Geomechanics and Engineering, *Vol. 22, No. 4 (2020) 329-337*
DOI: https://doi.org/10.12989/gae.2020.22.4.329

Compressibility and hydraulic conductivity of calcium bentonite treated with pH-responsive polymer

Hyunwook Choo[1a], Youngmin Choi[2b], Young-Uk Kim[3c], Woojin Lee[4d] and Changho Lee*[5]

[1]Department of Civil Engineering, Kyung Hee University, Yongin, South Korea 17104
[2]SK Engineering & Construction Co., Ltd., Seoul, South Korea
[3]Department of Civil and Environmental Engineering, Myongji University, Yongin, South Korea 17058
[4]School of Civil, Environmental, and Architectural Engineering, Korea University, Seoul, South Korea 02841
[5]Department of Civil Engineering, Chonnam National University, Gwangju, South Korea 61186

(Received August 16, 2019, Revised July 9, 2020, Accepted July 16, 2020)

Abstract. Polyacrylamide (PAM) possesses high water absorption capacity and a unique pH-dependent behavior that confer large potential to enhance the engineering performance of clays. In this study, calcium bentonite was treated with a nonionic PAM. Flexible-wall permeability test and the consolidation test were performed at different pH values to evaluate the effects of PAM treatment on the hydraulic and consolidation properties. Test results demonstrate that index properties are affected by the adsorbed PAM on clay surface: a decrease in specific gravity, a decrease in net zeta potential, and an increase in liquid limit are observed due to the PAM treatment. At a given pH, the compressibility of the treated clay is greater than that of the untreated clay. However, the compression indices of untreated and treated clays can be expressed as a single function of the initial void ratio, regardless of pH. Hydraulic conductivity is reduced by PAM treatment about 5 times at both neutral and alkaline pH conditions under similar void ratios, because of the reduction in size of the water flow channel by PAM expansion. However, at acidic pH, the hydraulic conductivity of the treated clay is slightly higher than the untreated clay. This reflects that the treated bentonite with PAM can be beneficially used in barrier system for highly alkaline residues.

Keywords: polyacrylamide; calcium bentonite; hydraulic conductivity; compression index

1. Introduction

The common type of natural bentonite in the world is a calcium bentonite (i.e., smectite clay with calcium as the predominant exchangeable cation) (Egloffstein 2001, Murray 2002). While the sodium bentonite, which is smectite clay with sodium as the predominant exchangeable cation, has been beneficially used in various engineering areas, including as a hydraulic barrier system, slurry trenches, and pile installations, due to its very low hydraulic conductivity, the use of calcium bentonite is relatively limited comparing with the sodium bentonite. Note that the hydraulic conductivity (K) of clay is mainly governed by the size and tortuosity of water flow channels in the porous media (Choo *et al.* 2018, Jang *et al.* 2011, Mesri and Olson 1971): the double layer thickness of calcium bentonite is generally smaller than that of sodium bentonite (Mitchell and Soga 2005, Terzaghi *et al.* 1996); and the microstructure of calcium bentonite is a coarse dispersed structure, due to face to face particle aggregation by calcium ion (Ece *et al.* 1999, Egloffstein 2001). Therefore, calcium bentonite shows a higher K than sodium bentonite.

Since polymers have high applicability, the works of polymer enhanced soil properties are of growing interest in the geotechnical engineering (Arasan *et al.* 2016, Arasan and Nasirpur 2015, Choo *et al.* 2020, Kolay *et al.* 2016, Kwon *et al.* 2019, Scalia IV and Benson 2016, Tian *et al.* 2019). In various types of polymers, the polyacrylamide (PAM) possesses high flocculation ability and high water absorbency; therefore, it has been usefully applied in various fields, such as wastewater treatment (Bolto 1995), agriculture (Barvenik 1994), and soil erosion control (Green *et al.* 2004) as well as PAM may be useful to prevent fines migration by changing the surface charge of clay (Zheng *et al.* 2018). Recently, sodium bentonite treated with PAM was studied to use the amended bentonite (or the bentonite-PAM composite) in the geotechnical engineering fields (Bishop *et al.* 2014, Kim and Palomino 2011, Kim *et al.* 2012). Because PAM is a pH-responsive polymer, these previous studies demonstrated that 1) due to the expandable nature of the PAM at alkaline medium (pH > 9), the bentonite-PAM composite could have lower K than untreated bentonite; 2) at relatively acidic medium (pH < 6), the observed K of the composite was higher than that of untreated bentonite; and 3) the bentonite-PAM composite showed higher compression and swelling indices than untreated bentonite.

