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Mineralogical evidence of alkaline corrosion of montmorillonite in GMZ bentonite

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Abstract: During the operation of underground repository of high-level radioactive waste, the highly alkaline solution generated by groundwater corroding lining concrete will diffuse into the bentonite buffer barrier, resulting in the degradation of barrier property. The KOH solution with different pH values was used to simulate the alkaline solution, and a one-year contact diffusion test at room temperature was conducted. Then, X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectrometry (EDS) were performed to investigate the effect of slow diffusion on the mineralogy of bentonite. The XRF test results show that when the pH of KOH solution was greater than 12.6, the content of silicon began to decrease, that is, montmorillonite, quartz, cristobalite and other Si-containing minerals in bentonite were dissolved. At the same time, the content of K increased, indicating that the bentonite had an ion exchange reaction with the alkaline solution, a large amount of K⁺ ions in the solution entered the montmorillonite crystal layer. The XRD test results show that the 001 peak of montmorillonite mineral started to shift to the right at pH=12.6, the peak widths widened, and the peak intensity reduced considerably. When the pH>13, the crystal interlayer space decreased from 1.385 3 nm (13.853 Å) to 1.221 0 nm (12.210 Å), indicating that the crystal layer of montmorillonite was compressed. With the increase of the pH value, the content of minerals such as montmorillonite and quartz decreased significantly, and the contents of illite, clinoptilolite and feldspar minerals increased slightly. The SEM test results show that part of the montmorillonite crystal layer overlapped with the pH of the solution increasing, and then some cracks and holes were generated. As a result, the cracks can accelerate the dissolution of montmorillonite. In the one-year contact diffusion test, the diffusion depth of the KOH solution with pH=13.8 exceeded 7.5 mm, and the newly formed illite crystallites were observed on the contact surface between the alkaline solution and the bentonite. It is confirmed that the strong alkaline solution will cause montmorillonite dissolution and illitization.

Keywords: bentonite; montmorillonite; KOH solution; pH value; diffusion test; corrosion

1 Introduction

The safe disposal of high-level radioactive waste is a major environmental issue related to the sustainable development of the nuclear industry. The deep geological disposal method based on multi-barrier system has been considered as the most safe and reliable method^[1]. The first candidate site for China's high-level waste repository is located in Beishan, Gansu^[2] (see Fig. 1).

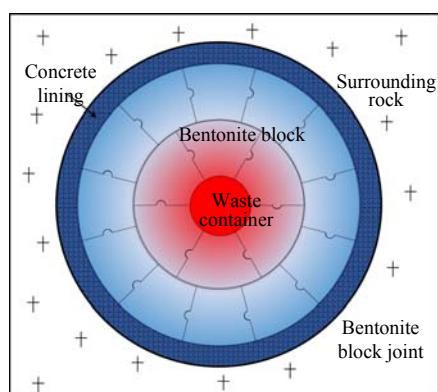


Fig. 1 Conceptual design of high-level buffer barrier in China

The underground laboratory began to construct in June 2021, and was expected to complete and put into use in 2050. As the most important artificial barrier of the repository, the bentonite buffer block is filled between the waste container and the concrete lining in the form of high-density compacted block. Then the radioactive waste is sealed because of bentonite excellent performance, such as high dilatibility, low permeability and strong adsorption.

During the operation of the repository, the lining concrete is corroded under the action of groundwater, the highly alkaline cement hydration products are dissolved continuously, and then diffuse into the bentonite buffer barrier slowly, which affect the performance of bentonite to a certain degree. Previous researches revealed that the pH value of highly alkaline solution released by concrete lining can be as high as 13 under the action of groundwater^[3]. Many scholars have investigated the chemical reaction experimentally as the bentonite contacted with alkaline solution, and it is clear that dissolution and phase change occur in montmorillonite^[4–5], and non-swelling minerals are generated when bentonite contacts with alkaline solution. Higher pH value and test temperature of alkaline solution

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dissolve more montmorillonite, and generate more secondary minerals^[6]. However, the final dissolution rate of montmorillonite minerals is related to the generation rate of secondary minerals. When they are roughly the same, the dissolution reaches a relative equilibrium^[7].

The candidate of buffer backfill material for China's high-level radioactive waste repository is GMZ Na-bentonite. Many scholars have conducted a series of swelling, permeability and erosion tests on compacted GMZ bentonite using NaOH solution with different pH values to simulate cement solution. The results demonstrated that the swelling force of bentonite decreases with the increase of pH value of alkaline solution and test temperature^[8], while the permeability coefficient and porosity increase, and montmorillonite minerals are dissolved^[9–10].

Based on the previous work^[11], KOH solution was used to simulate the alkaline solution produced by the degradation of lining concrete, and a one-year indoor

contact diffusion test was carried out. With the help of X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive spectroscopy (EDS), the changes of mineral composition and microstructure of bentonite were investigated. Additionally, the effects of pH value of alkaline solution and time duration on the dissolution and phase change process of montmorillonite in bentonite were explored. It provides a theoretical basis for the construction of high-level radioactive waste geological repository in China.

2 Materials and methods

2.1 Materials

The material used in this study is GMZ Na-bentonite, whose basic physical properties are shown in Table 1. The main mineral is montmorillonite, with a content of 46.6%, and the associated minerals are quartz, feldspar and cristobalite.

