Mechanical Behavior and Constitutive Model for Loess Samples under Simulated Acid Rain Conditions

xia ye

Sichuan University - Wangjiang Campus: Sichuan University

Enlong Liu (✉ liuenlong@scu.edu.cn)

Sichuan University - Wangjiang Campus: Sichuan University

Baofeng Di

Sichuan University - Wangjiang Campus: Sichuan University

yayang yu

Sichuan University - Wangjiang Campus: Sichuan University

Research Article

Keywords: Acid rain, Saturated loess samples, Mechanical properties, Porous medium material, The double hardening model, pH values

Posted Date: April 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-355110/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Scientific Reports on March 9th, 2022. See the published version at <https://doi.org/10.1038/s41598-022-08199-9>.

Mechanical Behavior and Constitutive Model for Loess Samples under Simulated Acid Rain Conditions

Xia Ye ^a, Enlong Liu ^b, Baofeng Di ^c, Yanyang Yu ^d

^a Ph.D. Student, Institute of Disaster Management and Reconstruction, Sichuan University, Chengdu 610041,

China

^b Professor, State Key Laboratory of Hydraulics and Mountain River Engineering, College of Water Resource

and Hydropower, Sichuan University, Chengdu 610065, Sichuan, China

^c Professor, Institute of Disaster Management and Reconstruction, Sichuan University, Chengdu 610041, China

^d Ph.D. Student, State Key Laboratory of Hydraulics and Mountain River Engineering, College of Water

Resource and Hydropower, Sichuan University, Chengdu 610065, Sichuan, China

Corresponding author: Professor Enlong Liu; Email: liuenlong@scu.edu.cn.

ABSTRACT: In this paper, the sulfuric acid solution is diluted to pH 5.0, 4.0 and 3.0 to simulate the acid rain condition, and the triaxial compressional tests and scanning electron microscope are carried out to study the mechanical properties and evolution of the microstructure of the saturated loess samples. The results demonstrate that acid rain increases the porosity of loess samples, and the pore distribution is not uniform, so that the mechanical properties of loess samples change. With the decrease of pH value, the peak value of the deviatoric stress and the volumetric contraction of loess samples decreases, which causes the strength of soil to decrease. Furthermore, the framework of the chemical-mechanical model for loess under the action of acid rain is established, in which the loess is considered as porous medium material, and the variable of acid rain at different pH values through the degree of chemical reaction is

taken into account in the double-hardening model, and the model is also verified by the triaxial test results finally.

KEYWORDS: Acid rain; Saturated loess samples; Mechanical properties; Porous medium material; The double hardening model; pH values;

1 Introduction

In recent years, the problem of acid rain is very common, many scholars have found that acid rain will not only destroy the living environment of biological communities, but also aggravate other soil pollution (Wang et al., 2018; Zhu et al., 2018; Liang et al., 2020). Acid rain can accelerate the loss of mineral composition and change the soil structure. As we know, acid rain can corrode buildings, roadbed and pavement, dissolve soil on the surface of roadbed and pavement, and make cracks appear, resulting in reduced strength, thereby damaging the roadbed and pavement, and causing certain risks. For the loess areas located in western zone in China, acid rain can also change the mechanical features and thus damage the ground there. Therefore, the effect of acid rain on the mechanical properties of loess samples should be studied, which can provide a guidance for protecting the building located in loess areas there.

A large number of experimental studies have found that acid rain has an impact on soil strength and other mechanical indicators. In terms of rocks, the indoor uniaxial, shear and triaxial tests on rocks corroded by different pH values are carried out, and find that it significantly reduces the strength of rocks and causes damage to the rock structure. The corrosion mechanism of acid rain on rock samples is also preliminarily discussed (Ding and Feng, 2009; Xu et al., 2012; Han et al., 2013). The influence of acid rain on the stability of slope is explored, conducted relevant chemical weathering experiments under the action of acid rain, and analyzed the weakening mechanism of acid rain on slope (Zhao et al., 2009; Zhao

et al., 2019). The leaching effect of acid rain on calcareous sandy loam is simulated, and different pH aggravates the loss of phosphorus in the soil (Jalali and Naderi, 2012). Huang et al. (2021) found that high temperature and acid chemical solution could affect the mechanical characteristics of rock mass through the physical thermophysical test and Brazilian splitting test of red sandstone samples. The changes of the mechanical properties of composite fine grained soil under the influence of acids with different pH values is investigated. Because the internal structure of the soil is changed by acid rain, the compressive strength and shear strength parameters of the soil are reduced (Sarkary et al., 2012). (Gratchev and Towhata, 2011; Gratchev and Towhata, 2016; Bakhshipour et al., 2016a; Bakhshipour et al., 2016b; Bakhshipour et al., 2017) they conducted experiments on the influence of acid rain on soil compression characteristics, which led to significant changes in mineral structure with the decrease of pH values. The study of acid concentration on the mechanical properties of soil is also carried out. Acid has a great influence on the mechanical properties of soil (Hassanlourad et al., 2017; Chavali and Ponnappureddy, 2018; Koupai et al., 2020). Liu et al. (2020) used the laboratory permeability test of undisturbed loess to study the permeability characteristics under the action of three kinds of acid erosion, found the influence of acid concentration on the permeability coefficient, and analyzes its mechanism from the perspective of microstructure changes. It can be seen that the erosion of acid rain will damage the structure of soil and has a very adverse effect on the mechanical properties of soil. The above-mentioned scholars mainly conduct related experiments on rock and soil by acid rain, but did not conduct related research on the constitutive relationship.

In recent years, some scholars have studied the constitutive relations of soils (permafrost, over-consolidated soil, saturated soil and rocks) through porous media theory (Yao et al., 2009; Zhang et al., 2012; Shen and Shao, 2016; Zhang, 2017; Liu et al., 2018; Liu and Lai, 2020). Constitutive models of

65 the chemical-mechanical behavior of soil under porous media theory are also proposed. (Gawin et al.,
 66 2006; Martinelli et al., 2013) they proposed a thermal fluidization model that takes into account the fine
 67 and microscopic scale of concrete hardening. A high-precision hydrothermal chemical model for early
 68 self-drying phenomena is proposed (Luzio and Cusatis, 2009; Jendele et al., 2014). These scholars have
 69 studied the chemical-mechanical model of concrete materials, but have not applied this method to soil
 70 materials. For geotechnical materials, the following scholars have done the related research. Sherwood
 71 (1993) modified the basic thermodynamic parameters of Biot and the chemical potential related to the
 72 pore fluid. (Hueckel, 1997; Gajo et al., 2002) they considered that clay is contaminated in the stress
 73 history and study the electro-chemical-mechanical constitutive equation under the elastoplastic condition
 74 from the perspective of mass concentration. Nova et al. (2003) proposed a strain hardening elastoplastic
 75 model considering the internal plastic strain, weathering and chemical effects of bonded geomaterials.
 76 Boukpeti et al. (2004) proposed a model to consider the chemical plastic behavior of organic polluted
 77 liquids on clay under vertical flow. Shale was studied and permeability parameters are determined to
 78 solve the chemical pore elasticity of the cylinder (Detournay et al., 2005; Bungler, 2010; Sarout and
 79 Detournay, 2011). Guimaraes et al. (2007) proposed a thermo-fluid-mechanical coupling model
 80 considering the transport of the reaction from the perspective of the total analytical concentration.
 81 Kyokawa et al. (2020) established an electro-chemical-mechanical model by considering the deformation
 82 characteristics of the chemical composition changes of pore fluids in expansive soil. Song and Menon
 83 (2019) applied the principle of state primitives to unsaturated clays and establishes a non-local chemical-
 84 hydrodynamic model at the same chemical loading rate. The microstructure of the soil is studied, and the
 85 macroscopic model of saturated soil is derived by extending the pore scale to macroscopic scale through
 86 the theory of homogenization (Moyne and Murad, 2002; Buscarnera and Das, 2012). Thomas and Clearl

