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The paper was published in the proceedings of the 3rd International Symposium on Coupled Phenomena in Environmental Geotechnics and was edited by Takeshi Katsumi, Giancarlo Flores and Atsushi Takai. The conference was originally scheduled to be held in Kyoto University in October 2020, but due to the COVID-19 pandemic, it was held online from October 20th to October 21st 2021.

Alkaline degradation of GMZ bentonite as HLW barrier in China

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ABSTRACT

Gaomiaozi (GMZ) bentonite is a suitable buffer material for underground repository barrier of high-level waste (HLW) in China. Strong alkaline cementitious material formed from the corroded lining concrete by groundwater will penetrate into bentonite buffer, meanwhile, the temperature of the barrier will rise under the radiant heat from the decay of the radionuclide. The laboratory tests were conducted to simulate the diffusion of KOH solution into bentonite under elevated temperature conditions and investigate the changes in mineral composition and microstructure of GMZ bentonite by X-ray diffraction (XRD), nitrogen adsorption and scanning electron microscopy (SEM). The results confirmed that alkaline dissolution of montmorillonite minerals in GMZ bentonite is increased with both pH value of the alkaline solution and the temperature. For example, montmorillonite content decreased from initial 44.4% to 25.9% in severe situation. The degree of alkaline corrosion of bentonite is inversely proportional to the distance between the contact interface of bentonite and alkaline solution and visible macro fissures were observed by naked eyes at the interface. Within 2mm of the surface, the wing-like gels produced by montmorillonite hydration were dissolved apparently; and beyond 4mm, the bentonite retained its original microstructure. The results reveal the adverse effects of alkaline corrosion of GMZ bentonite on the long-term performance of buffer barriers should be paid great attention.

Keywords: GMZ bentonite, montmorillonite, alkali solution, microstructure, degradation

1 INTRODUCTION

Deep geological disposal based on the multi-barrier system has been adopted for high-level radioactive waste (HLW). In China's HLW disposal buffer barrier system (Zhang et al., 2013), high-density compacted bentonite blocks are filled between the waste tank and the lining concrete (Fig. 1). The good sealing performance and strong adsorption performance of bentonite material can control the migration of nuclide effectively. After the repository construction, the concrete will undergo some chemical effects from the groundwater and produce strong alkaline solution (Faucon et al., 1998). The alkaline solution will penetrate into the bentonite blocks, superposing the radiant heat, bentonite blocks will degrade over time.

Many researchers have studied the thermochemical degradation of bentonite. It is clear that when bentonite contact with alkaline solution, montmorillonite, the main mineral in bentonite, will suffer alkaline dissolution and transformation of mineral (Nakayama et al., 2004 and Pusch, 2008), generate non-swelling minerals (Taylor, 1987 and Gaucher et al., 2004), weaken the swelling property of bentonite. Furthermore, the concentration of alkali solution, the temperature and the type of alkali metal ions had important relations with the dissolution of clay minerals in bentonite and the formation of secondary minerals (Gaucher et al., 2006 and Fernandez

et al., 2009). At a certain temperature and pH value, the dissolution rate of montmorillonite is a linear equation about the reaction time, the OH⁻ ion concentration and the temperature (Yamaguchi et al., 2007), the higher the concentration of alkali solution and the temperature, the more montmorillonite was dissolved and the more secondary minerals were generated (Savage et al., 2002 and Bauer and Velde, 1999). In addition, the types of secondary minerals vary depending on the alkali metal ion (Karlund et al., 2007). The buffer backfill material in repository of HLW in China is GMZ sodium bentonite (Wen, 2005). A series of swelling, infiltration and erosion experiments were carried out on GMZ bentonite with NaOH solutions of different pH values at different temperatures, the results showed that with the increase of the pH value and the temperature, the swelling pressure of bentonite gradually decrease, the montmorillonite were dissolved, and the permeability and porosity increase (Ye et al., 2014 and Chen et al., 2012).

In this study, the contact diffusion test between GMZ bentonite and KOH solution with different pH values was carried out under a certain temperature, simulating the chemical corrosion of bentonite under the highly alkaline environment induced by the degradation of cement and the radiant heat in the repository. Then, the mineral composition and microscopic structure of the bentonite after the experiments was determined by X-ray

diffraction (XRD), nitrogen adsorption and scanning electron microscopy (SEM). A comprehensive evaluation was made on the performance degradation of GMZ bentonite buffer backfill material under the combined action of chemical solution and radiant heat.

