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## Shear characteristics of compacted bentonites immersed in KOH and KOH-NaOH solutions

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## ABSTRACT

This paper elucidates the influence of alkaline solutions on shear characteristics of bentonite and bentonite–sand mixtures. The compacted Ca–bentonite and bentonite–sand mixtures were immersed in 0.1 mol/L–KOH and KOH–NaOH solutions at 40 °C. Triaxial compression tests were executed using the immersed specimens. The mineral composition, montmorillonite content, expansivity of montmorillonite, mean layer charge, and leachable cations of the samples were investigated. The shear characteristics of the compacted bentonite changed after the immersion in alkaline solutions. The reduction of dry density, likely induced by the dissolution of minerals, and the K-exchange of montmorillonite are related to the decrease in shear strength. K-exchanged montmorillonite behaved as a pseudo-non-swelling layer. It is suggested that the precipitation of secondary products, composed of mainly calcium, contributed to the increase in shear strength. The change in the shear characteristics of the compacted bentonite was interpreted as primarily resulting from a combination of dissolution and precipitation.

**Keywords:** bentonite, ion exchange, dissolution, precipitation, triaxial compression

## 1 INTRODUCTION

Owing to its low permeability, compacted bentonite is used as engineered barriers in radioactive waste disposal sites to delay nuclide migration. For low-level radioactive waste disposal in Japan, a cementitious material is formed adjacent to the compacted bentonite (JSCE, 2007; Namioka et al., 2014). The compacted bentonite will continually interact with an alkaline solution derived from leaching of the cementitious materials. The mineralogical alteration of bentonite under alkaline conditions has been well documented (Gaucher and Blanc, 2006; Savage et al., 2007). The mineralogical alteration of bentonites is attributed to the dissolution of its primary minerals and the subsequent precipitation of secondary phases. The permeability of compacted Na-bentonite increases along with the dissolution of montmorillonite in an NaOH solution (Miyoshi et al., 2011; Yamaguchi et al., 2013). The microstructure and mechanical properties, the internal friction angle, and the effective cohesion of the mixture of the Na-bentonite and argillite change as a result of the dissolution and precipitation of minerals in portlandite-saturated water (Cuisinier et al. 2008; 2009). Not only sodium hydroxide but also potassium hydroxide dominates the faster stage in leaching of the cementitious material (Atkinson, 1985). The swelling pressure was attenuated for compacted Na-bentonite infiltrated with K<sup>+</sup> salt/alkaline solutions (He et al., 2019). The reduction of the interlayer spacing of montmorillonite via K<sup>+</sup> exchange could be a significant

factor in the attenuation of the swelling pressure. K<sup>+</sup> is an important factor in the illitization of smectite along with pH and other factors (Eberl et al., 1986). Furthermore, the K<sup>+</sup> fixation in the montmorillonite interlayer could induce the loss of swelling capacity (Kaufhold and Dohrmann, 2010). Hence, the coupled influence of K<sup>+</sup> and high pH on the mechanical behavior of the compacted bentonite is complex.

This study aims to investigate the influence of KOH and KOH-NaOH solutions on the shear characteristics of the compacted bentonite.

## 2 SAMPLE

The sample used in this study included Ca-bentonite (Kunibond, Kunimine Industries Co., Ltd.), mined from Miyagi prefecture in Japan. The physico-chemical properties of the bentonite are listed in Table 1 (Watanabe and Yokoyama, 2016). The amount of cation leached by 1 mol/L-NH<sub>4</sub>Cl solution was used as a value close to the amount of exchangeable cation.

Table 1. Physico-chemical properties of bentonite (Watanabe and Yokoyama, 2016).

Particle density of soil (Mg/m <sup>3</sup> )		2.68
Amount of methylene blue adsorbed (mmol/100g)		117.8
Amount of leachable cation (meq/100 g)	Na <sup>+</sup>	14.3
	Ca <sup>2+</sup>	62.0
	K <sup>+</sup>	2.0
	Mg <sup>2+</sup>	15.7
	Total	94.0

The leachable  $\text{Ca}^{2+}$  was dominant in the bentonite. Assuming that 150.5 mmol/100g of methylene blue (MB) was adsorbed on the pure montmorillonite (Watanabe and Yokoyama, 2020), the montmorillonite content is estimated to be 78.3%. The bentonite was mixed with sand. The mixing ratio of bentonite was 30%.

