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Research Paper

Effect of cations on consolidation and permeability of polymerized bentonite

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ABSTRACT

Properties of a novel material “polymerized bentonite (PB)” and a traditional untreated bentonite (UB) were investigated through two series of laboratory tests (i.e., consolidation test and filter press test). Three different test liquids included of deionized water, 0.6 M NaCl and 0.6 M $CaCl_2$ were used in this study. The results of consolidation tests indicated that the compression index (C_c) and swelling index (C_s) decreased, while the coefficient of consolidation (c_v) increased with the increasing in concentration and valence of cation in the solutions. Comparison between two materials in the cationic solutions, the PB had higher C_c and C_s value, but it gave lower c_v value compared with that of the UB. The results of estimated permeability (k_{filter}) from the test results of the filter press showed that the PB gave lower values of k_{filter} for all the test solutions compared with those of the corresponding UB due to the polymer “locked” Na^+ ions carried by the bentonite particles and partially prevented it to be replaced by higher cation charge. Based on the results of permeability, it is suggested that the PB can provide better barrier properties against aggressive cationic solutions compared to that of the UB.

1. Introduction

Sodium bentonite is widely used as a liner material in waste landfill systems due to its high swelling capacity and low water permeability (*k*). However, when it interacts with cationic solutions (e.g., sea water, leachate, etc.), the swelling capacity of the sodium bentonite dramatically decreases (Jo et al., 2001; Razakamanantsoa et al., 2012) due to the cations reduce the thickness of diffuse double layer (DDL) around the bentonite particles (Mitchell and Soga, 2005; Chai and Shen, 2018).

To improve the swelling capacity of the bentonite, technique of polymerizing the sodium bentonite has been used (Bohnhoff and Shackelford, 2013; Di Emidio et al., 2015). Prongmanee et al. (2018) produced the polymerized bentonite (PB) by dispersing the sodium bentonite into an aqueous sodium acrylate monomer, then proceed a polymerization process by using a free radical polymerization. They reported that the produced PB showed higher swelling capacity and lower value of *k* in aggressive cationic solutions compared with that of the untreated bentonite (UB).

For key parameters to consider a proper liner material for landfill systems, not only the swelling capacity and the value of *k* are considered, but also consolidation is one of important parameter used. Consolidation parameters, such as compression index (C_c) is used to evaluate the

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settlement of the liner material due to weight of the landfill waste. Coefficient of consolidation (c_v) is used to determine its rate of settlement and the value of k. There are considerable literatures investigate on the consolidation behavior of the bentonite in cationic solutions (Mishra, 2005; Yukselen-Aksoy et al., 2008; Dutta and Mishra, 2016). However, few researchers investigate on the consolidation behavior of the newly PB material in the cationic solutions.

The main purpose of this study aims to investigate the consolidation parameters and permeability of the PB in aggressive cationic solutions through a series of consolidation tests and filter press tests. The test results of the PB in aggressive cationic solutions were reported and compared with those using the corresponding untreated bentonite (UB).

2. Materials and methods

2.1 Sodium bentonite

The sodium bentonite used namely “Super Clay” is from Wyoming, USA (Tang et al., 2014). The chemical properties of the sodium bentonite are listed in **Table 1**. The value of pH was measured using the liquid from the UB and deionized water with a solid/liquid ratio of 1/10. The value of *CEC* measured using atomic absorption spectrophotometry is 77 meq/100g. The bentonite mainly consisted of dioctahedral smectite mineral and its content was approximately 85 % of the total weight (Chai and Shen, 2018). The bentonite used for all the tests was screened passing sieve No. 200 (< 75 μm).