Table 1 Basic properties of GMZ bentonite

Specific gravity	Particle size/mm	Natural water content/%	Plastic limit/%	Liquid limit/%	Plasticity index	Montmorillonite content/%	Cation exchange capacity/(mmol·kg ⁻¹)	Main cations/(mmol·kg ⁻¹)			
								Na ⁺	1/2 Mg ²⁺	K ⁺	1/2 Ca ²⁺
2.70	<0.075	9.56	32	228	196	46.6	555.4	371.7	13.4	32.1	75.8

Previous researches demonstrate that properties of bentonite vary with the pH value of the solution obviously. The pH value of alkaline solution produced by cement degradation can be as high as 12.4–13.5^[4]. In the early stage, K⁺, Na⁺, Ca²⁺ and OH⁻ are the dominant species of the solution, and the content of K⁺ is about twice that of Na⁺^[4]. Subsequently, the pH value of the alkaline solution is controlled by the portlandite which is dissolved from cement, and finally it equilibrates with calcium silicate hydrate (C-S-H) type gel minerals^[12], the pH value ranges from 10 to 12.6. Therefore, KOH solution was selected for contact diffusion test in this study. pH values of alkaline solution were set as 10.0, 12.0, 12.6, 13.0, 13.5 and 13.8, respectively. Deionized water was added as the control group. Table 2 presents the parameters of alkaline solution.

Table 2 The parameter of alkaline solutions

Solution	Concentration C(M)	Designed pH	Measured pH	Redox potential/mV	Electrical conductivity/(mS·cm ⁻¹)
Deionized water	—	7.0	6.78	8	0.006 1
	1×10 ⁻⁴	10.0	8.42	-33	0.014 7
	0.01	12.0	11.97	-299	2.320 0
KOH	0.04	12.6	12.52	-333	8.590 0
	0.10	13.0	12.90	-354	20.840 0
	0.30	13.5	13.32	-380	60.500 0
	0.60	13.8	13.62	-396	116.400 0

2.2 Apparatus and methods

In order to simulate the radial diffusion process of solution in compacted bentonite samples. The reaction device for the contact diffusion test is shown in Fig. 2^[13].

The device is a rigid unit, whose material is 316 stainless steel. It can withstand both high temperature and highly alkaline corrosion; O-ring is placed between the upper and lower parts to ensure good sealing performance. Apart from allowing the solution to pass through, the internal perforated tube plays an important role in supporting the inner wall of the cylindrical bentonite sample and limiting its inward swelling deformation after absorbing water. The top opening is to add alkaline solution into the device, then the alkaline solution can diffuse to the bentonite through the small holes on perforated tube.

Bentonite with 12% water content was prepared by spray mixing method, and it was sealed and maintained for 24 hours to make it uniform. The sample pressing device, complete with the contact diffusion test device, was designed, and it could strictly control the dry density and realize the close fitting between the sample and the inner wall of the device. The GMZ bentonite was prepared into a hollow cylinder with a dry density of 1.80 g/cm³. The height is 30 mm, the inner and external diameters are 15 mm and 30 mm, respectively. A 50 kg jack was used for compaction at a rate of 2 kN/min, and the pressure was maintained for 5 min after the set dry density was reached. The perforated tubes and filter paper were put in the middle of the hollow cylinder sample for preventing the migration and swelling of bentonite particles to the alkaline solution. Then the sample was saturated by vacuum saturation method, the pumping process lasted 3 h, and the negative pressure was kept for 10 h. After saturation, the distilled water in the perforated tube was sucked out, and the prepared alkaline solution

with different pH values was injected. The contact diffusion test was conducted at room temperature (20–25 °C) for one year. During the first 6 months, the alkaline solution was replaced once a month to simulate the continuous dissolution of highly alkaline solution from the lining concrete in the early stage under the action of groundwater, then it was not replaced in the following 6 months to simulate the equilibrium state of the dissolution of cement solution.

After the contact diffusion test, the samples were taken from the bentonite at different diffusion depths after reacting with different pH alkaline solution. And several tests, namely XRD, XRF, SEM and EDS tests, were conducted to measure and analyze the mineral composition and microstructure. Then the impact of different pH alkaline solution on the performance of bentonite was analyzed, and the degradation of bentonite performance was quantitatively analyzed and qualitatively evaluated.

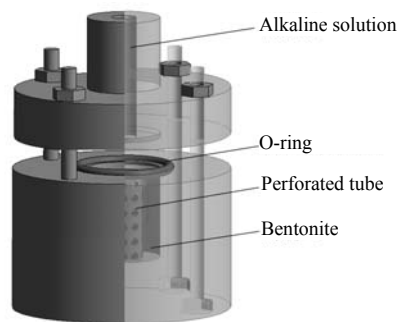


Fig. 2 The device of contact diffusion test

2.2.1 XRF test

The X-ray fluorescence spectrometer consists of an excitation source (X-ray tube) and a detection system. It is a fast, non-destructive material measure method used for elemental analysis and chemical analysis. X-ray fluorescence refers to the secondary X-ray emitted from the sample when it is excited by high-energy X-ray. Specific energy or wave length features of X-ray are produced for different elements. By measuring these X-ray fluorescence, the detection system converts the collected information into element types and contents in the samples. The employed X-ray fluorescence spectrometer with model Magic-2403 is produced by Philips, Netherlands, and the element range from Na to U can be measured.

2.2.2 XRD test

The X-ray diffractometer mainly consist of X-ray generator, goniometer, X-ray detector, and X-ray system control device. The phase composition and structure of the sample can be identified qualitatively by comparing the diffraction pattern of the sample with that of the known crystalline substance, then the quantitative analysis of the sample phase composition can be obtained by analyzing and calculating diffraction intensity of the sample. The employed X-ray diffractometer with model Ultima IV is produced by Rigaku Corporation, Japan. its radiation is Cu-K α , working

voltage is 40 kV, current is 40 mA, and the step size is 0.02°. The scanning process adopts continuous scanning with the temperature of 20 °C. In this study, the diffraction angle 2θ ranges from 3° to 80°, and the test results were analyzed and processed by the software Jade.