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*Corresponding author, Associate Professor
E-mail: changho@jnu.ac.kr
[a]Assistant Professor
E-mail: choohw@khu.ac.kr
[b]Junior Manager, Infra Engineering Team
E-mail: choiym@sk.com
[c]Professor
E-mail: yukim@mju.ac.kr
[d]Professor
E-mail: woojin@korea.ac.kr

http://www.techno-press.org/?journal=gae&subpage=7
ISSN: 2005-307X (Print), 2092-6219 (Online)

Table 1 Chemical composition of the calcium bentonite

Component	SiO_2	Al_2O_3	Fe_2O_3 [a]	CaO	K_2O	MgO	Na_2O	TiO_2	MnO	P_2O_5	LOI [b]
Weight %	65.06	15.43	3.94	2.33	2.06	1.28	1.24	0.52	0.11	0.09	6.77

[a]: Fe_2O_3 = total Fe; [b]: Loss on ignition

Table 2 Index properties of the tested clays

Sample	G_s	LL (%)	PL (%)	S_a (m^2/g)	pH	CEC (cmol/kg)	USCS
Untreated	2.51	86.76	35.83	260.56	8.48	89.65	CH
Treated	2.47	121.53	38.10	263.62	8.46	89.21	CH

Note: G_s = specific gravity; LL = liquid limit; PL = plastic limit; S_a = specific surface; CEC = cation exchange capacity; USCS = unified soil classification system; pH = values at a solid content of 2%

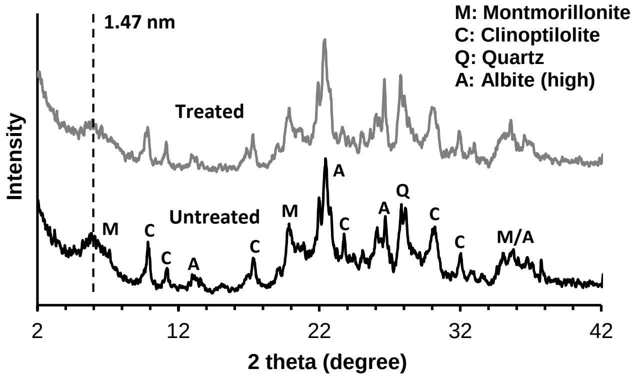


Fig. 1 X-ray diffraction (XRD) patterns of untreated and treated clays

Note that these previous studies are based only on sodium bentonite. Furthermore, the compressibility and hydraulic conductivity results of previous studies on bentonite treated with PAM were obtained under limited experimental conditions: the maximum applied vertical stress was 87 kPa; and the effect of the void ratio, which is the important parameter in determining the compressibility and hydraulic conductivity, was not considered in the analysis of the results.

In order to systematically characterize the effects of PAM treatment on the compressibility and hydraulic conductivity of the calcium bentonite, the calcium bentonite surface was first treated with a nonionic PAM in this study. The flexible-wall permeability test was conducted at three different pH values of 1.84, 6.62, and 12.65 and at varying void ratios ranging from 1.63 to 3.08. In addition, the consolidation test with vertical effective stress ranging from 5 kPa to 640 kPa were conducted at varying pH (pH = 1.84, 6.62, and 12.65) and at initial void ratio values ranging from 1.53 to 4.18. The zeta potential of both untreated and treated clays was also measured in this study to explore the effect of PAM treatment on the electrical charge of bentonite.

2. Materials and methods

2.1 Materials

2.1.1 Bentonite

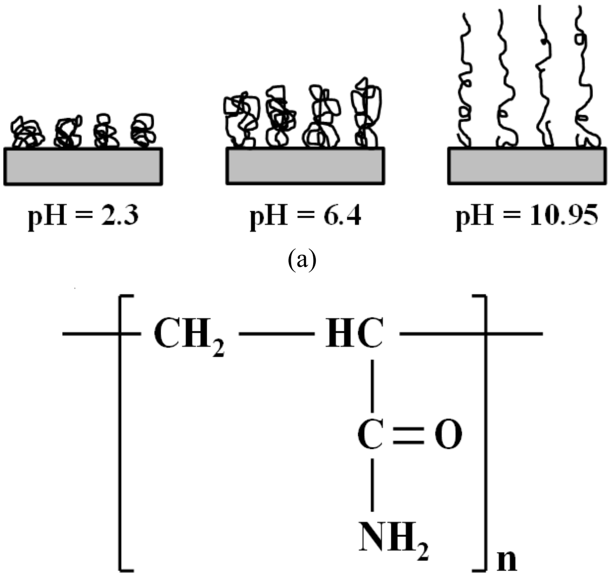
A calcium bentonite produced by Donghae Chemicals Industrial, South Korea was used as the base material in this study. The clay was sieved through a No. 200 sieve to minimize large-sized impurities. Fig. 1 shows the mineralogy of the bentonite measured using X-ray diffractometry (Philips, X'Pert MPD), and reveals that the main clay mineral is montmorillonite. Table 1 shows the chemical composition of the bentonite that was measured using X-ray fluorescence (XRF) spectrometry (Philips, PW2404). Since the Na^+ / Ca^{2+} ratio (= 0.53) was smaller than 1, the bentonite used in this study reveals a calcium bentonite. The specific gravity (G_s) was measured as 2.51 (ASTM-D854) (Table 2). The plastic limit (PL) was determined to be 35.83% according to the traditional thread-rolling method (ASTM-D4318), and the liquid limit (LL) was determined to be 86.76% according to the fall cone method (BS-1377). Therefore, in accordance with the Unified Soil Classification System (ASTM-D2487), the calcium bentonite used in this study can be classified as a clay with high plasticity (CH). The specific surface area (S_a) was determined by the methylene blue spot test to be 260.56 m^2/g (Santamarina *et al.* 2002), and the natural pH value at 2% solid content was 8.48. The cation exchange capacity (CEC) was measured according to the ammonium acetate method to be 89.65 meq/100g (Chapman 1965).

