



# Article Statistical Damage Model of Rock Based on Compaction Stage and Post-Peak Shape under Chemical-Freezing-Thawing-Loading

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Abstract: The deterioration of rock mechanical properties under chemical-freezing-thawing-loading will seriously threaten the stability and safety of engineering rock mass, so the study of its constitutive model has very important theoretical and engineering application significance. In view of the deficiency that the existing statistical damage constitutive model cannot describe the nonlinear characteristics of the compaction stage and the post-peak shape, the compaction index is introduced to measure the stress-strain nonlinear characteristics caused by the iso-compression of the pores in the rock, and the post-peak correction coefficient is introduced to optimize the post-peak shape of rock loading. Assuming that the strength and failure of rock microunits obey the Weibull distribution, on the basis of using the Drucker-Prager strength criterion to measure the strength of rock microunits, a statistical damage model for rock considering the compaction stage and post-peak shape under chemical-freezing-thawing-loading is established. Finally, it is compared with the test curve. The results show that the calculation curve of the established chemical-freezing-thawing-loading rock statistical damage model has the same trend as the rock uniaxial compression test curve. Furthermore, it can better describe the rock stress-strain law with different chemical solutions and different freezethaw cycles, which fully reflects the rationality and accuracy of the constructed constitutive model. The research results can provide a theoretical basis for the calculation of deformation and failure of rocks under chemical-freezing-thawing-loading.

**Keywords:** chemical erosion; freeze-thaw cycles; constitutive model; Weibull distribution; pore compaction; post-peak shape

# 1. Introduction

On the one hand, engineering rock masses in cold regions are chemically eroded by water, acid rain and many ions in groundwater, causing changes in the mineral composition and structure inside the rock [1,2]. On the other hand, under the influence of seasons and alternation of day and night, rocks are damaged by freeze-thaw cycles under repeated freezing and thawing of water and chemical solutions [3–5], and the rock mass is always under a certain stress field condition. Therefore, under the action environment of chemical erosion, freeze-thaw cycles and loads, the internal microscopic defects of the rock gradually generate and expand, and the damage accumulates, thereby deteriorating the physical and mechanical properties of the rock mass. This affects the safety of rock mass engineering in cold regions at all times and it makes the research on the mechanical damage of rock under chemical-freezing-thawing-loading extremely important in theory and engineering practice. Establishing an objective and reasonable constitutive model is one of the keys to explore and study the mechanical properties of rock under chemical-freezing-thawing-loading.



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A large number of scholars first carried out rock mechanics test and damage constitutive theory research under a single chemical erosion or freeze-thaw environment, and made useful progress. In terms of chemical erosion tests, Hutchinson et al. [6], Cai et al. [7], Li et al. [8], and Gong et al. [9] carried out experimental research on the corrosion mechanics of limestone and sandstone with different chemical solutions, and the results showed that chemical erosion will change the mineral composition of the rock and affect the parameters such as uniaxial compressive strength and elastic modulus. Han et al. [10] carried out chemical corrosion sandstone mechanical tests and proposed to use porosity changes to describe the microstructure damage variables. In terms of freeze-thaw tests, Yang et al. [11] studied the damage extension mechanism of rocks, water migration, ice formation and structural damage changes under freeze-thawcycles and discussed the effects of freeze-thaw cycles on the deterioration of physical and mechanical properties of rocks. Zhou et al. [12] first performed freeze-thaw cycles on sandstone, and then conducted NMR tests and impact load tests to analyze the microscopic damage characteristics and dynamic mechanical parameters of sandstone. Yahaghi et al. [13] studied the physical and mechanical properties and failure behavior of Tasmanian sandstone in various freeze-thaw cycles through a P-wave test, uniaxial compression test and a Brazilian split test after freeze-thaw cycles. Li et al. [14] carried out research on rock freeze-thaw cycles and uniaxial compression tests, analyzed the freeze-thaw degradation mechanism, and applied the test results to the stability evaluation of rock mass slopes in open-pit mines. The above laboratory experiments show that chemical erosion and freeze-thaw cycles have damage effects on rocks, which are mainly reflected in the reduction of elastic modulus, mechanical strength, and peak strain increase.

In the study of the constitutive model of chemical erosion, Chen [15] established a microscopic damage evolution constitutive model of rock under uniaxial compression under different pH values, concentrations, and types of chemical solution corrosion by introducing chemical corrosion damage factors. Chen et al. [16] proposed an evolutionary neural network constitutive model to describe the stress-strain characteristics of rocks under chemical corrosion. Lin et al. [17] introduced the damage variable correction coefficient affected by porosity and established a statistical damage constitutive model of rock under chemical corrosion based on the Drucker-Prager strength criterion and the two-parameter Weibull distribution. In terms of freeze-thaw cycles, Fang et al. [3] established a statistical damage constitutive model for rocks under freeze-thaw and load conditions, and clarified the method for determining model parameters, and analyzed the relationship between elastic modulus, peak stress, and freeze-thaw cycles. Huang et al. [18] derived a statistical damage constitutive model for rocks under freezing-thawing-loading conditions based on Weibull distribution and maximum tensile strain yield criterion and applied the model to analyze the stability of tunnels under thermal-water-mechanical coupling conditions in cold regions. Feng et al. [19] carried out the freezing-thawing cycle test of saturated sandstone, established a freezing-thawing damage model based on the energy evolution law, and used this model to perform theoretical calculations on the uniaxial compression test. Zhang et al. [20] proposed the concepts of freeze-thaw damage, load damage and total damage, established a freezing-thawing-loading rock damage model, and described the damage evolution and macroscopic damage behavior of the meso-structure of rock materials through damage variables and constitutive equations.

