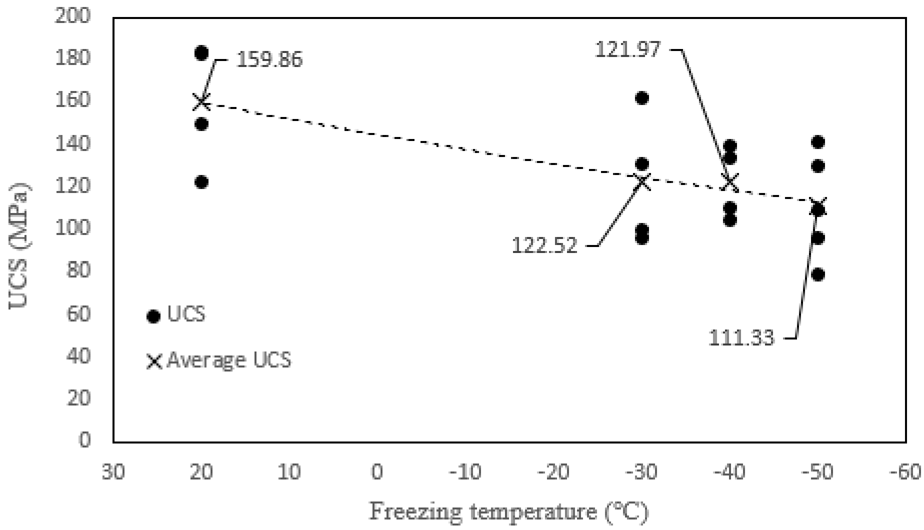


Figure 4. The variation of uniaxial compressive strength (UCS) for tonalite subjected to freeze-thaw cycles (G1 and G3).

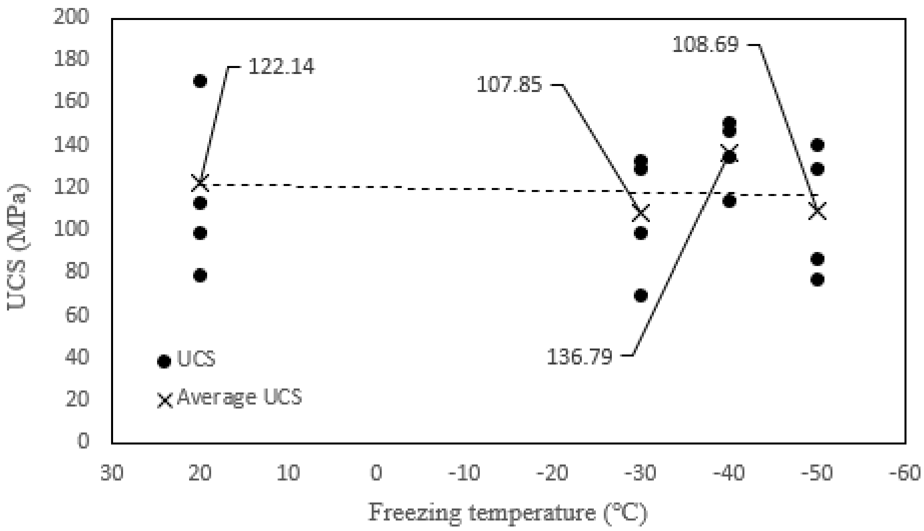


Figure 5. The variation of UCS for tonalite subjected to combined effect of chemical corrosion and freeze-thaw cycles (G2 and G4).