2.1.2 Polyacrylamide (PAM)

A nonionic PAM (Yangfloc N-100P, OCI-SNF) was used in this study to synthesize the treated calcium bentonite, or the calcium bentonite-PAM composite. Fig. 2(a) shows that at a low pH, the nonionic PAM contracts; while at a high pH, it extends. These conformational states of the PAM could assign pH-dependent engineering properties of the clay-PAM composite. The molecular weight and charge density of the PAM used in this study were 8.5 × 10^6 g/mol and -0.56 ~ -1.23 meq/100g (data from the manufacturer), respectively. Fig. 2(b) shows the chemical structure of nonionic PAM. The carbonyl oxygen (–C=O) of PAM molecules can form hydrogen bonds between PAM and the clay surface. Additionally, the ion-dipole interactions can occur between the polar group (–NH_2) of PAM molecules and the interlayer cations of clay (Kang *et al.* 2018, Ruiz-Hitzky and van Meerbeek 2006). Therefore, the PAM can adsorb onto the mineral surface of the bentonite.

2.2 Bentonite-PAM composite

The treated clay with the PAM was synthesized through the solution intercalation technique according to the method suggested by Besra *et al.* (2004) and Kim and Palomino



(a)

(b)

Fig. 2 Nonionic polyacrylamide (PAM): (a) schematic illustration of the conformational state of adsorbed PAM at different pH values (after Besra *et al.* 2004) and (b) chemical structure of PAM (after Barvenik 1994)

(2011). First, 300 g of the dried clay was mechanically blended with 6 L of deionized water for 24 hours to ensure complete dispersion. Next, 1 L of the nonionic PAM solution was poured into the slurry. The concentration of PAM in the slurry was 1.88 g/L (= 131.6 mg of the PAM for 100 g of the clay). Note that the concentration of 1.88 g/L was chosen because the swell index of the PAM treated clay, determined according to ASTM-D5890, reached the maximum value (≈ 7.4 mL/2g) at the concentration of 1.88 g/L (data not shown). After continuous stirring for 24 hours, the slurry was allowed to settle for 1 hour. The supernatant liquid was drained out, and then the slurry was dried in an oven at 110 °C. Before performing all experiments, the dried clay-PAM composite was ground with a mortar and pestle, and the ground soil was sieved with a No. 200 sieve. Table 2 shows the index properties of the treated bentonite. The specific gravity (G_s) of the PAM treated clay was 2.47, which is slightly smaller than that of the untreated clay, due to the low G_s of the PAM (i.e., G_s of the acrylamide = 1.12). The PL and LL of the treated clay were 38.10% and 121.53%, respectively. The specific surface area (S_a), cation exchange capacity (CEC), and pH of the treated clay were similar to those of the untreated clay. Fig. 1 shows that the XRD pattern of the treated clay is similar to the XRD pattern of the untreated clay. Since the clay intercalated with PAM shows a larger basal spacing than the untreated clay (Kim and Palomino 2011, Ray and Okamoto 2003), no clear change in the basal spacing of treated clay (d_{001} value ≈ 1.47 nm) implies that the PAM molecules might be adsorbed onto the external clay surface.

2.3 Preparation of testing specimen

The testing specimens for both consolidation and flexible wall permeability tests were prepared by using a specially designed small centrifuge facility (Kim *et al.* 2004). The centrifuge has 2 arms of 100 cm long. Two cylinders containing clay slurry were symmetrically connected to the arms. Note that consolidation and flexible wall permeability tests were conducted at three different pH values (i.e., pH = 1.84, 6.62, and 12.65), because the bentonite-PAM composite shows pH-dependent behavior, due to the change in the conformation of the PAM (Fig. 2(a)). Therefore, pore fluids with three different pH values (i.e., pH = 1.84, 6.62, and 12.65), which were controlled by HNO_3 and NaOH, were used to prepare the slurry specimen, and the initial water content of the slurry was 2 times the liquid limit, to ensure homogeneous and fully saturated specimens. The clay slurry was consolidated by a centrifugal force, and the centrifugal force acting on the center of specimen (F) can be calculated as:

$$F = \frac{W}{g} \cdot \omega^2 \cdot r \tag{1}$$

where W = sum of the half weight of the specimen and an external weight applied on the top of the specimen; g = gravitational acceleration; ω = angular velocity; and r = distance between the center of the centrifuge facility and the middle of the specimen. The F in Eq. (1) was controlled to have the preconsolidation stress of approximately 50 kPa.

2.4 Experimental methods

2.4.1 Measurement of Zeta potential

To explore the effect of PAM treatment on the surface charge of the bentonite, the zeta potentials of both untreated and treated clays were measured by a zeta potential analyzer (Otsuka Electronics, ELSZ-1000) with a standard cell (flow cell). 0.6 g of soil was dispersed in 1 L of 0.01 M NaCl solution, and then rested for 24 hours. After the rest time, pH of the dispersion was adjusted from pH 2.8 to 11.8 by using HNO_3 or NaOH solution.