Table 1. Chemical properties of the sodium bentonite

Property	Unit	Value
Chemical composition		
SiO_2	%	73.8
Al_2O_3	%	13.8
Fe_2O_3	%	4.3
MgO	%	1.6
CaO	%	1.5
Na_2O	%	1.7
K_2O	%	0.5
LOI	%	1.6
Total	%	98.8
Cation exchange capacity, *CEC*	meq/100g	77.0
Soil pH (ASTM 4972)	-	9.3

2.2 Polymerized bentonite (PB)

The PB used in this study was produced using a free radical polymerization process with the optimum conditions proposed by Prongmanee et al. (2018). The optimum conditions for producing the PB are: using sodium acrylate as the monomer and potassium persulfate (KPS) as the initiator, pH of 7.0, the initiator (I) to monomer (M) ratio, I/M, of 0.2 and the monomer content of 10% with respect to the mass of a bentonite to be polymerized. A procedure for producing the PB is as follows;

1) Sodium acrylate monomer ($C_3H_3NaO_2$) was produced by mixing acrylic acid ($C_3H_4O_2$) with a sodium carbonate (Na_2CO_3) solution.
2) A certain amount of initiator was dissolved in the sodium acrylate monomer solution.
3) Then, the solution was removed an oxygen (O_2) by circulating with nitrogen gas for 30 min. After that, the temperature of the mixture was increased above its decomposed temperature, the polymerization process was performed for 2.5 h.
4) The PB was oven dried at 105 °C. Then, the dried PB was milled, and screened by the number 200 sieve (< 75 μm).

2.3 Test liquids

Three different liquids namely, deionized water, 0.6 M NaCl and 0.6 M $CaCl_2$ were used. The 0.6 M NaCl was used to simulate the sea water (Miyahara et al., 2015). The 0.6 M $CaCl_2$ is an aggressive divalent cation solution. These chemical solutions were chosen to evaluate the performance of the PB against aggressive di-valence and mono-valence cation solutions. **Table 2** reported the results of pH and electro-conductivity (*EC*) of the test liquids.

Table 2. Properties of the test liquids

Liquids	pH	*EC* (mS/cm)
Deionized water	6.99	0.0
0.6 M NaCl	6.21	11.1
0.6 M $CaCl_2$	6.94	16.6

2.4 Consolidation test

The consolidation tests were conducted following ASTM D2435 except the thickness of the sample used was 10 mm (it will be explained in the later section).

Oven dried powder of the PB or the untreated bentonite (UB) was thoroughly mixed with 2.0 times its liquid limit (w_l) and the slurry was cured for at least 24 h. After that, the slurry was pre-consolidated under a vertical effective stress (σ_v') of 50 kPa in an oedometer ring 60 mm in diameter and 20 mm in height for about 3 days. After the pre-consolidation, the specimen had a height approximately 16 mm which is smaller than 20 mm height for the standard oedometer ring test. So, it was decided to trim the specimen to 10 mm in thickness for the oedometer test by pushing the specimen into a 60 mm in diameter and 10 mm in height ring and cutting the extra PB or UB by a wire saw. The consolidation test was carried out with σ_v' from 10 kPa to 1280 kPa, by doubling the stress for each subsequent step. Initial water content (w_i), initial void ratio (e_i) and the value of w_l of the PB and the UB in deionized water and aggressive cationic solutions are given in **Table 3**. Generally, the w_l of soil is controlled by (1) water in diffuse double layer (DDL), and (2) water in micro-pores structure (Sridharan and Prekash, 1999). It is considered that the reduction of liquid limit (w_l) in deionized water of the PB compared with that of the UB is because with the sodium polyacrylate disperses the particles of bentonite (Prongmanee et al., 2018), resulting in the PB particles tend to from dispersive micro-structure and reduced amount of water held in the micro-pores (Du et al., 2016). In cationic solutions, the PB provided higher w_l value. It is postulated that the polymer "fixed" more Na^+ on the surface of the bentonite particles and resulted in thicker DDL (Prongmanee et al., 2018).

Table 3. Initial water content (w_i), and initial void ratio (e_i) of the PB and UB

Liquid	UB			PB		
	w_i	e_i	w_l	w_i	e_i	w_l
Deionized water	332	10.17	621	291	7.82	499
0.6 M NaCl	100	2.86	142	156	4.37	267
0.6 M $CaCl_2$	82	2.36	132	113	3.19	184

2.5 Filter press test

An alternative method to determine the value of *k* is from the test result of filter press test (Rosin-Paumier et al., 2010; Rosin-Paumier and Touze-Foltz, 2012). This method provides quick evaluation of the value of *k* compared with those of traditional permeability and consolidation tests.