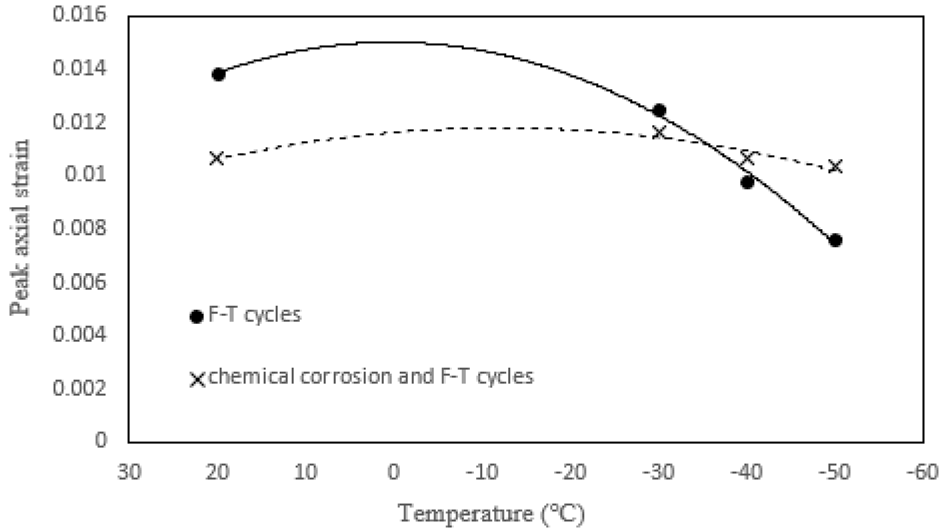


Figure 6. The peak axial strain ε_f of tonalite specimens.

3.2.3. The Compressive Stress-Strain Curves for the G4

The stress-strain curves for the tonalite specimens subjected to the combined effects of chemical corrosion and cyclic freeze-thaw weathering are shown in Figure 7. Compared with the control group, the peak stress of tonalite specimens subjected to combined effect is found to decrease with decreasing temperature. The peak strain of tonalite specimens submitted to the combined effect is shown to increase slightly. However, there are several factors that may affect peak strain, and these should be considered. Based on the stress-strain curves at −30 °C and −40 °C, the compaction stage was found to be longer compared with the control group in strain. The compression stage at −50°C is not significant, indicating that the internal structure deteriorates faster. The combination of chemical corrosion and freeze-thaw cycles is found to have a physical softening effect on tonalite, as the peak strain for the specimens at −30 °C, −40 °C and −50 °C are all higher than the untreated specimen. Moreover, this softening effect is most distinct for the tonalite specimen with −50 °C minimum freeze-thaw temperature combined effect. Understandably, the ductility of tonalite specimens decreases as a result of the combined effects of freeze-thaw cycles and chemical corrosion.

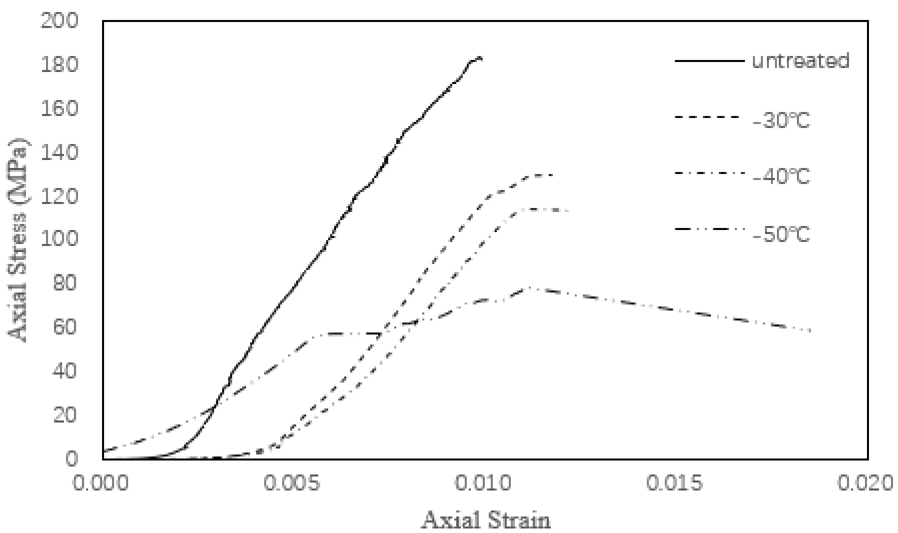


Figure 7. Compressive stress-strain curves for tonalite of subjected to combined effect weathering (G4).

3.3. Three-Point Bending Test

The critical stress intensity factor (K_{IC}) of tonalite specimens can be calculated according to the three-point bending test. The K_{IC} of tonalite specimens treated with nitric acid at pH = 1 (G1&G2) are shown in Figure 8. Generally speaking, the K_{IC} of G2 decreases with the increase of soaking time. The K_{IC} of granite specimens soaked in nitric acid at pH = 1 of soaking time 30, 60 and 90 days are 5.9%, 12.6% and 12.8% of the original value, respectively. The trend of reduction is very fast from 30 days to 60 days, but the decline is almost the same from 60 days to 90 days.