2.4.2 Consolidation test

The consolidation tests were performed according to ASTM-D2435 (2011). The oedometer cell was made of stainless steel type 316 to minimize the chemical reaction between the cell and the pore fluid. The specimen ring was 60 mm in inner diameter and 20 mm in height, with a wall thickness of 4 mm. The preconsolidated specimen using the small centrifuge facility was trimmed, and carefully inserted into the ring. The inner space of the oedometer cell was filled with the fluid of the same pH adopted in the preparation of the preconsolidated specimens, and a seating stress (5 kPa) was applied for more than 24 hours until the settlement of the specimen was equilibrated. The vertical effective stress was incrementally doubled during each of the seven loading steps, until the vertical effective stress reached 640 kPa. Each loading step lasted at least 24 hours. After the 24 hours loading, if the specimen had not reached 100% primary consolidation, determined from time-settlement readings (i.e., root time method), additional time was allowed, until reaching 100% primary consolidation. Settlement was measured using a linear variable differential transformer (LVDT) transducer (Macro sensors, repeatability error < 0.6 μm) with DC power supply

(Agilent, E3634A) and data logger (Agilent, 34970A).

2.4.3 Flexible-wall permeability test

The hydraulic conductivity tests were performed according to ASTM-D5084 (2003). The preconsolidated specimen was trimmed to be 50 mm in diameter and 30 mm in height. Note that the minimum size of the specimen specified by ASTM-D5084 was 25 mm in diameter and 25 mm in height. Tests were conducted under three different pH values of permeant fluids (i.e., pH = 1.84, 6.62, and 12.65). The hydraulic conductivity of the specimen was measured with the falling head method using a flexible-wall permeability cell (Geocomp, 3300) with a pressure panel (Trautwein, M100000).

3. Results and discussion

3.1 Zeta Potential (ζ)

Fig. 3 plots the zeta potential (ζ) of the tested materials as a function of pH, and shows that as the pH increases, the net ζ of both untreated and treated clays increases until pH of around 10, and then with further increasing pH, very slightly decreases. Numerous previous studies on the measurement of zeta potential for natural soils have observed an increase in net ζ with increasing pH, due to the high concentration of OH^- and the consequent expansion of the double layer (Goh *et al.* 2011, Hussain *et al.* 1996, Vane and Zang 1997, Yukselen and Kaya 2003). Thus, the net ζ of tested materials increases with an increase in pH. However, for calcium clays, Chorom and Rengasamy (1995) reported that the net ζ can decrease at a high pH due to the formation of calcium carbonate. Thus, at high pH values, the net ζ of the tested materials very slightly decreases.

The net ζ of the treated clay is smaller than that of the untreated clay at pH ~7, which is the pH without addition of the pH adjusting solution, reflecting the effect of PAM adsorption on the clay surface charge (İşçi *et al.* 2006, Nasser and James 2006, Theng 2012). Note that the nonionic PAM adsorbed on the clay surface neutralizes the surface charge of clay particle (Kang *et al.* 2018); thus, the net ζ of treated clay generally shows smaller values than that of untreated bentonite. Additionally, Fig. 3 demonstrates that as the pH decreases from 7 to 3, the difference between the ζ values of untreated and treated clays becomes larger. However, as the pH increases from pH 7 to 12, the ζ of the treated clay converges to that of the untreated clay. Because the variation of zeta potential may correspond with the conformational state of adsorbed PAM according to pH, the above findings reflect: 1) the contracted or highly coiled form of PAM at low pH (Fig. 2(a)) can strongly neutralize the surface charge of clay particle because of the increased clay surface coverage by the highly coiled PAM (or increase in the degree of occupancy of surface with the train segments); 2) at higher pH values, the adsorbed PAM would be extended, due to an intra-coil repulsion through a hydrolysis reaction (Besra *et al.* 2004, Kim *et al.* 2012, Yu and Somasundaran 1996) (Fig. 2(a)); and thus the neutralizing of the surface charge by the adsorbed polymer would be reduced because of the decrease in the region of attached segments of polymer on a clay surface (or increase in trail segments). Consequently at high pH, the zeta potential of treated clay approaches that of untreated clay (Fig. 3).

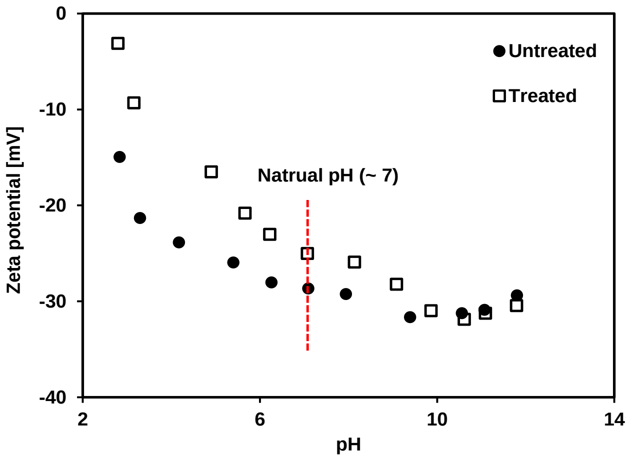


Fig. 3 Variations of zeta potential of untreated and treated clays as a function of pH

