Experimental Study on the Dissolution of Calcite and Montmorillonite in High-Pressure Open Flow Systems

Authors: Zhao Yu, Jiang Yu, Zhao Yu

Date: 2020-03-26T00:00:00+00:00

Abstract

Water-rock (soil) chemical interaction (CWRI) is of particular significance in the development process of rainfall-induced landslides. On one hand, rainwater dissolution causes damage to the rock-soil mass; on the other hand, it generates a large amount of secondary clay minerals. The enrichment of dissolution-induced damage and secondary clay minerals on the slip surface leads to a reduction in the shear strength of the slip surface, which constitutes the primary cause of slip surface formation. This study employs a high-pressure open-flow system to simulate the mechanochemical environment of the slip surface, taking common slip surface minerals—calcite and montmorillonite—as examples, to investigate the dissolution rates and controlling factors of slip surface mineral reactions, thereby revealing the formation mechanism of slip surfaces and their process kinetics/mechanochemical effects. Experimental results demonstrate that: 1) Mineral dissolution rates increase with increasing pressure, but different minerals exhibit different pressure responses; 2) As solution pH decreases and H+ activity gradually increases, mineral dissolution rates are significantly enhanced; 3) The flow rate effect on mineral dissolution is highly complex, being related to pressure, pH, and mineral type; 4) Mineral dissolution does not follow stoichiometric relationships. These experimental results reveal that dissolution on the slip surface is intimately coupled with soil damage and the evolution of slip surface strength, while slip surface depth, mineral type, and groundwater pH jointly determine the dissolution rates and transformation characteristics of minerals on the slip surface. An increase in slip surface depth or in easily dissolvable minerals accelerates the slip surface formation process. Increased groundwater acidity accelerates the water-rock reaction rate, thereby accelerating the rate of slip surface strength reduction.

Full Text

Experimental Study on the Dissolution of Calcite and Montmorillonite in High-Pressure Open Flow Systems

Yu Zhao[1],*, Yu Jiang[1],[2]
[1]Institute of Mountain Hazards and Environment, Chinese Academy of Sciences, Chengdu, Sichuan 610041, China
[2]University of Chinese Academy of Sciences, Beijing 100049, China
Corresponding Author: Yu Zhao, Email: zhaoyu@imde.ac.cn

Abstract

Water-rock (soil) chemical interaction (CWRI) plays a fundamental role in the formation processes of rainfall-induced landslides. On one hand, rainwater dissolution causes damage to rock and soil masses; on the other hand, it generates substantial secondary clay minerals. The enrichment of dissolution damage and secondary clay minerals on the sliding surface leads to reduced shear strength, representing the primary mechanism for sliding surface formation. This study employs a high-pressure open flow system to simulate the chemo-mechanical environment of sliding surfaces, using common sliding surface minerals—calcite and montmorillonite—as examples to investigate dissolution rates and controlling factors, thereby revealing the formation mechanism and chemo-mechanical processes of sliding surfaces. Experimental results demonstrate: (1) mineral dissolution rates increase with pressure, though different minerals exhibit varying pressure responses; (2) as solution pH decreases and H activity increases, mineral dissolution rates rise significantly; (3) flow rate effects on mineral dissolution are complex, depending on pressure, pH, and mineral type; and (4) mineral dissolution does not follow stoichiometric relationships. These findings reveal that dissolution on sliding surfaces is closely linked to soil damage evolution and sliding surface strength degradation. Sliding surface depth, mineral composition, and groundwater pH collectively determine dissolution rates and transformation characteristics. Increased sliding surface depth or more soluble minerals accelerate sliding surface formation, while increased groundwater acidity enhances water-rock reaction rates, thereby accelerating sliding surface strength reduction.