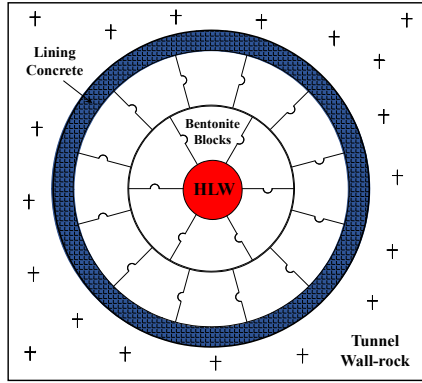


Fig. 1. Conceptual design of high-level buffer barrier for China.

2 MATERIALS AND METHODS

2.1 Materials

The material used in this study was GMZ sodium-based bentonite (Zhang et al., 2020). The main mineral was montmorillonite with a content of 44.4%, and the associated minerals were quartz, feldspar and cristobalite. Its specific gravity is 2.70, liquid limit is 228%, the plastic limit is 32%, the particle size is less than 0.075mm. The natural moisture content is 9.56%.

2.2 Experimental methods

The reaction device is specially manufactured as shown in Fig. 2 (Pusch et al., 2003). Using spray stirring method obtained GMZ bentonite with an initial water content of 12% (Zhang et al., 2012), then press it into the reaction device at one time by static compaction method, the dry density was set to 1.80kg/cm³. Subsequently, the sample was saturated under vacuum, and KOH solution with pH values of 12.6, 13.0 and 13.5 was injected, placed the device in a constant temperature water box, the test was started at 30°C and 60°C, respectively. The devices were opened after 28 days of reaction, then XRD, SEM, and physical adsorption tests were performed, the effects of temperature and pH value on mineral composition and microstructure of bentonite were analyzed.

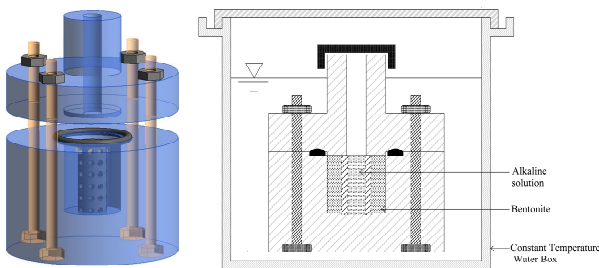


Fig. 2. Contact diffusion test reaction device.

3 EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 XRD analysis results

After the contact diffusion test, the bentonite under different test conditions were divided into three layers along the diffusion direction, which are A, B, and C from the inside to the outside (Fig. 3), and each layer was about 2cm thick. Then, the sub-sample was freeze-dried (Zhang et al., 2011) and grind into powder, the mineral composition was analyzed by XRD test.

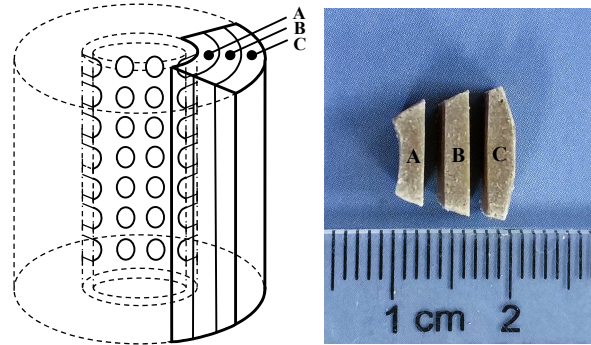


Fig. 3. Sampling locations and sub-sample photos of bentonite at different diffusion depths.

Figure 4 is the XRD patterns of bentonite sub-samples in layer A under different temperatures and different pH values. On the left is the pattern of bentonite, the diffraction angle is 5°~75°, and the right side shows the XRD pattern of montmorillonite minerals, the diffraction angle is 5°~7°, corresponds to the first peak in the left picture. It can be seen that the diffraction intensity of the montmorillonite mineral is decrease significantly with the increase of the pH value of KOH solution and the temperature. The montmorillonite was dissolved gradually (Cama et al., 2000), and the higher the pH value and the temperature, the more montmorillonite was dissolved.