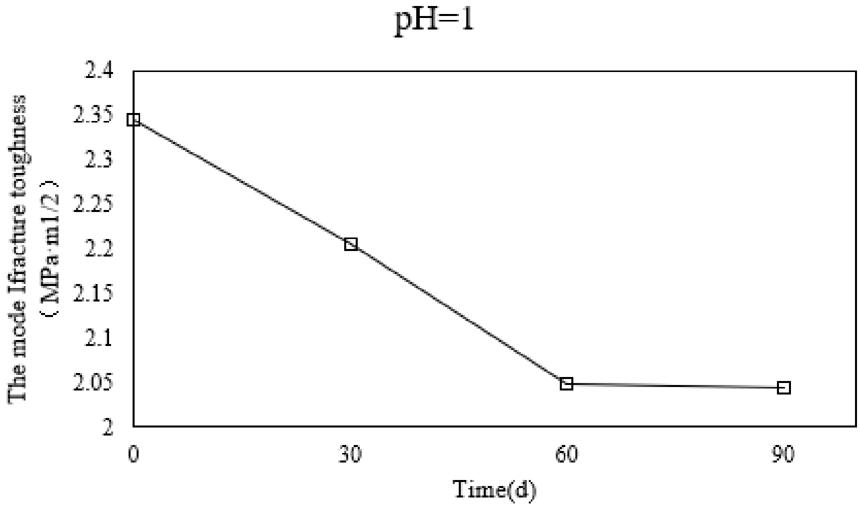


Figure 8. The K_{IC} of tonalite specimens after nitric acid treatment at pH = 1.

The K_{IC} of tonalite specimens under freeze-thaw (G3) and the combined effect of chemical corrosion and freeze-thaw cycles (G4) are shown in Figure 9. K_{IC} of untreated tonalite specimens is 2.34 MPa. The K_{IC} of G3 and G4 both decreases as the freezing temperature reduces. The K_{IC} of tonalite specimens with freezing temperatures of −30 °C, −40 °C and −50 °C are 82.2%, 82.0% and 86.1% of G1. The K_{IC} of tonalite specimens combined effect of chemical corrosion and after −30, −40, and −50 °C freeze-thaw cycles decreased by 1.3%, 5.2% and 9.3% of G2. It can be seen that the K_{IC} of G4 declined less than the K_{IC} of G3 compared with the control group. In the G3, the K_{IC} is slightly increased at a freezing temperature of −50 °C, which can be attributed to the error caused by the discreteness of the tonalite itself.

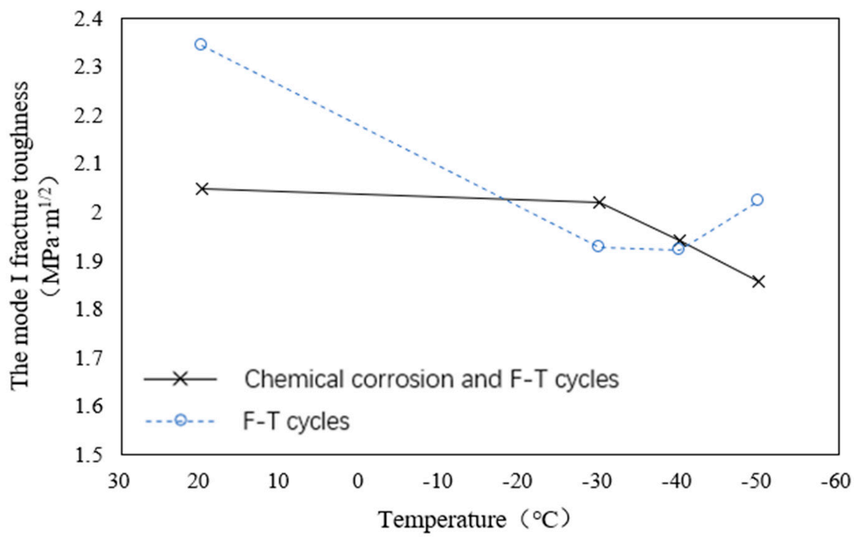


Figure 9. The K_{IC} of tonalite specimens under freeze-thaw (G3) and the combined effect of chemical corrosion and freeze-thaw cycles (G4).