2.2.3 SEM-EDS test

Scanning electron microscope consists of electron gun, magnetic lens, scanning coil, and sample chamber. The morphology, composition and crystal structure of the samples are obtained by imaging the secondary electronic signals generated by the interaction of electrons and materials. The energy spectrometer mainly consists of control system, X-ray signal detection system, signal conversion and storage system, data output and display system, which can detect the surface elements of samples and analyze the chemical composition of substance quantitatively. German Zeiss Auriga scanning electron microscope was employed to observe the microstructure of the bentonite sample surface after the contact diffusion test, and energy spectrum was used to analyze the elements on the sample surface. Before the test, FD-2A freeze dryer was used to dehydrate the bentonite sample for minimizing the disturbance of the dehydration process on its microstructure, and then Hitachi E-1010 ion sputtering instrument was used to gild the sample surface.

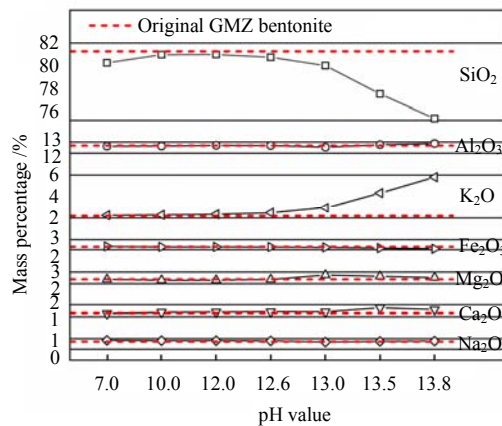
3 Results and analysis

3.1 XRF analysis

Table 3 shows the XRF results of bentonite after one-year contact diffusion test, and the relationship between the chemical composition and the pH value of the solution is showed in Fig. 3. It can be seen that the Si content starts to decrease when the pH value of KOH solution is greater than 12.6, and this trend becomes more intense when the pH of solution is greater than 13, that is, siliceous minerals in bentonite, such as montmorillonite, quartz, cristobalite, have been dissolved^[14]. William et al.^[15] found that the dissolution of montmorillonite minerals increase the Si content in solution, that is, the Si content in soil decreases. Meanwhile, the solubility of quartz or amorphous silicon dioxide increase with the increase of test temperature, pressure and pH value. Fernández et al.^[16] used MX-80 bentonite to react with alkaline solution, and found that the Si content in the solution increases with the test duration. Fig. 4 also illustrates that the content of K, Al, Mg, and Ca increase slightly, and Na and Fe contents remain unchanged. The increase of K in bentonite mainly occurs when pH>12.6, indicating that a large amount of K⁺ in solution intrude the interlayer of montmorillonite. The reason may be that the interlayer charge of montmorillonite decreases due to the dissolution of Si, and K⁺ compensates the deficiency of positive charge in the interlayer position, resulting in a significant ion exchange reaction between bentonite and alkaline solution^[17].

Table 3 Chemical analysis of bentonite samples (weight percentage $w_t\%$)

Solution	Composition /%								Total oxide /%
	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	Fe ₂ O ₃		
Original GMZ bentonite	81.23	12.69	2.36	1.28	0.69	2.19	2.34		102.78
pH=7 Deionized water	80.19	12.63	2.35	1.24	0.81	2.25	2.38		101.85
pH=10.0, KOH	80.93	12.64	2.27	1.36	0.78	2.28	2.33		102.59
pH=12.0, KOH	80.95	12.71	2.28	1.37	0.78	2.34	2.33		102.76
pH=12.6, KOH	80.70	12.69	2.34	1.40	0.77	2.47	2.32		102.69
pH=13.0, KOH	79.94	12.54	2.75	1.39	0.66	2.96	2.29		102.53
pH=13.5, KOH	77.37	12.77	2.63	1.75	0.72	4.35	2.22		101.81
pH=13.8, KOH	75.15	12.88	2.52	1.60	0.75	5.81	2.16		100.87

**Fig. 3** Chemical composition of bentonite after one-year reaction with different pH KOH

3.2 XRD analysis

After the contact diffusion test, the bentonite sample was divided into five layers from the inside out (see Fig. 4), each layer is about 1.5 mm thick. Since some bentonite was squeezed into the perforated tube inevitably, this part was also taken out as the sample in the innermost perforated tube. The samples reacting with different pH solution and at different diffusion depths were selected for XRD test, and the results are shown in Figs. 5 and 6. Table 4 lists the statistical results of 001 peak parameters of montmorillonite.