To sum up, the damage research on single chemical and freeze-thaw factors has achieved relatively fruitful results, but most of the rocks in the actual engineering rock are subject to two or more damage effects, which makes the current theoretical research and engineering applications still have a large gap. In recent years, Chen [21–24], Wang [25], and Li et al. [26] carried out experimental studies on the mechanical properties of rocks immersed in different chemical solutions and subjected to freeze-thaw cycles. Li et al. [27] studied the pore change law and damage evolution mechanism of sandstone under chemical solution erosion by nuclear magnetic resonance and carried out sandstone freeze-thaw cycle tests with different solutions, indicating that the combined effect of chemical corrosion

and freeze-thaw cycles can relatively slow down the damage aggravation. Due to limited test conditions and complex influencing factors, the research on rock mechanics under multi-field coupling is in its infancy, and there is no report on the research on the constitutive model of rock under the combined action of chemical-freezing-thawing-loading. In addition, the traditional constitutive model still has some shortcomings. First, the traditional constitutive model simplifies the compaction stage as a linear feature for processing, and the chemical-freezing-thawing action leads to a large increase in the internal pores of the rock, the compaction effect of rock is much more significant during the mechanical test than in the natural state, so the nonlinear change of compaction stage cannot be ignored for the constitutive model of rock under chemical-freezing-thawing-loading. Second, the degree of fitting of the post-peak shape is relatively low. Cao et al. [28], Zhang et al. [29], Zhang et al. [30], and Bilen et al. [31] carried out research on the evaluation of brittleness and plasticity indicators in the process of rock damage. It is worth noting that the brittleness of the rock is weakened and the plasticity is enhanced after chemical erosion and freeze-thaw cycles. The traditional constitutive model cannot well reflect the post-peak shape changes of the plastic enhancement caused by chemical and freeze-thaw damage.

To sum up, the current rock environment is not considered enough, and the existing constitutive model cannot better describe the whole process of rock deformation and failure, resulting in great differences between the current model and the rock stress-strain curve in engineering practice. Therefore, based on previous research, this paper first considers the coupling effect of chemical erosion and freeze-thaw cycles, assumes that the strength of rock micro units obeys the Weibull distribution, and introduces the compaction index, a post-peak correction coefficient, threshold stress, and threshold strain. A statistical damage constitutive model of rock under chemical-freezing-thawing-loading is established. Then, it is compared with the rock uniaxial compression test curve of the literature [21] to verify the rationality and accuracy of the established model. Finally, the total damage evolution equation under the action of chemical-freezing-thawing-loading is used to describe the rock meso-damage evolution and macro-mechanical performance response, which provides a theoretical reference for rock multi-field coupled damage research.

# 2. Statistical Damage Model of Rock under Chemical-Freezing-Thawing-Loading

#### 2.1. Chemical-Freeze-Thaw Damage Variable and Damage Model

Tang et al. [32] put forward the concept of chemical damage earlier and defined it as the deterioration process of rock (mass) material or structure caused by water-rock chemistry. Water-rock chemistry affects the physical state and micro-structure of rocks, weakens the connection between mineral particles, increases rock mass deformation, decreases strength, and significantly reduces the elastic modulus. Because the elastic modulus of rock is easier to analyze and measure during chemical erosion, the damage variable  $D_{\rm C}$  of rock chemical erosion can be expressed as:

$$D_{\rm C} = 1 - \frac{E_{\rm C}}{E_0} \tag{1}$$

where  $E_C$  is the elastic modulus of rock after chemical erosion damage,  $E_0$  is the elastic modulus of natural rock before chemical erosion.

Due to the freeze-thaw cycles, a large number of meso-cracks are bound to occur in the rock, and the cracks gradually expand with the increase of the number of cycles, and the elastic modulus also decreases significantly, indicating that the freeze-thaw cycles cause damage to the rock and so the elastic modulus is also selected in this paper. To represent the freeze-thaw damage variable, so the freeze-thaw damage variable  $D_T^{T}$  is defined as

$$D_{\rm T}^n = 1 - \frac{E_{\rm T}^n}{E_0'}$$
(2)

where  $E_T^n$  is the elastic modulus after *n* times of freeze-thaw, and  $E_0'$  is the initial elastic modulus without freeze-thaw.

Figure 1 is a schematic diagram of the damage state of the rock, where a is the rock in the initial state, b is the rock after chemical erosion, c is the rock that has undergone chemical-freezing-thawing action, and d is the rock that has been subjected to chemical-freezing-thawing-loading. Based on the generalized Lemaitre strain equivalence principle [33], the natural initial state of the rock is regarded as the first damage state, and the state after chemical damage is regarded as the second damage state, then

$$\sigma_{\rm C} = \sigma_0 (1 - D_{\rm C}) \tag{3}$$

The generalized strain equivalence principle is applied again, chemical damage is regarded as the first damage state, and the total damage state caused by chemical-freezing-thawing action is regarded as the second damage state, then

$$\sigma_{\rm T} = \sigma_{\rm C} (1 - D_{\rm T}^n) \tag{4}$$

The damage model of chemical-freezing-thawing action is

$$\sigma_{\rm T} = \sigma_0 (1 - D_{\rm C}) (1 - D_{\rm T}^n) = E_0 \varepsilon (1 - D_{\rm C}) (1 - D_{\rm T}^n) = E \varepsilon$$
(5)

where *E* is the elastic modulus after chemical-freezing-thawing action;  $\sigma_0$  is the effective stress in the natural initial state;  $\sigma_C$  is the effective stress in the chemical damage state;  $\sigma_T$  is the effective stress in the chemical-freezing-thawing state.



Figure 1. Schematic diagram of rock damage state.