3.4. Factors Influencing the Mechanical Properties of Tonalite under the Combined Effect of Chemical Corrosion and Freeze-Thaw Cycles

Several factors can affect the mechanical properties of tonalite subjected to the coupled effect of freeze-thaw weathering and chemical corrosion. The influence factors have been separated into internal and external causes. Internal causes include (but are not limited to) the type of rock, the development of cracks, density, porosity and permeability. External causes include freezing methods (i.e., freezing times, freezing cycles and freezing temperature), initial moisture content, water supply condition, and the stress state of the rock. Based on analysis of the results of the experiments carried out in this work, the factors that affect the mechanical properties of tonalite specimens subjected to the combined effect of freeze-thaw weathering and chemical corrosion are summarized as follows:

(1) Freezing temperature

At different freezing and thawing temperatures, the UCS of tonalite specimens does not differ much. However, the peak strain decreases with decreasing freezing temperature. The K_{IC} of specimens decreases as the freezing temperature reduces.

(2) Chemical reaction of minerals

Based on the comparison of the peak strains for G3 and G4 specimens, it can be inferred that cementation takes place inside the specimens. This enhances the peak strain and the peak stress of G4. Otherwise, the UCS and K_{IC} of samples subjected to combined effect should be much lower compared with those subjected to freeze-thaw or chemical corrosion. Additionally, a cream suspension liquid was found in the experimental container when tonalite was soaked in nitric acid solution. Thus, minerals of tonalite undergo hydrolysis when the pH of the chemical solution is sufficiently low:

① Plagioclase (Albite):

$$NaAlSi_3O_8 + 4H^+ = Al^{3+} + 3SiO_2 + 2H_2O + Na^+ \tag{1}$$

② Mica:

$$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = 3Al^{3+} + 3SiO_2 + K^+ + 6H_2O \tag{2}$$

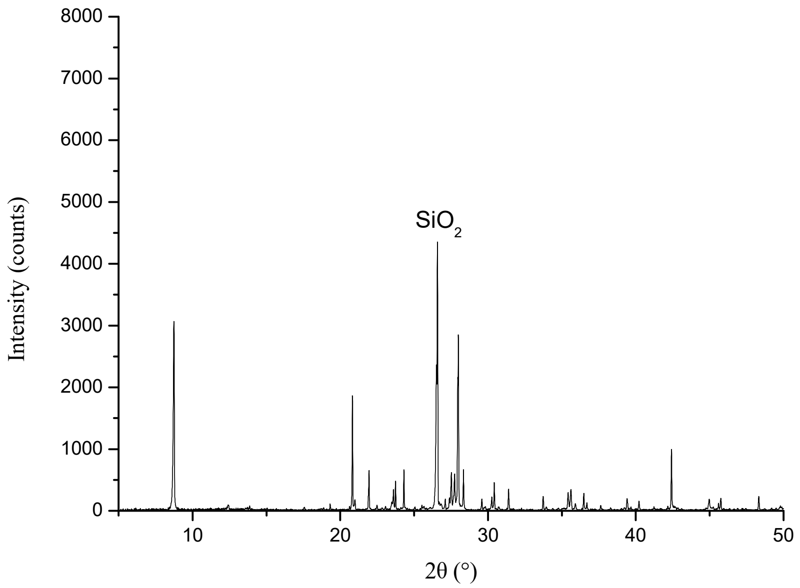
③ K-feldspar:

