Deterioration Characteristic of Mudstone Due to Freeze-Thaw Action Using Electrical Impedance Spectroscopy

J.C. Hu, H.F. Wang, J. Zhao

Abstract. Determining the damage of rocks after freeze-thaw cycles is an important subject for natural building rocks used in cold regions. Freeze-thaw test is an important method for determining the deteriorations of stones due to freeze-thaw action. To understand the mechanisms of rock deterioration in cold regions, the electrical impedance spectroscopy technique can be utilized to investigate the mechanical properties of mudstone because of freeze-thaw test. Firstly, the initial rock properties including mineral composition, microstructure, water absorbing capacity and the thermogravimetric properties are measured for assessing damage characteristic of mudstone due to freeze-thaw action. Then, an instrument is designed for measurement electrical impedance spectroscopy of the specimens during freeze-thaw test. Finally, the capacitance, resistance and the parameter indicating dispersive effect \( \phi \) are analyzed from Nyquist curve of electrical impedance spectroscopy of mudstone specimens. The variation of above parameters abides by the law which their values changes at 12 of freeze-thaw cycles. The results show the specimen crack occurs obviously at 12 of freeze-thaw cycles. It proved the electrical impedance spectroscopy is a useful method to research rock cracking due to freeze-thaw action.

Keywords: mudstone, freeze-thaw test, electrical impedance spectroscopy, capacitance, resistance, constant phase element.

1. Introduction

Rock deterioration is a topic of concern in many fields such as geologic materials and cultural/historical sculptures and monuments. In cold regions, rocks are subjected to freeze-thaw action and therefore deteriorate more quickly. Rock weathering is promoted by repeated freezing and thawing of water in the voids of rock, and its damage depends on the temperature, rock type and moisture content in cold regions (Matsuoka, 1990). Chen et al. (2004) have subjected to freeze-thaw tests rock specimens prepared from welded tuff with a degree of saturation from 0% to 95%. When the initial degree of saturation exceeded 70%, the rock was damaged significantly, and the degree of saturation in the surface layer was higher than that in the center of the frozen specimen (Chen et al., 2004). Rock deterioration is the result of the number of freeze-thaw cycles, temperature, rock type, applied stress and moisture content in cold regions (Chen et al., 2004; Tan et al., 2011). A statistical model was developed for predicting the percentage loss values in uniaxial compression strength from intact tests of impact strength, modulus of elasticity and water absorption (Bayram, 2012). The changes of the mass and volume ultrasonic velocities, the complete stress-strain curves, uniaxial compressive strengths, frost resisting coefficient, weathering degree, dynamic elastic modulus and acoustic emission parameters for marble specimens were obtained before and after freeze-thaw action. The main physical and mechanical characteristics of marble were summed up under cycles of freeze-thaw test (Wu et al., 2006). Of course, except for above-mentioned details, the researchers use many methods to investigate rock deterioration during freeze-thaw cycles, such as CT scanning test (Yang & Pu, 2002), gloss test (Ozcelik et al., 2012), ultrasound propagation speed test (Inigo et al., 2013). However, little information of rock damage was obtained in real-time during the freeze-thaw test. In the present paper, rock deterioration due to freeze-thaw test was investigated with electrical impedance spectroscopy.

Electrical impedance spectroscopy (EIS) has been used extensively to characterize the electrical properties of materials as a function of frequency (Gersing, 1998; Pan et al., 2003; Prabakar & Rao, 2007; Li, 2003). The EIS results are used to interpret impedance spectra in terms of resistance and capacitance associated with the physicochemical properties of the sample under test (Zhang et al., 1990; Zhang & Willison, 1991; Bhatt & Nagaraju, 2009). Many researchers (Olson et al., 1995; Perron & Beaudoin, 2002; Hu et al., 2007) have used EIS to estimate the physical state of various porous solid samples. The EIS was used to measure physical-mechanical properties of rock including fault breccia, sandstone and limestone (Kahraman & Alber, 2006; Kahraman et al., 2015; Saltas et al., 2014; Su et al., 2000), and also to monitor CO2 or oil migration within saturated rock (Kirichek et al., 2013; Liu et al., 2015). For im-