Figure 5(a) illustrates the XRD results of bentonite samples in the innermost perforated tube after reacting with different pH alkaline solutions for one year. It can be seen that the peak intensity of montmorillonite in bentonite greatly reduces with the gradual increase of pH value, so do its content in general, which is similar with the short-term test results^[11]. At the same time,

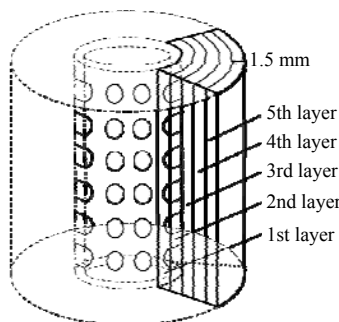
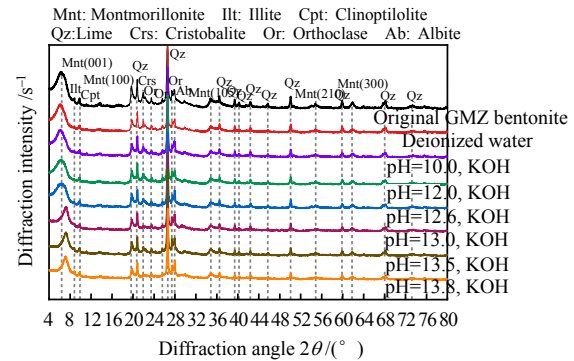
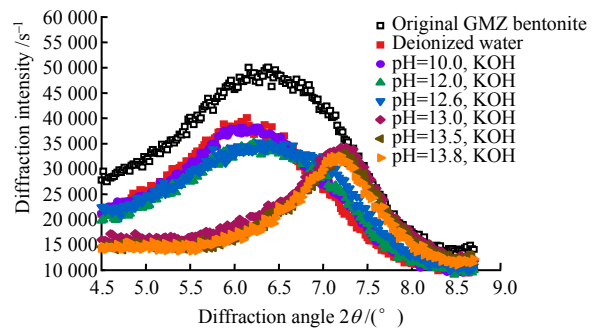
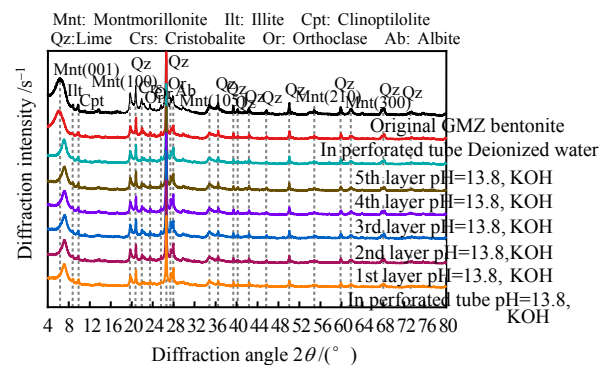
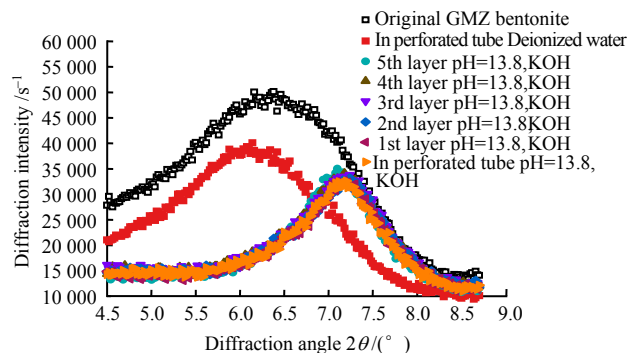
**Fig. 4** Sampling diagram of bentonite at different diffusion depths**(a)** Relationship between XRD diffraction pattern and pH value of bentonite in the perforated tube**(b)** Relationship between XRD diffraction pattern and pH value of montmorillonite in the perforated tube**Fig. 5** XRD patterns of bentonite and montmorillonite at different pH in the perforated tube**(a)** XRD diffraction patterns of bentonite at different diffusion depths**(b)** XRD diffraction patterns of montmorillonite at different diffusion depths**Fig. 6** XRD patterns of bentonite and montmorillonite at different diffusion depths (pH=13.8, KOH)

Table 4 Parameters of the 001 peak of montmorillonite

No.	Solution	pH	Sampling position	2θ /(°)	d /nm	Half peak width /(°)	Intensity	Integral area	Montmorillonite content /%
1	—	—	Original soil	6.38	1.385 3	2.183	50 133	178 639	46.6
2	Deionized water	7.0	In perforated tube	6.14	1.439 4	2.315	40 100	156 234	40.8
3	KOH	10.0	In perforated tube	6.06	1.458 4	2.558	38 167	137 746	38.5
4	KOH	12.0	In perforated tube	6.22	1.420 9	2.753	35 283	126 358	33.0
5	KOH	12.6	In perforated tube	6.28	1.407 4	3.053	35 250	127 346	33.2
6	KOH	13.0	In perforated tube	7.26	1.217 6	1.146	34 300	94 269	24.6
7	KOH	13.5	In perforated tube	7.24	1.221 0	1.077	33 217	83 552	21.8
8	KOH	13.8	In perforated tube	7.20	1.227 7	1.011	32 583	74 396	19.4
9	KOH	13.8	1st layer	7.18	1.231 2	1.031	32 667	75 093	19.6
10	KOH	13.8	2nd layer	7.24	1.225 2	1.077	33 217	76 118	19.9
11	KOH	13.8	3rd layer	7.24	1.226 8	1.058	33 783	76 517	20.0
12	KOH	13.8	4th layer	7.18	1.236 9	1.043	34 167	77 459	20.2
13	KOH	13.8	5th layer	7.10	1.245 0	1.013	35 033	77 864	20.3

the contents of quartz and cristobalite also reduce obviously^[18], which confirms the results of XRF. In addition, the contents of illite and clinoptilolite increase slightly^[19], and so do albite and K-feldspar^[20]. From the patterns of 001 peak of montmorillonite in Fig. 5(b), it can be seen that the height of montmorillonite 001 diffraction peak of the bentonite sample is significantly weakened after reacting with deionized water. The reason is that the bentonite colloidal particles show the migration characteristics in the low ionic strength aqueous solution. At the contact interface between the aqueous solution and bentonite, the montmorillonite continues absorbs water and migrates into the solution in the gel form, resulting in the loss of some montmorillonite and the reduction of its content^[21]. In addition, according to the Bragg equation:

$$2d \sin \theta = n\lambda \quad (1)$$

where d is the crystal plane spacing; θ is the diffraction half angle; n is the diffraction order, $n = 1$; λ is the wavelength of X-ray, and the wavelength of Cu target is 0.154 18 nm (1.541 8 Å).