(1999) proposed an unsaturation-thermo-mechanical coupling model from the perspective of the osmotic potential and chemical solute concentration of expanded clay. Lei et al. (2016) established a thermodynamic framework for unsaturated expansive clay and took into account the situation of ionic expansive clay. These scholars mainly explore the chemical ion exchange that occurs inside the rock and soil, and the chemical concentration changes caused by ion exchange, which are taken into account in the constitutive model.

Even though the above-mentioned scholars have made a lot of contributions to the simulated acid rain test and the chemical-mechanical model, few researches have been done on the mechanical model considering the internal chemical reaction of acid rain on loess samples. This paper mainly conducts the triaxial tests of saturated loess samples under simulated acid rain conditions, and in the chemical-mechanical framework the double hardening model is formulated to consider the chemical reactions under the action of acid rain to the saturated loess samples.

2 Influence of Simulated Acid Rain on the Mechanical Properties of Loess

Samples

2.1 Materials and Test Methods

The material used here is loess samples extracted from Xi'an area of China. The intact loess is crushed into a 2 mm sieve to make triaxial samples. All samples are compacted in 4 layers according to the dry density of 1.7 g/cm^3 , with the diameter of 39.1mm and the height of 80mm. The test conditions are sulfuric acid solutions with pH 5.0, 4.0 and 3.0, and the control group is clean water (pH 6.9). The above prepared specimen is put into sulfuric acid solution for vacuum suction saturation. The specimens

are placed on a strain-controlled triaxial instrument for consolidated drained (CD) tests. The confining pressures are 50, 100, 200, and 400 kPa, respectively. The degree of saturation of the samples tested are more than 0.95 and the loading rate is 0.08mm/min. Afterwards, the loess samples with different pH values are sprayed with metal powder on the surface after treatment, and the surface microstructure is studied by the scanning electron microscope SEM.

2.2 Stress-Strain Relationships

The deviatoric stress $q=\sigma_1-\sigma_3$ –axial strain ε_1 curves and volumetric strain ε_v –axial strain ε_1 curves under different confining pressures in the consolidated drained tests of saturated loess samples are shown in Fig. 1 and Fig. 2, respectively. Fig. 1 and Fig. 2 show that (1) the loess samples present strain-hardening behavior under confining pressures ranging from 50 to 400kPa; and (2) the loess samples contract under various confining pressures and all the samples fail by bulging. The higher the confining pressures, the higher the peak value of the deviatoric stress and volumetric contraction. During the consolidation process, the bonds between loess particles are heavily damaged under confining pressures. Thus the strength is mainly contributed by the sliding of the loess particles in the shearing process, which leads the loess samples to present strain-hardening behavior and contraction. The higher the confining pressure, the more the bonds damage of loess particles is at the end of consolidation, which cause larger slippage of loess particles in the shear process and thus a larger peak value of deviatoric stress.

The deviatoric stress $q=\sigma_1-\sigma_3$ –axial strain ε_1 curves and volumetric strain ε_v –axial strain ε_1 curves under different acidic conditions in the consolidated drained tests of saturated loess samples are shown in Fig. 3 and Fig. 4, respectively. It can be concluded that the mechanical properties of loess

samples are significantly affected by the pH value. (1) Under confining pressures ranging from 50 to 400kPa, the deviatoric stresses of the loess samples under acidic conditions are smaller than that under clear water. (2) The volumetric contraction of the loess samples under acidic conditions is smaller than that under clear water under various confining pressures. From the molar stress circle drawn on the obtained results, the expressions of c -pH value and φ' - pH value are obtained as follows:

$$\begin{aligned} \varphi' \\ = -0.1923(-lg s)^2 + 2.5271(-lg s) \\ + 18.428 \end{aligned} \quad (1)$$

$$\begin{aligned} c \\ = -0.4959(-lg s)^2 + 6.1694(-lg s) \\ + 2.6869 \end{aligned} \quad (2)$$

where s is the concentration of sulfuric acid, $pH = -lg s$. The equations (1) and (2) show that with the decrease of pH value, both c decreases and φ' decrease. Due to the action of acid rain, the loess interior is eroded, which leads to the decrease of c and φ' . Therefore, compared with clear water, the bonds of loess particles under different acidic conditions are weaker, and the loess samples is more likely to be damaged. The lower the pH value, the lower the peak value of the deviatoric stress, and the lower the volumetric contraction.

2.3 SEM Images of Loess Sample under Different Acidic Conditions

Fig. 5 shows the microstructure of loess sample after being saturated with clear water and sulfuric acid solutions of different pH values. The microstructure of loess sample has undergone significant changes. It can be seen from Fig. 5(a) that the soil sample is very dense and has no obvious pores under

clear water conditions. It shows that the cementation of immersion in clean water is strong, and a higher deviatoric stress value is required to destroy. By comparing Fig. 5(b), (c), (d) and (a), it can be seen that with the decreasing pH value, the sulfuric acid solution corrodes the dense structure into a pore structure, so the pores gradually increase. In addition, even large pores appear, and the pore distribution is gradually uneven. Due to the increase of internal pores, the void ratio of loess sample increases, resulting in a decrease in deviatoric stress.

3 Constitutive Model for Loess under Acid Rain Conditions

3.1 Constitutive Model Considering Chemical Reaction

Complex chemical reactions will take place in the process of loess samples immersed in sulfuric acid solution. The main component of sulfuric acid solution is sulfuric acid, and calcium carbonate is involved in the reaction in loess. In this case, the main equations for chemical reaction that occurred can be simplified as follows:

(

3)

For the macroscopic model of chemical reaction with sulfuric acid, it is considered that the loess is a porous medium material. In the chemical reaction process, the solid part of the material is formed by the precipitation of unreacted loess and the slightly water-soluble $CaSO_4$ generated by the reaction. The condition for the reaction to occur is that the aqueous sulfuric acid solution diffuses into the unreacted

loess through the precipitate of CaSO_4 that has been formed. The aqueous sulfuric acid solution is then consumed until the chemical reaction can no longer occur. Therefore, the reaction is controlled by the diffusion of the sulfuric acid solution through the compound layer. In order to be able to take this chemical reaction into account in the constitutive equation, this paper adopts the chemical-mechanical constitutive model was proposed to describe the influence of chemical reactions on soil properties from the macroscopic level (Coussy, 1995; Ulm and Coussy, 1996). The loess consisting of skeleton and fluid is a porous medium material. The deformation of loess is considered to be caused by the irreversible behavior of the soil skeleton indicated by the plastic strain ε^p and the hardening variable χ . In addition, for the fluid phase saturated porous space of loess, the sulfuric acid solution is reactive and can react with loess. The conservation of mass of the reaction:

$$\begin{aligned} & \frac{dm_{sa}}{dt} \\ & = -\nabla_X M_{sa} \\ & + m_{\rightarrow sa}^\circ \end{aligned}$$

where dm_{sa} is the change in the mass of the sulfuric acid per unit of macroscopic volume. $\nabla_X M_{sa}$ is the external rate of sulfuric acid fluid mass supply. $m_{\rightarrow sa}^\circ$ is the rate of mass consumption of the sulfuric acid during the chemical reaction.