Figure 5 shows the XRD patterns of GMZ bentonite at different temperatures and different diffusion depths, the pH value of KOH solution is 13.5. It can be seen that the diffraction intensity of the montmorillonite mineral is gradually increases along the diffusion direction. Layer A has the lowest diffraction intensity, the montmorillonite was eroded significantly, and the diffraction intensity was still relatively high in layers B and C, close to the undisturbed bentonite sample. By comparing the sub-samples with different test temperatures, it was found that the effect of the temperature is not significant.

In order to quantitatively evaluate the relationship between the dissolution of montmorillonite and the pH value of the alkali solution, the temperature and the diffusion depths. The percentage of montmorillonite mineral after chemical corrosion was obtained by semi-quantitative analysis of the diffraction results (Table 1). It can be found that during the diffusion of KOH solution to bentonite, the content of montmorillonite gradually

decreases with the increase of the pH value and the temperature. The degree of montmorillonite erosion decreased significantly along the diffusion layer, it can be concluded that the KOH solution has not yet diffused to the B and C layers. In the most extreme case of this

study, the alkaline solution pH=13.5, temperature T=60°C, in diffusion layer A, the amount of montmorillonite dissolved reaches the maximum, and the content decreased from the initial 44.4% to 25.9%.

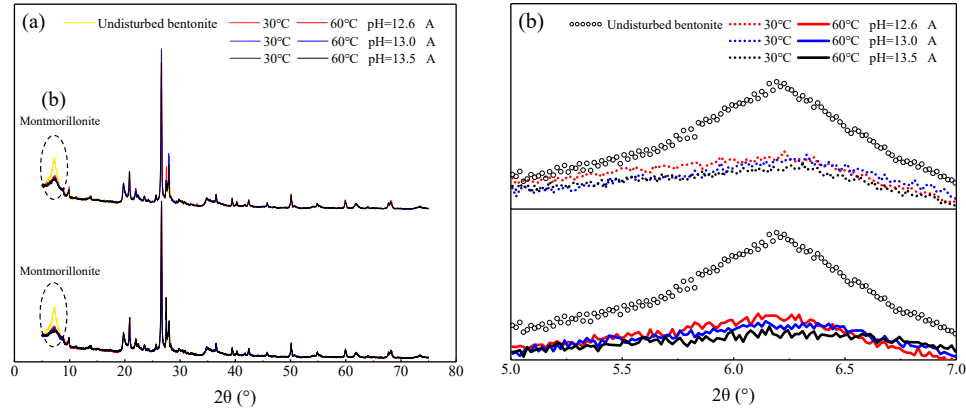


Fig. 4. XRD patterns of bentonite at different temperatures and different pH values.

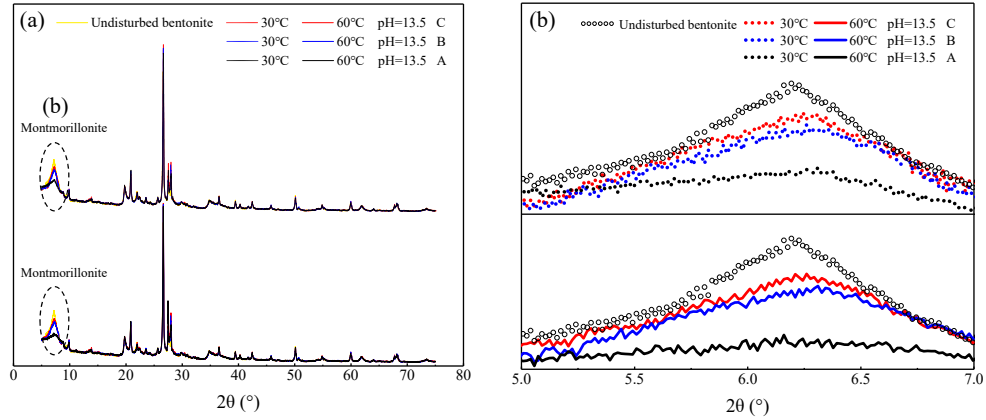


Fig. 5. XRD patterns of bentonite at different temperatures and different diffusion depths.

Table 1. Contact diffusion test conditions and calculated montmorillonite mineral content.