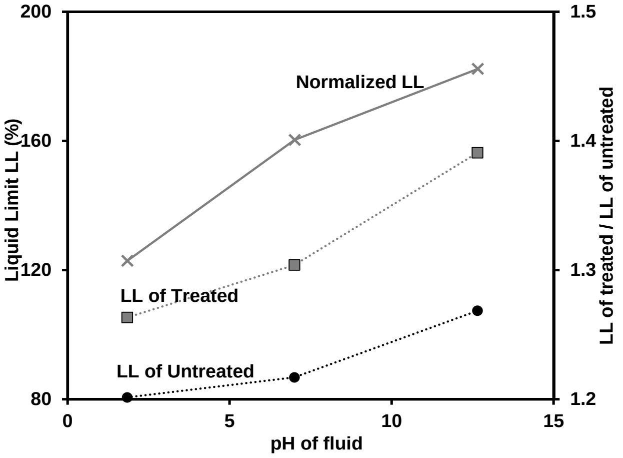


Fig. 4 Variations of liquid limit of untreated and treated clays as a function of pH of fluid: LL = liquid limit; normalized LL = LL of treated clay / LL of untreated clay

3.2 Liquid limit of PAM treated clay

Fig. 4 shows the variations of liquid limit (LL) of both untreated and treated clays as a function of fluid pH. It is remarkable that the pore fluid chemistry (e.g., pH and concentration) greatly affects the behavior of fine-grained soils, because the pore fluid determines the particle-to-particle interaction. Fig. 4 shows that the values of LL of both treated and untreated clays increase with an increase in pH. Note that LL can be defined as a lower limit of viscous flow, which is strongly related to the diffuse double layer (DDL) thickness (Holtz and Kovacs 1981, Sridharan *et al.* 1986). Because the water in the DDL is more viscous than free water, an increase in pH is expected to result in an increase in LL, as shown in Fig. 4, due to the increase in the

DDL thickness. Additionally, it is notable that alkaline pH condition was achieved through the addition of NaOH solution. This results in that some Na cations can enter the interlayer of treated and untreated clays (i.e., cation exchange between Ca and Na). Because sodium bentonite has higher LL and swelling capacity than calcium bentonite, LL can increase with an increase in pH for both treated and untreated clays.

Fig. 4 also demonstrates that the LL of treated clay is always greater than that of untreated clay. It is known that the DDL thickness of treated clay depends on the density of polymer in the outer (diffuse) double layer: if the polymer segments density in outer layer can be assumed to be small, the DDL thickness of the treated clay may be comparable to that of untreated clay; while, if the polymer density in outer layer is high, the DDL thickness can be expanded in the presence of adsorbed polymers (Vincent 1974). Thus, it can be postulated that 1) at a high pH, the DDL thickness of treated clay is greater than that of untreated clay because of an increase in segment density in outer layer, resulting from the extension of adsorbed PAM (Fig. 2(a)); and 2) at a low pH, DDL thickness of treated clay is comparable to that of untreated clay because of a decrease in segment density in outer layer, resulting from the highly coiled PAM which may mainly locates at Stern layer (Fig. 2(a)). Thus, the higher LL of treated clay can be partially attributed to the greater DDL thickness of treated clay. In addition, PAM molecules has great affinity for water, leading to the additional adsorption of water on the PAM. Consequently, at a given pH, LL of treated clay can be greater than that of untreated clay.

Fig. 4 also demonstrates that the normalized LL, which is the ratio between the LL of treated and untreated clays, increases with an increase in pH, which reflects the effect of the conformational state of PAM according to pH on LL. With an increase in pH, the adsorbed PAM on clay surface can be extended, as shown in Fig. 2(a). Note that the extended PAM molecules allow more water molecules absorbed onto the PAM. Additionally, the DDL thickness of treated clay at high pH may be greater than that of untreated clay. Therefore, the highest normalized LL can be observed at the highest pH.

3.3 Consolidation characteristics

Fig. 5 shows the consolidation curves (variation of the void ratio according to the vertical effective stress) of the untreated and treated clays at three different pH values of the pore fluid. It can be observed in Fig. 5 that as the pH decreases, the initial void ratios (e_i), which are defined as the void ratios at 5 kPa of the vertical effective stress in this study, of both untreated and treated clays decrease. In addition, the void ratio of treated clay is greater than that of untreated clay at the same pH value of the pore fluid. From this aspect, it is notable that the initial mixing water content in the preparation of slurry specimens was two times the liquid limit (LL) in Fig. 4. Because the LL increases with an increase in pH of the pore fluid and the LL of the treated clay is greater than that of untreated clay as shown in Fig. 4, e_i increases with an increase in pH, and as well, the initial water content (or e_i) of treated clay is greater than that of untreated clay.