θ shows a negative correlation with d . After reacting with deionized water, the 001 peak of montmorillonite gradually widens, shifts to the left, and the diffraction angle decreases. The crystal plane spacing increases from 1.385 3 nm (13.853 Å) of the original bentonite sample to 1.439 4 nm (14.394 Å), indicating that the crystallinity of the montmorillonite decreases after water absorption, and the crystal layer swells^[22]. After reacting with KOH solution with pH=10, the 001 peak of montmorillonite is close to that of deionized water with pH=7, indicating that alkaline solution with pH=10 has little effect on montmorillonite. With the increase of pH value, the 001 peak gradually shifts to the right, the diffraction angle increases, and the crystal plane spacing d gradually decreases. When pH=12.6, an obvious right shift trend is observed, and the peak is very wide, and becomes very asymmetric^[23]. When pH>13, the diffraction angle θ shifts to the right in general, and the crystal plane spacing finally drops to 1.221 0 nm (12.210 Å). The montmorillonite crystal layer is compressed, and the dilatibility is reduced, resulting

in the so-called crystal layer collapse^[20].

Figure 6(a) presents the XRD results of bentonite at different diffusion depths after the diffusion reaction with KOH solution with pH=13.8 for one year. It can be seen that the montmorillonite 001 peaks of bentonite samples within the range of five layers from inside out shift to the right and the peaks decrease significantly (see Fig. 6(b)). In other words, the alkaline solution with pH=13.8 has passed through five test layers after one year, the diffusion distance is more than 7.5 mm, and the outermost layer of bentonite has been corroded. Montmorillonite is a clay mineral with a three-layer lamellar structure consisting of two layers of silicon oxide tetrahedron and one layer of aluminum oxide octahedron. It contains water and some exchangeable cations between crystal structural layers, and has high ion exchange capacity. During the diffusion of KOH solution to bentonite, K^+ can enter the crystal layer of montmorillonite since the ion exchange capacity of K^+ is greater than that of Na^+ ^[24], it exchanges with Na^+ on interlayers, and then rapidly diffuses in bentonite.

Since the test is conducted for one year, the sample is not disassembled until the reaction time, so KOH solution may have diffused to the outermost layer in an earlier time, that is, the diffusion depth of alkaline solution is greater than 7.5 mm in one year. This process includes the ion exchange reaction, the dissolution of montmorillonite, the formation of new minerals, and the change of the internal pore structure of bentonite. At the same time, the change of concentration gradient in the diffusion process ultimately affects the diffusion rate of alkaline solution in bentonite.

In order to quantitatively evaluate the relationship between the pH value of alkaline solution and the dissolution of montmorillonite, semi quantitatively analysis was conducted for the XRD results. The montmorillonite content is 46.6% in the natural GMZ bentonite. After the diffusion test, the relative proportion of montmorillonite was calculated according to the ratio of montmorillonite 001 peak integral area of each sample to that of the original bentonite, then 46.6% was multiplied for normalization, and the percentage content of montmorillonite after chemical corrosion

was obtained (see Table 4). Table 4 illustrates that the montmorillonite content in the inner wall of diffusion test decreases sharply with the increase of pH value of alkaline solution, indicating that montmorillonite is dissolved: the montmorillonite content decreases from 46.6% to 19.4% after one year under the corrosion of highly alkaline solution with pH=13.8. In the bentonite outside the perforated tube, the montmorillonite also dissolved obviously, and the dissolution degree was weakened outward in turn.

3.3 SEM-EDS analysis

Figure 7 presents the electron microscope photos of bentonite reacting with deionized water, KOH solution with pH=12.6 and pH=13.8 for one year. We can clearly observe the hydrated bentonite in deionized water (see Fig. 7(a)), swelling of montmorillonite after absorbing water, the lamellar crystal layer structure, and there is no obvious crack. After reacting with KOH solution with pH=12.6 (see Fig. 7(b)), some crystal layers of montmorillonite overlap, resulting in some cracks and holes. And the crystal layer structure of montmorillonite changes significantly after reacting with KOH solution with pH=13.8 (see Fig. 7(c)). The solution with high ionic strength reduces the thickness of its double electric layer^[25–26], the crystal layers of lamellar structure are compressed and overlapped, and the pinnate colloid produced by montmorillonite

hydration is dissolved^[27], resulting in a 10 μm crack. The newly formed fractures can provide a convenient hydraulic channel for further diffusion of alkaline solution and accelerate the infiltration of alkaline solution.

Figure 8 presents the energy spectrum of bentonite sample after reacting with alkaline solution. The sample is divided into three layers by lyophilization, which corresponds to the positions of 1st, 3rd and 5th layers in Fig. 4. The section elements are obtained by surface scanning under 5000 times magnification. Since the atomic numbers of all the elements are less than 32 in bentonite, the data obtained from the K line system are selected as the results of the semi quantitative element analysis. By comparing the samples reacting with the same solution at different diffusion depths, it is found that each element content detected in bentonite gradually increases along the diffusion direction, that is, the dissolution of montmorillonite gradually slows down with the increase of diffusion depth. Compared with the samples reacting with different solutions at the same diffusion depth, the contents of Mg, Al and Si in bentonite gradually decrease with the increase of pH value of the solution^[28], that is, the montmorillonite is dissolved. K increases significantly when pH=13.8, which is consistent with the XRF results.

