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Influence of Alteration on Engineering Properties of Bentonite in Highly Alkaline Condition

Influence de modification sur les propriétés de construction mécanique de Bentonite dans la condition extrêmement Alcaline

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ABSTRACT: This study investigated the changes in the shear, permeability, and swelling characteristics of bentonite being altered by exposure to alkaline conditions. The main reactions between the bentonite and alkaline solutions were dissolution and precipitation. The bentonite and bentonite-sand mixture were immersed in alkaline solutions, NaOH and Ca(OH)₂, to make the specimen chemically altered. Triaxial compression tests, permeability tests, and swelling pressure tests were conducted using the specimen. Shear strength and residual stress decreased as materials in the bentonite dissolved. Based on SEM-EDS observation, shear strength supposedly increased upon bonding with the precipitate.

RÉSUMÉ : Cette étude a enquêté sur les changements dans le tondage, la perméabilité et les caractéristiques se gonflant de bentonite être changée par l'exposition aux conditions alcalines. Les réactions principales entre le bentonite et les solutions alcalines étaient la dissolution et la précipitation. Le bentonite et le mélange de bentonite-sable ont été plongés dans les solutions alcalines, NaOH et Ca(OH)₂, pour rendre l'échantillon chimiquement changé. Les épreuves de compression de Triaxial, les épreuves de perméabilité et les épreuves de pression se gonflant ont été conduites en utilisant l'échantillon. La force de tondage et la tension persistante ont diminué comme le matériel dans le bentonite dissous. Basé sur l'observation de SEM-EDS, tondez la force censément augmentée après le fait de vous attacher avec le précipité.

KEYWORDS: Radioactive waste, Bentonite, Alkaline solution, Alteration, Swelling, Shear, Permeability

1 INTRODUCTION

Engineered barriers in radioactive waste disposal facilities are constructed of bentonite and cementitious materials to control nuclide migration. The bentonite is exposed to alkaline solutions generated by leaching of the cementitious materials and is chemically altered by reaction with these solutions (Savage et al., 2007). It is expected that these alterations change the engineering properties of bentonite, such as permeability, swelling, and shear characteristics, over very long time scales.

The hydraulic conductivity of Na-type bentonite increases during alkaline alteration, along with the dissolution of montmorillonite (Yamaguchi et al., 2013; Miyoshi et al., 2011). Mixtures of Na-type bentonite and argillite undergoing alkaline alteration exhibit modified internal friction angles and effective cohesion (Cuisinier et al., 2009). Previous studies have mainly focused on the alkaline alteration of Na-type bentonite. Montmorillonite in bentonites contains various exchangeable cations and these cations strongly influence the swelling behavior of the bentonite due to osmotic pressure. Na-saturated montmorillonite has a higher shear strength than does Ca-saturated montmorillonite (Warkentin and Yong, 1960). Ca/Na ion exchange reactions can occur in highly compacted bentonite based on the Ca/Na selectivity coefficient of the montmorillonite (Karlund et al., 2011).

Consequently, it is important to understand the interactions between cement and bentonite that occur in radioactive disposal facilities, and to investigate how the bentonite is altered by alkaline conditions. The changes in the engineering properties of Ca-type bentonite were investigated in this study in order to evaluate the long-term stability of engineered barriers in radioactive disposal facilities.

2 SAMPLE AND SPECIMEN

Ca-type bentonite sold commercially as Kunibond by Kunimine

Industries Co., Ltd. was used and its physicochemical properties are listed in Table 1. The leachable (exchangeable) cations were determined by leaching the bentonite five times with 1 mol/L-NH₄Cl solution. The dominant leachable ion was Ca²⁺. The montmorillonite content of this bentonite was approximately 84%, as estimated by methylene blue absorption (JBAS 107-91).

The specimens were produced using both the bentonite and bentonite-sand mixtures. The ratio of bentonite to sand was 3 to 7 dry weight. The median diameter of the sand grains was 0.2 mm. Each specimen was 40 mm in height and 20 mm in diameter and were generated by applying a static axial load. The dry densities and effective bentonite densities of the specimens are listed in Table 2. The dry density of the bentonite-sand mixture was calculated from its maximum dry density to be 1.81 Mg/m³. The effective density of the bentonite was set to the same value as that of the bentonite-sand mixture.