$$KAlSi_3O_8 + 4H^+ = Al^{3+} + 3SiO_2 + 2H_2O + K^+ \tag{3}$$

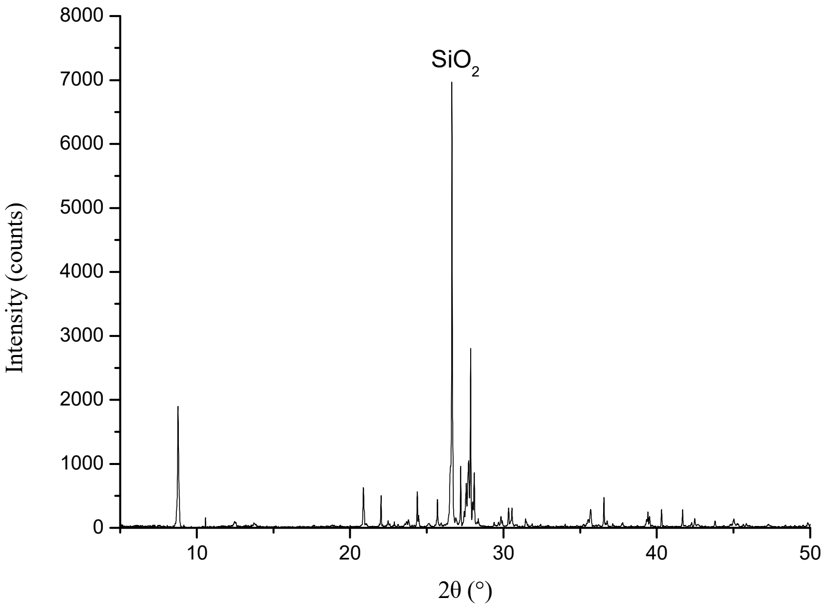
Free SiO_2 particles are generated during the hydrolysis of several minerals, as indicated in the above equations. Consequently, suspended SiO_2 particles become much denser. In the HNO_3 solution, suspended SiO_2 particles are absorbed by the tonalite specimens, into the pores and cracks. When the tonalite specimens are removed from the container, a silica gel was generated because of water evaporation. This silica gel enhances the cohesion and the peak strain of the samples. This phenomenon also verifies why the UCS of G3 is close to that of G4.

3.5. XRD Analysis

To confirm the existence and changing conditions of the silica gel, XRD was used to analyse the tonalite specimens. The results before and after acid treatment are presented in Figure 10. As the phase content is proportional to the diffracted intensity, the diffracted intensity of the main peak was selected to compare the changing SiO_2 content. The diffracted intensities for G1 and G2 specimens are 4351 and 6966. The SiO_2 of the specimen subjected to the nitric acid solution was noticeably increased. As expected, the content of other minerals was found to decrease.



(**a**)