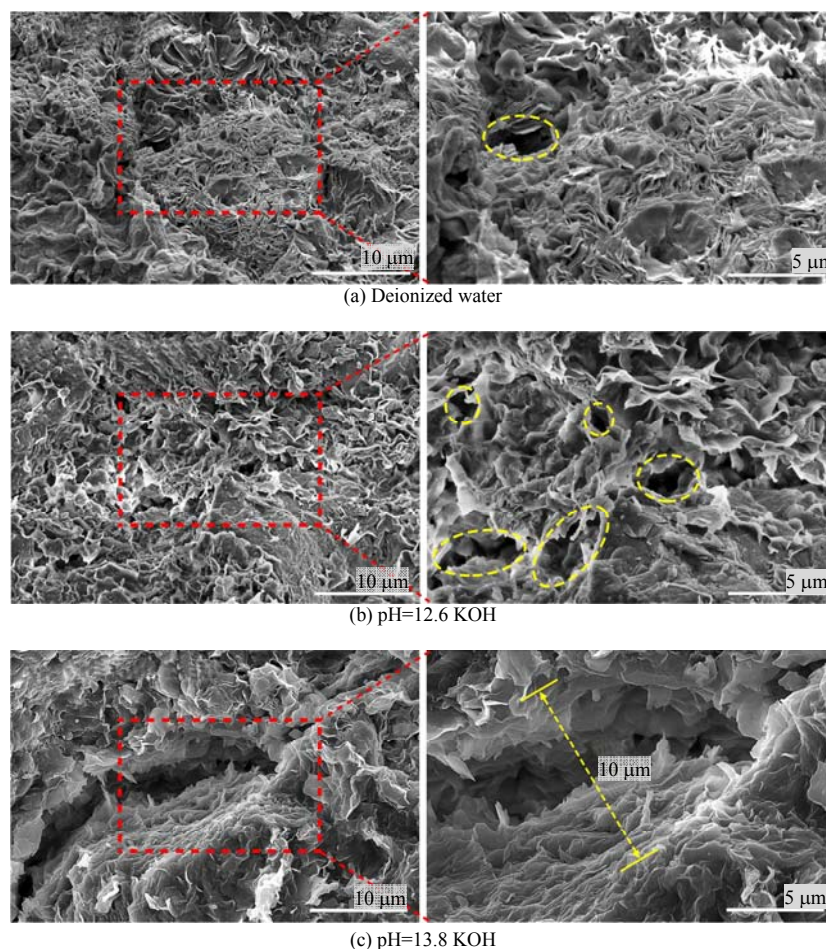


Fig. 7 SEM images of the bentonite samples

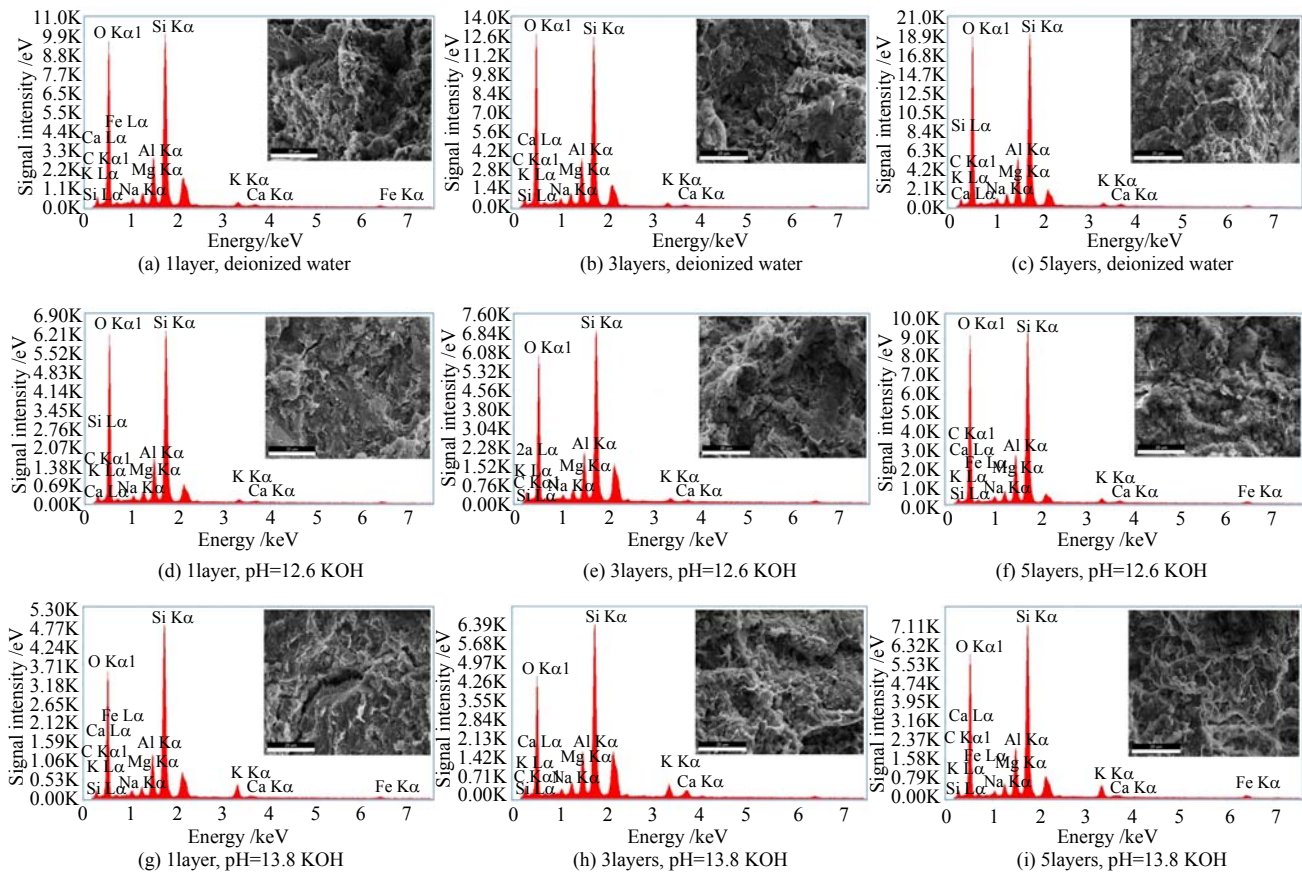


Fig.8 Energy spectra of bentonite samples

4 Alkaline dissolution and mineral phase change of montmorillonite

This study aims at analyzing the mineralogical evidence of chemical corrosion of montmorillonite in GMZ bentonite by the diffusion of highly alkaline solution. The short-term diffusion test results in Zhang et al.^[11] demonstrated that the dissolution rate of montmorillonite is positively related to the pH value of alkaline solution, test temperature and reaction time. After diffusion with KOH solution with pH=13.5 for 28 days, significant dissolution of montmorillonite occurred within 2 mm of the contact zone, and no new minerals were detected. In this study, the reaction duration is one year, more pH ranges are set, and more measured data indicate the weak change of bentonite minerals in low pH condition. When pH>12.6, significant ion exchange occurs in bentonite, and the main mineral components in bentonite, such as montmorillonite, quartz and cristobalite, are dissolved. After reacting for one year with KOH solution of pH=13.8, the diffusion depth in bentonite exceeds 7.5 mm, and the montmorillonite along the distance is dissolved to various degrees. The dissolution depth and degree slow down gradually.

4.1 Alkaline dissolution of montmorillonite

Montmorillonite is mainly eroded by basic igneous rock in alkaline environment, and it is alkalescence. Therefore, it can not be dissolved by low pH alkaline solution. When the pH value of KOH solution is less than 12.6, alkaline solution hardly impacts on bentonite.

The dissolution of montmorillonite is due to the destruction of its Al-O-Si bond by OH⁻, so the dissolution begins to occur as the pH and the concentration of OH⁻ gradually increase^[29].

The determination of montmorillonite dissolution rate is based on the concentration of Si and Al in solution currently. At the same time, the mineral dissolution is related with its structure. The structure of montmorillonite is two layers of silicon oxide tetrahedron sandwiched together with one layer of aluminum oxide octahedron. Under the action of alkaline solution, the silicon oxide tetrahedron first dissolves. Then a large amount of Si are always lost at the initial stage of montmorillonite dissolution^[30], which is consistent with the results of this study. As the content of Si produced by montmorillonite dissolution increases, it limits its further dissolution in turn. Cama et al.