### 3 EXPERIMENTAL PROCEDURE

#### 3.1 Immersion test

The specimen, covered with a filter with pore size  $0.25 \times 0.075 \mu\text{m}$  to prevent sample loss, was held in a container made of stainless steel, and it was immersed in 300 mL of 0.1 mol/L-KOH or 0.1 mol/L-KOH-NaOH solutions (0.05 mol/L each), i.e., immersion solution. The volume change of specimen was restrained by the container, having porous end pieces at the top and bottom faces of specimen. After vacuuming air for saturation of the specimens to minimize the effect of atmosphere on precipitation, the specimen in the immersion solution was stored at 40 °C. The immersion solution was replaced once every month to prevent chemical equilibrium between the solution and specimen. The pH of the immersion solution was measured using a pH meter with a glass electrode at room temperature. The concentrations of K, Na, Ca, Al, and Si in the immersion solution were determined by the inductively coupled plasma-atomic emission spectrometry technique. The initial conditions of the specimens immersed in the alkaline solutions are listed in Table 2.

Table 2. Initial conditions and immersion period of specimens.

Case	Sample	Solution	Initial dry density ( $\text{Mg/m}^3$ )	Immersion period (days)
KB100-K-32	Ca-bentonite	KOH	0.98	32
KB100-K-223			0.96	223
KB100-K-726			0.97	726
KB30-K-41	Ca-bentonite-sand mixture	KOH	1.75	41
KB30-K-223			1.74	223
KB30-K-700			1.77	700
KB30-K-1043	Ca-bentonite	KOH-NaOH	0.98	1043
KB30-K-737	Ca-bentonite-sand mixture		1.74	737

#### 3.2 Triaxial compression test

Consolidated-undrained triaxial compression tests with reference to JGS 0523-2009 were performed with the specimens used in the immersion tests. The specimen was taken out of the container, and the wet weights and sizes of the specimens were measured to calculate their wet density. The dry density was calculated based on the water content after the triaxial compression test.

A 5 mL capacity burette was used to measure a small volume of drainage in consolidation. The

thickness of a rubber membrane was 0.15 mm. Following the immersion test, the immersion solution was used in the triaxial compression test to maintain constant chemical conditions of the liquid phase. A backpressure of 300 kPa was applied. More than 0.9 of B-value was obtained, and subsequently, the consolidation stress of 200 kPa was applied isotropically. Undrained shearing was performed at a strain rate of 0.01%/min.

#### 3.3 Solid phase analysis

After the triaxial compression test, the specimen was divided into the top, middle, and bottom parts and washed using 80% alcohol to reduce the pH of pore water to prevent the further dissolution of minerals. The washed samples were analyzed via powder X-ray diffraction (XRD) to investigate their mineral compositions. For the oriented samples, a particle fraction, 2–0.2  $\mu\text{m}$  in Stokes' diameter, was collected by centrifugal sedimentation. The illitization of the montmorillonite was analyzed by XRD patterns after the ethylene glycol solvation (Watanabe, 1988) and the Sr-exchange treatment. The mean layer charge (MLC) of the montmorillonite was measured by the treatment of alkylammonium using the method proposed by Olis et al. (1990) and Sato et al. (1996). The leachable cations of the sample were identified after five rounds of leaching with a 1.0 mol/L- $\text{NH}_4\text{Cl}$  solution. The MB adsorbed on the sample was measured by the spot method with reference to JIS Z 2451, where the washed sample was oven-dried at 110 °C before the adsorption.

## 4 RESULTS AND DISCUSSION

### 4.1 Leaching behavior

The pH and concentrations of Na, Ca, Si, and Al in the outer solution during the immersion tests are shown in Fig. 1. The pH was almost constant at approximately 13 during the immersion test.

In the KOH solution, K concentration was temporarily decreased for approximately 40 days and maintained almost constant. Na concentration rapidly increased at the beginning of the test, and afterward gradually decreased. Ca concentration was primarily detected; however, after approximately 100 days, it was below the detection limit. It is supposed that the ion exchange from  $\text{Na}^+$  or  $\text{Ca}^{2+}$  to  $\text{K}^+$  proceeded. Al concentration was less than  $1 \times 10^{-2}$  mmol/L, close to the detection limit during the immersion test. Si concentration gradually increased and reached an upper concentration after 200 days. This indicated that the dissolved minerals were mainly composed of Si, although any mineral composed of Al may have been dissolved slightly.