Due to the occurrence of chemical reactions, the Clausius-Duhem inequality associated with the deformable porous continuum can be derived:

$$\begin{aligned} & \Phi' + \Phi_{sa} + \Phi_{th} \\ & \geq 0 \end{aligned}$$

(5)

where Φ_{th} is the thermal dissipation. Φ_{sa} is the dissipation associated with the transport of the sulfuric acid.

Considering the early immersion of soil in acid solution, the dissipation is mainly caused by the irreversible skeleton evolution of loess and the chemical reaction between sulfuric acid solution and calcium carbonate, so the expression is as follows:

$$\Phi' = \Phi_{\rightarrow sa} + \Phi_s \geq 0 \quad (6)$$

$$\Phi_{\rightarrow sa} = -\mu_{sa} m_{\rightarrow sa}^{\circ} \geq 0 \quad (7)$$

where $\Phi_{\rightarrow sa}$ is the dissipation related to the chemical reaction between sulfuric acid solution and calcium carbonate, μ_{sa} is the chemical potential difference. It shows the thermodynamic imbalance between the sulfuric acid solution and the chemical composition of calcium carbonate involved in the reaction. Chemical dissipation $\Phi_{\rightarrow sa}$ can be written in the equivalent form:

$$\Phi_{\rightarrow sa} = A'_m \frac{d\xi}{dt} \geq 0 \quad (8)$$

where A'_m is the affinity of the chemical reaction, which is related to chemical potential difference μ_{sa} . ξ is the degree of chemical reaction, which is related to the mass reaction rate $m_{\rightarrow sa}^{\circ}$. The diffusion of sulfuric acid solution through the compound layer is the main mechanism to control the reaction between sulfuric acid and calcium carbonate. The chemical affinity is related to the degree of reaction, activation energy and temperature, whose expression is as follows:

$$213 \quad A'_m$$

$$214 \quad = k \frac{d\xi}{dt} \exp \left(\frac{E'_a}{RT} \right)$$

215 The dissipation associated with the skeleton is written as:

$$216 \quad \Phi_s$$

$$217 \quad = \sigma: \frac{d\varepsilon}{dt} + \mu_{sa} \frac{dm_{sa}}{dt} - S \frac{dT}{dt}$$

$$218 \quad - \frac{d\psi}{dt}$$

$$219 \quad (10)$$

220 Denoting g_f^{eff} as the specific Gibbs potential of the effective solution, we write:

$$221 \quad \mu_{sa}$$

$$222 \quad = g_f^{eff}(P, T)$$

223 The chemical activity A of the saturating solution is then defined as the ratio of the two densities

224 according to:

$$225 \quad A = \frac{\rho_{sa}^{eff}}{\rho_{sa}}, A$$

$$226 \quad \geq 1$$

227 By substituting (11) and (12) into the equation of state of the fluid, where $g_f = g_f^{eff}(P, T)$, it can

228 be obtained:

$$229 \quad \frac{\partial \mu_{sa}}{\partial p} = \frac{1}{A \rho_{sa}}, S_f$$

$$230 \quad = - \frac{\partial \mu_{sa}}{\partial T}$$

$$231 \quad \psi_s = \psi - m_{sa} \psi_{sa}^{eff}; S_s$$

$$232 \quad = S$$

$$233 \quad - m_{sa} S_{sa}$$

$$\Phi_s$$

$$= \sigma: \frac{d\varepsilon}{dt} + p \frac{d}{dt} \left(\frac{\phi}{A} \right) - S_s \frac{dT}{dt} - \frac{d\psi_s}{dt}$$

Since μ_{sa} replaces g_f , Φ_{sa} becomes:

$$\Phi_{sa}$$

$$= \left[-\frac{1}{A} \nabla_x p + \rho_{sa} (f - \gamma^{sa}) \right]$$

$$\cdot \vartheta$$

A is the chemical activity, and for the pure component, $A=1$. Therefore, formula (15) is written as:

$$\Phi_s$$

$$= \sigma: \frac{d\varepsilon}{dt} + p \frac{d\phi}{dt} - S_s \frac{dT}{dt} - \frac{d\psi_s}{dt}$$

The system intrinsic dissipation includes the dissipation caused by the evolution of the permanent skeleton of loess and the dissipation related to the chemical reaction between the sulfuric acid solution and calcium carbonate, and the expression is written as:

$$\Phi' = \sigma: \frac{d\varepsilon}{dt} + \mu_{sa} \frac{dm_{sa}}{dt} - S \frac{dT}{dt} - A'_m \frac{d\xi}{dt} - \frac{d\psi}{dt} \quad (18)$$

Free energy is expressed by temperature, the total strain, plastic strain, m_{sa} , hardening parameters and the degree of chemical reaction:

$$\psi$$

$$= \psi(T, \varepsilon, \varepsilon^p, \chi, m_{sa}, \xi$$

$$)$$

$$(19)$$

By substituting the free energy into dissipation, we can get:

$$\begin{aligned} \Phi' = & \left(\sigma - \frac{\partial \psi}{\partial \varepsilon} \right) : d\varepsilon - \left(S + \frac{\partial \psi}{\partial T} \right) dT - \left(A'_m + \frac{\partial \psi}{\partial \xi} \right) d\xi + \left(\mu_{sa} - \frac{\partial \psi}{\partial m_{sa}} \right) dm_{sa} + \sigma : d\varepsilon^p + \zeta d\chi \\ \geq & 0 \end{aligned}$$

Referring to Coussy (2004), from Equation (20) we can be obtained the following:

$$\begin{aligned} \sigma = \frac{\partial \psi}{\partial \varepsilon} = - \frac{\partial \psi}{\partial \varepsilon^p}, S = - \frac{\partial \psi}{\partial T}, \mu_{sa} = \frac{\partial \psi}{\partial m_{sa}}, \zeta = - \frac{\partial \psi}{\partial \chi}, \quad A'_m \\ = - \frac{\partial \psi}{\partial \xi} \end{aligned} \quad (21)$$

Alternatively, use of energy G defined by:

$$\begin{aligned} G \\ = \psi_s \\ - p\phi \end{aligned}$$

Formula (21) becomes:

$$\begin{aligned} \sigma = \frac{\partial G}{\partial \varepsilon}, S = - \frac{\partial G}{\partial T} + s_{sa} m_{sa}, \phi = \frac{m_{sa}}{\rho_{sa}} = - \frac{\partial G}{\partial p}, \zeta = - \frac{\partial G}{\partial \chi}, \quad A'_m \\ = - \frac{\partial G}{\partial \xi} \end{aligned} \quad (23)$$