3 EXPERIMENTAL PROCEDURE

3.1 Immersion test

A compacted specimen was held in a polyacetal resin container

Table 1. Physico-chemical properties of bentonite.

Water content [%]	14.4	
Particle density of soil [Mg/m ³]	2.68	
Methylene blue absorption [mmol/100g]	117.8	
Amount of leachable cation [meq/100g]	Na ⁺	14.3
	Ca ²⁺	62.0
	K ⁺	2.0
	Mg ²⁺	15.7

stable toward alkali (see Fig. 1(a)). Each specimen was

Table 2. Conditions of specimens.

Specimen No.	¹ Sample	Solution used in immersion test	Immersion period [d]	Initial dry density [Mg/m ³]	Initial effective bentonite density [Mg/m ³]
Na1-1	Bentonite	0.1 mol/L NaOH	279	0.94	0.94
Na1-2			322	0.94	0.94
Na1-3			581	0.94	0.94
Na1-4			² >800	0.94	0.94
Ca1-1		0.005 mol/L Ca(OH) ₂	500	0.94	0.94
Ca1-2			515	0.94	0.94
Ca1-3			711	0.94	0.94
Ca1-4			² >800	0.94	0.94
Na2-1	Bentonite-sand mixture	0.1 mol/L NaOH	225	1.75	0.97
Na2-2			273	1.75	0.97
Na2-3			532	1.75	0.97
Na2-4			² >800	1.75	0.97
Ca2-1		0.005 mol/L Ca(OH) ₂	393	1.75	0.97
Ca2-2			421	1.75	0.97
Ca2-3			645	1.75	0.97
Ca2-4			² >800	1.75	0.97

¹Ca-type bentonite was used in all cases. ²Immersion test is continued.

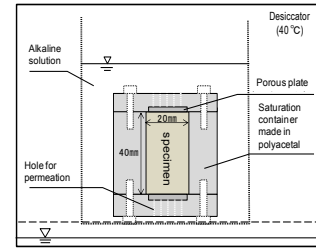
immersed in 300 mL of 0.1 mol/L-NaOH (pH 13.0) or 0.005 mol/L-Ca(OH)₂ (pH 12.5) outer solution at room temperature. After placing the specimens under vacuum to remove air and saturate them with solution, the specimen and the outer solution were put in a desiccator and stored at 40°C. The outer solution was changed every two weeks to keep the solute concentration below the saturation level. The pH of the outer solution was measured using a pH meter with a glass electrode. The concentrations of Na, Ca, Si, and Al in the outer solution were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

3.2 Triaxial compression test

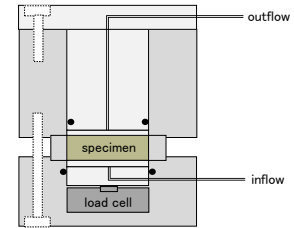
Triaxial compression tests as described in JGS 0523-2009 were conducted on the specimens used in the immersion tests. The specimens were carefully removed from the saturation containers and quickly mounted in the triaxial compression apparatus. The small volume of drainage water generated during consolidation was measured using 5 mL burettes. The membrane was 0.15 mm thick. The porous end metals and tubes were made of stainless steel. The solution obtained from the immersion test was used in the triaxial compression tests to maintain the chemical composition of the liquid phase. The specimen was first confined to a pressure of 100 kPa to prevent volume change by swelling, then a 300 kPa backpressure was applied to increase saturation. A B-value greater than 0.90 was obtained for each experiment. A consolidation stress of 100 to 200 kPa was applied. Un-drained shearing with a rate strain of 0.01%/min was carried out.

3.3 Permeability and swelling pressure test

Changes in permeability and swelling pressure during exposure to alkaline conditions were observed at room temperature by using the apparatus illustrated in Fig. 1(b). The dry density of the bentonite-sand mixture was as shown in Table 2. Each specimen was 10 mm in height and 30 mm in diameter. A load cell was set under the specimen to measure the swelling pressure. The alkaline solutions NaOH and Ca(OH)₂ permeated from the bottom of the specimen. N₂ gas pressure was applied to increase the hydraulic gradient in order to prevent reaction



(a) Saturation container



(b) Permeability and swelling test

Figure 1. Schematic image of experimental apparatus.

between the alkaline solution and CO₃²⁻. Hydraulic conductivity was calculated based on Darcy's law.