Number	Temperature (°C)	pH	Concentration (M)	Time (day)	Diffusion layer	Montmorillonite content (%)
I	30	12.6	0.04	28	A	29.8
	30	12.6	0.04	28	B	38.9
	30	12.6	0.04	28	C	40.7
	30	13.0	0.10	28	A	29.0
	30	13.0	0.10	28	B	38.2
	30	13.0	0.10	28	C	39.6
	30	13.5	0.30	28	A	28.0
	30	13.5	0.30	28	B	36.7
	30	13.5	0.30	28	C	39.0
II	60	12.6	0.04	28	A	28.9
	60	12.6	0.04	28	B	37.9
	60	12.6	0.04	28	C	39.3
	60	13.0	0.10	28	A	28.5
	60	13.0	0.10	28	B	37.4
	60	13.0	0.10	28	C	38.6
	60	13.5	0.30	28	A	25.9
	60	13.5	0.30	28	B	35.6
	60	13.5	0.30	28	C	37.8

3.2 Microstructure characterizations

(1) Microstructure by SEM

The microstructure of bentonite sub-samples after the contact diffusion test was observed by SU-1500 scanning electron microscope. The photos of the samples under different conditions at a magnification of 2000 times were selected for analysis.

Fig. 6 shows the pictures of bentonite with different diffusion layers at different temperatures, the pH of the KOH solution is 13.5. It can be seen the wing-like colloids produced by the hydration of montmorillonite were basically dissolved in layer A (Wang et al., 2014). The structure of montmorillonite was become more fragmented and scattered, with more fissures and holes, which provides a convenient way for the infiltration of the alkaline solution, and accelerates the reaction between the internal bentonite and the alkaline solution. This is because the bentonite is in an alkaline environment, the exchangeable cations on the clay mineral surface will exchange with potassium ions in the solution, and the montmorillonite mineral will also undergo a dissolution reaction with hydroxide ions (Takase, 2004), that is, the agglomerate structure produced by hydration of montmorillonite mineral becomes broken.

In the middle layer B, the complete agglomerate structure of the montmorillonite mineral was gradually destroyed, but no significant dissolution was found in mineral edge. In the layer C, the sub-sample basically maintains the original mineral form of montmorillonite. It can be concluded that the significant dissolution of montmorillonite minerals in bentonite mainly occurs within 0~2 mm from the contact surface, the result is consistent with the XRD.

(2) Nitrogen adsorption

The pore structure of bentonite was measured by ASAP2020M nitrogen adsorption instrument. The pore diameter distribution of bentonite is relatively concentrated, most in the range of 2~50 nm (Xiang et al., 2016), and nitrogen adsorption is an effective test method.

Table 2 shows the microstructure parameters of bentonite sub-samples under different test conditions. Compare the sub-samples that react with the KOH solution in different pH value, it was found that as the increase of the pH value, the BET surface area of the sub-sample gradually increases, the BJH average pore size gradually decrease. Compare the sub-samples with different diffusion layers, it was found that along the direction of diffusion layer, the BET surface area gradually decreases, and the BJH average pore size increase, it can be concluded that along the direction of the diffusion layer, the reaction between bentonite and alkaline solution is gradually slowing down or even not reacting to diffusion layers B and C. This result is consistent with the SEM result. With the increase of the pH value, the dissolved amount of bentonite is increase, the large aggregate particles of bentonite gradually change into small particles, as a result, the specific surface area of the bentonite is increases, the pore diameter changes from large to small. Compare the sub-samples with different temperatures, the results found as the temperature increases, the BET surface area also increases, the BJH average pore size decreases, illustrates the temperature promotes the reaction between bentonite and alkaline solution (Bauer and Velde, 1999). As a result, the reaction was more complete and the dissolved amount of montmorillonite in bentonite was increases.