By differentiating the above equation of state, a complex equation of state can be obtained:

$$\begin{aligned} d\sigma \\ = \frac{\partial^2 G}{\partial \varepsilon^2} : (d\varepsilon - d\varepsilon^p) + \frac{\partial^2 G}{\partial \varepsilon \partial p} dp + \frac{\partial^2 G}{\partial \varepsilon \partial T} dT \\ + \frac{\partial^2 G}{\partial \varepsilon \partial \xi} d\xi \end{aligned} \quad (24-a)$$

$$\begin{aligned} dS = - \frac{\partial^2 G}{\partial T^2} dT - \frac{\partial^2 G}{\partial \varepsilon \partial T} : (d\varepsilon - d\varepsilon^p) - \frac{\partial^2 G}{\partial T \partial p} dp - \frac{\partial^2 G}{\partial T \partial \xi} d\xi \\ + s_s m_{sa} \end{aligned} \quad (24-b)$$

$$\begin{aligned} dA'_m = - \frac{\partial^2 G}{\partial \xi \partial \varepsilon} : (d\varepsilon - d\varepsilon^p) - \frac{\partial^2 G}{\partial \xi \partial T} dT - \frac{\partial^2 G}{\partial \xi \partial p} dp - \frac{\partial^2 G}{\partial \chi \partial \xi} d\chi \\ - \frac{\partial^2 G}{\partial \xi^2} d\xi \end{aligned} \quad (24-c)$$

In the process of reaction between sulfuric acid solution and remolded loess, we believe that the

temperature change can be ignored, so $dT=0$. The strain in incremental form is expressed as:

$$\begin{aligned}
& d\varepsilon \\
& = D^{-1}:d\sigma + d\varepsilon^p + ad\xi \\
& + bdp \\
& (25)
\end{aligned}$$

where $D = \frac{\partial^2 G}{\partial \varepsilon^2}$ is the elastic stiffness tensor, $a = D^{-1}:\frac{\partial^2 G}{\partial \varepsilon \partial \xi}$ is the chemical expansion coefficient tensor. $b = D^{-1}:\frac{\partial^2 G}{\partial \varepsilon \partial p}$ is the Biot's tangent tensor. For the isotropic case, $a = \beta_s \mathbf{1}$, Equation (25) becomes:

$$\begin{aligned}
d\varepsilon - d\varepsilon^p &= \frac{1}{3G} d\sigma_s + \left(\frac{1}{K}\right) d\sigma_m \\
&- \beta_s d\xi \quad (26)
\end{aligned}$$

where $\sigma'_m = \frac{1}{3}(\sigma_1 + 2\sigma_3)$, $\sigma_s = \left(\frac{3}{2}s_{ij}s_{ji}\right)^{1/2} = \sigma_1 - \sigma_3$, $\sigma_m = \sigma'_m - p$. The axial stress, confining pressure, the mean stress and the shear stress under the condition of triaxial compression are denoted by σ_1 , σ_3 , σ'_m and σ_s . The stress deviatoric tensor are denoted by s_{ij} .

The standard principle of applying ideal plasticity is written:

$$\begin{aligned}
& \sigma \in C_E \Leftrightarrow F(\sigma, p, \zeta) \\
& \leq 0 \\
& (27)
\end{aligned}$$

In the formula, $F(\sigma, p, \zeta)$ is the loading function. When the loading point remains constant at the boundary of C_E in the elastic domain ($F = dF = 0$), the plastic variable ε^p and χ will evolve. In a standard plastic model, the hardening development often only relates to the plastic hardening variable χ ($\zeta = \zeta(\chi)$), but to the loess dipped in acid rain has also been chemical hardening phenomenon. Therefore, the hardening force is expressed by hardening variables and the degree of chemical reaction:

$$\zeta = \zeta(\chi, \xi) \quad (28)$$

With regard to the development of plastic variables, the hardening law and flow law are written:

$$\begin{aligned} d\varepsilon^p &= d\lambda \frac{\partial g(\sigma, p, \zeta)}{\partial \sigma} \\ d\chi &= d\lambda \frac{\partial g(\sigma, p, \zeta)}{\partial \zeta} \end{aligned} \quad (29-b)$$

In the formula, the plastic multiplier is denoted by $d\lambda$, and the plastic potential is denoted by $g(\sigma, p, \zeta)$. The consistency conditions are obtained:

$$dF = 0 \Leftrightarrow \frac{\partial F}{\partial \zeta} \frac{\partial \zeta(\chi, \xi)}{\partial \chi} d\chi = -d_\chi F = -d\lambda H \quad (30)$$

Among them, $d_\chi F$ is the sub-derivative of F when χ is constant; and the hardening modulus is denoted by H . Then, through the above formula and the hardening law, the expressions of H and $d\lambda$ are obtained:

$$d\lambda = \frac{d_\chi F}{H} = \frac{1}{H} \left(\frac{\partial F}{\partial \sigma} : d\sigma + \frac{\partial F}{\partial p} dp + \frac{\partial F}{\partial \zeta} \frac{\partial \zeta}{\partial \xi} d\xi \right) \quad (31)$$

$$H = - \frac{\partial F}{\partial \zeta} \frac{\partial \zeta}{\partial \chi} \frac{d\chi}{d\lambda}$$

$$= - \frac{\partial F}{\partial \zeta} \frac{\partial \zeta}{\partial \chi} \frac{\partial g(\sigma, p, \zeta)}{\partial \zeta}$$

According to the Drucker hypothesis, the inherent dissipation convexity and non-negativity of the loess can be obtained:

$$\varphi dt = d\lambda \left(\sigma : \frac{\partial g}{\partial \sigma} + p \frac{\partial g}{\partial p} + \zeta \frac{\partial g}{\partial \zeta} \right) \geq 0, F = dF = 0 \quad (33)$$

Because the plastic multiplier $d\lambda$ is not negative, according to the law of hardening and flow, plastic increment $d\varepsilon^p$ is represented by thermodynamics $\frac{\partial g(\sigma, p, \xi)}{\partial \sigma}$ and $\frac{\partial g(\sigma, p, \xi)}{\partial p}$, and $d\chi$ is represented by thermodynamics $\frac{\partial g(\sigma, p, \xi)}{\partial \xi}$. Furthermore, the elastic domain develops and changes because of the hardening force is affected by the degree of chemical reaction, even if there is no plastic evolution in the loess specimen ($d\lambda = 0$), the hardening variable χ remained unchanged in dt duration. The degree of chemical reaction ξ is defined according to physical chemistry as:

$$\xi = \frac{sV - n_B(0)}{v_B} \quad (34)$$

where s is the concentration of sulfuric acid solution; v_B is the measurement coefficient of the chemical reaction, and -1 is used for this reaction; $n_B(0)$ is the amount of the substance at the beginning of the chemical reaction. It is considered that the initial volume V_0 during the entire reaction is equal to the volume V when the reaction is completed, so $n_B(0) = s_0V$. Therefore, the above formula becomes:

$$\xi = \frac{(s - s_0)V}{v_B} \quad (35)$$

For ξ dimensionless treatment is Z :

$$Z = \frac{\xi}{N_0} \quad (36)$$

N_0 is the amount of sulfuric acid before the chemical reaction.