^[31] obtained a negative correlation between the dissolution rate of montmorillonite and Si content in solution through a series of tests:

$$\text{Rate} = \left(\frac{3.7 \times 10^{-17}}{C_{\text{Si}}} \right) \quad (2)$$

where Rate is the dissolution rate of montmorillonite; and C_{Si} is the concentration of Si in the solution.

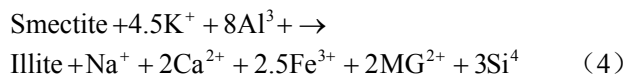
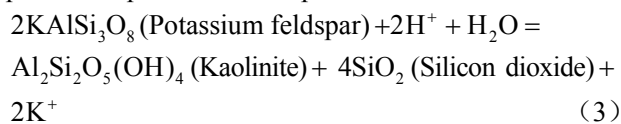
Meanwhile, Kuwahara^[29] found that the dissolution of montmorillonite in alkaline solution was characterized by the gradual disappearance of soil particles edge through microscope, which was related to the layer by layer dissolution of its lamellar structure. At a certain

temperature and pH value conditions, the dissolution rate depends on the surface area of montmorillonite particles. In addition, the dissolution rate of montmorillonite is also subject to a number of external conditions, such as saturation, ionic strength, time, etc.

4.2 Transformation of montmorillonite minerals under alkaline conditions

The change of montmorillonite is usually related to the type of adsorbed cations^[32]. In the meantime, all of the temperature, pressure, chemical composition and content in pore fluid play a decisive role in the mineral transformation. In this study, KOH, highly alkaline solution was used, and K^+ exchanges with bentonite easily and exists in the interlayer of montmorillonite^[18].

The study of montmorillonite illitization shows that the K^+ content is necessary in the illitization process, when the temperature is low, the K^+ content is the main control factor. During the diagenesis of stratum, it is found that the conversion reaction from smectite to illite was achieved by K^+ in the dissolution process of potassium feldspar:



This reaction is a spontaneous reaction with low energy consumption. As long as there is a transformation from smectite to illite, potassium feldspar in the stratum will continue dissolving during burial diagenesis until it is dissolved completely^[33].