#### 2.2. Statistical Distribution Function

Rock is a natural material composed of a variety of minerals. Due to the heterogeneity of the microscopic structure inside the rock arising from the geological environment and mineral composition, the mechanical properties of the micro units that make up the rock may have large differences, and the micro cracks and fractures are also randomly distributed. It is a reasonable and effective way to use statistical functions to describe the strength of rock micro units. At present, the commonly used distribution functions in rock statistical damage constitutive models include the Weibull distribution, normal distribution [34], power function distribution, lognormal distribution, etc. According to the literature [35,36], the Weibull probability distribution function has the characteristics of peak effect and simple integral calculation, which can better describe the process of rock deformation and failure. Therefore, this paper assumed that the generation and expansion of cracks under the action of chemical-freezing-thawing obey the Weibull distribution function, and the strength of micro units also obeys the Weibull statistical distribution, and the probability density function p(x) is

$$p(x) = \frac{m}{F} \left(\frac{x}{F}\right)^{m-1} \exp\left[-\left(\frac{x}{F}\right)^{m}\right]$$
(6)

The distribution function P(x) is

$$P(x) = 1 - \exp\left[-\left(\frac{x}{F}\right)^{m}\right]$$
(7)

where *x* is the micro units' strength value of the rock under chemical-freezing-thawing, *m* and *F* are parameters related to the Weibull distribution function affecting the shape and size of rock micro units, which change with the change of chemical and freeze-thaw conditions. Therefore, chemical and freeze-thaw damage will affect parameters *m* and *F*. According to the existing research, this paper assumes that m(C, T) and F(C, T) are similarly affected by chemical and freeze-thaw damage, and also according to the extended Lemaitre strain equivalence principle mentioned above, we can obtain

$$\begin{array}{c} m(C) = m_0(1 - D_C) \\ F(C) = F_0(1 - D_C) \end{array} \right\}$$
(8)

$$\begin{array}{l} m(C,T) = m(C)(1-D_{T}^{n}) \\ F(C,T) = F(C)(1-D_{T}^{n}) \end{array} \right\}$$

$$(9)$$

where  $m_0$  and  $F_0$  are the Weibull parameters of the rock without chemical erosion, m(C) and F(C) are the Weibull parameters of the rock after chemical erosion, m(C, T) and F(C, T) are the Weibull parameters of the rock under different chemical and freeze-thaw conditions.

According to Equations (8) and (9), the Weibull parameters of rocks under different chemical erosion and freeze-thaw cycles are

$$\begin{array}{l} m(C,T) = m_0(1 - D_C)(1 - D_T^n) \\ F(C,T) = F_0(1 - D_C)(1 - D_T^n) \end{array} \right\}$$
(10)

Assuming that the total number of micro units in the rock is N, the number of damaged micro units under a certain stress level is  $N_{\rm F}$ , and the damage variable D is defined as the ratio of the number of damaged micro units to the total number of micro units, namely

$$D = \frac{N_{\rm F}}{N} \tag{11}$$

When the stress is loaded to the  $p(\sigma)$  state, the micro units start to be destroyed one after another, and the number of micro units that have been destroyed is

$$N_{\rm F} = \int_0^{p(\sigma)} N \cdot p(\sigma) \mathrm{d}\sigma = N \int_0^{p(\sigma)} p(\sigma) \mathrm{d}\sigma \tag{12}$$

From Equations (11) and (12), the rock damage variable D can be obtained as

$$D = \frac{N \int_0^{p(\sigma)} p(\sigma) d\sigma}{N} = \int_0^{p(\sigma)} p(\sigma) d\sigma$$
(13)

Substituting Equations (7) and (10) into Equation (13), we can get

$$D = 1 - \exp\left[-\left(\frac{p(\sigma)}{F_0(1 - D_C)(1 - D_T^n)}\right)^{m_0(1 - D_C)(1 - D_T^n)}\right]$$
(14)

There is an obvious threshold for rock damage under loading [37]. When the stress state is lower than the threshold stress, the stress-strain relationship of the rock is mainly in the stage of pore compaction and linear elasticity, and the damage caused by the load to the interior of the rock is almost zero and can be ignored. At this time, the total damage is caused by chemical erosion and freezing-thawing, therefore, the damage variable is

$$D = 1 - (1 - D_{\rm C})(1 - D_{\rm T}^n) = 1 - \frac{E_{\rm C}}{E_0'} \cdot \frac{E_{\rm T}^n}{E_0''}$$
(15)

Combining Equations (14) and (15), the damage evolution equation in the process of rock loading under chemical-freezing-thawing action can be obtained as

$$D = \begin{cases} 1 - (1 - D_{\rm C})(1 - D_{\rm T}^n) & (0 \le \varepsilon \le \varepsilon_{\rm u}) \\ 1 - \exp\left[-\left(\frac{p(\sigma)}{F_0(1 - D_{\rm C})(1 - D_{\rm T}^n)}\right)^{m_0(1 - D_{\rm C})(1 - D_{\rm T}^n)}\right](\varepsilon > \varepsilon_{\rm u}) \end{cases}$$
(16)

where  $\varepsilon_u$  is the strain at the rock damage threshold point, Equation (16) represents the relationship between the total rock damage D, chemical damage  $D_C$ , and freeze-thaw damage  $D_T^n$  under loading conditions.

According to Lemaitre's strain equivalence principle [38] and the concept of effective stress, the strain produced by the nominal stress (stress measured by the test) on the damaged material is equivalent to the strain caused by the effective stress on the non-destructive material. Moreover, the post-peak shapes of the stress-strain curves of different rocks are not exactly the same during the loading process. For example, basalt, granite, and quartzite have high strength, and the stress decreases approximately vertically in the post-peak stage, which is prone to brittle failure. On the other hand, shale and sandstone have low strength, and the stress decreases slowly in the post-peak stage, showing good plasticity [39]. In order to be closer to the actual stress-strain law, this article introduces the post-peak correction coefficient  $\lambda$  to represent the plasticity, and the corrected damage model is

$$\sigma_i = \sigma_i^* (1 - \lambda D) \ (i = 1, 2, 3) \tag{17}$$

where  $\sigma_i$  is the nominal stress of the rock (MPa), and  $\sigma_i^*$  is the effective stress of the rock (MPa).

Due to the obvious elastic characteristics of rock stress-strain under chemical-freezingthawing action, according to the generalized Hooke's Law, it can be obtained

$$\varepsilon_i = \frac{1}{E} \left[ \sigma_i^* - \mu (\sigma_j^* + \sigma_k^*) \right] \quad (i, j, k = 1, 2, 3)$$
(18)

where  $\varepsilon_i$  is the strain;  $\mu$  is the Poisson's ratio; *E* is the elastic modulus.