3.2 Simulation of Triaxial Compression Tests

In order to model the mechanical features of loess under simulated acid rain conditions, the double hardening model is adopted (Shen, 1995; Liu and Xing, 2009), which can be revised to reflect both strain hardening phenomenon and strain softening phenomenon of the soil. For triaxial compression, we have $\varepsilon_s = \left(\frac{2}{3}e_{ij}e_{ji}\right)^{1/2} = \frac{2}{3}(\varepsilon_1 - \varepsilon_3)$, $\varepsilon_v = \varepsilon_1 + 2\varepsilon_3$. Strain deviation tensor is denoted by e_{ij} ; the axial strain, shear strain and radial strain are respectively denoted by ε_1 , ε_s and ε_3 . σ_m is the effective stress, $\sigma_m = \sigma'_m - p$. When the loess is under triaxial compression: the current elastic interval is written as:

$$F(\sigma_m, \sigma_s, \zeta) \leq 0 \quad (37)$$

The constitutive equation is written as:

$$F(\sigma_m, \sigma_s, \zeta_1, \zeta_2) = \frac{\sigma_m}{1 - (\eta/\zeta_1)^n} - \zeta_2 = 0 \quad (38)$$

where $\zeta_1(\varepsilon_s^p, \xi)$, $\zeta_2(\varepsilon_v^p, \xi)$ are expressed as a hardening parameter; n is the parameter related to the over-consolidation ratio; and $\eta = \frac{\sigma_s}{\sigma_m}$. The expression of the hardening parameter $\zeta_1(\varepsilon_s^p, \xi)$, $\zeta_2(\varepsilon_v^p, \xi)$ are written as:

$$\begin{aligned} & \zeta_1(\varepsilon_s^p, \xi) \\ &= \alpha_c(\xi)\alpha_{m0} \left[1 - a_1 \exp\left(-\frac{\varepsilon_s^p}{a_2}\right) \right] \end{aligned} \quad (39)$$

$$\zeta_2(\varepsilon_v^p, \xi) = \left[1 - a_3 \left(\frac{\xi}{N_0} \right) \right] \sigma_{c0} \exp(\beta \varepsilon_v^p) \quad (40)$$

$$\alpha_c(\xi)$$

$$= \alpha_0$$

$$+ N_{s0} \frac{\xi}{N_0}$$

where the material parameters are α_{m0} , a_1, a_2 and c_3 ; and the reference pressure is σ_{c0} .

Using the associated flow rule, the yield function F is consistent with the plastic potential function

g , namely $F=g$. We can get the $d\varepsilon_v^p$ and $d\varepsilon_s^p$:

$$d\varepsilon_v^p$$

$$= d\lambda$$

$$\frac{\partial g}{\partial \sigma_m}$$

(42-a)

$$d\varepsilon_s^p$$

$$= d\lambda$$

$$\frac{\partial g}{\partial \sigma_s}$$

(42-b)

Meeting the consistency condition, the expression of H and $d\lambda$ are written as:

$$d\lambda = \frac{1}{H} \left[\frac{\partial F}{\partial \sigma_m} d\sigma_m + \frac{\partial F}{\partial \sigma_s} d\sigma_s + \left(\frac{\partial F}{\partial \zeta_1} \frac{\partial \zeta_1}{\partial \xi} + \frac{\partial F}{\partial \zeta_2} \frac{\partial \zeta_2}{\partial \xi} \right) d\xi \right] \quad (43)$$

$$H$$

$$= - \frac{\partial F}{\partial \zeta_1} \frac{\partial \zeta_1}{\partial \chi_1} \frac{d\chi_1}{d\lambda}$$

$$- \frac{\partial F}{\partial \zeta_2} \frac{\partial \zeta_2}{\partial \chi_2} \frac{d\chi_2}{d\lambda}$$

384 Putting $d\chi_1 = d\varepsilon_s^p = d\lambda \frac{\partial F}{\partial \sigma_s}$ and $d\chi_2 = d\varepsilon_v^p = d\lambda \frac{\partial F}{\partial \sigma_m}$ into (44), it becomes:

385 H

$$386 = -\frac{\partial F}{\partial \zeta_1} \frac{\partial \zeta_1}{\partial \varepsilon_s^p} \frac{\partial F}{\partial \sigma_s}$$

$$387 - \frac{\partial F}{\partial \zeta_2} \frac{\partial \zeta_2}{\partial \varepsilon_v^p} \frac{\partial F}{\partial \sigma_m}$$

388 where

$$389 \frac{\partial F}{\partial \sigma_m} = \frac{1 - (1+n)\left(\frac{\eta}{\zeta_1}\right)^n}{\left(1 - \left(\frac{\eta}{\zeta_1}\right)^n\right)^2}, \frac{\partial F}{\partial \sigma_s} = \frac{n\left(\frac{\eta}{\zeta_1}\right)^{n-1}}{\zeta_1 \left(1 - \left(\frac{\eta}{\zeta_1}\right)^n\right)^2}, \frac{\partial \zeta_1}{\partial \xi} = \alpha_{m0} \left[1 - a_1 \exp\left(-\frac{\varepsilon_s^p}{a_2}\right) \right] \frac{N_{s0}}{N_0},$$

$$390 \frac{\partial \zeta_2}{\partial \xi} = -\sigma_{c0} \exp(\beta \varepsilon_v^p) \frac{a_3}{N_0}, \frac{\partial F}{\partial \zeta_1} = \frac{-n\sigma_m \eta^n}{\zeta_1^{n+1} [1 - \left(\frac{\eta}{\zeta_1}\right)^n]^2}, \frac{\partial F}{\partial \zeta_2} = -1, \frac{\partial \zeta_2}{\partial \varepsilon_v^p} = \beta \zeta_2.$$

$$391 \frac{\partial \zeta_1}{\partial \varepsilon_s^p} = \frac{1}{a_2} (\zeta_1 - \alpha_c(\xi) \alpha_{m0}) .$$

392 Hence, the shear and volumetric strain increments composed of elasticity and plasticity:

$$393 d\varepsilon_v = d\varepsilon_v^E + d\varepsilon_v^p$$

$$394 = A_1 d\sigma_m + A_2 d\sigma_s$$

$$395 + A_3 d\xi$$

396

397 (46-a)

$$398 d\varepsilon_s = d\varepsilon_s^E + d\varepsilon_s^p = B_1 d\sigma_m + B_2 d\sigma_s + B_3 d\xi \quad (46-b)$$