At present, many different arguments exist in the mechanism and kinetic process of montmorillonite illitization. Some scholars believe that montmorillonite

dehydrates firstly, and Al^{3+} in octahedron replaces Si^{4+} in tetrahedron, which causes the increase of interlayer negative charge valence, leading to K^+ entering the crystal layer^[34], and then the mixed layer of illite and montmorillonite begin to form until stable illite is formed. In this process, illite inherits the structure of 2:1 clay mineral in the original montmorillonite, and only the chemical compositions are changed between crystal layers, that is, K^+ and Al^{3+} replace Si^{4+} and Na^+ . Other scholars believe that montmorillonite and illite are quasi stable minerals, and montmorillonite is dissolved firstly in the process of the illitization of montmorillonite, and fine illite recrystallizes on the surface of montmorillonite until the formation of illite aggregates. The so-called mixed layer stage of illite and montmorillonite does not exist in this process. The mixed layer of illite and montmorillonite observed on the XRD patterns is actually a very small dioctahedral illite aggregate. Only illite crystalizes to form larger particles, the peak of illite mineral can be displayed on the XRD patterns^[35].

After reacting with KOH solution with pH=13.8 for one year, the scanning electron microscope photos and energy spectrum of the sample are shown in Fig. 9. It can be observed that a lot of irregular small tabular illite crystals are formed in bentonite^[17, 20]. Because XRD can only detect crystals larger than size ranging from 50 to 100 μm , and the signals of smaller crystals can not be detected, the XRD patterns of this research (see Fig. 5) fail to detect significant changes in illite content. Whilst, the small illite microcrystals observed in this study can not explain the specific formation process, while it can be sure that a large amount of Si in bentonite is lost, and K intrudes into the bentonite, which promotes the transformation of montmorillonite to illite.

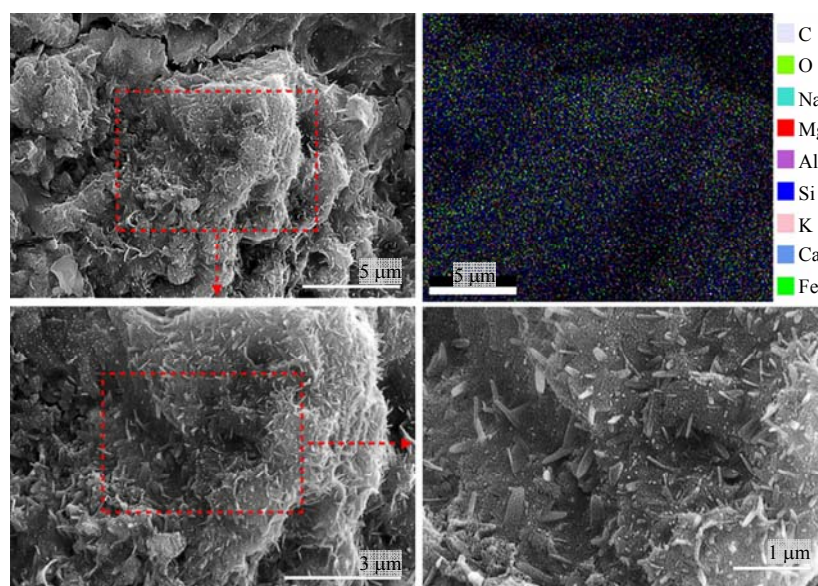


Fig. 9 SEM photos and energy spectrum of bentonite (pH=13.8, KOH)

The real contact reaction between bentonite and concrete should be carried out in the underground

laboratory in the future. However, it can only be investigated through indoor test up to now. The alkaline

corrosion of montmorillonite and the formation of illite microcrystals in GMZ bentonite discovered in this study will limit the normal exertion of bentonite swell potential. For instance, it may hinder the bentonite to fill masonry joints and surrounding rock crack effectively in the underground repository of high-level radioactive waste. This reminds us that we should pay close attention to the degradation of the buffer barrier caused by concrete lining of the repository, and avoid possible problems by developing low alkaline cement with excellent performance, or thickening the bentonite buffer barrier, then the construction scheme of China's high-level radioactive waste underground repository can be optimized.

5 Conclusions

The KOH solution was used to conduct the contact diffusion test of GMZ Na-bentonite at room temperature for one year. The bentonite was sampled layer by layer, and its elements, mineral composition and microstructure were analyzed. The montmorillonite corrosion and illitization trends were observed in GMZ bentonite under highly alkaline conditions, which confirmed that the original excellent swelling potential is at risk of deterioration and degradation. The following conclusions are drawn:

(1) The mineral changes of GMZ bentonite are closely related to the pH value of alkaline solution. PH=12.6 is a key mutation point. The change of bentonite minerals is very weak below this pH value. Once it is exceeded, the content of siliceous minerals, such as montmorillonite, quartz and cristobalite in bentonite decrease significantly with the increase of pH value, while the contents of feldspar minerals, such as albite, K-feldspar, illite and clinoptilolite increase gradually.

(2) When the pH of KOH solution is greater than 12.6, montmorillonite minerals in GMZ bentonite dissolves and exchanges ions with the solution. By stratified sampling, it is found that the diffusion depth of KOH solution with pH=13.8 in bentonite exceeds 7.5 mm within one year, and illite microcrystals are formed at the surface between alkaline solution and bentonite.

(3) The change of microstructure demonstrates that the highly alkaline solution leads to the overlapping of montmorillonite crystal layers in bentonite, the pinnate colloid generated by hydration is dissolved, and the cracks and holes generated accelerate the dissolution of montmorillonite.

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