2.5.1 Test methods

The procedures of the filter press test are almost the same as the fluid loss test (ASTM D 5891) except that in filter press test, the volume of out-flow liquids need to be recorded all over the test, while the fluid loss test only needs to be collected the out-flow volumes from 7.5 ± 0.1 min to 30 ± 0.1 min (Totally 22.5 min) period. **Fig. 1** shows the filter press apparatus in schematic picture. The test procedures are as follows;

a. Oven dried untreated bentonite (UB) or the polymerized bentonite (PB) of 18.0 g was dispersed into a 300 ml of a desired liquid, i.e. deionized water, or 0.6 M NaCl, or 0.6 M $CaCl_2$ by a mechanical mixer.
b. The filter paper of 60 mm in diameter was firstly placed on the porous stone. The filter paper used is a Whatman no. 50 filter paper. Then, the mixture slurry was poured into the filtration cell (cylinder with 60 mm in diameter and 120 mm in height).
c. The vertical pressure of 700 kPa was directly applied on the top of the loading piston. The O-ring was attracted to the piston to prevent the liquid leaked during the filter press test.
d. The volume of the out-flow liquid was recorded with elapsed time. The volume of the out-flow liquid was recorded by a graduated cylinder of 10 ± 0.1 ml. The test duration was 1 hour (Rosin-Paumier et al., 2010).

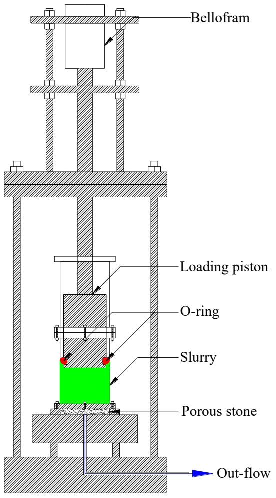


Fig. 1. Fluid loss test apparatus.

After test, the slurry was drained out and left a thin film layer called "filter cake". The thickness of the filter cake was measured by a digital caliper Vernier. The water content and dry mass was (W_s) were measured to determine the initial void ratio (e_0). The value of e_0 is calculated following Eq. [1].

$$e_0 = \frac{H_v}{H_s} \qquad [1]$$

$$H_s = \frac{W_s}{G_s \cdot \rho_w \cdot A} \qquad [2]$$

$$H_v = H - H_s \qquad [3]$$

where H_s is solid height which is calculated from Eq. [2], H_v is void height and it is determined by Eq. [3], W_s is dry mass of the filter cake, ρ_w is density of water, *A* is cross sectional area of the filter cake, *H* is the total thickness of the filter cake after performed filter press test.

The results of thickness, water content and initial void ratio (e_0) are listed in **Table 4**. The values of water content as shown in **Table 4** were the measured water content following ASTM D2216, and all cases were duplicate. The obtained high value of water content is because the thin film cake contains very low amount of dried mass with very high amount of water.

Table 4. Results of thickness (*H*), water content (*w*) and initial void ratio (e_0) of filter cake

Materials	Liquids	*H* (mm)	W_s, (g)	*w* (%)	e_0
UB	Deionized water	0.6	1.3	2890	36.3
UB	0.6 M NaCl	1.0	13.3	377	12.2
UB	0.6 M $CaCl_2$	1.2	18.6	284	11.8
PB	Deionized water	0.3	0.9	3830	31.2
PB	0.6 M NaCl	0.2	2.2	3590	21.2
PB	0.6 M $CaCl_2$	1.1	17.0	380	17.1

2.5.2 Calculation methods

The fluid loss volume (V_f) in milliliters is calculated by Eq. [4].

$$V_f = 2 \times V \qquad [4]$$

where *V* is the filtrated volume for last 22.5 min interval (collected filtrate volume from 7.5 to 30.0 min).