399 where

$$400 A_1 = \frac{1}{K} + \frac{1}{H} \frac{\partial F}{\partial \sigma_m} \frac{\partial F}{\partial \sigma_m}, A_2 = \frac{1}{H} \frac{\partial F}{\partial \sigma_m} \frac{\partial F}{\partial \sigma_s}, A_3 = \frac{1}{H} \left(\frac{\partial F}{\partial \zeta_1} \frac{\partial \zeta_1}{\partial \xi} + \frac{\partial F}{\partial \zeta_2} \frac{\partial \zeta_2}{\partial \xi} \right) \frac{\partial F}{\partial \sigma_m} - \beta_s$$

$$401 B_1 = \frac{1}{H} \frac{\partial F}{\partial \sigma_m} \frac{\partial f}{\partial \sigma_s}, B_2 = \frac{1}{3G} + \frac{1}{H} \frac{\partial F}{\partial \sigma_s} \frac{\partial F}{\partial \sigma_s}, B_3 = \frac{1}{H} \left(\frac{\partial F}{\partial \zeta_1} \frac{\partial \zeta_1}{\partial \xi} + \frac{\partial F}{\partial \zeta_2} \frac{\partial \zeta_2}{\partial \xi} \right) \frac{\partial F}{\partial \sigma_s} .$$

402 3.3 Model Validation

The parameters of consolidated drained tests are as follows: $E = E_0 \left(\frac{\sigma_{c0}}{P_a} \right)^m$, $E_0 = -48.177(-lg s)^2 + 1582.1(-lg s) + 293.47$, $m = -0.0196(-lg s) + 0.8246$. σ_{c0} is the reference pressure when $\varepsilon_v^p = 0$. In this paper, the confining pressure of the conventional triaxial consolidated drained shear tests under the corresponding conditions is 50, 100, 200 and 400kPa, respectively. Standard atmospheric pressure is represented by P_a . The values of K and G are determined by $K = \frac{E}{3(1-2\nu)}$ and $G = \frac{E}{2(1+\nu)}$, Poisson's ratio $\nu = 0.2$. The initial pore ratio is represented by e_0 , $e_0 = 0.712$. λ represents the slope of the isobaric consolidation curve, and κ represents the slope of the rebound curve. It is available in the $\nu - \ln p$ plane: $\lambda = 0.088$, $\kappa = 0.008$. $\beta = \frac{1+e_0}{\lambda-\kappa} = 21.4$, $n=1.4$, α_{m0} is a model parameter related to n and effective internal friction Angle φ' . $\varphi' = -0.1923(-lg s)^2 + 2.5271(-lg s) + 18.428$. The expression is as follows:

$$\alpha_{m0} = 1.25^n \sqrt{1+n} \frac{6 \sin \varphi'}{3 - \sin \varphi'}$$

According to the value of the effective internal friction angle under different acidic conditions, the different values of α_{m0} can be obtained. $N_{s0} = 0.0002$, $a_3 = 0.001$, $\beta_s = -0.001$, $\alpha_0 = 1.0043 \left(\frac{\sigma_{c0}}{P_a} \right)^{-0.131}$, $a_1 = 0.0003(-lg s)^2 - 0.0122(-lg s) + 0.9681$, $a_2 = -0.0008(-lg s)^2 + 0.0102(-lg s) - 0.0379$. As can be seen from Fig. 6 and Fig. 7. The results show that the deviatoric stress-axial strain curves and volumetric strain-axial strain curves of saturated loess can be simulated by a double-hardening model considering the influence of concentration. The simulated results of the model under all confining pressures present strain-hardening behavior and contract, which is consistent with the tested results of loess and whose peak value is very close to the tested results. For the simulated results, the higher the confining pressures, the higher the peak of the deviatoric stress and volumetric contract. The simulated results at different pH values can be the same as the tested results of saturated loess. With

the decrease of pH values, the peak of the simulated deviatoric stress and volumetric contract decrease.

Although the simulated values are slightly different from the experimental results, the double hardening model can better reflect the deformation behavior of saturated loess.

3.4 Parameter Sensitivity Analysis

Fig. 8-14 shows the calculated results when the model parameters change when the acidic condition is pH 5 and the confining pressure is 200kPa, including a_1 , a_2 , a_3 , α_0 , β_s , n and N_{s0} . The model calculated results can reflect the main mechanical behavior of loess. From the deviatoric stress–axial strain curves, it show that with the decrease of N_{s0} and a_3 , the loess samples present strain hardening behavior; With the decrease of a_1 , β_s and n , the loess samples behave strain softening slightly to strain hardening, and the deviatoric stress peak value decreases; While the reduction of a_2 and α_0 , the loess samples behave strain hardening slightly to strain softening. For volumetric strain change, with the decrease of a_1 , a_2 , β_s and n , the loess samples contract more heavily. With the decrease of α_0 , a_3 , and N_{s0} , the loess samples dilate more heavily. On the whole, the values of a_1 , a_2 and a_3 have the greatest impact on the simulation results, that is, the most sensitive. The value of α_0 and N_{s0} have the second effect, and β_s and n have the least effect.

4 Conclusions

1. By performing the CD experiments of acid rain on loess samples, we found that with the increase of acid rain concentration, the peak of the deviatoric stress decreases, and the samples contracts less. Through SEM analysis of the microstructure, it is found that the cementation failure caused by acid rain erosion on loess is the reason for the reduction of strength.

2. A thermodynamic framework for the chemical and mechanical coupling of loess under acid rain conditions is proposed. The chemical reaction degree of sulfuric acid and calcium carbonate is taken into account in the framework and the elastoplastic constitutive relation is established.

3. Different pH values are introduced into the double hardening model through the degree of chemical reaction, and the mechanics and deformation behavior of the loess under different acid rain conditions can be well simulated by the proposed model.

Consent to Participate Since this study did not recruit any human subjects, this section does not apply.

Consent to Publish Since this study is not attempting to re-publish/publish any third party or author's previously published material, this section does not apply.

Ethical approval Since this study did not recruit any human and/or animal subjects, this section does not apply.

Acknowledgments We thank the anonymous reviewers for their comments on our paper.

Authors' contributions All the authors have designed this study equally. XY collected, analyzed and interpreted the results of the study. And XY drafted the initial manuscript. YY helped XY do the experiment. EL and BD have revised and restructured the manuscript.

Funding This research was supported by National Science Foundation of China (Grant No. 41790431)

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflict of interest The authors declare that they have no conflict of interest.

References

465 Boukpeti N, Charlier R, Hueckel T (2004) Modelling contamination of clays. Elsevier Geo-
 466 Engineering Book Series 2:523–528. DOI: 10.1016/S1571-9960(04)80093-4
 467 Bungler AP (2010) The mandel-cryer effect in chemoporoelasticity. .International Journal for Numerical
 468 and Analytical Methods in Geomechanics 34(14):1479–1511. DOI: [http://orcid.org/0000-0002-0696-](http://orcid.org/0000-0002-0696-7066)
 469 7066
 470 Bakhshipour Z, Asadi A, Huat BBK, Sridharan A (2016) Effect of Acid Rain on Geotechnical
 471 Properties of Residual Soils. Soils and Foundations 56(6): 1008-1020. DOI:
 472 10.1016/j.sandf.2016.11.006
 473 Bakhshipour Z, Asadi A., Huat BBK, Sridharan A (2016) Long-Term Intruding Effects of Acid Rain on
 474 Engineering Properties of Primary and Secondary Kaolinite Clays. International Journal of Geosynthetics
 475 and Ground Engineering 2(3). DOI: 10.1007/s40891-016-0059-1
 476 Buscarnera G, Das A (2016) Chemo-mechanics of cemented granular solids subjected to precipitation
 477 and dissolution of mineral species. International Journal for Numerical and Analytical Methods in
 478 Geomechanics 40(9). DOI: 10.1002/nag.2486
 479 Bakhshipour Z, Asadi A, Sridharan A, et al. (2017) Acid Rain Intrusion Effects on The Compressibility
 480 Behaviour of Residual Soils. Journal of Environmental Geotechnics 1-38. DOI: 10.1680/jenge.15.00081
 481 Coussy O (1995) Mechanics of Porous Continua. John Wiley and Sons, Chichester, U.K.
 482 Coussy O, Ulm F (1996) Creep and plasticity due to chemo-mechanical couplings. Archive of Applied
 483 Mechanics 66:523-535. DOI: 10.1007/BF00808142
 484 Coussy O (2004) Poromechanics, John Wiley & Sons, Ltd.

