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# Micro-damage evolution and macro-mechanical property degradation of limestone due to chemical effects

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ABSTRACT

Nuclear Magnetic Resonance (NMR) imaging in combination with mechanical tests are carried out to investigate the influence of chemical solutions on porosity change, micro damage and macro mechanical property degradation of limestone samples under external stress. The NMR images and $T_2$ values for compression stage, micro damages emergence stage, micro damages development stage and fracture and collapse stage are obtained and analysed. The results of the corrosive influence of chemical solutions with different pH values and immersion periods on the mechanical property degradation of limestone samples are investigated. By choosing porosity as the damage variable, the micro damage of the samples during triaxial compression are calculated. It can be concluded that pH values of the chemical solutions change the porosity and micro damage evolution of the rock, which is the root reason for its mechanical properties degradation. The chemical erosion also has a significant influence on the micro crack propagation in the limestone samples under triaxial compression.

## 1. Introduction

Underground rock mass is often surrounded by water, containing complex chemical icons and different pH values, which may have complex effects on the mechanical properties of the underground rocks.[1] This is because the presence of water often contains different chemicals, and the reaction between chemical icons with rock is a significant factor that accelerates failure progress, leads to mechanical characteristics decrease of rock, or causes geological disasters, such as land slope and earthquakes.[2–4] In underground storage constructions, such as nuclear waste storage[5,6] and underground reservoirs,[7] the water has a significant influence on the stability of these underground constructions. Research on mechanical properties of chemical corroded rock is one of the important topics in ground water reservoirs, oil drilling, $CO_2$ injection, toxic material or nuclear waste disposal, slope and dam foundation and underground rock engineering structures, *etc*.

Over the past few years, efforts have been made to investigate the mechanical response of the rocks to chemical effects, in particular the injection of $CO_2$ into sedimentary rocks.[8–11] Grgic et al.,[12] conducted triaxial coupled $CO_2$ injection tests on oolitic limestone under temperature and mechanical stresses conditions. With the help of a specific "flow-through" triaxial cell, which can measure very low strain rates, the petrographical evolutions and long-term mechanical properties of the oolitic limestone were investigated. Results shows that $CO_2$ is not a significant role in the chemistry of carbonate reservoirs. This is because the $H_2O$-$CO_2$-calcite reaction did not induce reservoir compaction. Combined with fluid flow-through experiments (brine and $CO_2$-rich brine), Hangx et al.,[13] performed conventional triaxial creep experiments on carbonate and quartz cemented Captain Sandstone from the Goldeneye field. The carbonate cement dissolution effects on mechanical properties, as well as on the failure strength of the sandstone were studied. Guen et al.[14] conducted experiments on low and high $P_{CO_2}$ (8 MPa) aqueous fluids injection tests. Results show that there is a positive correlation between fluid flow rate and strain rate of the sample. Hangx et al.,[13] conducted the test under in situ reservoir conditions, the effect of carbonate cement dissolution on mechanical properties of the sandstone were investigated. Gaus et al.[15] investigated the $CO_2$–rock interactions. By using the research data, the possibly affect the safety and/or feasibility of the $CO_2$ storage scheme were analysed.

Meanwhile, some studies have also been conducted to investigate the chemical solution effects on the mechanical properties of the rock. Grgic et al.,[16] used acoustic emission to study the influence of water, oil and alcohol solutions on the macro mechanical properties of sandstone samples. The results show that there is a close relationship between acoustic

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emission events and the shape of the creep curve. Creep characteristics of micro cracks can be revealed by studying the static elastic properties of rocks. Chai et al.,[17] immersed clayey rocks into different chemical solutions and observed that the expansion effect of clayey rocks relies on the concentration of aqueous solution and the expansion effect decrease with the increase of concentration of the solution. Carrying out uniaxial tests on chemical corroded limestone samples, Feng et al.,[15] studied the coupling effect of multiple cracks propagation law and found that the crack evolution of the chemical corroded samples during the uniaxial loading is very complex, which depends on the pH value of the chemical solution, concentration of chemical ions in solution, mineral composition of the rock and pre-existing cracks, etc. Mohtarami et al.,[18] used extended finite element method (XFEM) to model fracturing graded brittle rocks by chemical corrosion, and investigated the crack propagation by considering different corrosive solutions under various mechanical loading in three-point and four-point bending tests both numerically and experimentally.

However, the existing studies so far have been mainly focusing on the macro and mesoscopic mechanical properties of rock under the chemical environment, such as the degradation of rock strength and elastic modulus, macro crack propagation, expansion effect of rocks, fracture toughness, etc. Under the effect of chemical solutions, large changes would occur at micro scale within rocks. Microstructural changes can cause macro-mechanical changes.[19] Thus, the study on micro damage and mechanical property degradation of chemical corroded rocks is of great importance. However, there is little research on this issue, and thus the prediction of the mechanical behaviour of chemical corroded rocks and effective coupled chemical-mechanical modeling become very difficult.