Keywords: Mineral dissolution, high-pressure open flow system, calcite, montmorillonite

Introduction

Landslides have become the second most destructive geological disaster after earthquakes in China [1], with approximately 90% of landslides being rainfall-related [2]. The essence of rainfall-induced landslides lies in the interaction between groundwater (converted from rainwater) and slope rock-soil masses. Water-rock (soil) interactions primarily include mechanical, physical, and chemical processes [3], with chemical interactions being relatively understudied despite their fundamental significance in landslide formation. Slope masses exist in erosive hydrogeological environments where chemical water-rock interaction (CWRI) plays a foundational role in landslide incubation, necessitating dedicated research.

CWRI encompasses hydration, hydrolysis, dissolution, ion exchange, and redox reactions [4], with mineral dissolution representing the core process [5], occurring at initial defects within particles or crystals and in rock fracture zones [6-7]. Influencing factors include mineral characteristics (chemical composition, crystalline properties, particle geometry, specific surface area) and environmental conditions (temperature, groundwater, pH, organic matter) [5,8]. Field investigations reveal non-uniform rock weathering, with varying degrees of weathering even within the same area, indicating the discontinuous nature of CWRI [9]. This phenomenon arises partly from different mineral responses to groundwater environments, and studying single-mineral dissolution reactions can deepen understanding of overall rock-soil mass dissolution.

Numerous laboratory simulation studies on CWRI have demonstrated significant degradation of rock-soil structure and mechanical properties [10-11]. Zhou et al. [12] conducted saturation tests on silty mudstone and argillaceous siltstone, showing that ion concentration changes in reaction solutions generally follow exponential and reaction-diffusion equations. Zhao et al. [13] immersed clay and silty clay in different solutions, noting that dissolution curves exhibited slight S-shapes, characteristic of autocatalytic reactions. Shan et al. [14] performed immersion experiments on purplish-red loose soil, revealing that different immersion conditions trigger distinct chemical reactions that weaken over time and eventually reach equilibrium. Tao [15] noted that sliding zones exist in reducing environments due to microbial activity, but rainwater infiltration during rainfall events introduces dissolved oxygen, shifting conditions to oxidizing environments. Under aerobic conditions, initial oxidation of low-valence elements releases SO ^{2} and Cl ions, which combine with H to create acidification (decreasing pH). Later, silicate mineral transformation and carbonate dissolution cause alkalinization (increasing pH). Under anaerobic conditions, carbonate minerals dissolve while silicates transform slowly, causing gradual pH changes.

While these studies yielded valuable results, they neglected pressure effects and employed closed systems. Landslide masses exist under geostress conditions where pressure significantly influences CWRI. Moreover, rainfall recharge continuously supplies reactants and removes products, driving chemical reactions in sliding zone soils far from equilibrium. Conventional atmospheric-pressure closed systems poorly reflect actual geological conditions, whereas high-pressure open flow systems can overcome these limitations.

This study investigates dissolution characteristics of common landslide minerals (calcite and montmorillonite) using a high-pressure open flow system to explore dissolution patterns under various conditions, understand factor effects on dissolution rates, and analyze underlying mechanisms.

Experimental Methods

Experimental System

The experimental system comprises a high-pressure titanium reactor, fluid pump, back-pressure controller, and computer monitoring/recording system [Figure 1: see original paper]. The reactor has an inner diameter of 0.638 cm and length of 21.6 cm, operating as a continuous stirred-tank reactor (CSTR). The fluid pump controls solution inflow rates (0.5-8 ml/min).

Figure 1. Schematic diagram of the experimental system [16]: 1. Reservoir; 2. Pump; 3. Titanium tube; 4. Preheater; 5. High-pressure reactor; 6. Temperature controller; 7. Back-pressure controller; 8. Pressure gauge; 9. Conductivity meter; 10. Computer control system; 11. Sampling port; 12. Gas column.

Sample Preparation

Numerous studies indicate that sliding zone soils primarily consist of clay minerals (montmorillonite, kaolinite, illite) and detrital minerals (quartz, calcite, feldspar). Duan et al. [16] demonstrated that clay minerals and calcite readily undergo water-rock chemical reactions, generating secondary minerals and soluble salts that degrade rock-soil microstructure. Peng et al. [17] noted that calcite dissolution dominates in red-bed soils during saturation-desaturation cycles, intensifying with repeated cycles.