Substitute Equation (17) into Equation (18) to get

$$\varepsilon_i = \frac{1}{E(1-\lambda D)} \left[ \sigma_i - \mu(\sigma_j + \sigma_k) \right] \quad (i, j, k = 1, 2, 3)$$
(19)

when  $\varepsilon_i > \varepsilon_u$ , substitute Equation (14) into Equation (19) to get

$$\varepsilon_{i} = \frac{1}{E\left(1 - \lambda + \lambda \exp\left[-\left(\frac{p(\sigma)}{F_{0}(1 - D_{C})(1 - D_{T}^{R})}\right)^{m_{0}(1 - D_{C})(1 - D_{T}^{R})}\right]\right)} \left[\sigma_{i} - \mu(\sigma_{j} + \sigma_{k})\right]$$

$$(i, j, k = 1, 2, 3)$$
(20)

Sorted out

$$\sigma_{i} = E\varepsilon_{i} \left( 1 - \lambda + \lambda \exp\left[ -\left(\frac{p(\sigma)}{F_{0}(1 - D_{C})(1 - D_{T}^{n})}\right)^{m_{0}(1 - D_{C})(1 - D_{T}^{n})} \right] \right) + \mu(\sigma_{j} + \sigma_{k})$$

$$(i, j, k = 1, 2, 3; \varepsilon_{i} > \varepsilon_{u})$$

$$(21)$$

Substituting Equation (5) into Equation (21), the rock damage equation considering chemical-freezing-thawing-loading can be obtained as:

$$\sigma_{i} = E_{0}(1 - D_{\mathrm{C}})(1 - D_{\mathrm{T}}^{n})\varepsilon_{i}\left(1 - \lambda + \lambda \exp\left[-\left(\frac{p(\sigma)}{F_{0}(1 - D_{\mathrm{C}})(1 - D_{\mathrm{T}}^{n})}\right)^{m_{0}(1 - D_{\mathrm{C}})(1 - D_{\mathrm{T}}^{n})}\right]\right) + \mu(\sigma_{j} + \sigma_{k}) \qquad (i, j, k = 1, 2, 3; \varepsilon_{i} > \varepsilon_{\mathrm{u}})$$

$$(22)$$

## 2.3. The Representation of Micro Units' Strength

At present, many scholars have introduced the commonly used rock strength criteria, such as the maximum tensile strain strength criterion, the Mohr–Coulomb strength criterion, the Drucker–Prager strength criterion and the Hoek-Brown strength criterion, etc. The Drucker–Prager strength criterion considers the effect of intermediate principal stress and the effect of hydrostatic pressure, which makes up for the main defect of the Mohr–Coulomb strength criterion. In view of this, this paper adopts the Drucker–Prager strength failure criterion as the measurement method of the strength of the rock micro units, and the strength of the micro units  $p(\sigma)$  is expressed as follows

$$p(\sigma) = \alpha_0 I_1 + \sqrt{J_2} \tag{23}$$

$$\alpha_0 = \frac{\sin\varphi}{\sqrt{9+3\sin^2\varphi}} \tag{24}$$

where  $\varphi$  is the rock internal friction angle;  $I_1$  is the first invariant of the stress tensor;  $J_2$  is the second invariant of the stress deviator.

It can be obtained by combining Equation (19)

$$\sigma_1^* = \frac{\sigma_1}{1 - \lambda D} = \frac{\sigma_1 \varepsilon_1 E}{\sigma_1 - \mu(\sigma_2 + \sigma_3)}$$
(25)

$$\sigma_2^* = \frac{\sigma_2}{1 - \lambda D} = \frac{\sigma_2 \varepsilon_1 E}{\sigma_2 - \mu(\sigma_1 + \sigma_3)}$$
(26)

$$\sigma_3^* = \frac{\sigma_3}{1 - \lambda D} = \frac{\sigma_3 \varepsilon_1 E}{\sigma_3 - \mu(\sigma_1 + \sigma_2)}$$
(27)

Then,

$$I_1 = \sigma_1^* + \sigma_2^* + \sigma_3^* = \frac{E\varepsilon_1(\sigma_1 + 2\sigma_3)}{\sigma_1 - 2\mu\sigma_3}$$
(28)

$$\sqrt{J_2} = \sqrt{\frac{1}{6} \left[ (\sigma_1^* - \sigma_2^*)^2 + (\sigma_2^* - \sigma_3^*)^2 + (\sigma_3^* - \sigma_1^*)^2 \right]} = \frac{E\varepsilon_1(\sigma_1 - \sigma_3)}{\sqrt{3}(\sigma_1 - 2\mu\sigma_3)}$$
(29)

Substitute Equations (28) and (29) into Equation (23) to get

$$p(\sigma) = \frac{\alpha_0 E \varepsilon_1(\sigma_1 + 2\sigma_3)}{\sigma_1 - 2\mu\sigma_3} + \frac{E \varepsilon_1(\sigma_1 - \sigma_3)}{\sqrt{3}(\sigma_1 - 2\mu\sigma_3)}$$
(30)

# 2.4. Statistical Damage Constitutive Model Considering Chemical-Freezing-Thawing Effect in Compaction Stage

The entire deformation process of the rock sample under uniaxial compression can be represented by the full stress-strain curve shown in Figure 2 [40]. This shows that the deformation and failure of the rock is divided into four stages, which are the pore and fracture compaction stage (*OA* stage), elastic deformation to the stable development stage of micro-elastic cracks (*AC* stage), among them, the *AB* stage is the elastic deformation stage, and the *BC* stage is the stable development stage of micro-elastic cracks, unstable rupture development stage (*CD* stage), and post-rupture stage (after point *D*).



Figure 2. Total stress-strain curve of rock deformation.

