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Electrochemical modification of the porosity and zeta potential of montmorillonitic soft rock

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Abstract. The porosity (including the specific surface area and pore volume-diameter distribution) of montmorillonitic soft rock (MSR) was studied experimentally with an electrochemical treatment, based on which the change in porosity was further analyzed from the perspective of its electrokinetic potential (ζ potential) and the isoelectric point of the electric double layer on the surface of the soft rock particles. The variation between the ζ potential and porosity was summarized, and used to demonstrate that the properties of softening, degradation in water, swelling, and disintegration of MSR can be modified by electrochemical treatment. The following conclusions were drawn. The specific surface area and total pore volume decreased, whereas the average pore diameter increased after electrochemical modification. The reduction in the specific surface area indicates a reduction in the dispersibility and swelling-shrinking of the clay minerals. After modification, the ζ potential of the soft rock was positive in the anodic zone, there was no isoelectric point, and the rock had lost its properties of softening, degradation in water, swelling, and disintegration. The ζ potential increased in the intermediate and cathodic zones, the isoelectric point was reduced or unchanged, and the rock properties are reduced. When the ζ potential is increased, the specific surface area and total pore volume were reduced according to the negative exponent law, and the average pore diameter increased according to the exponent law.

Keywords: montmorillonitic soft rock; electrochemical modification; specific surface area; pore volume-diameter, ζ potential, isoelectric point.

1. Introduction

The specific properties of montmorillonitic soft rock (MSR) are softening, degradation in water, swelling, and disintegration, which have a tremendous effect on the stability of the rock and on soft rock engineering. In controlling the stability of soft rock and in the field of soft rock engineering, all the existing theories and methods have focused on passive support, anchorage, and cement grouting, which depend on changes in the external factors affecting the soft rock. However, these strategies have great limitations and do not address the aging factor (Wang *et al.* 2000, Wang and

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Fan 2000, Jiang *et al.* 2001, Onargan *et al.* 2004). Studies of the long-term stability of soft rock and soft rock engineering that are based on modifying the physicochemical properties of the soft rock have fundamental scientific significance and value in engineering applications.

Previous studies have shown that the modification of MSR with electrochemical methods is an effective management strategy (Mikhajlovich 2001, Zhou *et al.* 2008, Mikhajlovich 2006). Titkov *et al.* (1961, 1965), and Song *et al.* (1998) studied the mechanical properties of modified and unmodified mudstones experimentally, and demonstrated that the tensile strength of modified mudstone is increased. Titkov *et al.* (1961, 1965), Gray (1969), Adamson *et al.* (1966), and Harton *et al.* (1967) studied the mineralogical composition, crystal structure, and newly formed minerals experimentally, and their results indicated that fundamental changes occur in the physicochemical properties of MSR after electrochemical treatment. Chilingar (1970), Aggour *et al.* (1992, 1994), and Schifano *et al.* (2001) studied the effects of the electrical potential gradient on the permeability of sandstone and oil shale. Their results indicate that the permeability of oil shale and sandstone is augmented as the electrical potential gradient increases because of changes in the crystal structures of the rocks. Bernabeu *et al.* (2001) studied the porous system of Bateig stone, and showed that electrochemical treatment can consolidate porous rocks, prevent decay, and improve its resistance to water and weathering.

The properties of softening, degradation in water, swelling, and disintegration of MSR are closely related to its specific surface area and the pore volume-diameter distribution (Sondi *et al.* 1996, Sondi *et al.* 1997). Because MSR has active physicochemical properties and a high specific surface area, the water molecules in the pore fracture of MSR will be transported and enriched, which causes an increase in the thickness of the water-adsorbing film on the surfaces of the fine particles of the MSR. The increment in the thickness of the diffusion layer in the electric double layer weakens the physicochemical coupling, appearing as inner crystalline swelling and osmotic swelling of the clay minerals, and causing softening, degradation in water, swelling, and disintegration of MSR (Madsen and Vonmoos 1989, Tuller 2003, Schifano 2001, Bernabeu *et al.* 2001, Tan and Kong 2006). To solve the problem, we experimentally investigated the modification of the porosity and zeta (ζ) potential of MSR caused by electrochemical treatment, and examined a new method of modifying the properties of softening, degradation in water, swelling, and disintegration of MSR.