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pedance spectra, the qualitative interpretations are that the grain-interior response lies at highest frequency, the sample-electrode response at low frequency and the grain boundary response at the mid-frequencies, and the qualitative interpretations take parameters from the impedance spectra which can show some properties of rock (Kahraman & Alber, 2006; Kahraman et al., 2015; Hu et al., 2007; Huebner & Dillenburg, 1995).

The authors have developed a method for simultaneous measurement of rock deterioration and impedance characteristics of rock because of freezing and thawing. A feature of the impedance spectra, the frequency dispersion (or depression) angle, was found to contain information of pore structure and the related parameters of mass transfer of unfrozen water, pore blocking. The ultimate goal of this work is to provide useful information for the development of a frost resistance test based on electrical measurement methods.

2. Materials and Methods

2.1. Rock specimens

Test specimens were prepared from mudstone produced in Northern Liaoning province, China. The mudstone consists of quartz (32.9%), sodium feldspar (24.7%), clay mineral (42%) (including illite 23%, kaolinite 18%, chlorite 19%, illite smectite mixed layer 40%) and a small amount of calcite. The X-ray diffraction (XRD) tests are shown in Fig. 1 and 2, for the mudstone and clay minerals, respectively.

The mudstone, which has a relatively low strength, has been classified as a soft rock in civil engineering. It is a clay-bearing rock, and scanning electron microscope (SEM) images showing the microcharacteristics and microcracks of the specimen are given in Fig. 3 and Fig. 4, respectively. The figures show that the samples are compact. Fig. 3 includes some micropores whose size is 10-20 μm. In the sample picture in Fig. 4, which has an amplification of 1000 times, there are some fractures and their size is 5-10 μm.

2.2. Physical and mechanical properties

The porosity of a rock specimen was determined by two means, namely, water absorption capacity and water intrusion method. In the water saturation, specimens were immersed in two ways, one is saturated under certain pressure, and the other is saturated under natural conditions. The saturation velocity of specimen is very important regarding rock deterioration. Saturation velocity of specimen is described with water absorption content, water absorption velocity and the rate of change of water absorbing capacity with time.

The water absorption content, \( \omega_c \), was calculated from Eq. 1:

![Figure 1 - XRD spectrum diagram showing the mineral compositions of specimen.](Image)
where \( \omega_0 \) is the water content of specimen in natural conditions; \( m_{wt} \) is the specimen weight after water absorption; \( m_s \) is the dry weight of specimen.

The change of water absorbing capacity with time is shown in Fig. 5.

In order to describe rock strength change with its water absorbing capacity, the strength softening coefficient \( \eta(t) \) was used, which is calculated from Eq. 2:

\[
\eta(t) = \frac{\sigma_u}{\sigma_c}
\]
where $\sigma_u$ is the uniaxial compression strength value with time; $\sigma_c$ is the uniaxial compression strength standard value.

The uniaxial compression tests and the rock water content measurements were performed using standard methods. The summarizing values are shown as Table 1.

### 2.3. Thermal analysis test

In order to investigate the relation of mudstone physical properties and temperature, the weight change of specimens with temperature in Simultaneous Thermal Analysis (STA) was measured using the Ntisch STA 409 PC/PG, and the result is given in Fig. 6. The result shows that the thermogravimetric (TG) properties of mudstone are more complex than those of the single minerals.