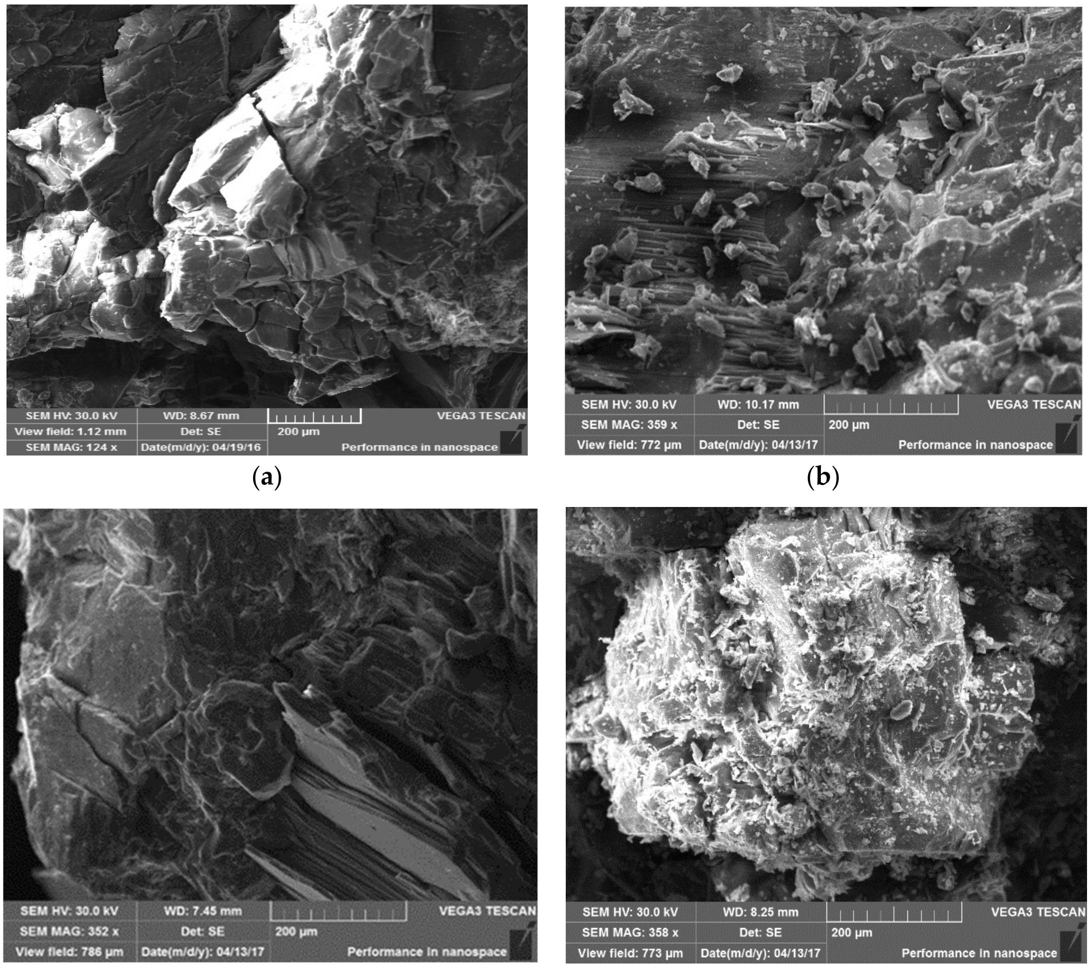


(**b**)

Figure 10. Powder diffraction patterns from tonalite after the treatment: (**a**) untreated (G1); (**b**) pH = 1, 60day (G2).

3.6. SEM Observation

SEM was used to observe the tonalite surface, which is destroyed on the microscale. The microstructures of different groups of samples under 200 μm scale are shown in Figure 11. In comparison to the G2 specimen (Figure 11b), the amount of fragmental minerals on the G2 specimen is less than G4. In comparison to the G3 specimen (Figure 11c), the surface of the G4 specimen is shown to absorb far more mineral particles (Figure 11d). This is because the G4 specimen was subjected to the combined effect of chemical corrosion and freeze-thaw cycles. However, there are no fragmental minerals on the G1 specimen, which is similar to the G3 specimen. Both G1 and G3 specimens were not subjected to chemical corrosion. Thus, the tonalite specimen subjected to freeze-thaw cycles (G3) only generates cracks or pores where cementation is weak, and these are not filled with colloidal particles. Furthermore, the surface shape of the minerals becomes more irregular because of the coupling effect.

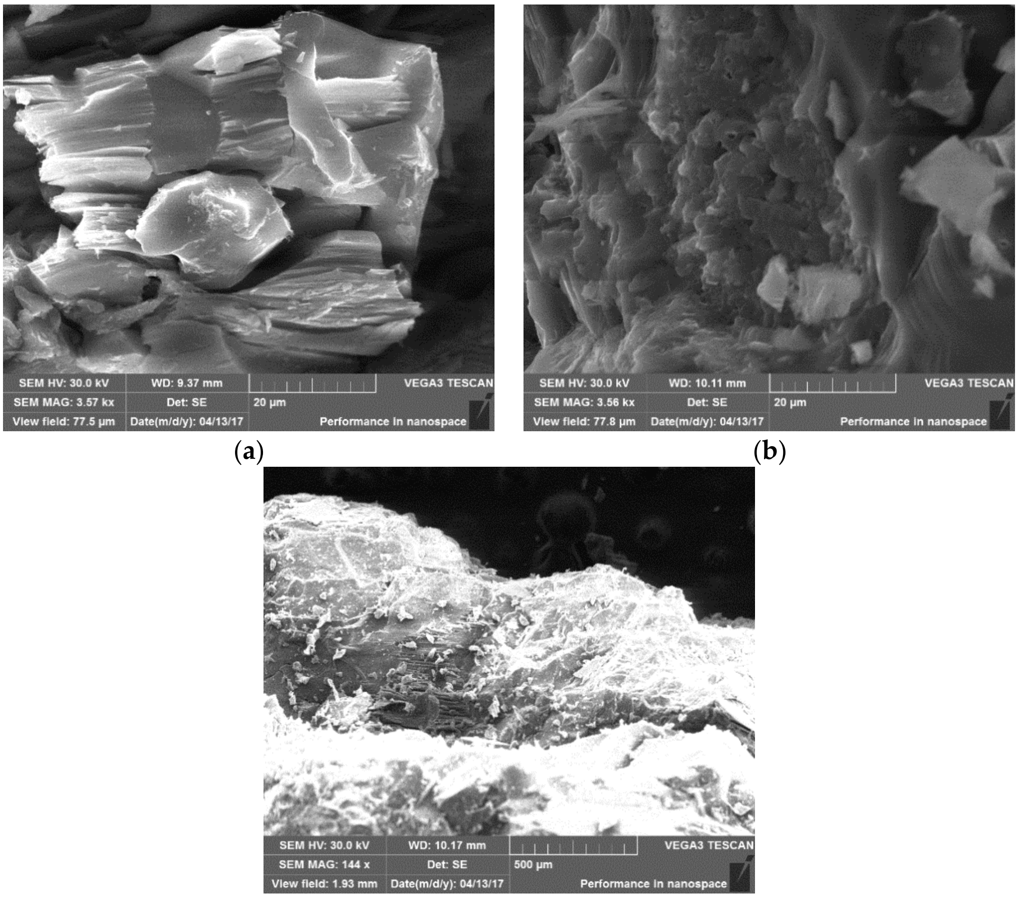


(**a**) (**b**)