Before the peak, stress generally increases with increasing strain, but the rate of stress growth is not exactly the same. In the compaction stage, due to the compaction of the internal pores of the rock, the stress increases slowly with the strain, showing an upward concave shape; then in the elastic deformation stage, the stress increases rapidly with the strain and is basically linear elastic. To establish a constitutive model that conforms to the nonlinear characteristics of rock deformation in Figure 2, the existence of pores in the rock needs to be considered, and under the action of chemical erosion and freeze-thaw, the rock crystal plane is prone to dissolve small cavities, resulting in many secondary cracks and pores. The original pores in the rock sample are further expanded or more micro-cavities are formed, which promotes changes in the deformation and failure mechanism of the rock. To sum up, the compaction effect of rock pores is more obvious under the action of chemical-freezing-thawing, and it is particularly important to simulate the nonlinear characteristics of the compaction stage. In addition, chemical erosion and freeze-thaw cycles will also destroy the connection between the particles in the rock and the crystal itself, so that the rock changes from brittleness to plasticity, that is, the brittleness of the rock decreases and the plasticity increases, and the stress-strain curve of the rock sample fall slowly after the peak.

After multiple fittings, it was found that the exponential function can well describe the stress-strain characteristics considering the pore compaction in the *OC* stage. This paper defines a parameter  $\alpha$  to measure the pore compaction of the rock, which is called the compaction index, and its value is related to the rock type, damage and stress state. It can be expressed as

$$\tau = \sigma_{\rm u} \left(\frac{\varepsilon}{\varepsilon_{\rm u}}\right)^{\alpha} \tag{31}$$

where  $\sigma_u$  is the stress value at the ultimate elastic strain  $\varepsilon_u$ .

The influence of the compaction index on the shape of the stress-strain curve is shown in Figure 3. The boundary yield point of the compaction stage, the elastic deformation to the stable development stage of micro-elastic cracks (*OC* stage) and the unstable rupture development stage (*CD* stage) is  $C(\varepsilon_u, \sigma_u)$ , the peak point is  $D(\varepsilon_s, \sigma_s)$ , where the peak strain is  $\varepsilon_s$  and the peak stress is  $\sigma_s$ . With the increase of  $\alpha$ , the degree of concave on the curve is more obvious,  $\alpha < 1$ , indicating that there are fewer pores in the rock, when  $\alpha = 1$ , the pores in the rock are moderate, that is, the stress-strain curve increases linearly, on the contrary, when  $\alpha > 1$ , there are more pores in the rock.



**Figure 3.** Stress-strain relationship of rock with different values of  $\alpha$ .

When the stress state is lower than the threshold stress, the rock is mainly in the stage of pore compaction and linear elasticity, and the total damage is caused by chemical erosion and freeze-thaw cycles, the constitutive relationship of the rock can be well obtained by fitting the above exponential function. When the stress state exceeds the threshold stress, the damage is caused by the combined action of chemistry, freeze-thaw, and load, which can be described by the Weibull distribution function. Combining Equations (22) and (31), the statistical damage constitutive model of rock based on the Weibull distribution function and the Drucker–Prager strength criterion under chemical-freezing-thawing-loading can be obtained as,

$$\sigma_{i} = \begin{cases} \sigma_{u} \left(\frac{\varepsilon}{\varepsilon_{u}}\right)^{\alpha} & (0 \leq \varepsilon \leq \varepsilon_{u}) \\ E_{0}(1 - D_{C})\left(1 - D_{T}^{n}\right)\varepsilon_{i} \cdot \\ 1 - \lambda + \lambda \exp\left[-\left(\frac{p(\sigma)}{F_{0}(1 - D_{C})\left(1 - D_{T}^{n}\right)}\right)^{m_{0}(1 - D_{C})(1 - D_{T}^{n})}\right] + \mu\left(\sigma_{j} + \sigma_{k}\right) & (\varepsilon > \varepsilon_{u}) \end{cases}$$
(32)

of which

L

$$p(\sigma) = \frac{\alpha_0 E \varepsilon_1(\sigma_1 + 2\sigma_3)}{\sigma_1 - 2\mu\sigma_3} + \frac{E \varepsilon_1(\sigma_1 - \sigma_3)}{\sqrt{3}\sigma_1 - 2\mu\sigma_3}$$
(33)

# 3. Determination of Constitutive Model Parameters

3.1. Determine the Parameters m and F

In the triaxial and uniaxial tests of rock under chemical-freezing-thawing, the parameters *E* and  $\mu$  in the model proposed in this paper can be measured by the rock mechanics test after chemical-freezing-thawing. As can be seen from the above description, the stress has a distinct peak value. The stress-strain curve satisfies the model (32) at the stress peak, we can get

$$\sigma|_{\varepsilon=\varepsilon_{\rm s}} = \sigma_{\rm s} = E\varepsilon_{\rm s} \left( 1 - \lambda + \lambda \exp\left[ -\left(\frac{p(\sigma_{\rm s})}{F}\right)^m \right] \right) + 2\mu\sigma_3 \tag{34}$$

The first derivative of the stress-strain curve is zero at the peak, that is

$$\frac{\frac{\partial \sigma_{1}}{\partial \varepsilon_{1}}}{\varepsilon = \varepsilon_{s}} = 0$$

$$\varepsilon = \varepsilon_{s}$$

$$= E \left\{ 1 - \lambda + \lambda \left\{ \exp\left[ -\left(\frac{p(\sigma_{s})}{F}\right)^{m} \right] + \varepsilon_{s} \exp\left[ -\left(\frac{p(\sigma_{s})}{F}\right)^{m} \right] \left\{ -m\left(\frac{p(\sigma_{s})}{F}\right)^{m-1} \right\} \frac{\partial p(\sigma_{s})}{\partial \varepsilon_{1}} \right\} \right\}$$

$$(35)$$

of which

$$\frac{\partial p(\sigma_{\rm s})}{\partial \varepsilon_1} = E \frac{\sqrt{3}\alpha_0(\sigma_{\rm s} + 2\sigma_3) + (\sigma_{\rm s} - \sigma_3)}{\sqrt{3}(\sigma_{\rm s} - 2\mu\sigma_3)} \tag{36}$$