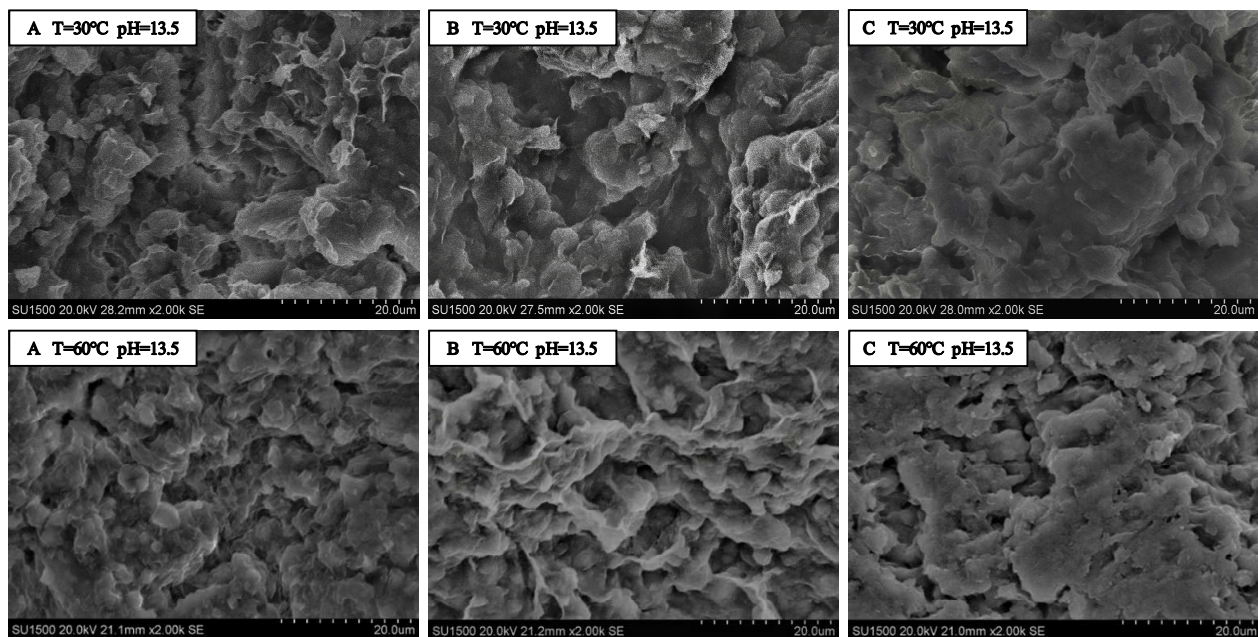


Fig. 6. SEM pictures of bentonite at different temperatures and different diffusion depths.

Table 2. Microstructure parameters of bentonite sub-samples at different states.

The pH value of KOH solution	Temperature (°C)	Time (days)	Time (days)	BET Surface Area (m ² /g)	BJH Average Pore size (nm)
12.6	60	28	28	23.143	8.474
13.0	60	28	28	26.614	8.199
13.5	30	28	28	27.948	8.305
13.5	60	28	28	28.737	8.001
13.5	60	28	28	28.585	8.144
13.5	60	28	28	28.288	8.612

The pore size distribution curve of bentonite sub-sample was calculated by the BJH method (Fig. 7). It can be seen that the pore volume and pore size of each sample are typical bimodal, and the pore size of the bentonite mainly concentrated between 2~5nm and 10~100nm.

With the increase of pH value, the pores of bentonite sub-sample gradually increased, while the volume of pores gradually decreased along the direction of diffusion layer, it was further proved that the alkaline solution had not diffused to the layers B and C.

Figure 7(a) shows the pore size distribution curve of bentonite sub-samples with different pH values, and Fig. 7(b) is the curve at different temperatures. It can be found that with the increase of the pH value of the alkaline solution and the temperature, the volume of the pores in the bentonite sub-sample shows an increasing trend, the pore volume in the range of 10~100nm increases significantly, while the change of pore volume in the range of 2~5nm is not very obvious. This is because the bentonite can fill its own tiny pores through hydration during the saturation process. However, when the alkali solution diffuses into the bentonite, a series of reactions occur between the alkali solution and the montmorillonite mineral in the bentonite, and the wing-like colloid produced by the hydration of the montmorillonite will continue to be dissolved, making its complete structure gradually destroyed (Chen et al., 2012). The higher the pH value of the alkaline solution and the temperature, the more intense the dissolution reaction and the more pores are produced.