(**c**) (**d**)

Figure 11. SEM images of tonalite in different groups: (**a**) G1; (**b**) G2; (**c**) G3 and (**d**) G4, under 200 µm.

Images of the G4 tonalite microstructure on different scales are presented in Figure 12. Figure 12a shows the intercrystalline crack, which is easily generated and leads to specimen failure. Figure 12b shows that parts of mineral exhibit irregularly shaped cavities and the number of pores and cracks has increased. An image under 500 µm scale is shown in Figure 12c. This shows a mass of grey-white fragments on the surface of the specimen fragment. This indicates that the specimen has absorbed a large number of colloidal particles, which have filled the pores and cracks on the tonalite surface. Fang showed that the combined effect of chemical corrosion and freeze-thaw weathering generates two different types of pores: one is due to the weakening of cement, which results in larger pores and the other one is also due to the weakening of cement but with pores filled with colloidal particles. However, the composition and the effectiveness of colloidal particles were not confirmed.



(a) (b) (c)

Figure 12. SEM images of G4 tonalite specimens under different scales: (**a**,**b**) G4, under 20 μm; (**c**) G4, under 500 μm.

4. Discussion and Conclusions

Based on the above results, it can be indicated that the creation of colloidal SiO_2 particles is the main factor which leads to the cementation effect in tonalite specimens, especially the tonalite specimens subjected to the coupled effects. Without freeze-thaw cycles, chemical corrosion can only cause a slight decrease in Young's moduli. The Young's moduli of tonalite specimens subjected to the combined effect (G4) are distinctly lower compared with those of G2 and G3. Chemical corrosion does further damage to specimens with freeze-thaw cycles. The results of XRD and SEM can prove that the SiO_2 particles are absorbed into cracks and voids. The results show that UCS of tonalite specimens subjected to the combined effect (G4) is not lower compared with that of G3. As more cracks and pores are generated in the specimens due to freeze-thaw cycles, SiO_2 colloidal particles can move into specimens with the acid solution. In addition, the result of peak strain shows that SiO_2 colloidal particles can increase the peak strain of tonalite specimens subjected to freeze-thaw cycles.

This paper presented the laboratory experiments such as the Young's modulus test, the uniaxial compression test, three-point bending test, XRD and SEM test of the tonalite samples subjected to the combined effect of freeze-thaw cycles and chemical corrosion. The following conclusions can be drawn from the results presented in this study:

(1) The Young's modulus of several tonalite specimens subjected to the combined effect of chemical corrosion and freeze-thaw weathering is far less than that found for the specimens subjected only to either chemical corrosion or freeze-thaw weathering. Based on Figure 3, nitric acid solution amplifies the damage caused by freeze-thaw cycles.

(2) The peak strain of tonalite specimens subjected to the combined effect decreases with decreasing freezing temperature. Moreover, the peak strain of tonalite specimens subjected to the coupled effect is the highest. While the UCS of tonalite specimens submitted to the coupled effect decreases with decreasing freezing temperature, the values are not significantly different at each temperature. It can be shown that the nitric acid solution has a softening effect on the tonalite specimen.

(3) The K_{IC} of tonalite specimens decreases with the increase of soaking time in HNO_3 (pH = 1), but the decline is almost the same from 60 days to 90 days. It can also be seen that the K_{IC} of G4 declined less than the K_{IC} of G3 compared with the control group.

(4) Based on the results of SEM, it was verified that colloidal particles are generated when tonalite specimens are subjected to nitric acid. Following the combined effect, a number of pores and cracks will be filled by colloidal particles. This process enhances the cohesion of the tonalite specimen and decreases the damage that results from freeze-thaw weathering.

(5) The main failure mode in tonalite specimens is intercrystalline crack when the specimens are subjected to both chemical corrosion and freeze-thaw weathering.

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