In the KOH-NaOH solution, K and Na concentrations maintained constant value during the immersion tests. Ca concentration gradually decreased along with the number of exchanging the immersion

solution, although data during 100–600 days was at the detection limit or below. The same concentrations of Al and Si as in the case of KOH solution were obtained. Therefore, there was no influence of the coexistence ion of an initial immersion solution on a leaching behavior of Al and Si resulted from the composite reaction of dissolution and precipitation.

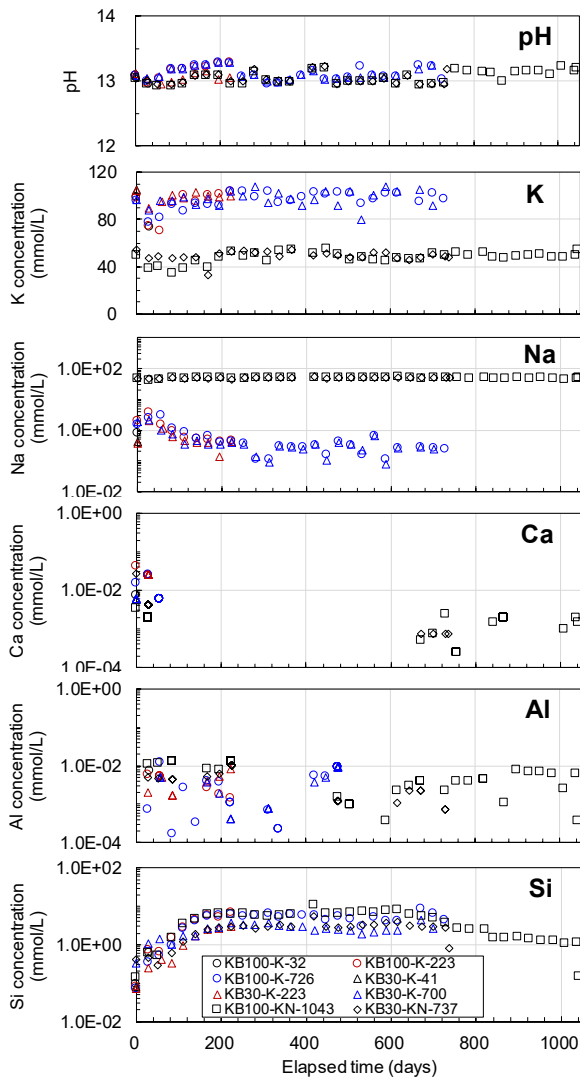
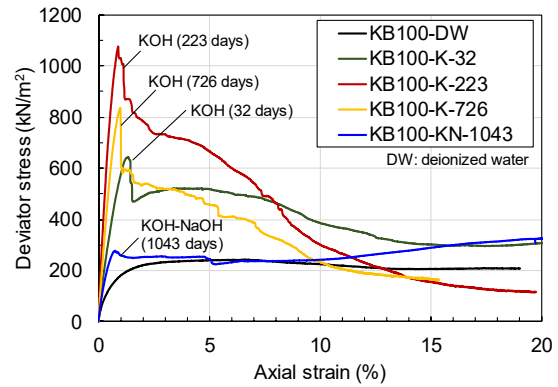


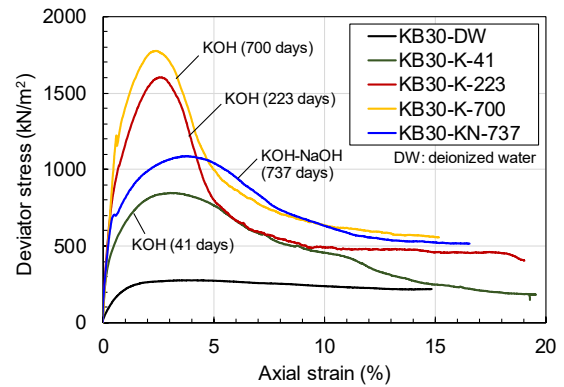
Fig. 1. pH and concentrations of the outer solution in the immersion test.