485 Chavali, Ponnareddy (2018) Swelling and compressibility characteristics of bentonite and kaolin clay
 486 subjected to inorganic acid contamination. *International Journal of Geotechnical Engineering* 12(5). DOI:
 487 10.1080/19386362.2017.1299418
 488 Detournay E, Sarout J, Tan C, Caurel J (2005) Chemoporoelastic parameter identification of a reactive
 489 shale. vol. 125 of *Solid Mechanics and its Applications* 125–132.
 490 Ding WX, Feng XT (2009) Damage effect and fracture criterion of rock with multi-preexisting cracks
 491 under chemical erosion. *Chinese Journal of Geotechnical Engineering* 31(6): 899-904.
 492 Gajo A, Loret B, Hueckel T (2002) Electro-chemo-mechanical couplings in saturated porous media:
 493 elastic–plastic behaviour of heteroionic expansive clays. *International Journal of Solids and Structures*
 494 39(16):4327–4362. DOI: 10.1016/S0020-7683(02)00231-7
 495 Gawin D, Pesavento F, Schrefler BA (2006) Hygro-thermo-chemo-mechanical modelling of concrete at
 496 early ages and beyond. Part I: hydration and hygro-thermal phenomena. *International Journal for*
 497 *Numerical Methods in Engineering* 67 (3):299–331. DOI: 10.1002/nme.1615
 498 Guimaraes LDN, Gens A, Olivella S (2007) Coupled thermo-hydro-mechanical and chemical analysis
 499 of expansive clay subjected to heating and hydration. *Transport in Porous Media* 66(3):341–372. DOI:
 500 10.1007/s11242-006-0014-z
 501 Gratchev I, Towhata I (2011) Compressibility of natural soils subjected to long-term acidic contamination.
 502 *Environmental Earth Sciences* 64(1). DOI: 10.1007/s12665-010-0838-2
 503 Gratchev I, Towhata I (2016) Compressibility of soils containing kaolinite in acidic environments. *KSCE*
 504 *Journal of Civil Engineering* 20(2). DOI: 10.1007/s12205-015-0141-6

505 Hueckel T (1997) Chemo-plasticity of clays subjected to stress and flow of a single contaminant.
 506 International Journal for Numerical and Analytical Methods in Geomechanics 21(1):43–72. DOI:
 507 10.1002/(SICI)1096-9853(199701)21:1<43::AID-NAG858>3.3.CO;2-T
 508 Han TL, Chen YS, Shi JP, et al. (2013) Experimental study of mechanical characteristics of sandstone
 509 subjected to hydrochemical erosion. Chinese Journal of Rock Mechanics and Engineering 32(S2): 3064-
 510 3072.
 511 Hassanlourad M, Khatami MH, Ahmadi MM (2017) Effects of sulphuric acid pollutant on the shear
 512 behaviour and strength of sandy soil and sand mixed with bentonite clay. International Journal of
 513 Geotechnical Engineering 11(2). DOI: 10.1080/19386362.2016.1193662
 514 Huang Z, Zeng W, Wu Y, Li SJ, Gu QX, Zhao K(2021) Effects of temperature and acid solution on the
 515 physical and tensile mechanical properties of red sandstones. Environmental Science and Pollution
 516 Research. DOI: 10.1007/s11356-020-11866-x
 517 Jendele L, Smilauer V, Cervenka J (2014) Multiscale hydro-thermo-mechanical model for early-age and
 518 mature concrete structures. Advances in Engineering Software 72 (2):134–146. DOI:
 519 10.1016/j.advengsoft.2013.05.002
 520 Jalali M, Naderi E (2012) The Impact of Acid Rain on Phosphorus Leaching from a Sandy Loam
 521 Calcareous Soil of Western Iran. Environmental Earth Sciences 66(1):311-317. DOI: 10.1007/s12665-
 522 011-1240-4
 523 Koupai JA, Fatahizadeh M, Mosaddeghi MR (2020) Effect of pore water pH on mechanical properties
 524 of clay soil. Bulletin of Engineering Geology and the Environment: The official journal of the IAEG
 525 79(1). DOI: 10.1007/s10064-019-01611-1

526 Kyokawa H, Ohno S, Kobayashi I (2020) A method for extending a general constitutive model to
 527 consider the electro-chemo-mechanical phenomena of mineral crystals in expansive soils. *International*
 528 *Journal for Numerical and Analytical Methods in Geomechanics* 44(6). DOI: 10.1002/nag.3026
 529 Luzio GD, Cusatis G (2009) Hygro-thermo-chemical modeling of high performance concrete. I: theory.
 530 *Cement and Concrete Composites* 31 (5):301–308. DOI: 10.1016/j.cemconcomp.2009.02.015
 531 Liu EL, Xing H (2009) A double hardening thermo-mechanical constitutive model for overconsolidated
 532 clays. *Acta Geotechnica* (4): 1-6. DOI: 10.1007/s11440-008-0053-4
 533 Lei XQ, Wong H, Fabbri A, Limam A, Cheng YM (2016) A chemo-elastic-plastic model for unsaturated
 534 expansive clays. *International Journal of Solids and Structures* 88-89. DOI:
 535 10.1016/j.ijsolstr.2016.01.008
 536 Liu, EL, Lai YM, Wong H, Feng JL (2018) An elastoplastic model for saturated freezing soils based on
 537 thermo-poromechanics. *International Journal of Plasticity* 107:246-285. DOI:
 538 10.1016/j.ijplas.2018.04.007
 539 Liu H, He JT, Zhao Q, Wang TX, Guo CY (2020) Experimental study on the evolution law of seepage
 540 microscopic characteristics of undisturbed loess polluted by acid. *Rock and soil mechanics* 41(03):765-
 541 772.
 542 Liu EL, Lai YM (2020) Thermo-poromechanics-based viscoplastic damage constitutive model for
 543 saturated frozen soil. *International Journal of Plasticity* 128:102683. DOI: 10.1016/j.ijplas.2020.102683
 544 Liang CJ, Ma YJ, Li LR(2020) Comparison of plasma membrane H⁺-ATPase response to acid rain
 545 stress between rice and soybean. *Environmental Science and Pollution Research* 27(6). DOI:
 546 <http://orcid.org/0000-0001-7704-4309>