According to Equations (34) and (35), we can get

$$m = -\frac{\sigma_{\rm s} - 2\mu\sigma_3}{[\sigma_{\rm s} - 2\mu\sigma_3 + (\lambda - 1)E\varepsilon_{\rm s}]\ln\frac{\sigma_{\rm s} - 2\mu\sigma_3 + (\lambda - 1)E\varepsilon_{\rm s}}{\lambda E\varepsilon_{\rm s}}}$$
(37)

$$F = \frac{p(\sigma_{\rm s})}{\left\{\ln\left[\frac{\lambda E\varepsilon_{\rm s}}{\sigma_{\rm s} - 2\mu\sigma_{\rm s} + (\lambda - 1)E\varepsilon_{\rm s}}\right]\right\}^{1/m}}$$
(38)

of which

$$p(\sigma_{\rm s}) = \frac{\alpha_0 E \varepsilon_{\rm s}(\sigma_{\rm s} + 2\sigma_3)}{\sigma_{\rm s} - 2\mu\sigma_3} + \frac{E \varepsilon_{\rm s}(\sigma_{\rm s} - \sigma_3)}{\sqrt{3}(\sigma_{\rm s} - 2\mu\sigma_3)}$$
(39)

#### 3.2. Determine the Parameter $\alpha$

The deformation and failure generated in the rock mechanics test is a process of continuous change. The stress-strain curve has the same change law before the elastic deformation to the stable development stage of micro-elastic cracks and the unstable rupture development stage, which is continuous at point  $C(\varepsilon_u, \sigma_u)$ , we can get

$$\lambda E \varepsilon_{\mathbf{u}} \exp\left[-\left(\frac{p(\sigma_{\mathbf{u}})}{F}\right)^{m}\right] + 2 \mu \sigma_{3} = \alpha \sigma_{\mathbf{u}} \left(\frac{\varepsilon}{\varepsilon_{\mathbf{u}}}\right)^{\alpha}$$
(40)

of which

$$p(\sigma_{\mathbf{u}}) = \frac{\alpha_0 E\varepsilon_1(\sigma_{\mathbf{u}} + 2\sigma_3)}{\sigma_{\mathbf{u}} - 2\mu\sigma_3} + \frac{E\varepsilon_1(\sigma_{\mathbf{u}} - \sigma_3)}{\sqrt{3}(\sigma_{\mathbf{u}} - 2\mu\sigma_3)}$$
(41)

$$\frac{\partial \sigma_1}{\partial \varepsilon_1} \left| \begin{array}{l} \sigma = \sigma_{\mathbf{u}} \\ \varepsilon = \varepsilon_{\mathbf{u}} \end{array} \right| = \lambda E \exp\left[ -\left(\frac{p(\sigma_{\mathbf{u}})}{F}\right)^m \right] \left\{ 1 - \frac{m}{F} \left[ \left(\frac{p(\sigma_{\mathbf{u}})}{F}\right)^m \right] \right\} = \alpha \frac{\sigma_{\mathbf{u}}}{\varepsilon_{\mathbf{u}}} \left(\frac{\varepsilon}{\varepsilon_{\mathbf{u}}}\right)^{\alpha - 1}$$
(42)

The parameter  $\alpha$  can be determined by combining Equations (40) to (42). At the same time, the parameter  $\alpha$  can also be obtained by fitting the exponential function curve and it can be obtained by substituting the above formula for verification.

#### 3.3. Determine the Parameter $\lambda$

The value of the post-peak correction coefficient  $\lambda$  is the key to ensure that the rock statistical damage constitutive model can accurately describe the post-peak shape of the rock stress-strain curve. For the post-peak stress path of the rock during the loading process, the smaller the mean square error of the stress calculated by the damage constitutive model, the better the practicability of the parameter  $\lambda$  for the rock. The stress mean square error calculated by the established damage model can be expressed as

$$MSE = \frac{1}{m} \sum_{i=1}^{m} \left( \sigma_1^{M} - \sigma_1^{E} \right)^2$$
(43)

where  $\sigma_1^{\text{M}}$  is the axial stress obtained by substituting the parameter into Equation (32), and  $\sigma_1^{\text{E}}$  is the axial stress obtained from the test.

Therefore, when the mean square error of the axial stress is the smallest, it can be considered that the post-peak stress-strain curve of the rock obtained by the established damage model is the most accurate, and the corresponding  $\lambda$  at this time is the optimal solution.

# 4. Model Verification and Analysis

In order to verify the rationality of the statistical damage model of rock under the action of chemical-freezing-thawing-loading, the uniaxial compression test results of granite with different chemical solutions and different freeze-thaw cycles in the literature [21] were selected for comparative analysis. The freeze-thaw equipment in the literature [21] is the CABR-HDK9A rapid freeze-thaw test machine researched and produced by Jianyan Building Materials Co., Ltd. of China Academy of Building Research, Beijing, China and its freeze-thaw temperature is -20 °C $\sim$ 20 °C. The uniaxial compression test adopts the microcomputer-controlled rigid servo triaxial compression testing machine produced by Xi'an Lichuang Material Testing Technology Co., Ltd., Xi'an China, and its maximum load is 2000 kN.

The samples were soaked in  $H_2O$ , 1 mol  $L^{-1}$  NaOH solution and 1 mol  $L^{-1}$  HNO<sub>3</sub> solution with pH  $\approx$  7.0 for 90 days. Then the sample was put into the rapid freeze-thaw test machine, add  $H_2O$  with pH  $\approx$  7.0, 1 mol  $L^{-1}$  NaOH solution and 1 mol  $L^{-1}$  HNO<sub>3</sub> solution, respectively, and freeze-thaw cycles at -15 °C $\sim$ 20 °C. The cycle is about 4 h. The uniaxial compression test was carried out on the frozen thawed granite by using a microcomputer-controlled rigid servo triaxial compression tester. The test adopted a stress control method and applied an axial load at a rate of 0.8 MPa/s until the sample failed. The samples were divided into three grades of freeze-thaw cycles: 0, 75, and 100 cycles, with twelve samples in each grade, including four samples in  $H_2O$ , NaOH solution and HNO<sub>3</sub> solution, as shown in Table 1. The obtained uniaxial compression test data are shown in Table 2.