3.4 Solid phase analysis

After the triaxial compression tests, the specimens were sectioned into top, middle, and bottom samples and washed five times with 80% alcohol to reduce the pH of the pore water and thus prevent the dissolution of particles during subsequent steps. The washed samples were analyzed by X-ray diffraction to investigate changes in mineral composition. The montmorillonite content of each sectioned sample from the specimens after the triaxial compression tests was estimated using the methylene blue absorption test described in JBAS 107-91. The amount of methylene blue absorbed of pure montmorillonite was 140 mmol/100 g. The composition of the exchangeable cations of montmorillonite was estimated by leaching a sample five times with 1 mol/L-NH₄Cl solution. Changes in the area of the specimens were determined by observation with an electron probe microanalyzer (EPMA) and scanning electron microscope (SEM).

4 RESULTS

4.1 Leaching behavior

The relation between pH or ion concentration of the outer solution and elapsed time is shown in Fig. 2. The pH of the outer solution remained essentially constant throughout the immersion tests. The Na ion concentration of the NaOH solution remained constant because the outer solution was frequently changed whereas the Na ion concentration in the Ca(OH)₂ solution was detected and gradually decreased. The concentration of Si gradually increased in the NaOH solution between 100 and 400 days to a maximum value, then gradually decreased. The concentration of Si slightly decreased in the Ca(OH)₂ solution as well, although the concentration was lower than in the NaOH solution, showing that a higher pH resulted in a higher Si concentration. Leached Al, a constituent of montmorillonite, was not detected during immersion. The bentonite mixture showed same leaching behaviors.

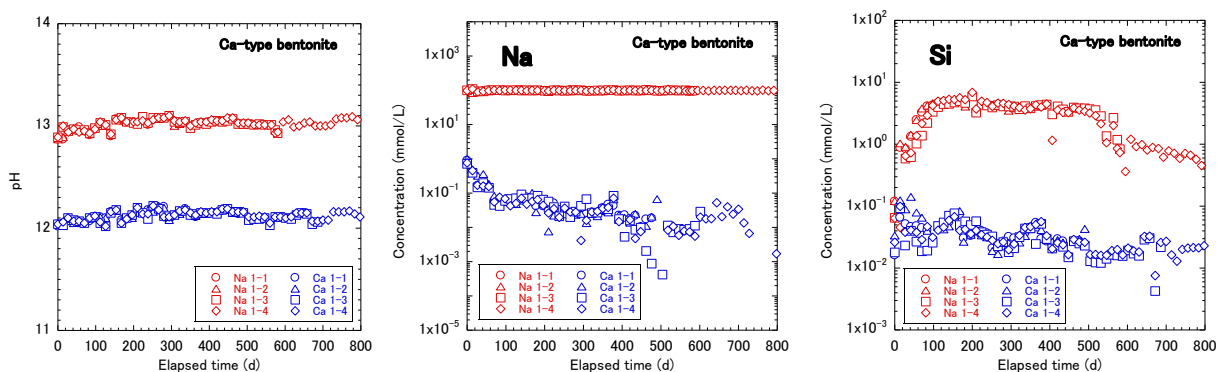


Figure 2. pH and ion concentrations in immersion tests of the bentonite.