This study uses high-purity montmorillonite and calcite samples to understand dissolution characteristics of clay and detrital minerals. Samples were ground, sieved, and ultrasonically cleaned in acetone for 1 hour to remove fine surface particles. Since mineral dissolution depends strongly on surface area, specific surface areas were measured using a Micromeritics Tristar 3000 instrument: calcite (20-40 mesh) measured 1.2046 m^2/g, while montmorillonite (10-20 mesh) measured 26.7954 m^2/g.

Experimental Conditions and Procedure

CWRI environmental factors include temperature, groundwater pH, pressure, and flow rate. Since surface temperature variations are relatively minor and have limited impact, experiments were conducted at constant temperature.

Landslide masses exist in geostress fields where stress increases with sliding zone depth. CWRI active zones occur in rock fractures where significant stress concentration exists at crack tips, with concentration factors several to over ten times higher than normal conditions [18]. Therefore, this study applied elevated pressures of 1, 14, and 28 MPa.

In shallow subsurface environments, water-rock reactions predominantly occur under acidic conditions. Rainwater dissolves atmospheric CO , resulting in weak acidity ($pH < 7$). Acid rain phenomena further lower pH values, with literature [19] reporting minimum monthly average pH values of 3.75 in the Three Gorges

Reservoir area. Additionally, plant roots and microbial activity in surface soils produce CO and organic acids, reducing infiltrating rainwater pH. Therefore, studying pH effects on mineral dissolution holds practical significance. Experiments used HCl solution and double-distilled water at pH 3.5 and 7.

Slope seepage fields are dynamic, related to groundwater levels, internal slope structure, and mineral composition. During rainfall, groundwater levels and hydraulic heads rise, increasing flow rates. Fractures and cracks serve as infiltration channels, while clay minerals significantly reduce seepage velocity. Since dissolution rates vary with flow rate, this study examined flow rate effects using 1.00, 2.00, and 3.00 ml/min.

Prior to experiments, input solution conductivity was measured to monitor output solution conductivity changes. Each parallel experiment used samples with identical particle size, mass, and surface area at constant temperature (22°C) and pressure (P = 1, 14, 28 MPa), with flow rates changed stepwise from low to high (L = 1.00, 2.00, 3.00 ml/min). After 40 minutes, flow rates were altered, and reaction steady state was determined by measuring output solution conductivity over time. Following 30 minutes of stabilization, output samples were collected (three samples per condition, one every 20 minutes) and analyzed using inductively coupled plasma spectroscopy (IRIS) for concentration and composition.

Experiments included calcite dissolution in pure water and HCl solution, and montmorillonite dissolution in pure water. Mineral dissolution rates were determined from elemental concentration changes, with average values from three parallel determinations representing dissolution rates under each condition. Results for calcite and montmorillonite are shown in and .

Table 1. Calcite dissolution results (Ca^2 concentration) at pH = 3.7

Flow Rate	Pressure	28 MPa
1 ml/min		
2 ml/min		
3 ml/min		

Table 2. Montmorillonite dissolution results at pH = 7, flow rate = 2 ml/min

14 MPa	28 MPa

Results and Discussion

Pressure Effects

As shown in [Figure 2a: see original paper], calcite dissolution rates increase with pressure. Under conditions of pH = 3.7 and flow rate = 3 ml/min, increasing pressure from 1 MPa to 28 MPa raised output Ca^{2} concentration from 9.7333 mg/L to 10.5667 mg/L (8.56% increase). However, the relationship is non-linear: when pressure increased from 1 MPa to 14 MPa, dissolution rate increased by 7.53%, but further increasing pressure from 14 MPa to 28 MPa yielded only a 0.95% increase, indicating a significant decline in enhancement. This demonstrates that pressure effects on dissolution rates have limitations.