### 2.4. Freeze-thaw test

The freeze-thaw test was conducted in a temperature-controlled chamber, and before the test, specimens have been saturated. The freeze-thaw cycle occurred in distilled water from 12 °C to -20 °C. The temperature variation of the freeze-thaw cycle was done as shown in Fig. 7. In the temperature-controlled chamber, a special apparatus shown in Fig. 8 is prepared for the EIS measurement of specimen. Two containers were installed on both sides of the apparatus to ensure the specimen is always in the saturated state. Between the container and specimen, there are the electrodes which connect to the electrochemical workstation. The apparatus in the temperature-controlled chamber ensures specimen real-time monitoring during the freeze-thaw cycle. A freeze-thaw cycle took 4 h, about 2 h for freezing and 2 h for thawing.

### 2.5. Electrical impedance spectroscopy test

For evaluating the specimen damage degree because of freeze-thaw action, the EIS test was conducted after each freeze-thaw cycle till the specimen was clearly damaged. The Nyquist curves (Crossley, 1975) of EIS are shown in Fig. 9, where the symbol for impedance is, as usually, $Z$. In these figures, there are six Nyquist curves: before the freeze-thaw action, after six cycles, nine cycles, twelve cycles, fifteen cycles and eighteen cycles of the freeze-thaw action.

### Table 1 - Summary of test results.

<table>
<thead>
<tr>
<th>Name</th>
<th>Time (h)</th>
<th>Water absorbing capacity (mL)</th>
<th>Water content (%)</th>
<th>Uniaxial compression strength (MPa)</th>
<th>Strength softening coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN-1</td>
<td>/</td>
<td>/</td>
<td>0</td>
<td>68.31</td>
<td>1.07</td>
</tr>
<tr>
<td>SN-2</td>
<td>saturated</td>
<td>7.50</td>
<td>1.11</td>
<td>63.67</td>
<td>0.99</td>
</tr>
<tr>
<td>SN-3</td>
<td>0</td>
<td>0</td>
<td>1.09</td>
<td>64.07</td>
<td>1.00</td>
</tr>
<tr>
<td>SN-7</td>
<td>saturated</td>
<td>9.27</td>
<td>1.36</td>
<td>30.31</td>
<td>0.47</td>
</tr>
<tr>
<td>SN-4</td>
<td>181.186</td>
<td>0.84</td>
<td>0.94</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>SN-5</td>
<td>180.731</td>
<td>0.70</td>
<td>0.58</td>
<td>64.72</td>
<td>1.01</td>
</tr>
<tr>
<td>SN-6</td>
<td>340.340</td>
<td>1.09</td>
<td>2.28</td>
<td>51.59</td>
<td>0.81</td>
</tr>
<tr>
<td>SN-8</td>
<td>505.500</td>
<td>1.44</td>
<td>1.07</td>
<td>31.75</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Figure 5 - Variation of water absorbing of specimen SN-6 and SN-8 with time.

Figure 6 - Variation of the specimen weight with temperature.
3. Results and Discussion

3.1. Initial rock properties

One of the factors influencing rock damage during freeze-thaw cycles is its minerals. Rock damage because of minerals has three mechanisms as follows. (1) Different thermal expansion coefficient of minerals in rock: when the temperature decreases from 12 °C to -20 °C, or increases from -20 °C to +12 °C, different expansion of minerals in rock will generate stress among minerals. When this stress exceeds the shear strength, damage occurs. (2) Minerals in rock are poor conductors of heat: during freeze-thaw cycle, the temperature gradient in rock is from the surface to the interior. So expansion degree from the surface to the interior has big differences, which will generate stress. The rock will be damaged when the stress exceeds the shear strength. (3) Some minerals can be deformed after absorbing water: the clay-bearing rocks such as shales, claystones, mudstones, and siltstones always contain clay minerals, especially montmorillonite, whose volume will expand when they are immersed in water. Expansion of clay minerals will generate pressure. When this pressure exceeds the tensile strength of rock, cracking occurs.