Various characterization techniques have been proposed to study the change of mechanical properties of rock after chemical erosion, including computerized tomography (CT) technique[20,21] and Nuclear Magnetic Resonance (NMR).[22,23] The NMR is powerful for investigating micro changes inside the samples in great details and also has wide applications in medical diagnosis, geotechnical engineering, oil and gas exploration, and recently in rock tests.[24–27] Li et al.,[28] used NMR to investigate the pore structure of the rock. Cai et al.,[2] investigated the changes of properties and mechanical characteristics of the rock after chemical erosion under identical loading conditions, including deformation and strength characteristics. Carpenter[29] used NMR imaging to the measurement of water content distributions in limestone. The hydraulic diffusivity of limestone is found to be an approximately exponential function of the water content, in agreement with experimental data on other porous materials.

By using NMR, this paper presents experimental research on the micro damage evolution of limestone treated with different chemical solutions over different immersion periods. NMR images and $T_2$ values (transverse relaxation time distribution which depends on the size of water-saturated pores) for limestone inner sections are obtained. Based on the experimental data, the micro damage evolution is investigated, and the compression stage, micro damages emergence stage, micro damages development stage, fracture and collapse stage of the chemical corroded limestone samples at different loading levels have been obtained and analysed. The influence and relationship between chemical solutions on porosity change as well as the degradation of macro mechanical properties of the limestone samples are summarised. These results will uncover the root reason for changes in mechanical properties of the chemical corroded sedimentary rocks, such as limestone, and reveal the influence of the chemical erosion on micro damage evolution of the rocks under triaxial compression.

## 2. Tested materials and experimental methods

### 2.1. Sample preparation

Sedimentary rock, such as sandstone and limestone, distributes extensively in the superficial lithosphere, which is the main place for underground constructions and engineering geological. Thus, limestone, a common sedimentary rock in southwest China, is selected as the test sample in this experiment. The limestone blocks, which are selected from a single block without macroscopic cracks from a tunnel construction site in Chongqing, are machined into cylindrical shapes with a length of 100 mm and a diameter of 50 mm. By X-ray diffraction (XRD) analysis it is found that the limestone samples are composed of 90% calcspar, quartz, cements and 1% accessory minerals. The microstructure of the limestone is oolithic, as shown in Fig. 1.

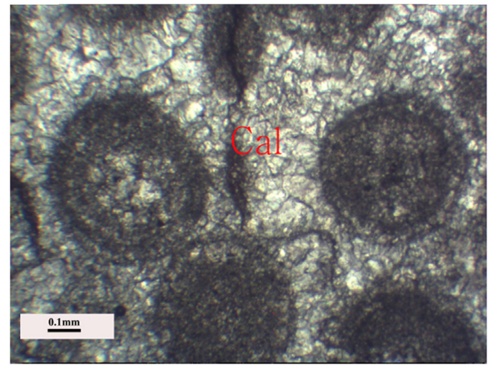


**Fig. 1.** Microscope image of a limestone sample: Cal, calcspar.

### 2.2. Chemical solutions

According to water sample analysis, which is collected from the tunnel construction site in Chongqing, the pH value of the water sample is 6.5 and the main icons are $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $Cl^-$ and $HCO^-$. To simplify the experimental study, the complex ionic composition of the water is replaced by $Na_2SO_4$ solution, which is made by NaCl solution added with $H_2SO_4$. There are three pH values (3, 5 and 7) of the $Na_2SO_4$ solution, and all initial concentrations of the chemical solutions are 0.01 mol $L^{-1}$.

### 2.3. Testing process

The samples are saturated using a vacuum saturation device. After saturation for 24 h, samples with similar initial porosity are selected using NMR and categorised into six groups to be immersed in distilled water and $Na_2SO_4$ solutions with three pH values (3, 5 and 7) for three designed periods (20d, 40d and 60d), as listed in Table 1.

When the samples reach the designed erosion period, NMR test is conducted to analyse the porosity change. After the NMR tests, the samples are taken out of the NMR machine and put into the triaxial pressure cell of the Rock 600-50 test system for triaxial compression tests. The confining pressure is gradually increased up to 10 MPa and then fixed. After that, a strain control mode is used for the axial loading at a rate of 0.02 mm $min^{-1}$ until the sample is ruptured.

After the chemical corrosion, the porosity and skeleton structure of the rock may largely change, which could influence the micro damage evolution of the rock under mechanical loading. Thus, it is necessary to study the micro damage evolution of the chemical corroded rock

**Table 1**
Group of samples.

| No. of specimen | pH | Time/d | No. of specimen | pH | Time/d |
|---|---|---|---|---|---|
| A-1 | 3 | 20 | C-1 | 3 | 60 |
| A-2 | 5 | 20 | C-2 | 5 | 60 |
| A-3 | 7 | 20 | C-3 | 7 | 60 |
| B-1 | 3 | 40 | D-1 | Distilled Water | 20 |
| B-2 | 5 | 40 | D-2 | Distilled Water | 40 |
| B-3 | 7 | 40 | D-3 | Distilled Water | 60 |