#### 4.2 Shear characteristics

The relation between the deviator stress and the axial strain is presented in Fig. 2. Following the immersion in alkaline solutions, the maximum deviator stress of the compacted bentonite increased up to 223 days-immersed in the KOH solution, while it dropped at 726 days-immersed. In the KOH-NaOH solution, the maximum deviator stress was further down. Those peaks were measured at an axial strain less than 1.5%. The residual stress of the specimens immersed for 223 and 726 days in the KOH solution was below that of the specimen saturated with deionized water (DW). The



(a) Bentonite content 100%



(b) Bentonite content 30%

Fig. 2. The relation between the deviator stress and the axial strain.

residual stress of the specimen immersed in the NaOH-KOH solution for 1043 days was almost the same or higher than that of the DW-saturated specimen.

In the bentonite-sand mixture, the maximum deviator stress of the compacted bentonite-sand mixture increased up to 700 days-immersed in the KOH solution. Furthermore, the specimen immersed in the KOH-NaOH solution for 737 days exhibited a relatively low peak despite having almost the same residual stress as that mentioned above. Here, the deviator stress of the bentonite-sand mixture slowly decreased after the peak, in contrast with that of the compacted bentonite, whereas the residual stress was almost the same or higher than that of DW-saturated specimen. Mixing sand mitigated a sudden drop in the deviator stress and reduction of residual stress by alkaline solutions.

The water content measured after the triaxial test is shown in Fig. 3. The water content increased along the immersion period. The dry density of specimen calculated based on the water content is presented in Fig. 4. The dry density decreased along with the immersion period. Because the dry density decreased, the water content of the saturated specimen increased. In the bentonite-sand mixture, despite the immersion periods being approximately the same, the dry density of the specimen immersed in the KOH-NaOH solution

was lower than that in the case of the KOH solution. It is presumed that the decrease in shear strength occurred due to the decrease in dry density.

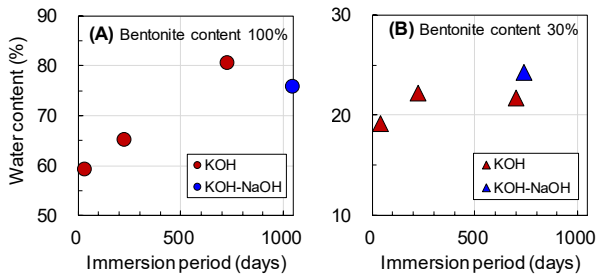


Fig. 3. Water content after the triaxial compression test.

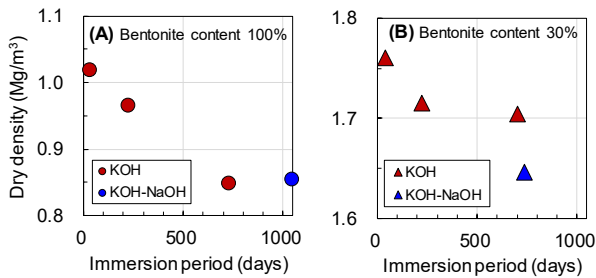


Fig. 4. Dry density of specimens used in triaxial compression tests.

### 4.3 Mineralogical changes

The XRD patterns of the compacted bentonite after the triaxial compression tests are shown in Fig. 5. The initial sample was mainly composed of montmorillonite, quartz, cristobalite, and feldspar. The mineral composition of the samples was unchanged after the immersion in the KOH solution. The 001 peak of montmorillonite shifted to a higher angle. The peaks of montmorillonite and cristobalite declined as the immersion period progressed. Although there is no quantitative analysis, considering Si release in the immersion test, cristobalite might be dissolved. Considering Al release during the immersion test, montmorillonite might be dissolved slightly. As a result of the methylene blue adsorption test, no change in the amount of methylene blue adsorbed was observed. It does not imply that montmorillonite was not dissolved. It is supposed that there was no change in the amount ratio of the montmorillonite to the accessory minerals containing secondary products. The same tendency described above was noticed for the bentonite-sand mixture.