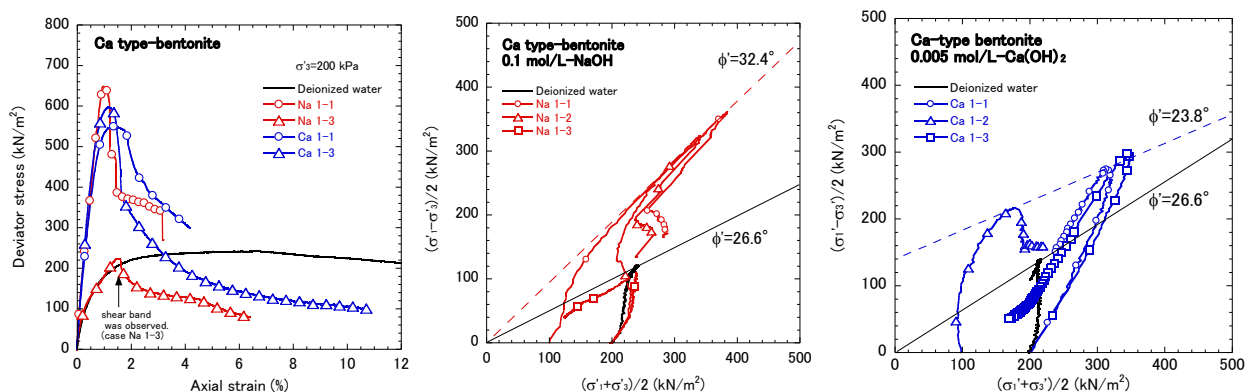


Figure 3. Stress-strain curves and effective stress path of the bentonite.

4.2 Shear characteristics

The obtained stress-strain curves and the effective stress path in the bentonite are presented in Fig. 3. The maximum deviator stress increased after immersion in alkaline solution, except for Na 1-3: in this case, immersion for 581 days in NaOH solution resulted in a shear band at 1.5% of the axial strain, and both the shear strength and residual stress decreased. In contrast, with Ca 1-3, immersion for 711 days in Ca(OH)₂ solution resulted in an increase in the shear strength and a slight decrease in the residual stress. Almost no reduction in shear stress or dry density was observed for the bentonite-sand mixture. Note that a longer immersion period in NaOH solution resulted in higher cumulative Si concentration. The dry density of the bentonite decreased from 0.94 to 0.49 Mg/m³ as the cumulative Si release increased.

The effective stress path shown in Fig. 3 represents the internal friction angle defined by the major and minor principal stresses. The internal friction angles of the bentonite and bentonite-sand mixture before immersion were 26.6° and 28.6°, respectively. For NaOH solution, the internal friction angle in both the bentonite and the bentonite-sand mixture immersed for 273 and 322 days increased to 32.5° and 34.5°, respectively. The internal friction angle decreased to approximately the initial value of the bentonite or the bentonite-sand mixture after immersion for 581 or 532 days, respectively. Remarkably, for Ca(OH)₂ solution, the cohesion intercept was obtained at the maximum deviator stress after alteration.

4.3 Hydraulic conductivity and swelling pressure

As depicted in Fig. 4, the swelling pressure of the bentonite-sand mixture when permeated with deionized water and NaOH solution was 200–300 kPa and 400–460 kPa, respectively.

The hydraulic conductivity gradually decreased, specifically when the hydraulic gradient increased. In steady state, the hydraulic conductivity of the bentonite-sand mixture when permeated with deionized water and NaOH solution was approximately 1×10^{-11} m/s and 2×10^{-12} m/s, respectively. Higher swelling pressure showed lower permeability in this experimental condition.

4.4 Alteration of bentonite

X-ray diffraction patterns of the bentonite immersed in NaOH solution are shown in Fig. 5. The peak due to cristobalite disappeared during immersion and disappeared earlier at the ends of the specimen than at the middle. This tendency was shown in the bentonite mixture as well. The peak due to montmorillonite shifted to a larger angle, meaning that the basal spacing became smaller. Several secondary minerals were not determined by X-ray diffraction following the triaxial compression tests. The methylene blue absorbed was not decreased after the triaxial compression test.

The study on leachable cations clarified Na/Ca ion exchange in these samples. Specifically, in NaOH solution, Ca ion exchanged with Na ion in montmorillonite as depicted in Fig. 6. However, cations exceeding the exchangeable capacity were extracted with NH₄Cl solution after alkaline alteration.

5 DISCUSSION

Solid-phase analysis showed that cristobalite likely dissolved in alkaline solution and that Si leached out in the immersion tests. Therefore, the dissolution of minerals causes the decrease in dry density of the specimen upon exposure to alkaline solutions and causes the reduction in shear strength and residual stress. The addition of sand would prevent the reduction of residual stress when dissolution is dominant.