Mineral dissolution rates relate to both reactive surface sites and locations with excess surface energy within mineral crystals (such as dislocations, stacking faults, exsolution lamellae boundaries, subgrain boundaries, and chemical impurities) [20]. According to solid mechanochemistry theory, a relationship exists between applied stress, reaction sites, and mechanochemical activity [21]:

P 00lnln(1)RTaPVRTa exp(2)PVaaRT 0 1a a

where is the standard-state reaction potential, a is thermodynamic activity, and V is molar volume. This indicates that increased pressure raises mineral crystal reaction sites, promoting dissolution—representing the intrinsic mechanism of pressure effects.

Different minerals exhibit varying pressure responses, with montmorillonite being far more sensitive than calcite. [Figure 3a: see original paper] shows Ca^{2} concentration curves for montmorillonite at pH = 7 and flow rate = 2 ml/min. Increasing pressure from 1 MPa to 28 MPa raised output Ca^{2} concentration from 0.7033 mg/L to 3.6767 mg/L (422.78% increase). In contrast, under pH = 3.7 and flow rate = 2 ml/min, calcite Ca^{2} concentration increased only from 9.77 mg/L to 10.47 mg/L (7.1% increase). Furthermore, while calcite dissolution rates increase with pressure but plateau above 14 MPa, montmorillonite shows enhanced pressure effects beyond 14 MPa.

Possible explanations include: (1) crystal property differences—Ca^{2} bonds are stronger in calcite, yielding weaker pressure responses; (2) montmorillonite typically exists as aggregates that disintegrate under higher pressure, increasing specific surface area and providing more reactive sites; and (3) montmorillonite' s higher specific surface area (26.7954 m^2/g vs. calcite' s 1.2046 m^2/g) generates more reaction sites through lattice dislocations under pressure.

pH Effects

As shown in [Figure 1b: see original paper], at 1 MPa, output Ca^{2} concentration at pH = 7 is significantly lower than at pH = 3.7. At 2 ml/min, Ca^{2} concentrations are 5.29 mg/L and 9.77 mg/L, respectively, demonstrating that mineral dissolution rates correlate negatively with pH under acidic conditions, consistent with previous research.

The intrinsic mechanism involves H attachment to oxygen atoms at crystal reaction sites, weakening metal-oxygen bonds and promoting dissolution [22]. This effect relates to H activity [23]:

()(01)nHkan   k Ha n

where k_ is the bulk dissolution rate (mass dissolved per unit time per unit mineral mass), a_H is H activity (higher at lower pH), and n_ relates to dissolution kinetics. At pH = 3.7, higher H activity yields greater reaction rates.

Flow Rate Effects

Flow rate effects on mineral dissolution are complex. At pH = 3.7, calcite dissolution rates increase with flow rate under 14 MPa and 28 MPa, but decrease with flow rate at 1 MPa. At pH = 7, dissolution rates show minimal flow rate dependence.

The intrinsic mechanism relates to H activity and reaction equilibrium. Under low pressure and pH = 7, calcite surface reaction sites and total H activity are relatively low. Increased flow rate transports H away from reaction interfaces before complete reaction with metal ions, reducing reaction activity and dissolution rates. Conversely, under high pressure and pH = 3.7, abundant surface reaction sites and high H activity allow sufficient reaction even at higher flow rates. Additionally, increased flow rate removes reaction products, driving dissolution away from equilibrium and increasing rates.

Chemical Composition Effects

As shown in [Figure 3b: see original paper], different ions exhibit distinct concentration characteristics. Si and Al^{3} show the highest concentrations, reflecting montmorillonite’ s aluminosilicate composition. K also shows relatively high concentrations due to weaker chemical bonds that facilitate preferential release.

With increasing pressure, all ion release rates increase except K , which decreases. Since sampling occurs after reaching steady state and K content is fixed in each sample, rapid reaction at high pressures depletes K before steady state, resulting in lower measured concentrations.