Another factor is pore water, which influences rock damage also through three mechanisms. (1) Expansion when water changes to ice: when the temperature decreases to below 0 °C, water begins to freeze in rock. If more than 90% of the pore volume is filled with water, expansion of water during freezing will generate pressure. When this pressure exceeds the tensile strength of the rock, cracking occurs. (2) Formation of ice lens or wedge: this is the persistent growth of a crystal large enough to disrupt the rock that contains enough water to feed further growth. A rock, such as mudstone, is a porous material in which pore water will not freeze immediately below 0 °C and can migrate during freezing. This phenomenon may be caused by the presence of dissolved chemicals and the relatively small sizes of the pores (Pigeon & Setier, 1997). (3) Hydraulic pressure: as ice grows in a pore or other space, owing to the expansion associated with freezing, unfrozen water is expelled from that space.

Before the freeze-thaw test, the mineral composition of specimens were obtained from the XRD test, as shown in Table 2 and Table 3. The specimen mainly contains quartz, sodium feldspar and clay mineral. Their thermal expansion coefficients are different, which will generate stress among minerals during freeze-thaw cycle and the specimen will be damaged. Simultaneously, the specimens will be damaged during freeze-thaw cycle because they are solids and minerals of their composition are poor conductors of heat. The mudstone contains 42% clay mineral. When specimens are immersed in water, part of clay mineral will contact with water and expand because of absorbing water. Expansion pressure can make the specimen crack open.

The water saturation method (Chen et al., 2004) showed that the porosity of the specimens varied from 5.8% to 6.8%, with an average of 6.3%. Fig. 3 and Fig. 4 show that the specimens contain a few micropores and microfractures. The previous tests show that the mudstones have water absorbing capacity under natural or pressure state. The mudstone contains a certain amount of absorbed water, crystal water and constitutional water, zeolite water and interlayer water from TG test shown in Fig. 6. The properties above mentioned can create internal pressures during freeze-thaw test. The first is the action of the unfrozen water being pushed into smaller spaces (including micropores and microfractures) and the resistance to this flow increases the hydrostatic pressure. Secondly, freezing typically occurs first at the outer surface, forcing the remaining water
inwards to create a saturated flow hydraulic pressure. Pressure is developed due to the resistance to the water flowing rapidly through the capillaries. The third involves saturated materials whereby an advancing ice front produces a hydrostatic compression that will create a tensile force within the constraining rock. Simultaneously, the heat transfers from the surface to the inner part of the specimen, or in the opposite direction. Because the minerals of specimen are poor conductors of heat and have different thermal expansion coefficient, stress will be generated among the minerals during freeze-thaw test. The water immersion also causes the clay minerals expansion.

3.2. EIS properties

Useful information is obtained from the data of EIS in the freeze-thaw test. However, the internal damage of rock during the freeze-thaw action can be expressed by the parameters from the data of EIS including capacitance properties, resistance properties, and constant phase element and so on.

3.2.1 Capacitance properties of Nyquist curves

The capacitance $C_p$ of mudstone is calculated from its Nyquist curves taken for every freeze-thaw cycle using Eq. 4 (Bhatt & Nagaraju, 2009) and the obtained values are plotted in Fig. 9.

$$X_p = \frac{R^2 + X^2}{R}$$

$$C_p = \frac{1}{2\pi f X_p}$$

where $R$ and $X$ are values of real and imaginary components of Nyquist curve at a frequency $f$, the value of $f$ is chosen such that these imaginary component values are nearly

![Figure 9 - The Nyquist curves of specimen after freeze-thaw cycles.](image)

Table 2 - Specimen mineral composition.

<table>
<thead>
<tr>
<th>Number</th>
<th>Kinds and percentage composition (%)</th>
<th>Clay mineral (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartz</td>
<td>Potassium feldspar</td>
</tr>
<tr>
<td>SN-1</td>
<td>32.9</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 3 - Specimen clay mineral composition.

<table>
<thead>
<tr>
<th>Number</th>
<th>Percentage composition (%)</th>
<th>Mixed-layer ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Smectite</td>
<td>Illite/Smectite</td>
</tr>
<tr>
<td>SN-1</td>
<td>/</td>
<td>40</td>
</tr>
</tbody>
</table>

maximum on the high frequency asymptote (HFA) part on Nyquist curve (Hu et al., 2007).