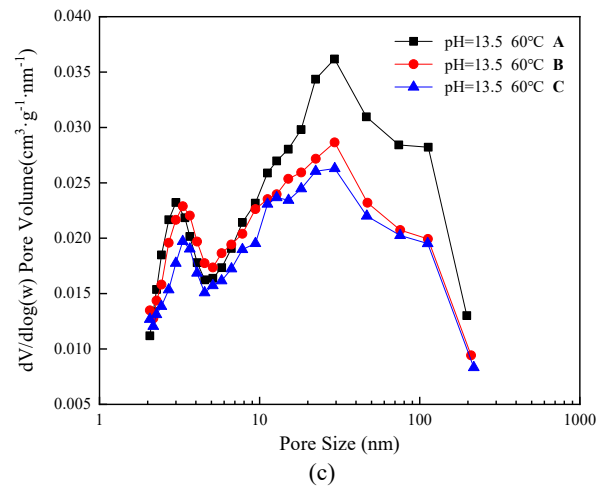
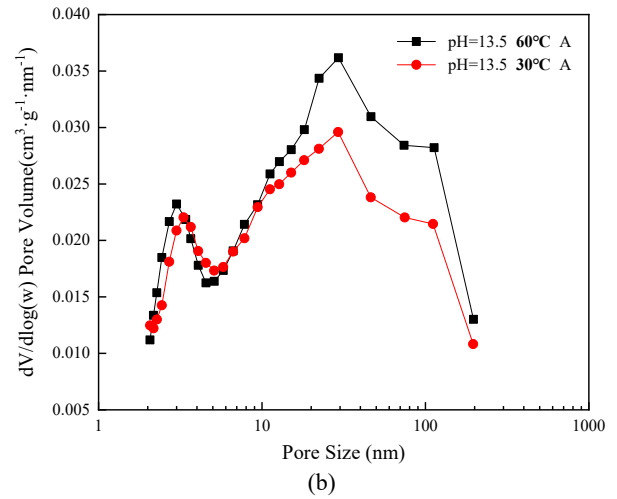
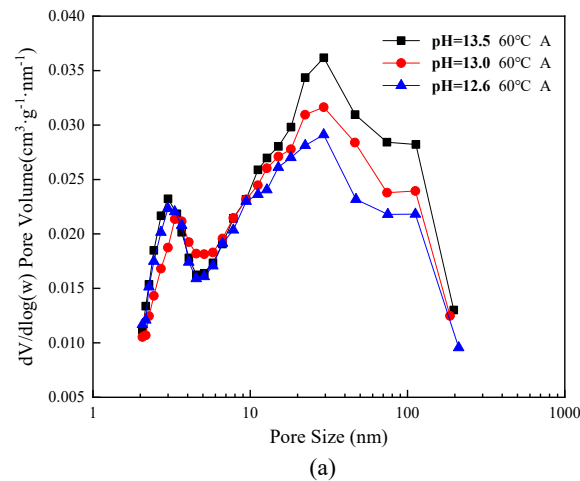


Fig. 7. Curves of pore size distribution of bentonite in different states.

Figure 7(c) is the pore size distribution curve of bentonite sub-samples with different diffusion layers. It can be seen that the volume of pores gradually decreased along the direction of diffusion layer. Layer A is the innermost sub-sample which in direct contact with the alkaline solution, the reaction is the most violent, and the volume of pore generated after the reaction is the most. The results of the layers B and C are similar, which further proves that the diffusion of the alkaline solution has not reached the two layers under the reaction time of 28d.

4 CONCLUSIONS

The contact diffusion experiments of GMZ bentonite and KOH solution was carried out to simulate the in-situ conditions of HLW repository. The result shows that the pH value of the alkaline solution and the temperature are important parameter affects the dissolution of montmorillonite mineral. The content of montmorillonite mineral gradually decreases with the increase of the pH value and the temperature. The montmorillonite dissolves most within 0~2mm of the interface between the bentonite and the alkaline solution, the content of montmorillonite decreased from 44.4% to 25.9%.

The effects on the microstructure features of bentonite were measured by means of both SEM and nitrogen adsorption. It was found that the wing-like gels produced by the hydration of montmorillonite were dissolved apparently, and the aggregate structure of montmorillonite was gradually destroyed, many cracks and holes were generated. With the increase of the pH value of the alkaline solution and the temperature, the BET surface area of bentonite sub-sample increases gradually, the BJH average pore size decreases, the pore volume increases gradually. Along the direction of diffusion layer, the result was opposite. The pore size of the bentonite mainly concentrates between 2~5nm and 10~100nm by the BJH method.

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