Normalizing different ion concentrations to Si concentration under identical pressure conditions yields . Results demonstrate that mineral dissolution does not follow stoichiometric relationships, possibly due to: (1) new phase precipitation on mineral surfaces, reducing effective reaction sites and causing preferential dissolution elsewhere; (2) secondary mineral dissolution with different stoichiometric coefficients; (3) preferential dissolution of certain components and leached layer formation (e.g., weak K bonds); and (4) chemical zoning, heterogeneous defects, or impurities in dissolving minerals [24].

Implications for Water-Mineral Dissolution in Sliding Surface Formation

Sliding surfaces contain diverse mineral particles with significantly different dissolution properties, creating heterogeneous dissolution that gradually enlarges and propagates microfractures. When fractures reach critical sizes, geostress-induced collapse generates additional microfractures, further promoting dissolution. Groundwater pH negatively correlates with dissolution rates, while higher seepage velocities enhance rainwater infiltration and groundwater discharge, accelerating solution renewal in microfractures and promoting dissolution. Under coupled media, chemical, and mechanical fields, sliding zone soil damage intensifies, cracks propagate, and eventual through-going failure triggers landslides.

Thus, dissolution at sliding surfaces causes significant microstructural changes, soil damage, and strength degradation. These dissolution patterns reveal that sliding surface depth, mineral composition, groundwater pH, and seepage velocity collectively control dissolution characteristics. Increased sliding surface depth or more soluble minerals accelerate landslide initiation and development, while increased groundwater acidity enhances water-rock reaction rates, accelerating sliding surface strength reduction and landslide formation.

Conclusions

Based on dissolution experiments of calcite and montmorillonite in high-pressure open flow systems, the following conclusions are drawn:

1. Mineral dissolution rates increase with pressure, but pressure enhancement has limitations. Different minerals exhibit varying pressure responses, with montmorillonite being far more sensitive than calcite. Increased pressure raises mineral crystal reaction sites, promoting dissolution.
2. Under acidic conditions, mineral dissolution rates correlate negatively with pH, with the intrinsic mechanism related to H activity in solution.
3. Flow rate effects on mineral dissolution are complex, depending on pressure, pH, and mineral type, with mechanisms related to H activity and reaction equilibrium.
4. Mineral dissolution does not follow stoichiometric relationships, possibly due to new phase precipitation, secondary mineral dissolution, preferential dissolution, or chemical zoning and heterogeneous defects.
5. Sliding surface depth, mineral composition, groundwater pH, and seepage velocity collectively control dissolution characteristics. Dissolution at sliding surfaces causes significant microstructural changes, soil damage, and strength degradation.

