Water-induced variations in micro characteristics of clay-bearing conglomerates at great depths in China

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Abstract. The micro characteristics, including micro-structural features of clay minerals and micro-pore textures of rock, change after the rock–water interaction and lead directly to rock deformation and deterioration. To understand the mechanism of the weakening process of rocks at great depths after interaction with water, we performed X-ray diffraction analysis, scanning electron microscopy, and mercury intrusion porosimetry experiments to investigate the mineral compositions, microstructures, and porosity characteristics of four clay-bearing conglomerate samples collected from Northeast China at great depths. In addition, the chemical analysis of the aqueous solutions was carried out to examine the variances of chemical compositions before and after the water absorption tests. The results showed that the dominant mineral components in the conglomerate samples were quartz, potash feldspar, plagioclase, and clay. The contents of clay minerals in all samples were relatively high and ranged from 8.9% to 14.9%, mostly containing a chlorite/montmorillonite mixed layer. The correlation analysis suggested that ion exchange occurred in the reactions between the conglomerate samples and water. The mixed layer of chlorite/montmorillonite expanded, spread, and flocculated after water absorption, jammed the pores, and reduced the porosity. A certain number of calcite particles formed on the surface of grains or surrounded the micro-pores, resulting in the blockage of pores and inducing the decrease in rock porosity. In addition, various occurrence features of the chlorite/montmorillonite mixed layer changed differently after interacting with water, leading to varied influences on the fractal characteristics of rocks.

1. Introduction

Deep soft rocks in natural state show a good mechanical performance; however, when absorbing a certain volume of water, the mechanical properties of rock mass will dramatically decrease, which will lead to a series of engineering problems, for example, the large deformation and collapse of soft rock tunnels [1-4]. The process of rock–water interaction is a kind of physical, chemical, and mechanical process in underground engineering. In this process, chemical elements are redistributed after water absorption. In addition, the micro characteristics, including micro-structural features of clay minerals and micro-pore textures of rock, change, leading directly to rock deformation and deterioration [5-7].

A number of works have been devoted to rock–water interaction, especially the chemical interactions to understand its mechanical effect. After absorbing a certain kind of solution, rock structures loosen and become porous, and their porosity enlarges [8-10]. Heggheim T. et al. discussed...
the changes in the composition and structures of rock minerals after their interaction with water [8]. With the utilization of computed tomography scanning images, Qiao et al. established the physical and chemical damage variable expression between sandy rock and water based on changes in the secondary porosity [11]. Wu et al. determine the pore evolution pattern by utilizing energy-dispersive X-ray spectroscopy spectrum analysis and mercury injection experiments [12]. Based on hydraulic experiments and the professional image analysis software Image-Pro Plus, Li et al. discussed the changes in pore structures by using scanning electron microscopy (SEM) images after water absorption tests and studied the characteristics of pore structure distribution [13].

In this paper, X-ray diffraction (XRD) analysis, SEM, and mercury intrusion porosimetry experiments were performed on clay-bearing conglomerate samples before and after water absorption tests. In addition, changes in the configuration of clayey minerals, pore distribution, and the fractal characteristics of conglomerates were analyzed in this paper.

2. Experimental

2.1 Sampling and preparation of conglomerate samples

The conglomerate samples used in this study were collected from Daqiang coal mine, which is located in Kangping county, Shenyang city, Liaoning province, China. The samples were collected at the depth interval of 1 052.59 m–1 053.81 m.

The specimens were drilled in situ and sealed in zip lock bags. Then, the rock samples were sealed with wax immediately to maintain their original state after being transported to the ground. The rock samples were processed to Φ55 mm×110 mm cylindrical cores in the laboratory by rock drilling, cutting, and grinding machines. The numbered samples were then dried in a vacuum drying oven for 1–2 days until their weights showed minimal changes. Table 1 lists the basic parameters of the four conglomerate samples investigated in this study.