2. Experimental specimen

The specimen of MSR, selected from the floor of the no. 1 coal seam at the mines of Wali (in the province of Shandong, China), is an argillaceous shale from Cenozoic Tertiary strata. The X-ray diffraction pattern (XRD) of the specimen is shown in Fig. 1. The mineralogical composition of the specimen was analyzed quantitatively with an adiabatic method. The mineralogical composition of the specimen was montmorillonite (33.26%), kaolinite (8.83%), quartz (47.11%), and albite (10.80%). Clearly, the main clay constituents were montmorillonite and kaolinite. The soft rock had the properties of softening, degradation in water, and strong swelling. The results of X-ray fluorescence (XRF) spectral analysis are shown in Table 1. The chemical composition of the specimen was mainly SiO₂ 60.65%, Al_2O_3 15.92%, TFe₂O₃ 5.39%, and LOI 5.39%.



Fig. 1 The X-ray diffraction pattern of the specimen

Table 1 Chemical composition of the specimen (%)

SiO ₂	Al_2O_3	TiO ₂	TFe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	LOI
60.65	15.92	0.63	5.39	0.09	1.46	0.98	1.96	2.35	0.28	10.29

3. Experimental apparatus

The experimental apparatus used for the electrochemical treatment in this study is shown schematically in Fig. 2. It consists predominantly of a beaker, electrode, sample, electrolyte, pH meter, DC power supply, current meter, and wire. The electrode geometry was chip-type, the anode was 2 mm thick aluminum, and the cathode was 0.5 mm thick red copper. The electrolyte consisted of $CaCl_2$, because the addition of salts and acids in the electrolyte can decrease the electroosmotic pressure and that alcohol increase it (Bernabeu *et al.* 2001, Schifano *et al.* 2001, Velde and Meunier



Fig. 2 The experimental apparatus of electrochemical modification

2008). The DC power supply provided a voltage output ranging from 0 to 250 V and a maximum current of 1.2 A. The wire was ASTVR 1×0.35 silk-covered wire.

The physical parameters of the unmodified specimen (original specimen) and the modified specimens (specimen after the electrochemical modification) in the anodic, intermediate, and cathodic zones, including the specific surface area, the pore volume, and the pore diameter, were measured using the low-temperature nitrogen adsorption technique. The measurement instrument was a Micrometrics Tristar 3000 gas adsorption analyzer, which can measure specific surface areas as small as $0.01 \text{ m}^2 \text{ g}^{-1}$ and a range of pore diameters of 1.7-300 nm.

The electrochemical parameters of the specimens, including their ζ potentials and isoelectric points, were measured with the electrophoretic method (Sabri 2004, Delgado *et al.* 1986, Horikawa *et al.* 1988, Velde and Meunier 2008). The measurement instrument was a microelectrophoresis unit (JS94H), the measured electrode was Ag, the switching time was 700 ms. The range of input pH values was 0-14, and 0.1 was treated as a unit.

4. Experimental studies

4.1 Preparation of the specimen

The MSR specimen was crushed and ground with a mortar and pestle, and then screened using a 300-mesh decimate sifter. The powdered specimen was then placed in a high-temperature cabinet at 100°C for 24 h to any remove moisture. An aliquot (20 mL) was taken as one share, so the specimen reached a total of 100 mL with five shares.

4.2 Experimental process

Electrochemical modification was applied for 120 h under electrical potential gradients of 0.5-2 V cm⁻¹ and an electrolyte concentration of 1 mol L⁻¹. The 20 mL dry powdered specimen was poured into a beaker, wetted for 24 h with the 1 mol L⁻¹ CaCl₂ electrolytes, and then treated with the appropriate electrical potential gradient. During this period, the pH values in the anodic, intermediate, and cathodic zones were measured with a pH meter at 4 h intervals. The powdered specimen was continuously modified by the electrochemical method for 120 h and then placed in the cabinet at 100°C for 24 h to dry.

The dry powdered specimen from the anodic, intermediate, and cathodic zones was picked and ground with a mortar and pestle, and screened with a 300-mesh decimate sifter after modification. Its physical parameters (specific surface area, pore volume, and pore diameter) were measured with the nitrogen adsorption technique.