Permeability from filter press test (k_{filter}) is determined by the Eq. [6]. The k_{filter} determines by assuming that the viscosity of filtrate was the same as the water. The value of k_{filter} can be obtained from Eq. [5] (Rosin-Paumier et al., 2010).

$$\omega = \left[\psi_{filter} \frac{2 \Delta P A \omega_t}{\rho g} \right]^{0.5} t^{0.5} \qquad [5]$$

$$k_{filter} = \psi_{filter} \cdot H \qquad [6]$$

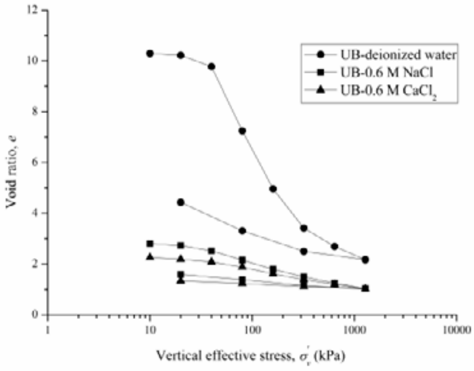
where ω is the filtrate volume, ω_t is the total filtrate volume, ΔP is the pressure gradient, *t* is time and *g* is the gravity acceleration. According to the relationship of ω and $t^{0.5}$ is linear relationship, the permittivity of filter cake (ψ_{filter}) (Eq. [5]) can be directly calculated from the constant value of the linear regression analysis (zero interception) (Rosin-Paumier et al., 2010).

3. Result and discussions

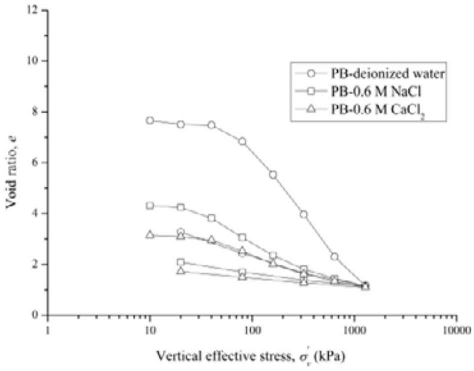
3.1 Results of consolidation test

The test results of the UB and the PB with different liquids are presented in **Figs. 2(a) and (b)**. In **Figs. 2(a) and (b)**, compression, i.e. initial void ratio (e_0) decrease as ion valence and concentration increase. Also, swelling behaviors of the materials are clearly affected by the cations charges and concentration.

Fig. 3 represent the results of compression index (C_c) in various liquids. **Fig. 3** shows C_c decrease with increasing of cation concentration and valence of cation. The decrease in C_c was found to be more significant for the UB in comparison to that of the PB in the aggressive cationic liquids.



(a) Untreated bentonite (UB)



(b) Polymerized bentonite (PB)

Figs. 2. Void ratio (*e*) - σ_v' value of (a) the UB, and (b) the PB

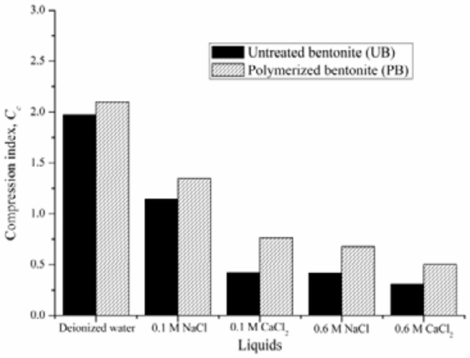


Fig. 3. Results of C_c with different liquids

In **Fig. 4**, it is clearly to see that the PB gave higher swelling index (C_s) value than that of the UB for all liquids. This is attributed that the PB had higher swelling capacity than that of the UB. This is because the polymer wrapped around the particles of the bentonite and the functional group (carboxylate salts, COO^-) of the sodium polyacrylate attracts some cations in the solutions preventing the cations enter the diffuse double layer of bentonite particles (Prongmanee et al., 2018).

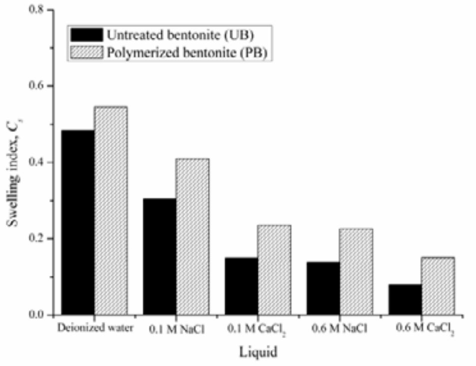


Fig. 4. Results of C_s with different liquids

The results of coefficient of volume change (m_v) are plotted with vertical effective stress (σ_v') as shown in **Fig. 5**. The value of mv initially tends to increase and then decreased with an increase of σ_v'. The m_v of both materials decrease with increase in the cation concentration and valence of cation. Under the same σ_v' value, the PB gave higher m_v value compared with that of the UB. The reason considered is that the PB had thicker DDL around the bentonite particles, resulting in higher water holding capacity of the particles, and higher compressibility.