The XRD patterns of the ethylene glycolated montmorillonite are shown in Fig. 6. In the initial sample, the peaks of montmorillonite were clearly detected. After the immersion in the KOH solution, the 002 and 003 peaks became much weaker, and the 001 reflection was asymmetrical with a low angle tail. In the sample of KB100-K-728, the 001 peak slightly shifted to a higher angle. This change in the 001 profile upon ethylene glycol solvation was also observed in the

randomly interstratified illite-montmorillonite (Brindley and Brown, 1980). However, according to the XRD patterns of the ethylene glycolated montmorillonite after the Sr-exchange treatment (Fig. 7), the 002 and 003 peaks were detected despite the longest immersion period. The result indicates that the K-exchange of montmorillonite occurred, rather than illitization. Based on the illite/smectite identification proposed by Watanabe (1988), the non-swelling layer approximately occupied 5–10% in the samples after the Sr-exchange, whereas 0–5% in the initial sample. Therefore, in the present study, the basal spacing of montmorillonite randomly collapsed because of the ion exchange with  $K^+$ , and it behaved as a pseudo-non-swelling layer.

MLC of the montmorillonite is shown in Fig. 8. Initially, MLC of the montmorillonite was 0.33–0.34. After the immersion in alkaline solutions, MLC was in the range of 0.30–0.34, and there was no systematic changing trend of MLC subjected to the immersion period. As there was no increase in the layer charge, no illitization occurred in those samples.

The amount of leachable cations of each part of the specimen after the triaxial compression test is shown in Fig. 9. After the immersion in alkaline solutions, the total amount of leachable cations increased, except for the middle part of KB100-K-32. In this sample, the leachable  $K^+$  relatively increased in the case of the same total amount of leachable cation as the initial sample, as the ion exchange from  $Na^+/Ca^{2+}/Mg^{2+}$  to  $K^+$  proceeded. It is suggested that the amount of leachable  $K^+$  increased due to K-exchange across all samples. Meanwhile, the amount of leachable  $Ca^{2+}$  was large in many samples, specifically in the upper and bottom of the specimen. Each side of the specimen had direct contact with an alkaline solution, and higher pH was maintained. It is indicated that the secondary product containing mainly Ca, which is stable in high pH, dissolved in the  $NH_4Cl$  solution. Considering that XRD diffraction could not detect new products, it might be the amorphous phase.

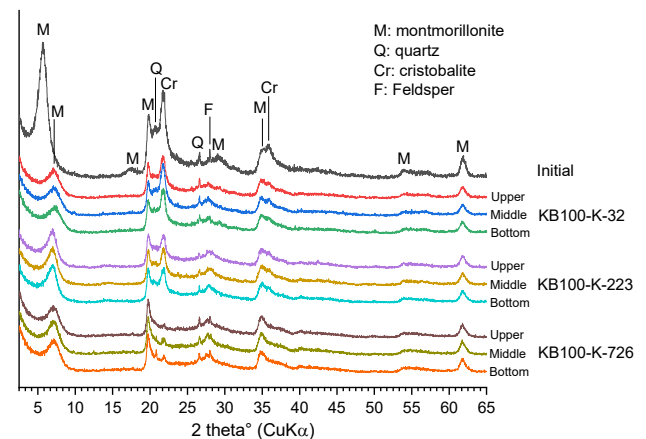


Fig. 5. XRD patterns of each part of the compact bentonites.

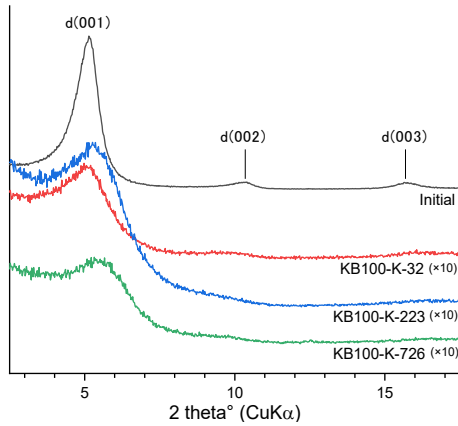


Fig. 6. XRD patterns of the ethylene glycolated montmorillonite.

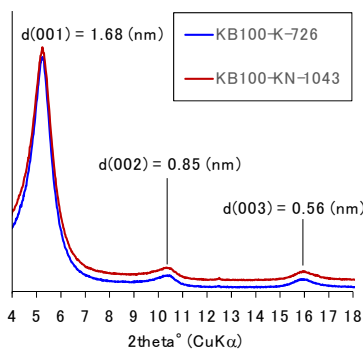


Fig. 7. XRD patterns of the ethylene glycolated montmorillonite after Sr-exchange treatment.