Table 1. Basic physical parameters of the conglomerate samples collected from Daqiang coal mine in Northeast China.

| NO. | Location depth (m) | Dry weight (g) | Dry density (g/cm³) | Natural water content (%) | Geological description |
|-----|--------------------|----------------|---------------------|---------------------------|------------------------|
| C-1 | 1052.59-1052.93    | 576.25         | 2.215               | 2.20                      | Gray-white, dense, no bedding, a small amount of small gray granular fillings |
| C-2 | 1051.59-1051.97    | 593.96         | 2.260               | 0.07                      | Gray, dense, a small amount of large gray granular fillings |
| C-3 | 1052.59-1052.93    | 569.81         | 2.227               | 0.23                      | Gray-white, dense, no bedding, a small amount of small gray granular fillings |
| C-4 | 1053.69-1053.81    | 578.36         | 2.243               | 2.87                      | Gray, dense, a small amount of big gray granular fillings |

2.2 Mineral compositions

XRD was utilized to investigate the mineralogical compositions of the conglomerate samples, and the results are shown in Table 2. As listed in Table 2, the dominant mineral components in the four conglomerate samples were quartz, potash feldspar, plagioclase, and clay. The contents of clay minerals in the four samples were relatively high and ranged from 8.6% (C-3) to 14.9% (C-4). In addition, the contents of their clayey minerals were mostly chlorite/montmorillonite mixed layer and very minimal amount of illite (1%–2%).

Table 2. Mineral compositions of rock samples as determined by XRD analysis.

| NO. | Mineral ingredient (%) | Clayey minerals (%) | Mixed layer (%) |
|-----|------------------------|---------------------|-----------------|
|     | quartz                 | potash feldspar     | plagioclase     | clay mineral | I | C/M | %M |
| C-1 | 37.3                   | 1.8                 | 52              | 8.9         | 2 | 98  | 45  |

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2.3 Experimental design
Two important kinds of rock form at great depths in water absorption, namely, those resulting from pressurized and non-pressurized water absorption. The former is caused by the existence of fissure water and results in water pressure on the surrounding rock in tunnels [14].

In 2010, the intelligent testing system for water absorption in deep soft rocks (ITSWADSR) was developed by HE Manchao [15]. The improved system (ITSWADSR) can perform two kinds of water absorption tests simultaneously.

In this paper, the water absorption tests of the dried rock samples were grouped into two kinds: the pressurized water absorption tests (C-1 and C-4) and non-pressurized water absorption tests (C-2 and C-3). Then, SEM and mercury intrusion porosimetry experiments were performed on clay-bearing conglomerate samples before and after the water absorption tests. The changes in the microcharacteristics, including the configuration of clayey minerals, pore distributions, and fractal characteristics of the conglomerate samples, were analyzed. In addition, chemical composition analysis of aqueous solution was carried out to determine the chemical changes after the water absorption tests.

3. Analysis of Microscopic Structures of Rock Samples Before and After Absorption Tests
After interacting with water, the mineral grains of soft rock generally showed a series of interfacial phenomenon, such as a double electric layer on the surface of grain and ionic exchange [16]. These factors directly influence the hygroscopic property of rocks. In general, the interfacial phenomenon of coarse mineral grains with small specific surface and low surface energy are considerably weaker than those of fine mineral grains with larger specific surface and higher surface energy. Thus, the changes in the configuration of minerals in rocks mainly indicate the changes in the morphology of clayey minerals.

According to the classified standard of capillary pore systems, a pore diameter between 0.2 and 500 μm is referred to as a capillary pore and characterized by water flow in pore channels if the external force is greater than the capillary force [17]. The thickness of the absorption film on the surface of pore is generally more than 0.1 μm, and water cannot easily flow within pores under normal condition, that is, when pores are less than 0.2 μm in diameter. Therefore, pores with a diameter of more than 0.2 μm play an important role in water absorption tests, whereas pores measuring less than 0.2 μm in diameter are regarded as invalid pores.

In this paper, we divided the pores into two types: valid (>0.2 μm) and invalid (≤0.2 μm) pores. The changes were analyzed in micro-pore structures with the distribution characteristics, the fractal characteristics of valid pores and the morphology of clayey minerals before and after the water absorption tests. The analysis of pore distribution characteristics and fractal characteristics of the valid pores were based on mercury injection experiments, which were applied on the rock samples before and after the water absorption tests. With SEM, we can intuitively observe the changes in the morphology of clayey minerals in rocks after the water absorption tests.

3.1. Pore distribution of rock samples before and after water absorption tests
Porosity is one of the most important parameters that significantly influence the physical–mechanical properties of rock. A valid porosity can be obtained as follows:

\[
\phi_v = \frac{V_{pe}}{V_e + V_p} \cdot 100\% \quad (1)
\]
where $V_{pe}$ is the rock effective pore volume whose diameter is greater than 0.2 $\mu m$, ml; $V_s$ is the skeleton volume of rock, ml; $V_p$ is the pore volume, ml.