References

[1] Duan, Y. Basic characteristics and development trends of geological hazards in China. *Quaternary Sciences* 1999, (03), 208-216. [2] Li, Y.; Meng, H.; Dong, Y.; Hu, S. Types and characteristics of geological hazards in China—Based on analysis of county-level geological hazard survey results. *The Chinese Journal of Geological Hazard and Control* 2004, (02), 32-37. [3] Wu, Y. Groundwater and geological hazards. *Underground Space* 1999, (04), 303-310+316-339. [4] Xu, Z.; Huang, R.; Fan, Z. Water-rock interaction in the process of landslide hazard formation—initiation. *Journal of Natural Disasters* 2005, (01), 1-9. [5] Xu, Z.; Huang, R.; Tang, Z. Dissolution kinetics of silicate minerals and its significance for landslide research. *Chinese Journal of Rock Mechanics and Engineering* 2005, 24 (9). [6] Chen, S.; Feng, X.; Li, S. Effects of chemical corrosion on mechanical properties of Xiaolangdi sandstone. *Rock and Soil Mechanics* 2002, (03), 284-287+296. [7] Tang, L.; Zhou, C. Failure mechanism of stressed rock mass under seepage and hydrochemical action. *Acta Scientiarum Naturalium Universitatis Sunyatseni* 1996, (06), 96-101. [8] Chen, J. *Water-Rock Chemical Interaction Process and Its Contribution to Landslide Formation.* Master' s Thesis, Kunming University of Science and Technology, 2006. [9] Wang, Z.; Shen, L.; Xu, Z. Chemical characteristics of groundwater in Touzhai landslide and its reflected water-rock (soil) interaction. *Hydrogeology & Engineering Geology* 2016, 43 (01), 111-116+123. [10] Tang, L.; Zhang, P.; Wang, S. Experimental study on rock fracture mechanical effects of water-rock chemical interaction. *Chinese Journal of Rock Mechanics and Engineering* 2002, (06), 822-827. [11] André, L.; Rabemanana, V.; Vuataz, F.-D. Influence of water-rock interactions on fracture permeability of the deep reservoir at Soultz-sous-Forêts, France. *Geothermics* 2006, 35 (5). [12] Zhou, C.; Deng, Y.; Tan, X.; Lin, C.; Wen, S. Study on chemical composition change rules of soft rock during water saturation. *Chinese Journal of Rock Mechanics and Engineering* 2004, (22), 3813-3817. [13] Zhao, Y.; He, S.; Cui, P. Study on mechanical-chemical behavior of rock and soil using solid mechanochemistry theory—A case study of purple soil in Chengdu. *Journal of Natural Disasters* 2002, (02), 70-74. [14] Shan, H.; Peng, S.; Liang, H.; Li, Y. Experimental study on chemical reaction characteristics of purplish-red loose soil in different water saturation environments. *Hydrogeology & Engineering Geology* 2018, 45 (05), 136-142. [15] Tao, Y. *Study on Water-Rock (Soil) Chemical Interaction at Landslide Sliding Zones in Red Bed Areas.* Chengdu University of Technology, 2017. [16] Duan, C.; Yang, H.; Qiu, Y. Study on influence of groundwater on soil structure characteristics and mechanical strength. *Gansu Water Resources and Hydropower Technology* 2018, 54 (08), 25-27+37. [17] Peng, S.; Shan, H.; Liang, H.; Cai, H.; Li, Y. Study on water-rock chemical interaction of red-bed soil during saturation-desaturation cycles in Three Gorges Reservoir area. *Journal of Guilin University of Technology* 2017, 37 (03), 444-450. [18] Zhao, Y. *Experimental Study on Mechano-Chemical Formation Mechanism of Sliding Surfaces.* Graduate University of Chinese Academy of Sciences, 2005. [19] Yang, X.; Zou, X.; Ma, T. Analysis of acid rain distribution characteristics in the Three Gorges Reservoir area of the Yangtze River.

Meteorological Monthly 2002, (10), 14-18. [20] Holdren, G. R.; Speyer, P. M. Reaction rate-surface area relationships during the early stages of weathering. II. Data on eight additional feldspars. *Geochimica et Cosmochimica Acta* 1987, 51 (9), 2311-2318. [21] Zhao, Y. Preliminary study on mechano-chemical autocatalysis in landslide fracture surface formation. In *Cross-Strait Symposium on Mountain Hazards and Environmental Conservation*, Chengdu, 1998; pp 278–282. [22] Welch, S. A.; Ullman, W. J. The effect of organic acids on plagioclase dissolution rates and stoichiometry. *Geochimica et Cosmochimica Acta* 1993, 57 (12), 2725-2736. [23] Zhang, R.; Hu, S.; Zhang, X. Experimental Study of Dissolution Rates of Fluorite in HCl–H O Solutions. *Aquatic Geochemistry* 2006, 12 (2), 123-159. [24] Zhang, R.; Zhang, X.; Guy, B.; Hu, S.; de Ligny, D.; Moutte, J. Experimental study of dissolution rates of hedenbergitic clinopyroxene at high temperatures: dissolution in water from 25 °C to 374 °C. *European Journal of Mineralogy* 2013, 25 (3).

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.