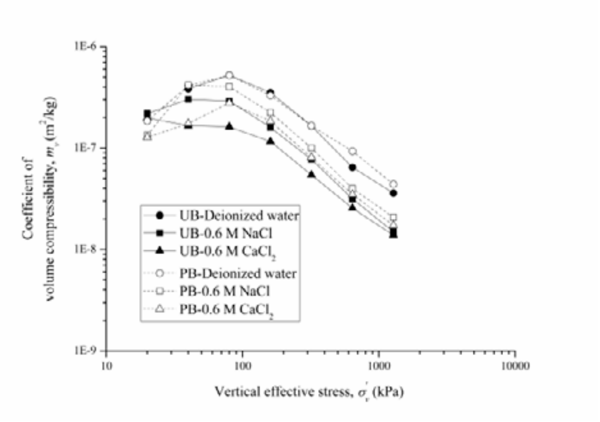


Fig. 5. Relationship between m_v value versus σ_v' values

The relationships between the coefficients of consolidation (c_v) and σ_v' are plotted in **Fig. 6**. The c_v values were determined using the square root of time (Taylor) methods for each loading stage of consolidation test. Generally, the c_v value decreased with increasing of vertical effective stress (σ_v'). For a given σ_v', c_v increased with the increase in the cation concentration and valence of cation. For the regular clay such as bentonite, it is commonly found that the c_v values decreased with increasing vertical effective stress (Das et al., 2017) due to the virgin compression behavior is controlled by physicochemical factors (Retnamony et al., 1998) indicating a slower rate of consolidation at higher vertical effective stress.

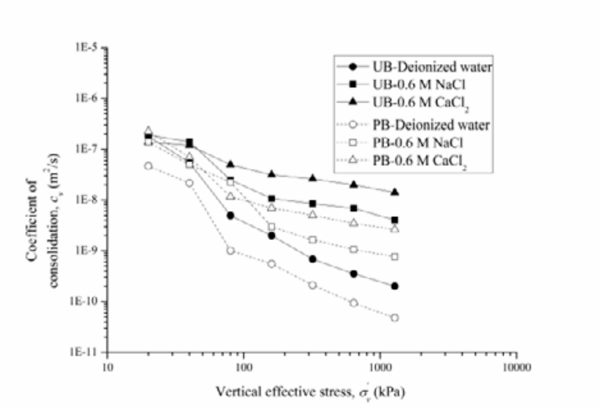


Fig. 6. Results of value of c_v versus σ_v' values

For further investigation, a time at 90% of consolidation (t_{90}), were plotted with the σ_v' as shown in **Fig. 7** for the UB and the PB, respectively. **Fig. 7** indicates that the t_{90} increase with increasing of σ_v' values. For effects of cations, t_{90} decreases with the increase in cation concentration and valence of cation, i.e. increase in rate of consolidation. For a given σ_v' values, the PB gave higher t_{90} than that of the UB.

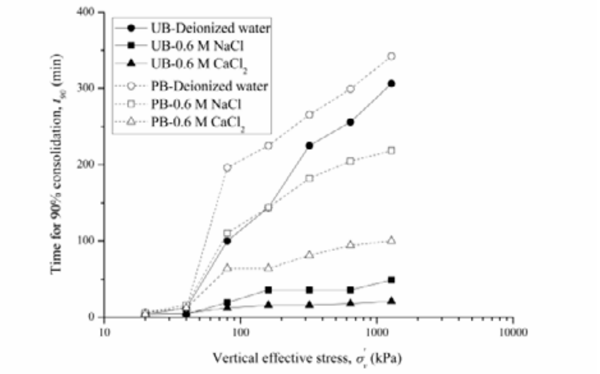


Fig. 7. Time for 90% of consolidation versus σ_v' values

According to the test results of consolidation, the PB showed higher compressibility and lower rate of consolidation in aggressive cationic solution compared with that of the UB.