Fig. 10 shows that the change rate of capacitance up to 9 freeze-thaw cycles is lower than that from 12 to 18 freeze-thaw cycles. The middle line of the curve is flat. This indicates that the mudstone crack induces a higher change rate as the freeze-thaw cycles increase past 12.

3.2.2. Resistance properties of Nyquist curves

The resistance of mudstone is calculated from its Nyquist curves taken for every freeze-thaw cycle using Eq. 5 (Bhatt & Nagaraju, 2009) and the obtained values are plotted in Fig. 11.

\[ R_x = \frac{R^2 + X^2}{X} \]  

(5)

where \( R \) and \( X \) are values of real and imaginary components of Nyquist curves at a frequency \( f \), the value of \( f \) being chosen such that these imaginary component values are nearly maximum on the HFA part on Nyquist curves (Hu et al., 2007).

Fig. 11 shows that the rate of change of resistance is high at the starting point of freeze-thaw test. From 12 to 18 freeze-thaw cycles, the line becomes flat. It indicates that the specimen offers decreasing resistance till 12 times, which means the mudstone crack is extending steadily during 12 times freeze-thaw cycles. After 12 freeze-thaw cycles, the crack does not extend due to the freeze-thaw action, the value of the curve is mainly the resistance of the solution contained in the specimen.

3.2.3. Constant phase element of Nyquist curves

A dispersive, frequency-dependent element or so-called constant phase element (CPE) can be introduced to account for the shape of the depressed complex plot (Perron & Beaudoin, 2002). The impedance contribution of this element can be expressed as follows:

\[ Z(CPE) = A_0^{-1}(j\omega)^{-\varphi} \]  

(6)

where \( \varphi = 1 - 2 / m(\alpha) \) and \( \alpha \) is the depression angle.

Therefore, \( \varphi \) can be used to represent the degree of perfection of the capacitor and represents a measure of how far the arc is depressed below the real impedance axis.

Previous work indicates a dependence of \( \varphi \) on the characteristics of the material pore size distribution (Hu et al., 2007). This work has suggested that a broad pore size distribution would result in a wide spread of relaxation times corresponding to a large dispersion angle. A narrow pore size distribution would result in a significantly reduced spread of relaxation times. The range of pore size distributions represented by the solution in specimen and porous conforms to these arguments (Perron & Beaudoin, 2002). The results of mudstone during freeze-thaw test are shown as Fig. 12, in which \( \varphi \) comes from the zone A of Fig. 9. The value of \( \varphi \) is increasing up till 12 freeze-thaw cycles. Then, the value starts to decrease from 12 to 18 freeze-thaw cycles. It indicates the uniformity of specimen...
getting better and better firstly, and uniform degree of pore size distribution variation becoming worse after 12 freeze-thaw cycles.

4. Conclusions

The designed instrument based on EIS is found quite suitable for rapid and nondestructive measurement of electrical properties of mudstone during freeze-thaw test. The designed instrument is also found quite suitable for the simultaneous measurement of capacitance and resistance of the specimen during freeze-thaw cycles. The change rate of capacitance showed the mudstone crack extending with the freeze-thaw cycles. The variation in resistance of mudstone specimen revealed that the mudstone crack extends steadily during 12 freeze-thaw cycles and from that time the crack connects the electrodes at both ends of the specimen. After 12 freeze-thaw cycles, the changes of resistance are smooth and steady, which shows that the crack does not extend due to the freeze-thaw action, the value of the curve being mainly the resistance of the solution contained in the specimen. The parameter indicating dispersive effect $\varphi$, which is increasing firstly and decreasing subsequently, shows the change rule of specimen crack at freeze-thaw test. Thus, the study of electrical properties of mudstone proved to be quite useful to study rock cracking during freeze-thaw test or other mechanical action.

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