**Table 1.** Uniaxial compression test scheme of granite with different chemical solutions and freezethaw cycles.

Solution Category	Soaking Time/d	Freeze-Thaw Range/°C	Freeze-Thaw Time/h	Freeze-Thaw Times <i>n</i>	Loading Rate/MPa/s	Number of Samples
H <sub>2</sub> O HNO <sub>3</sub> NaOH	90	-15~20	4	0	0.8	4 4 4
H <sub>2</sub> O HNO <sub>3</sub> NaOH	90	-15~20	4	75	0.8	4 4 4
H <sub>2</sub> O HNO <sub>3</sub> NaOH	90	-15~20	4	100	0.8	4 4 4

Table 2. Uniaxialtest data for different chemical solutions and freeze-thaw cycles.

Freeze-Thaw Times <i>n</i>	Solution Category	Elastic Modulus <i>E</i> /GPa	Peak Stress $\sigma_{ m s}/{ m MPa}$	Peak Strain $arepsilon_{ m s}/10^{-3}$	Threshold Stress $\sigma_{\rm u}/{ m MPa}$	Threshold Strain $\varepsilon_{ m u}/10^{-3}$
0	H <sub>2</sub> O	16.25	105.86	14.66	62.65	10.59
	HNO <sub>3</sub>	13.58	108.31	13.33	71.49	9.82
	NaOH	16.18	115.29	14.84	76.01	11.69
75	H <sub>2</sub> O	13.79	90.52	14.69	60.03	11.96
	HNO <sub>3</sub>	11.45	83.71	13.87	57.38	9.91
	NaOH	15.85	94.98	13.60	62.41	11.00
100	H <sub>2</sub> O	12.98	84.74	15.14	56.30	12.81
	HNO <sub>3</sub>	10.22	81.48	18.08	50.96	13.42
	NaOH	14.90	93.33	15.10	62.52	12.88

According to the data in Table 2, the variation laws of peak stress, peak strain, and elastic modulus of different freeze-thaw times under the same chemical solutions and

different chemical solutions under the same freeze-thaw times can be obtained, as shown in Figure 4. For the parameters of the constitutive model constructed in this paper, the parameters  $\alpha$ , *m*, *F* and  $\lambda$  of the constitutive model under different chemical solutions and freeze-thaw cycles can be obtained according to the experimental data of the literature [21] and the above parameter calculation process, as shown in Table 3. From Equation (32), the comparison between the theoretical stress-strain curve of granite under different chemical solutions and freeze-thaw cycles and the experimental curve of the literature [21] can be obtained, as shown in Figure 5.

Freeze-Thaw Cycles	Solution Category	α	т	F	λ
	H <sub>2</sub> O	2.51	15.15	41.57	0.95
0	HNO <sub>3</sub>	1.83	9.95	38.40	0.90
	NaOH	2.82	14.50	32.39	0.96
	H <sub>2</sub> O	3.85	1.16	126.29	1.81
75	HNO <sub>3</sub>	2.92	1.06	95.68	1.49
	NaOH	3.01	4.68	42.50	0.72
	H <sub>2</sub> O	2.71	2.59	35.23	1.02
100	HNO <sub>3</sub>	2.98	2.57	78.99	2.01
	NaOH	3.09	2.54	38.63	0.98

Table 3. Parameter values of constitutive model under different chemical solutions and freeze-thaw cycles.

It can be seen from Figures 4 and 5 that the typical total stress-strain curve change law of granite can be roughly divided into four stages as mentioned above: the pore and fracture compaction stage, elastic deformation to the stable development stage of microelastic cracks, the unstable rupture development stage, and the post-rupture stage. The compaction stage is mainly caused by the closure of micro-cracks and pores in the rock under uniaxial loading, and the compaction phenomenon is gradually obvious with the increase of the number of freeze-thaw cycles. At the post-rupture stage, with the increase of the number of freeze-thaw cycles, the stress drop phenomenon weakened and the plasticity gradually increased.

After 90 days of immersion in chemical solution without freeze-thaw, the peak stress of granite soaked in  $H_2O$  was basically unchanged, and the peak stress of granite soaked in  $HNO_3$  solution was slightly reduced. However, the mineral components in granite soaked in NaOH solution react with NaOH solution to repair the initial internal micro-cracks and pores but increase the peak stress. The elastic modulus of granite soaked in  $H_2O$  and NaOH solution did not change significantly, but the elastic modulus of granite soaked in  $HNO_3$  solution decreased. To sum up,  $HNO_3$  solution aggravated the damage and deterioration of granite, while NaOH solution has a certain inhibitory effect on rock damage. Under the same number of freeze-thaw cycles, the stress-strain curves of granite in  $H_2O$  and NaOH solutions were close to each other, while the stress-strain curves of rocks soaked in  $HNO_3$  solution changed greatly, mainly manifested as inconsistent shapes and uneven curves. Furthermore, its peak strain is quite different from the stress-strain curves in  $H_2O$  and NaOH solutions. The plasticity of the rock soaked in  $HNO_3$  solution was enhanced, the brittleness was weakened, and it was more easily damaged than that soaked in  $H_2O$  and NaOH solution.