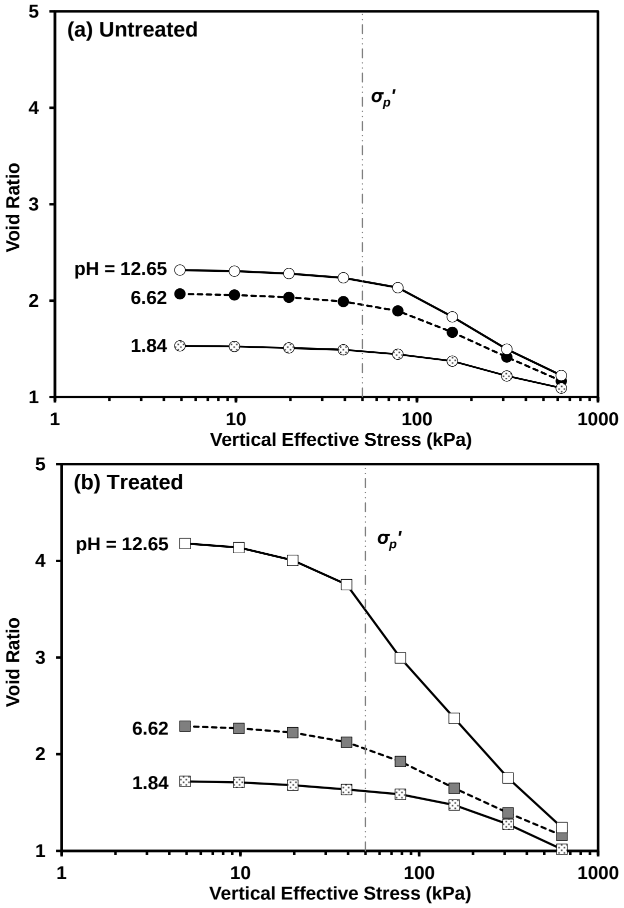


Fig. 5 Consolidation curves of (a) untreated and (b) treated clays at three different pH values of initial pore fluid: σ'_p =preconsolidation stress

Using the data in Fig. 5, the compression indices (C_c) of both untreated and treated clays were calculated and plotted as a function of pH of pore fluid in Fig. 6(a). Note that in this study, the C_c values were calculated using the void ratios at vertical effective stresses of 160 and 640 kPa to isolate the effect of preconsolidation stress on C_c. Fig. 6(a) clearly shows that the C_c increases with an increase in pH. Additionally at a given pH, C_c of treated clay is greater than that of the untreated, consistent with the result of (Bishop *et al.* 2014). However, due to the different void ratios according to pH values, the effect of the void ratio cannot be isolated in the evaluation of the effect of pH on C_c in Fig. 6(a). Note that it is well known that the compressibility (or C_c) of soils is significantly controlled by the void ratio or water content (Choo *et al.* 2017, Choo *et al.* 2016, Mitchell and Soga 2005). Therefore, the effect of pH on the C_c of the tested materials cannot be clearly established through Fig. 6(a). Instead, Fig. 6(a) indirectly demonstrates the effect of PAM treatment on C_c of tested materials. The differences in void ratios between the treated and untreated clays at pH of 1.84 and 6.62 are very similar (around 0.2). However, the differences in C_c between treated and untreated clays at pH of 1.84 and 6.62 are 0.30 and 0.04, respectively, reflecting the effect of the conformational state of the PAM on C_c. At a very low pH, the fabric of the treated clay shows less dispersed or more aggregated structure than that of

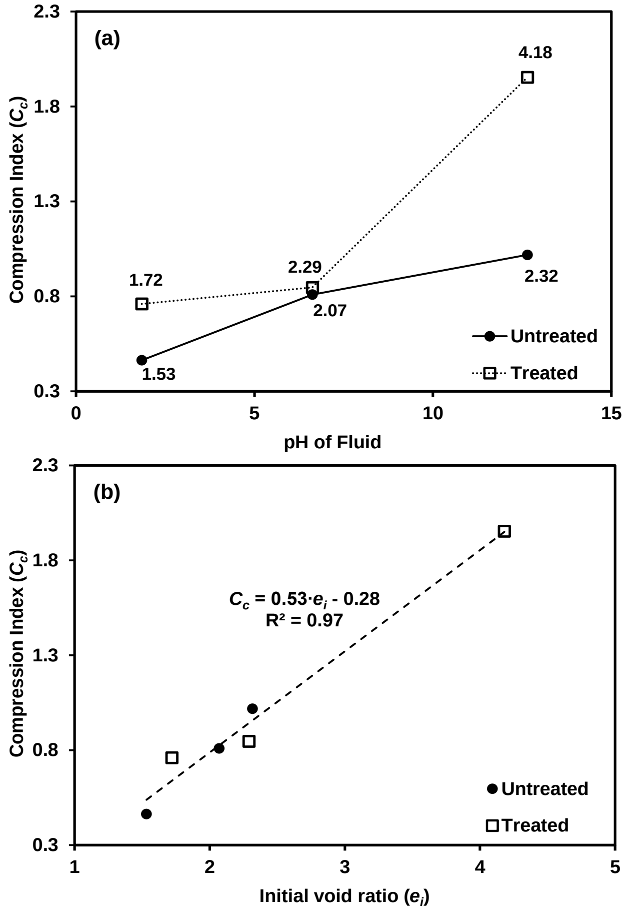


Fig. 6 Variation of compression index (Cc) as a function of (a) pH of fluid and (b) initial void ratio. Note the number next to each data point in the figure (a) denotes the initial void ratio; initial void ratio, e_i = void ratio at 5 kPa of vertical effective stress

untreated clay, because of the small repulsive force between particles as shown in zeta potential values in Fig. 3. Therefore, at a given applied stress and at a low pH, the treated clay can be more densely compacted than the untreated clay, resulting in a huge difference in C_c between untreated and treated clays at a pH of 1.84, in spite of the small difference in void ratio (Fig. 6(a)).