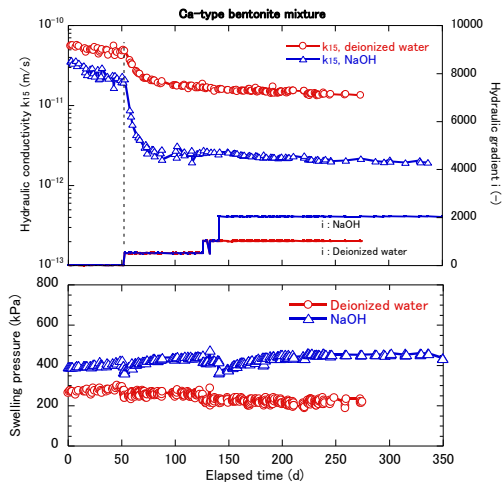


Figure 4. Hydraulic conductivity and swelling pressure when permeated with deionized water and NaOH solution.

In the leachable cations of the bentonite following the triaxial compression test, excessive leaching of Ca ion and Si ion by exposure to NH_4Cl solution suggests the presence of a soluble precipitate stable in alkaline conditions in the specimen. Savage et al. (2007) indicated that secondary minerals such as calcium silicate hydrate are the most likely to form in low temperature cement-bentonite systems. EPMA showed the presence of a Ca-rich precipitate on the edge of the specimen after alteration and a Ca-rich material on the surface of the montmorillonite was observed by SEM-EDS. As depicted in Fig. 7, the bonding effect by this non-crystallized precipitate apparently made the specimen hard.

6 CONCLUSIONS

This study investigated the changes in the shear, permeability, and swelling characteristics of bentonite being altered by exposure to alkaline conditions. The main reactions between the bentonite and alkaline solutions were dissolution and precipitation. Shear strength and residual stress decreased as materials in the bentonite dissolved. Based on SEM-EDS observation, shear strength increased upon bonding with the precipitate. The hydraulic conductivity and swelling pressure remained essentially constant in this experiment. It is important to understand the relation between the alteration and engineering properties of bentonite from both chemical and mechanical perspectives in order to assess its long-term safety for use in radioactive waste disposal facilities.

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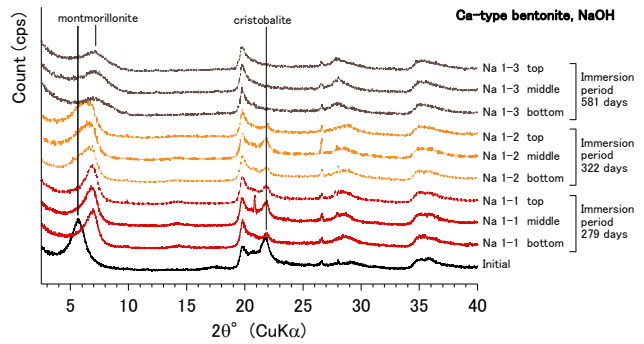


Figure 5. X-ray diffraction patterns of the bentonite.

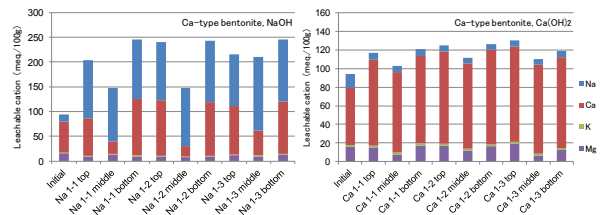


Figure 6. Leachable cation of the bentonite.

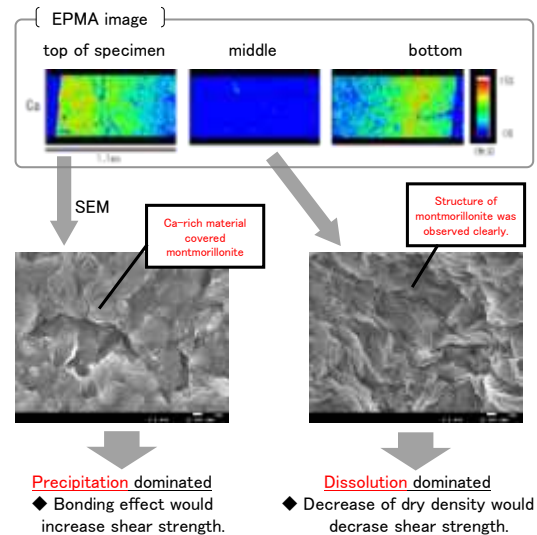


Figure 7. Mechanism of changes in engineering properties by alteration of bentonite.

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