Under the same solution immersion, the elastic modulus, peak stress, and threshold stress of granite in general decrease with the increase of freeze-thaw cycles, while the peak strain and threshold strain increase with the increase of freeze-thaw cycles. It was gradually obvious with the increase of freeze-thaw cycles, indicating the damage and deterioration effect of freeze-thaw cycles on granite. With the increase of the number of freeze-thaw cycles, the stress-strain curve of the rock soaked in HNO<sub>3</sub> solution changed significantly, and the plastic deformation was obvious after 75 freeze-thaw cycles; after 100 freeze-thaw cycles, the NaOH solution showed a certain plastic deformation phenomenon. It shows that in HNO<sub>3</sub> solution, the effect of freeze-thaw cycle on the mechanical properties of



granite is more obvious, while the effect of freeze-thaw cycle in  $H_2O$  and NaOH solution is relatively weak.

**Figure 4.** Changes of rock parameters under different chemical solutions and freeze-thaw cycles: (a) Elastic modulus; (b) Peak stress; (c) Peak strain; (d) Threshold stress; (e) Threshold strain.



**Figure 5.** Comparison of the stress-strain curves and the curves of literature [21] under different chemical solutions and freeze-thaw cycles: (a) Freeze-thaw 0 times; (b) Freeze-thaw 75 times; (c) Freeze-thaw 100 times.

The theoretical results obtained in this paper have the same general trend as the experimental results in the literature [21]. In particular, the granite stress-stress curve has a good degree of fitting in the compaction stage and the post-destruction stage and can reflect the variation law of stress with strain. It shows that the statistical damage model of rock considering the pore compaction and post-peak shape under the action of chemical-freezing-thawing-loading can reflect the uniaxial compression deformation characteristics of rocks under different chemical solution soaking and freeze-thaw cycles. Additionally, it can well characterize the whole process curve of rock stress-strain under different chemical solution immersion and freeze-thaw cycles, however, after the point (at which damage is generated), there is also a certain deviation between the model curve in this paper and the test data, and the deviation is reasonable. The range is due to the different failure criteria selected during the establishment of the equation, which results in the different setting parameters, and the experimental measurement errors.

According to Equation (16), the change law of damage variables under different chemical solutions ( $H_2O$  solution,  $HNO_3$  solution, NaOH solution) and freeze-thaw times (0 times, 75 times, 100 times) can be obtained, as shown in Figure 6. When the rock is

not loaded after chemical-freezing-thawing, some initial damage has already occurred. Additionally, under the same conditions of freeze-thaw times, the value of damage variable D is HNO<sub>3</sub> solution > H<sub>2</sub>O solution > NaOH solution. It shows that the HNO<sub>3</sub> solution is more likely to cause damage to the granite, followed by the H<sub>2</sub>O solution, and the NaOH solution has the least damage. Under the same chemical solution erosion conditions, the value of damage variable D is freeze-thaw 100 times > freeze-thaw 75 times > freeze-thaw 0 times, and shows that freeze-thaw cycles exacerbate rock damage. It can be seen from Figure 6 that the damage variables of the rock in the initial stage, namely the compaction stage, elastic deformation to the stable development stage of micro-elastic cracks, are all zero. When the load reaches the yield point, the damage variable starts to accumulate and rapidly increases to one, and the damage variable remains stable at one, that is, the rock is completely damaged.



**Figure 6.** Damage evolution curves of uniaxial compression under different chemical solutions and freeze-thaw cycles: (**a**) Freeze-thaw 0 times; (**b**) Freeze-thaw 75 times; (**c**) Freeze-thaw 100 times.

The deformation and failure laws of siltstone in the literature [25] and sandstone in the literature [41] are similar to the uniaxial compression test characteristics of granite with different chemical solutions and freeze-thaw cycles in the literature [21], and they are all in line with the damage constitutive model established in this paper. The space is limited here and they will not be repeated here. Only the uniaxial compression test of granite with

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different chemical solutions and different freeze-thaw cycles in the literature [21] is used as a representative for a detailed comparison.

# 5. Conclusions

In view of the necessity for rock damage research under chemical-freezing-thawingloading and the defects existing in the traditional rock constitutive model, this paper uses statistical damage theory, assuming that the rock micro units' strength under chemicalfreezing-thawing action obeys the Weibull distribution. It introduces the compaction index and a post-peak correction coefficient that were used to establish a statistical damage model for rock under the action of chemical-freezing-thawing-loading. Analyzing the damage evolution process combined with the rock uniaxial compression test curve, the main conclusions obtained were as follows:

- (1) The compaction index  $\alpha$  is introduced to characterize the compaction performance of the internal pores in the rock compaction stage, and fully reflect the nonlinear curve shape of the stress-strain in the undamaged stage. As the compaction index decreases, the compaction effect of the pores in the rock gradually weakens.
- (2) Taking the Drucker–Prager strength criterion as the damage basis of rock micro units, considering the damage threshold and the post-peak correction coefficient, a statistical damage constitutive model of rock under chemical-freezing-thawing-loading based on the Weibull distribution is established, and the determination of each parameter of the model was clarified.
- (3) There is a good correlation between the experimental curve and the theoretical curve calculated by the constitutive model, which can better describe the uniaxial stress-strain relationship under different chemical solutions and freeze-thaw cycles. With the increase in number of freeze-thaw cycles, the rock damage deteriorated seriously, the peak stress, elastic model and threshold stress became smaller, and the increase of plasticity led to the increase of peak strain and threshold strain. Under the same number of freeze-thaw cycles, the HNO<sub>3</sub> solution is more likely to cause damage to the granite, followed by the H<sub>2</sub>O solution, and the NaOH solution has the least damage. From the damage evolution curve, it can be seen that some initial damage has occurred in the rock after chemical-freezing-thawing. During the uniaxial compression process, the damage variable remains unchanged at first, and then begin to change and rapidly increase to one after loading to the yield point. It shows that the model is accurate and reasonable and can provide a theoretical basis for the study of deformation and failure under multi-field coupling conditions.
- (4) The Hoek–Brown strength criterion can be used for further research on the method of measuring the strength of rock micro units, and the model results of the Drucker– Prager strength criterion can be compared and analyzed, hoping to obtain some new discoveries.

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