Specimen suspensions were made from the measured powdered specimens. The powdered specimens (solid content 20%) were soaked for 72 h in distilled water and completely hydrated. The concentrated suspensions were diluted with distilled water, until the specimen particles could fall freely in response to gravity. The supernatant suspensions were discarded to eliminate any contamination with electrolyte. The residual suspensions were diluted with distilled water and H_2O_2 to remove organic matter, and then heated to eliminate superfluous H_2O_2 (Sondi *et al.* 1996, 1997). The heated suspensions were centrifuged with a high-speed agitator for 20 min and then allowed to stand for 24 h. The aqueous suspensions were taken out with a siphon method, and the bigger

particles at the bottom of the test tubes were discarded. The operation was repeated until the specimen suspensions were homogeneous. Samples (2 mL) of the homogeneous specimen suspensions were injected into test tubes and diluted with 0.01 mol L⁻¹ NaCl to a specimen suspension concentration of 1 g L^{-1} . The pH of the suspensions was adjusted with 0.1134 mol L^{-1} HCl solutions, measured with a pH meter, and then stable equilibrium. The adjusted suspensions were dispersed for 5 min with an ultrasonic disperser (Kq3200e). The dispersed suspensions (0.5 mL) were injected into an electrophoretic cup, in which a cross grid was inserted to adjust the focus, and the electrode was placed on a three-dimensional platform to measure the ζ potential.

5. Experimental results and analysis

5.1 Specific surface areas of the unmodified and modified specimens

Fig. 3 shows the adsorption-desorption isotherms of the unmodified specimen, where P is the equilibrated pressure, P_0 is the saturation pressure, and P/P_0 is the relative pressure ratio. The specific surface area is 21.8899 m² g⁻¹.

Fig. 4 illustrates the effects of the electrical potential gradient (E) on the variation in the specific surface area (S) of the modified specimen in the anodic, cathodic, and intermediate zones. As shown in this figure, with increasing electrical potential gradients, the specific surface areas of the modified specimens in the intermediate, cathodic and anodic zones were 5.4341-9.9116 m² g⁻¹, 3.0931-4.3216 m² g⁻¹, and 2.1537-2.3629 m² g⁻¹, respectively. After electrochemical modification, the specific surface areas in the intermediate, cathodic, and anodic zones were reduced by 54.72%-75.18%, 80.26%-85.87%, and 89.21%-90.16%, respectively. The reduction in the specific surface areas shows that the properties of dispersibility and swelling-shrinking of the clay minerals were reduced. Therefore, the properties of softening, degradation in water, swelling, and disintegration of the MSR were reduced.



Fig. 3 The adsorption-desorption isotherms of the unmodified specimen

Fig. 4 The specific surface areas of the modified specimen in the different zones vary with the electrical potential gradient

2.0



Fig. 5 Pore volume of the unmodified specimen varies with pore diameter

5.2 The pore volume-diameter distribution of the unmodified and modified specimens

Fig. 5 shows the variation in the pore volume of the unmodified specimen with pore diameter. As shown in the figure, when the pore diameter was 2-9 nm, the pore volume was 0.037-0.012 cm³ g⁻¹. With increasing the pore diameter, the pore volume was changed by Gauss law, and the maximum was 0.0196 cm³ g⁻¹. The total pore volume of the unmodified specimen was 33.169 mm³ g⁻¹, and the average pore diameter was 6.061 nm.

The effects of the total pore volume (P_{tv}) and the average pore diameter (P_{ad}) of the modified specimen in different zones on the electrical potential gradient are shown in Fig. 6. As shown in Fig. 6(a), with the increase in electrical potential gradient, the total pore volumes of modified specimens in the intermediate, cathodic, and anodic zones were 17.473-20.215 mm³ g⁻¹, 12.03-12.679 mm³ g⁻¹, and 9.738-10.749 mm³ g⁻¹, respectively. The specific surface areas and total pore volumes of the modified specimens in the three zones have the same variational trends. As shown in Fig. 6(b), the average pore diameters of the modified specimens in the anodic, cathodic, and intermediate zones were 21.086-21.275 nm, 19.096-19.462 nm, and 10.158-13.334 nm, respectively. The variation in the average pore diameters was in the reverse sequence to those in Fig. 4. and Fig. 6(a). It can be seen from the pore volume-diameter distribution of the modified specimens in the different zones under electrochemical treatment that the reduction in the specific surface area of the specimen is caused by the reduction in the total pore volume and the increase in the average pore diameter.

After electrochemical modification, the total pore volumes of the specimens decreased from $33.169 \text{ mm}^3 \text{ g}^{-1}$ to $9.738-20.215 \text{ mm}^3 \text{ g}^{-1}$, and the average pore diameter increased from 6.061 nm to 10.158-21.275 nm. The mechanism of electrochemical modification is as follows. Electrochemical phenomena such as electrolysis, electroosmosis, and electrophoresis, will affect the solid-liquid phase system in MSR. As shown in Fig. 1 and Table 1, the mineralogical composition and chemical composition of MSR is complex. Electrolysis generates many H⁺ and OH⁻ ions in the anodic and cathodic zones, respectively, which cause a variance in the pH values of the powdered specimen. The pH value was 1.5-4 in the anodic zone, 3-5.4 in the intermediate zone, and 12.5-13 in the cathodic zone during the process of electrochemical modification. The pH value has a significant