Fig. 6(b) shows the compression indices (C_c) of both untreated and treated clays according to the initial void ratio (e_i). It is evident in Fig. 6(b) that regardless of PAM treatment and pH, the C_c can be expressed as a unique function of e_i. Therefore, this unique relationship indicates that the effects of pH and PAM treatment on the compressibility are masked by the dominant effect of the void ratio on the compressibility. Consequently, the very high compressibility of treated clay at a high pH condition (i.e., pH = 12.65) can be attributed to the very high void ratio of PAM treated clay at a high pH condition, resulting from the expansion of adsorbed PAM at alkaline pH (Besra *et al.* 2004, Kim *et al.* 2012). Therefore, it can be postulated that the compressibility of PAM-bentonite composite can be controlled by controlling the void ratio (or the water content) of the composite.

3.4 Hydraulic conductivity (K)

Table 3 summarizes the flexible wall permeability test results. At the pH of 6.62 and 12.65, the measured hydraulic conductivity (K) of the treated clay is around 5 times lower than that of the untreated clay, although the void ratio (e) of the treated clay is larger than that of the untreated clay. Note that as mentioned previously, the K of soils is mainly determined by the size and tortuosity of water flow channels in the porous media. Therefore, because of an increase in size and a decrease in tortuosity of water flowable pore space, a higher K is expected with increasing e. Consequently, this result reflects that the conformational state of PAM affects the K of the PAM-bentonite composite specimens. In contrast, at the acidic pH, the measured K of the treated clay is around 4 times higher than that of the untreated clay, which can be partially attributed to the fact that the void ratio of the treated clay is larger than that of the untreated clay (Table 3).

Due to the limited number of data from flexible wall tests as shown in Table 3, the K values of both treated and untreated clays were estimated using the results of consolidation. According to the Terzaghi one-dimensional consolidation theory, the hydraulic conductivity can be estimated according to:

$$K = c_v \cdot m_v \cdot \gamma_w \tag{2}$$

where c_v = coefficient of consolidation; m_v = coefficient of volume change; and γ_w = unit weight of water. The c_v was determined by Taylor's square root of time method in this study, and Fig. 7 shows the estimated K values using Eq. (2), along with the data of Table 3. Note that under the similar void ratios, most of the estimated K values are slightly lower than the measured K, due to the influence of structural resistance on the estimated K (Chapuis 2012, Mesri and Olson 1971); however, the overall comparison between the measured K and estimated K using Eq. (2) shows a good agreement, as shown in Fig. 7. Fig. 7 clearly indicates that as noted earlier, the K of both treated and untreated clays increases with an increase in void ratio. Additionally, it can be observed in Fig. 7 that at a given void ratio, K decreases with an increase in pH values. Because the thickness of DDL increases with increasing pH, the water flowable pore size decreases with an increase in pH at a given void ratio. Additionally, the clay fabric at a high pH shows more dispersed structure than that at low pH. Furthermore, as mentioned previously, with an increase

Table 3 Measured hydraulic conductivities of tested untreated and treated clays

pH of permeant	Sample	Void ratio	Hydraulic conductivity (m/s)
1.84	Untreated	1.63	2.7×10^{-9}
	Treated	1.91	1.0×10^{-8}
6.62	Untreated	1.97	2.4×10^{-10}
	Treated	2.08	3.9×10^{-11}
12.65	Untreated	2.36	1.4×10^{-10}
	Treated	3.08	4.0×10^{-11}

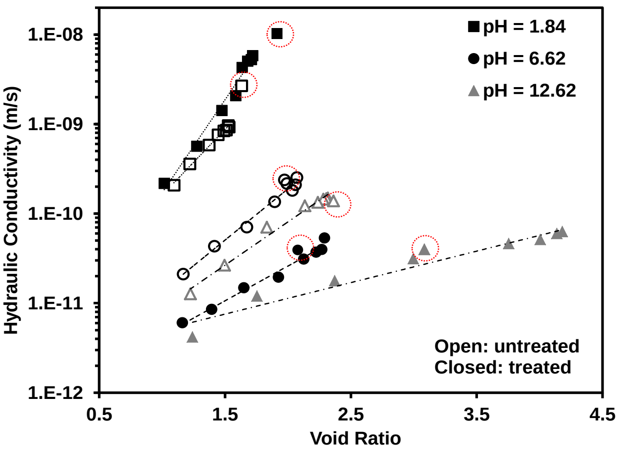


Fig. 7 Variations of hydraulic conductivity of both treated and untreated clays as a function of void ratio. Note the data in the dotted circle = measured hydraulic conductivity from flexible wall tests (Table 3); and the other data = estimated hydraulic conductivity from consolidation tests