The fractal dimension of rock samples before and after absorbing water can be calculated by the following [18]:

$$
\frac{\bar{V} - \bar{V}(d \geq 0.2 \mu m)}{\bar{V}} = \left( \frac{d}{d_{\text{max}}} \right)^{1-D}
$$

(2)

where $d$ is the diameter of micro-pore, $\bar{V}$ is the cumulative pore volume, and $\bar{V}(d \geq 0.2 \mu m)$ is the cumulative pore volume whose diameter is larger than $d$, and $d_{\text{max}}$ is the maximum diameter of pores in the rock sample.

Table 3 lists the micro-parameters associated with the pores for the four rock samples before and after the water absorption tests.

**Table 3 Pore texture parameters for the investigated conglomerate samples before and after the water absorption tests**

| No. | Porosity (%) | Effective porosity (%) | Fractal dimension |
|-----|--------------|------------------------|-------------------|
|     | Before       | After                  | Before | After |
| C-1 | 20.0535      | 16.7560                | 10.4992 | 5.5278 |
| C-2 | 16.7516      | 16.7185                | 5.1169  | 4.5813 |
| C-3 | 16.5886      | 14.4565                | 5.6962  | 4.4938 |
| C-4 | 15.3672      | 14.737                 | 4.5532  | 3.3453 |

As displayed Table 3, (1) the porosity and effective porosity of the four rock samples decreased after water absorption. After interacting with water, the mixed layer chlorite/montmorillonite expanded, resulting in the narrow channels of crevices blocking routes of water flow. Thus, the pore size and internal pore space decreased. Another factor that caused the decrease in porosity in rock samples was illite, which is vulnerable to be broken up from the particles under water shear stress and plugged the pore channels. (2) The fractal dimension of the valid pores in C-2, C-3, and C-4 decreased, whereas the opposite was observed for C-1, which indicated that the complexity of micro-pore structures of C-1 and increased heterogeneity after absorbing water. Illite can possibly either migrate through the micro-pores with water flow in the process of absorption or deposit and jam in the micro-pores. From Table 1, we can find that the highest content of illite was observed in C-1. In general, the size of illite particles were small, and after absorbing water, a large number of large pores (intergranular pores) in C-1 became micro-pores among the crystal grains of clayey mineral with a small diameter. Thus, the complexity of the pore structures increased, and the heterogeneity decreased. However, for C-2, C-3, and C-4, a large number of small pores were filled by chlorite/montmorillonite after absorbing water, whereas the large pores changed less. Therefore, the structure of pores became singular, and the heterogeneity increased.

3.2. SEM analysis of rock samples before and after absorbing water
To better analyze the variations of the micro-structural features of clay minerals (the type, crystal morphology and its occurrence feature), the morphology, and filling of micro-pores, we used SEM on the four samples before and after the water absorption tests.

Figures 1–4 display the comparisons of the micro-structural features of clay minerals and micropore textures of the four conglomerate samples before and after the water absorption tests.
As shown in Figure 1, the chlorite/montmorillonite mixed layer covering the surface of grains was mainly leaf-shaped or large with a honeycomb-shape (Figures 1(a-1) and 1(b-1)) for rock sample C-1. After interacting with water, the shape of the chlorite/montmorillonite mixed layer was mainly dominated by small honeycomb-shape (Figures 1(a-2) and 1(b-2)). New secondary minerals called calcspar were generated (Figure 1(a-2)). When meeting water, the hydration swelling was relatively fully, and the pores in the mixed layer easily shrunk, which resulted in the detachment of aggregations and weakened contact forces in clayey minerals or among the clayey minerals and particles. Therefore, the displacement and migration of particles occurred and induced the jam in pore throats, and the inter-granular pores in particles were backfilled by chlorite/montmorillonite mixed layer with honeycomb-shape. This condition led to the decrease in the porosity, rougher pore wall, and increase in the fractal dimension of valid pores.

![Micro-structural features of clay minerals and micro-pore textures in C-1](image)

**Figure 1.** Micro-structural features of clay minerals and micro-pore textures in C-1

Figure 2 shows that calcspar was generated on the surface of grains near the pores of rock sample C-2 after the water absorption test. Calcspar adhered poorly to the grains and easily jammed the micro-pores with water flow during the water absorption test. From Figure 2(a-2), a layer of organic film covered the wall or the surface of pores, and it led to a smoother pore wall and reduced fractal dimension of valid pores.
As shown in Figure 3, the shape of chlorite/montmorillonite mixed layer backfilled the micro-pores of rock sample C-3, which was mainly determined by pompom-like shape either in the original state or after water absorption test. In the process of water absorption, chlorite/montmorillonite mixed layer swelled, and the pores were jammed, which resulted in the reduced porosity (Figures 3(a-1) and 3(b-1)). In addition, a chlorite/montmorillonite mixed layer with thin film shape covered the surface of particles surrounding the pores, and the wall of pores became smoother after meeting water.