Fig. 6 Total pore volume and average pore diameter of the modified specimen in different zones vary with the electrical potential gradient

effect on the structural composition of MSR (Jayasekera and Hall 2007, Baraud *et al.* 1997). When the pH is extreme, either less than 4 or more than 9 (Schramm *et al.* 1991), the clay minerals in MSR are unstable, and fundamental changes may occur in the structural composition of soft rock. Electroosmosis causes the liquid electrolyte to flow to the cathodic zone and consolidate after the dehydration in the anodic zone, where the water that forms a film on the surfaces of the fine particles of the soft rock becomes thin, resulting in a reduction in the thickness of the electric double layer. Electrophoresis makes the fine particles of the soft rock move to the anodic zone and causes them to accumulate and coarsen. Conversely, it causes the organizational structure of the clay minerals to shrink, modifying the swelling of the clay minerals and their organizational structure, which prevents liquid phase flowing in pore throat destroy. These two aspects cause changes in the porosity of the soft rock after electrochemical modification: a reduction in the total pore volume, an increase in the average pore diameter, and a reduction in the specific surface area.

5.3 ζ Potentials and isoelectric points of unmodified and modified specimens

With a unit layer charge number of 0.25-0.6, montmorillonite has the properties of strong swelling and lattice substitution, which can make the crystal layer of montmorillonite expand completely after saturation, so it has a larger specific surface area. Electrochemical treatment can cause the water films on the surfaces of the fine particles of the soft rock to become thin, and the thickness of the diffusion layer in the electric double layer decreases. The ζ potential will increase according to the Stern model of the electric double layer. The porosity of soft rock, including the specific surface area and the pore volume-diameter distribution, is related to the electric double layer on the surfaces of the fine particles of soft rock. Consequently, the interrelation between the porosity and the ζ potential was further analyzed under the electrochemical treatment.

Fig. 7 shows a series of gray-scale images of the particulate motion in the unmodified specimen. The measured temperature was 17.6°C, the current 15.6 mA, the voltage 10 V, the switching time 700 ms, the pH 7.7, and the ζ potential -38.1127 mV. The anode was located on the right side of



Fig. 7 A series of gray-scale images of the particulate Fig. 8 ζ potential of the unmodified specimen varies with pH

the electrophoretic cup and the particles moved towards the anode. This phenomenon indicates that there were excess negative charges on the surfaces of the fine particles of the MSR.

The ζ potential of the unmodified specimen at different pH values is shown in Fig. 8. With increasing HCl solution, the pH value of the suspension decreased and the ζ potential increased from a negative to a positive value. When the ζ potential was zero, the isoelectric point was 6.5.

The ζ potentials of the modified specimens in different zones at different pHs are given in Fig. 9. The pH value in the anodic zone was reduced, indicating acidity, and the pH value in the cathodic zone was elevated, indicating alkalinity. As shown in Fig. 9(a), the pH value in the anodic zone was less than 2.5, the ζ potential of modified specimens was positive, and the isoelectric point did not exist. As shown in Fig. 9(b), the pH in the intermediate zone was 8.0, the ζ potentials under different electrical potential gradients ranged from -33.7522 to -29.4120 mV, and the isoelectric points were 6.4, 6.4, 6.4, and 6.5, respectively. Compared with those of the unmodified specimen, the ζ potential increased and the isoelectric point did not change. As shown in Fig. 9(c), the pH value in the cathodic zone was 10.1, the ζ potentials under different electrical potential gradients ranged from -22.2147 to -20.4368 mV, and the isoelectric points were 5.8, 5.8, 5.8, and 5.9, respectively. Compared with those of the unmodified speciments ranged from -22.2147 to -20.4368 mV, and the isoelectric points were 5.8, 5.8, 5.8, and 5.9, respectively. Compared with those of the unmodified speciments were 5.8, 5.8, 5.8, and 5.9, respectively. Compared with those of the unmodified speciments were 5.8, 5.8, 5.8, 5.8, 5.8, 5.9, respectively.