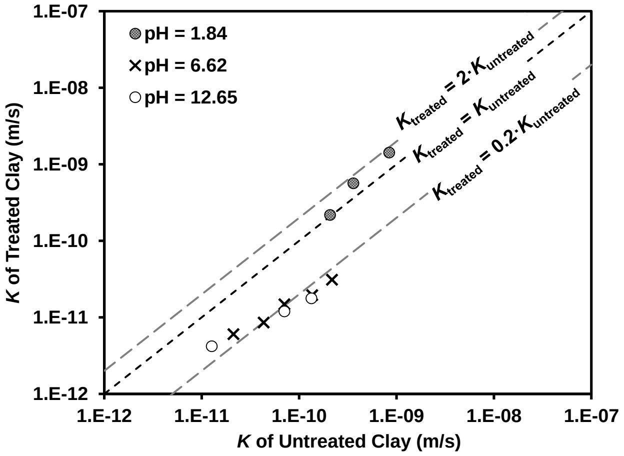


Fig. 8 Comparison between the *K* of untreated and treated clays under the similar void ratios: *K* = hydraulic conductivity

in pH values, the cation exchange between Ca and Na can be occurred, resulting in a decrease in *K* because sodium bentonite has a lower *K* than calcium bentonite. Consequently, the *K* decreases with an increase in pH of permeant fluid.

The comparison between the *K* of treated and untreated clays demonstrates that at neutral and high pH conditions, the *K* of treated clay is smaller than that of untreated clay. As mentioned previously, the DDL thickness of treated clay may be greater than that of untreated clay at relatively high pH values. Therefore, the *K* of treated clay is lower than that of untreated clay at neutral and high pH conditions. In addition, the smaller *K* of treated clay can be attributed to the presence of extended PAM, because with an expansion of the PAM by increasing pH (i.e., pH fluid = 6.62 and 12.65), the size of water flow channel of the treated clay could decrease; while, the tortuosity of water flow channel could increase. In contrast, at very acidic condition (pH of fluid = 1.84), the *K* of treated clay is slightly greater than that of untreated clay (Fig. 7). It can be assumed that due to the contraction of PAM at a low pH, the effect of PAM on the reduction of the size of water flow channel may disappear. In addition, DDL thickness of treated clay may be comparable to that of untreated clay at a low pH. In contrast, as reflected in the small net zeta potential values of treated clay at low pH values, the clay fabric of treated clay may be more aggregated, resulting in the *K* of treated clay at acidic condition being greater than that of untreated clay.

Finally, for the quantitative comparison between the *K* of untreated and treated clays, selected *K* values of treated and untreated clays under the similar void ratios in Fig. 7 are plotted together in Fig. 8. Fig. 8 shows that the *K* of treated clay is approximately 0.2 times the *K* of untreated clay except for the low pH condition, reflecting the possible use of the PAM-bentonite composite in a hydraulic barrier system for highly alkaline industrial residues such as steel slag, bauxite processing residue, ash from coal combustion, and others. However, in the case where the pH of fluid is very low (i.e., pH = 1.84), the *K* of treated clay is approximately one to two times the *K* of the untreated clay, reflecting that calcium bentonite treated with nonionic PAM should not be used in an acidic water environment. In addition, it is important to remark that the treated clay shows relatively higher compressibility compared to untreated calcium bentonite due to the increased liquid limit or water content. Therefore, the treated clay can be used in a hydraulic barrier system under the low applied stress condition such as the landfill cover. In contrast, the use of treated clay in a barrier system under the high applied stress condition should be carefully controlled or should be done after the sufficient compaction to reduce the void ratio of treated clay.

4. Conclusions

The effects of pH-responsible polymer treatment for calcium bentonite on the hydraulic and consolidation properties were explored according to three different pH conditions. The treated clay with the Polyacrylamide (PAM) was synthesized according to the solution intercalation technique. The following key observations were made in this study:

1. The net zeta potential of the treated clay is lower than that of the untreated clay because the nonionic PAM can neutralize the surface charge of clay particle. Because of the change in conformational states of PAM according to pH, the difference in zeta potential values between treated and untreated clays decreases with increasing pH.

2. The LL of the treated clay is always higher than that of the untreated clay because of the increased diffuse double layer thickness of treated clay and the great affinity for water of the PAM molecules.

3. The compression index (C_c) increases with an increase in pH, and at a given pH, C_c of treated clay is greater than that of the untreated clay. However, C_c of both untreated and treated clays can be expressed as a single function of the initial void ratio.

4. At the natural pH and alkaline pH, hydraulic

conductivity of the treated clay is around 0.2 times that of untreated clay under the similar void ratios because of the reduction in size of water flow channel by PAM expansion. However, at acidic pH, the hydraulic conductivity of the treated clay is slightly higher than that of the untreated clay.

Acknowledgments

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (NRF-2017R1C1B2004036).

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