3.2 Results of filter press test

The relationship of filtrate volume (ω) and square root time ($t^{0.5}$) are presented in **Fig. 8**. At a given elapse time, it is clearly seen that the UB had higher value of ω than that of the PB in the cationic solutions. While, in the deionize water both materials gave the similar ω value.

From test results in **Fig. 8**, the fluid loss volume (V_f) and permeability (k_{filter}) can be calculated by Eq. [5] and Eq. [6], respectively.

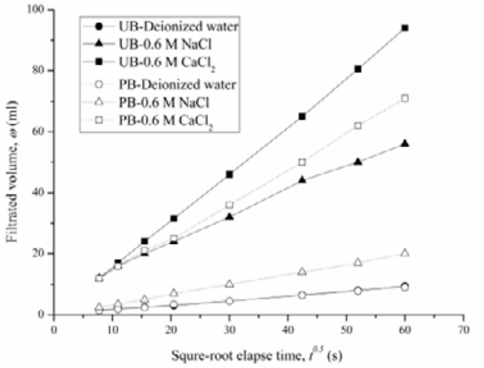


Fig. 8. Results of the filtrate volume versus square root of elapse time

In **Fig. 9**, the results of V_f show that the values of V_f increase with increasing of cation concentration and valence of cation in the solutions. In case of deionize water, both the PB and the UB had the similar V_f value. According to the requirement for the GCL material, the current industry standard is required the V_f must be less than 18.0 ml in deionized water (Von Maubeuge, 2002) and both materials gave the value lower than that of the minimum requirement value (**Fig. 9**). In salt solutions, the PB provided the lower V_f compared to that of the UB.

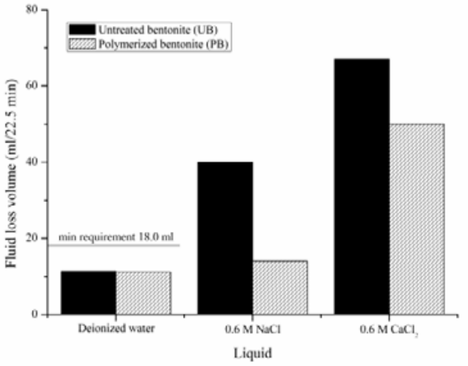


Fig. 9. Results of fluid loss volume with different liquids

In the similar way, **Fig. 10** shows the k_{filter} value of the PB and the UB with three permeated liquids. The test results confirm that the PB had lower permeability (k) when compared with that of the UB in cationic solutions due to the polymer "locked" Na^+ ions carried by the bentonite particles and partially prevented it to be replaced by Ca^{2+} ion (Deng et. al., 2006).

The test results of k_{filter} and k_{conso} from Prongmanee et al. (2018) were compared and reported in **Figs. 11(a) to (c)**. The results of k values are obviously shown that the k_{filter} yielded non-conservative value compared with the k_{conso} values under the same void ratio (e) condition. It is noted that the value of k_{conso} under the same e value with the filter press test can be estimated by using the proposed equation in **Figs. 11(a) to 11(c)**. This is attributed that the results from the filter press test are only qualitatively useful, i.e. only correct in tendency.