547 Moyne C, Murad MA (2002) Electro-chemo-mechanical couplings in swelling clays derived from a
 548 micro/macro-homogenization procedure. *International Journal of Solids and Structures* 39(25):6159–
 549 6190. DOI: 10.1016/S0020-7683(02)00461-4
 550 Martinelli E, Koenders EAB, Caggiano A (2013) A numerical recipe for modelling hydration and heat
 551 flow in hardening concrete. *Cement and Concrete Composites* 40 (2): 48–58. DOI:
 552 10.1016/j.cemconcomp.2013.04.004
 553 Nova R, Castellanza R, Tamagnini C (2003) A constitutive model for bonded geomaterials subject to
 554 mechanical and/or chemical degradation. *International Journal for Numerical and Analytical Methods in*
 555 *Geomechanics* 27(9):705–732. DOI: 10.1002/nag.294
 556 Sherwood J (1993) Biot poroelasticity of a chemically activeshale. *Proceedings of the Royal Society:*
 557 *Mathematical and Physical Sciences* 440(1909):365–377. DOI: 10.1098/rspa.1993.0021
 558 Shen ZJ (1995) Double hardening model of clay. *Rock and Soil Mechanics* 01:1-8.
 559 Sarout J, Detournay E (2011) Chemoporoelastic analysis and experimental validation of the pore pressure
 560 transmission test for reactive shales. *International Journal of Rock Mechanics and Mining Sciences*
 561 48(5):759–772. DOI: 10.1016/j.ijrmms.2011.04.009
 562 Sarkar G, Islam R, Alamgir M, et al. (2012) Effect of Acid Rain on Geotechnical Properties of Composite
 563 Fine-grained Soil. *International Journal of Applied Science & Engineering Research* 1(1):64-73. DOI:
 564 10.6088/ijaser.0020101007
 565 Shen WQ, Shao JF (2016) An incremental micro-macro model for porous geomaterials with double
 566 porosity and inclusion. *International Journal of Plasticity* 83:37-54. DOI: 10.1016/j.ijplas.2016.04.002

567 Song XY, Menon S (2019) Modeling of chemo-hydromechanical behavior of unsaturated porous media:
 568 a nonlocal approach based on integral equations. *Acta Geotechnica* 14(3). DOI: 10.1007/s11440-018-
 569 0679-9
 570 Thomas H, Cleall P (1999) Inclusion of expansive clay behavior in coupled thermo hydraulic mechanical
 571 models. *Engineering Geology* 54(1):93–108. DOI: 10.1016/S0013-7952(99)00065-4
 572 Ulm F, Coussy O, (1998) Couplings in early-age concrete: from material modeling to structural design.
 573 *International Journal of Solids and Structures* 35 (31): 4295–4311. DOI: 10.1016/S0020-7683(97)00317-
 574 X
 575 Wang M, Tang Y, Anderson CWN, Jeyakumar P, Yang JY (2018) Correction to: Effect of simulated acid
 576 rain on fluorine mobility and the bacterial community of phosphogypsum. *Environmental Science and*
 577 *Pollution Research* 25(23).DOI: <http://orcid.org/0000-0002-9841-8645>
 578 Xu J, Wu H, Cheng LZ, et al. (2012) Experimental study of shearing failure properties of sandstone under
 579 acidic conditions. *Chinese Journal of Rock Mechanics and Engineering* 31(S2): 3897-3903.
 580 Yao YP, Hou W, Zhou AN (2009) UH model: Three dimensional unified hardening model for over-
 581 consolidated clays. *Geotechnique* 59(5), 451–469.
 582 Zhao Y, Cui P, Hu LB (2009) Relation Between Evolution of Clay Shear Strength and Landslide Induced
 583 by Acid Rain-Taking Landslides in Three Gorges Reservoir Area for Example. *Journal of Rock*
 584 *Mechanics and Geotechnical Engineering* 28(3): 576-582.
 585 Zhang S, Leng W, Zhang F, Xiong Y (2012) A simple thermo-elastoplastic model for geomaterials.
 586 *International Journal of Plasticity* 34, 93-113. DOI: 10.1016/j.ijplas.2012.01.011
 587 Zhang Z (2017) A thermodynamics-based theory for the thermos-poro-mechanical modeling of saturated
 588 clay. *International Journal of Plasticity* 92, 164-185.

589 Zhu H, Wu CF, Wang J, Zhang XM (2018) The effect of simulated acid rain on the stabilization of
 590 cadmium in contaminated agricultural soils treated with stabilizing agents. Environmental Science and
 591 Pollution Research 25(18). DOI: 10.1007/s11356-018-1929-y
 592 Zhao XY, Li KP, Li X, et al. (2019) Experimental Study on Mechanism of Acid Rain-induced Slide of
 593 Gabbro Rock Slope. Journal of Engineering Geology 27(1): 152-161. DOI: 10.13544/j.cnki.jeg.2018-
 594 458
 595

Lists of Figures and Tables

Fig. 1 Deviatoric stress and axial strain curves of loess samples under different confining pressures (CD).

Fig. 2 Volumetric strain and axial strain curves of loess samples under different confining pressures (CD).

Fig. 3 Deviatoric stress and axial strain curves of loess samples under different values of pH (CD).

Fig. 4 Volumetric strain and axial strain curves of loess under different pH (CD).

Fig. 5 SEM micrographs of loess samples under acid rain conditions.

Fig. 6 Deviatoric stress and axial strain for tests and simulations (CD).

Fig. 7 Volumetric strain and axial strain for tests and simulations (CD).

Fig. 8 Simulated results with varying α_0

Fig. 9 Simulated results with varying α_1

Fig. 10 Simulated results with varying α_2

Fig. 11 Simulated results with varying α_3

Fig. 12 Simulated results with varying n

Fig. 13 Simulated results with varying β_s

Fig. 14 Simulated results with varying N_{s0}

Figures

(a) pH 6.9

(b) pH 5

(c) pH 4

(d) pH 3

Figure 1

Deviatoric stress and axial strain curves of loess samples under different confining pressures (CD).

Figure 2

Volumetric strain and axial strain curves of loess samples under different confining pressures (CD).

(a) Confining pressure=50kPa

(b) Confining pressure=100kPa

(c) Confining pressure=200kPa

(d) Confining pressure=400kPa

Figure 3

Deviatoric stress and axial strain curves of loess samples under different values of pH (CD).

(a) Confining pressure=50kPa

(b) Confining pressure=100kPa

(c) Confining pressure=200kPa

(d) Confining pressure=400kPa

Figure 4

Volumetric strain and axial strain curves of loess under different pH (CD).

(a) pH6.9

(b) pH5

(c) pH4

(d) pH3

Figure 5

SEM micrographs of loess samples under acid rain conditions.

(a) pH 6.9

(b) pH 5

(c) pH 4

(d) pH 3

Figure 6

Deviatoric stress and axial strain for tests and simulations (CD).

(a) pH 6.9

(b) pH 5

(c) pH 4

(d) pH 3

Figure 7

Volumetric strain and axial strain for tests and simulations (CD).

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 8

Simulated results with varying α_0

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 9

Simulated results with varying a_1

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 10

Simulated results with varying a_2

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 11

Simulated results with varying a_3

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 12

Simulated results with varying n

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 13

Simulated results with varying β_s

(a) Deviatoric stress and axial strain

(b) Volumetric strain and axial strain

Figure 14

Simulated results with varying N_{s0}