Figure 2. Micro-structural features of clay minerals and micro-pore textures in C-2

(a-1) Before water absorption
(a-2) After water absorption

(b-1) Before water absorption
(b-2) After water absorption
Figure 3. Micro-structural features of clay minerals and micro-pore textures in C-3

Figure 4 shows that calcispar was generated on the surface of grains near the pores for rock sample C-4 after the water absorption test. Calcispar adhered poorly to the grains and easily jammed the micro-pores with water flow in the process of absorbing water. In Figures 4(a-1) and 4(a-2), chlorite/montmorillonite mixed layer of inter-grain pore was outputted by anomalous honeycomb type, and chlorite/montmorillonite mixed layer swelled after meeting water, which reduced the pore space. In Figure 4(b-2), a layer of organic film covered the surface of the grains. This film resulted in a smoother pore wall, which reduced the fractal dimension of valid pores directly.
4. Aqueous Solution Analysis

Water analysis tests were applied to analyze the variances of the chemical compositions of aqueous solutions before and after the water absorption tests.

The chemical reactions that might have occurred in the reaction of water and rock are follows [20]:

\[
\text{KA}_{1:3}\text{Si}_{3:2}\text{O}_{10}\text{[Al}_{2}\text{Si}_{2}\text{O}_{5}]\text{OH}_{2}+2\text{K}^{+}+4\text{H}_{2}\text{SiO}_{4}\ (3) \\
\text{NaAlSi}_{3}\text{O}_{8}+2\text{H}^{+}+9\text{H}_{2}\text{O}→\text{Al}_{2}\text{Si}_{3}\text{O}_{6}(\text{OH})_{3}+2\text{Na}^{+}+4\text{H}_{2}\text{SiO}_{4}\ (4)
\]

As shown in Equations (3) and (4), potassium feldspar and soda feldspar can be transformed into kaolinite after dissolution.

Table 4 lists the chemical composition of aqueous solutions before and after the water absorption tests. As shown in Table 4, each chemical composition of aqueous solution after the water absorption tests was large. Thus, when interacting with water, clay minerals of the rock samples generally showed a series of interfacial phenomena, and they resulted in the solution of soluble minerals and ionic exchange in rocks. Therefore, the dissolution of soluble minerals and formation of secondary of minerals occurred.

**Table 4 Chemical composition of aqueous solution before and after the water absorption test**

| Sample | pH  | Degree of mineralization (mg/L) | Dissolved solids (mg/L) | The concentration of anion/cation (mmol/L) | The concentration of cation (mg/L) | Na⁺⁺K⁺ | Ca²⁺ | Mg²⁺ |
|--------|-----|---------------------------------|-------------------------|-------------------------------------------|----------------------------------|--------|------|------|
| Before | 7.55| 337.02                          | 262.91                  | 4.755                                     | 20.42                            | 47.95  | 7.55 |
| After  | 8.26| 450.69                          | 370.97                  | 6.049                                     | 96.52                            | 38.84  | 3.02 |

5. Conclusions

XRD analysis, SEM, and mercury intrusion porosimetry experiments were carried out to investigate the mineral compositions, microstructures, and porosity characteristics of four clay-bearing conglomerate samples collected from Northeast China at great depths. In addition, the chemical analysis of aqueous solutions were carried out to examine the variances of chemical compositions before and after the water absorption tests. The dominant mineral components in the conglomerate samples were quartz, potash feldspar, plagioclase, and clay. The contents of clay minerals in all samples were relatively high, ranged from 8.9% to 14.9%, and mostly contained chlorite/montmorillonite mixed layer. The main conclusions are summarized as follows.

Ion exchange occurred in the reactions between the conglomerate samples and water. The mixed layer of chlorite/montmorillonite expanded, spread, and flocculated after absorbing water, jammed the pores, and reduced the porosity, which led to the decreased porosity of conglomerates. A certain number of calcite particles formed on the surface of grains or surrounding micro-pores, resulting in the blockage of pores and inducing the decrease in rock porosity. In addition, various occurrence features
of chlorite/montmorillonite mixed layer changed differently after interaction with water, resulting in the varied influences on fractal characteristics of rocks.

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