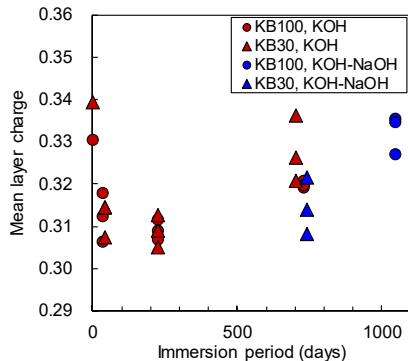


Fig. 8. Mean layer charge of the elutriation samples.

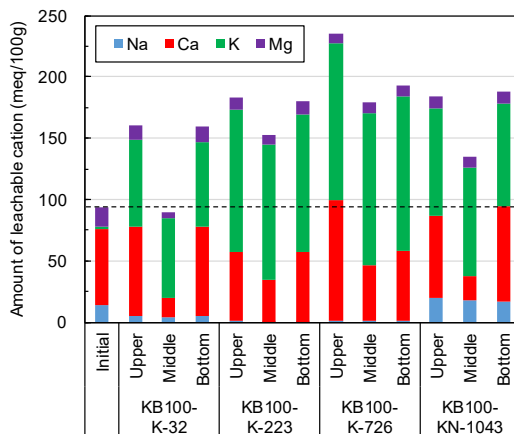


Fig. 9. Amount of leachable cation of each part of the compacted bentonites.

#### 4.4 Influence of alteration on shear characteristics

According to the results of the solid-phase analysis, the dissolution of minerals, mainly cristobalite, contributed to the reduction of dry density. As a result of composite reaction of dissolution and precipitation, there was no remarked difference in a Si leaching behavior between in KOH and KOH-NaOH solutions. In this experiment, there was no influence of K-Na composite on the leaching behavior; meanwhile, it was effective on the ion-exchange of montmorillonite. According to XRD analysis, K-exchanged montmorillonite also contributed to the reduction of a swelling property. Watanabe and Yokoyama (2018) reported that the swelling pressure of the compacted Ca-bentonite-sand mixture decreases after the permeation of the KCl solution if it subsequently changes the solution to deionized water. Therefore, it is assumed that the decrease in the shear strength was induced by those mineralogical changes.

Furthermore, the measurement of leachable cations demonstrated a possibility of forming the secondary product containing Ca. Savage et al. (2007) indicated that secondary minerals such as calcium silicate hydrate (CSH) are the most likely to form in low-temperature cement-bentonite systems. Cuisinier et al. (2009) reported that the dissolved chemical elements that combined with calcium takes part in the secondary formation of CSH and calcium carbonates. Thus, in the present study, it is assumed that the precipitation of secondary products composed of mainly Ca acts as a bond between soil particles, and accordingly, the increase in strength occurs. Watanabe and Yokoyama (2016) reported the increase and decrease in shear strength of compacted Ca-bentonites immersed in the NaOH solution. Except for the K-exchange of montmorillonite, the influence of dissolution and precipitation on the mechanical behavior was qualitatively similar to that in the present study. Those chemical reactions in the compacted bentonite proceed in parallel. Therefore, the change in shear characteristics of the compacted bentonite was observed as a result of a combination of dissolution and precipitation.

## 5 CONCLUSION

This study investigated the influence of KOH and KOH-NaOH solutions on the shear characteristics of compacted Ca-bentonite. The shear characteristics of the compacted bentonite considerably changed after the immersion in alkaline solutions. This was likely induced by both the dissolution of minerals, mainly cristobalite, and the precipitation of secondary products. Although differences of the leaching behavior between KOH and KOH-NaOH solutions were not observed, the release of Ca and other elements to pore water through ion-exchange to the  $K^+$  of montmorillonite likely formed the secondary products. The interaction of the



compacted bentonite with KOH or KOH-NaOH solutions was partially similar to that observed in a previous study using a NaOH solution. As the pseudo-non-swelling layer increases owing to the K-exchange of montmorillonite, it is noted that the mechanical behavior, which related to the swelling potential, might change when the pore water chemistry is changed as the experiment performed by Watanabe and Yokoyama (2018).

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