Through the statistics of this experimental datum, we found that the electrochemical method can modify the properties of softening, degradation in water, swelling, and disintegration of MSR. When the ζ potentials of clay minerals are less than -60 mV, the clay minerals are extremely dispersed; when the ζ potential is less than -40 mV, the clay minerals are strongly dispersed; when the ζ potential is less than -20 mV, the clay minerals are possibly dispersed; and when the ζ potential is



E 0.5V·cm⁻

E 1V·cm⁻¹

E 1.5V·cm⁻¹

10

11

E 2V·cm⁻¹

pН

(b) Intermediate zone

Fig. 9 ζ potentials of the modified specimens in different zones vary with pH

8

pH (c) Cathodic zone

less than -10 mV, the clay minerals are not dispersed (Sun *et al.* 2002). When the ζ potential on the surfaces of the clay mineral particles is strongly negative, the clay mineral properties of dispersibility and swelling-shrinking are strong. On the contrary, when the ζ potential is strongly positive, the clay mineral properties of dispersibility and swelling-shrinking are weak. Therefore, the clay mineral properties of dispersibility and swelling-shrinking can be estimated according to the value of the ζ potential, and the properties of softening, degradation in water, swelling, and disintegration of MSR can also be estimated. The ζ potential of the unmodified specimen was – 38.1127 mV, and the clay minerals were strongly dispersed. After electrochemical modification, the ζ potential in the anodic zone was positive, and the specimen had no properties of softening, degradation in water, swelling, or disintegration. The ζ potential in the intermediate zone ranged from -33.7522 to -29.4120 mV, and the rock properties were reduced. The ζ potential in the clay mineral modified specimen was and the properties of the specimen were reduced.

5.4 Correlation between porosity and ζ potential

pН

(a) Anodic zone

10

5

0

-5

5

6

-10 -15 -20 -25

Fig. 10 shows that the specific surface areas of the unmodified and modified specimens in different zones varied with the ζ potential. The fitted equation in Fig. 10 can be expressed as:



Fig. 10 The specific surface areas of the specimens vary with the ζ potential

$$S = (7.01E - 4)\exp(-0.27\zeta) + 2.61 \tag{1}$$

where S is the specific surface area and ζ is the ζ potential. The coefficient of correlation is 0.973. As shown in Fig. 10, as the ζ potential of the specimen increases, the specific surface area decreases according to the negative exponent law. After electrochemical modification, the ζ potential is more positive, the specific surface area is less, and the properties of dispersibility and swelling-shrinking of the clay minerals are reduced, which causes a reduction in the properties of softening, degradation in water, swelling, and disintegration of the MSR.

Fig. 11 shows that the porosity of the unmodified and modified specimens varied with the ζ potential. As shown in Fig. 11(a), as the ζ potential increased, the total pore volume decreased according to the negative exponent law. The fitted equation can be written as

$$p_{tv} = 0.018 \exp(-0.19\zeta) + 10.86 \tag{2}$$

where P_{tv} is the total pore volume. The coefficient of correlation is 0.955. As shown in Fig. 11(b),



Fig. 11 The porosity of the specimens varies with the ζ potential

as the ζ potential increased, the average pore diameter increased according to the exponent law. The fitted equation can be given as

$$p_{ad} = -0.376 \exp(-0.10\zeta) + 21.72 \tag{3}$$

where P_{ad} is the average pore diameter. The coefficient of correlation is 0.966.

6. Conclusions

(1) Electrochemical modification can reduce the specific surface area of MSR. After modification, the specific surface area decreases most in the intermediate zone, to an intermediate degree in the cathodic zone, and least in the anodic zone. The reduction in the specific surface area indicates a reduction in the properties of softening, degradation in water, swelling, and disintegration of the MSR.

(2) Electrochemical modification can change the pore volume-diameter distribution of MSR. After modification, the total pore volume of MSR decreased from 33.169 mm³ g⁻¹ to 9.738-20.215 mm³ g⁻¹, and the average pore diameter increased from 6.061 nm to 10.158-21.275 nm.

(3) Electrochemical modification can increase the ζ potential of MSR. The ζ potential of the unmodified specimen was -38.1127 mV, and the specimen was strongly dispersed. After modification, the potential of the specimen in the anodic zone was positive, the isoelectric point did not exist, and the specimen displayed no properties of softening, degradation in water, swelling, or disintegration. The ζ potentials in intermediate and cathodic zones increased, the isoelectric points were reduced or unchanged, and the rock properties were reduced.

(4) As the ζ potential increases, the specific surface area and the total pore volume are reduced according to the negative exponent law, and the average pore diameter increases according to the exponent law.

(5) Based on the porosity and ζ potential of the MSR, its properties of softening, degradation in water, swelling, and disintegration can be modified with an electrochemical method. This provides a theoretical reference and technical support for the increasing the long-term stability of soft rock, especially in soft rock engineering, by improving the physicochemical properties of the rock itself.

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