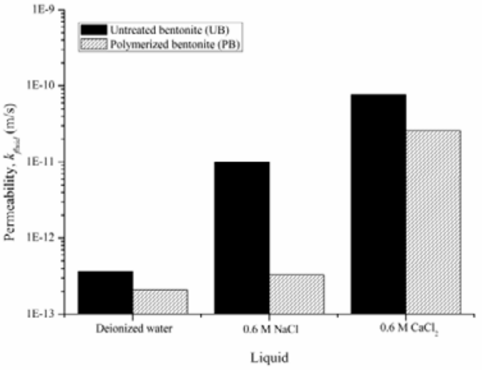


Fig. 10. Results of permeability (k) in various of liquid types

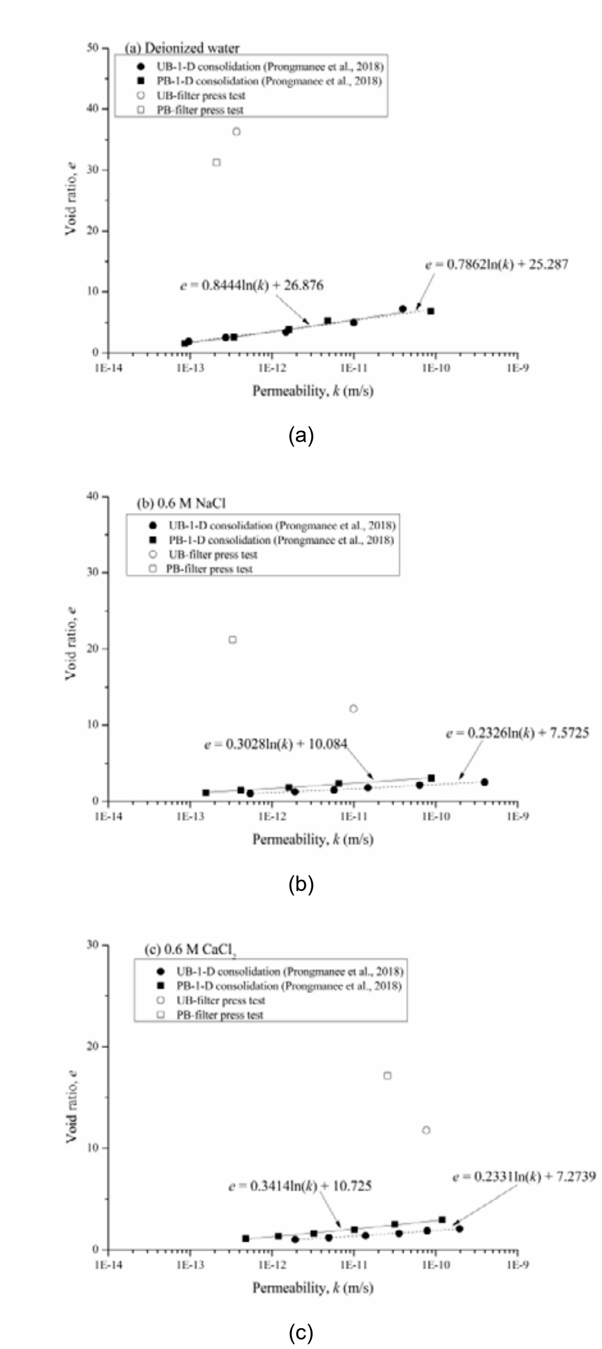
4. Conclusions

The consolidation tests and filter press tests of the polymerized bentonite (PB) were investigated experimentally and compared with those of the untreated bentonite (UB). Based on the test results, the conclusions can be drawn are as follows.

1. The PB yielded higher compression index (C_c) and swelling index (C_s) compared with that of the UB. This confirms that the PB had higher compressibility and swelling potential in cationic solutions. The results of coefficient of consolidation (c_v) shows that the PB had lower c_v compared with that of the UB.

2. Results of filter press indicate that the value of k_{filter} increases with increasing of the cation concentration and valence of cation. Under the same test conditions, the PB gave lower value of k_{filter} for all test liquids compared with that of the UB.

3. Based on the results of permeability, it is suggested that the PB can provide better barrier properties against aggressive cationic solutions compared to that of the UB.



(a)

(b)

(c)

Figs. 11(a) to (c) Comparison *k* values from two different test methods

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Symbols and abbreviations

C_c	Compression index
C_s	Swelling index
c_v	Coefficient of consolidation
m_v	Coefficient of volume change
t_{90}	Time at 90% of consolidation
k_{filter}	Permeability from filter press test
k_{conso}	Permeability from consolidation test
CEC	Cation exchange capacity
I/M	Initiator to monomer ratio
w_i	Initial water content
e_i	Initial void ratio
w_l	Liquid limit
e_0	Initial void ratio of filter cake
H_v	Void height
H_s	Solid height
W_s	Dry mass of the filter cake
ρ_w	Density of water
A	Cross sectional area of the filter cake
H	The total thickness of the filter cake
V_f	Fluid loss volume
V	Filtrated volume
ω	Filtrate volume at any time point
ω_t	Total filtrate volume
ΔP	Pressure gradient
t	Time
ψ_{filter}	Permittivity of filter cake
σ_v'	Radius of material point at initial state