

Research Article

Hydraulic Conductivity of Polymer-Amended Sand-Bentonite Backfills Permeated with Lead Nitrate Solutions

Sheng-Qiang Shen ¹ and Ming-Li Wei²

¹Ph.D. Candidate, Jiangsu Key Laboratory of Urban Underground Engineering & Environmental Safety, Institute of Geotechnical Engineering, Southeast University, Nanjing 210096, China

²Ph.D., State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan 430071, China

Correspondence should be addressed to Sheng-Qiang Shen; sqiangqiang110@163.com

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Hydraulic conductivity of sand-bentonite (SB) backfills amended with polyanionic cellulose (PAC) to lead nitrate ($\text{Pb}(\text{NO}_3)_2$) solutions was evaluated experimentally in this study. PAC-amended sand-bentonite (PSB) backfills were synthesized by mixing sand-bentonite mixture with 0.3 to 1.2% dry PAC (by total dry mixture mass) and mixed with a certain weight of conventional bentonite (CB) slurry. The rheology properties including the filtrate loss, viscosity, density, and pH testes of slurry with various bentonite dosages were measured to determine the reasonable CB dosage of slurry. The slump tests on PSB backfills with various mass slurries were conducted to determine the corresponding water content of backfills with slump 125 ± 5 mm. Under the applied pressure 100 kPa, the hydraulic conductivity to $\text{Pb}(\text{NO}_3)_2$ solutions (k_c) of PSB backfills with various PAC contents was evaluated based on the modified filter press (MFP) tests, to ascertain the optimum PAC content of PSB backfills when permeated with $\text{Pb}(\text{NO}_3)_2$ solutions. Index properties, including the specific gravity (G_s) and liquid limit (w_L) of PSB backfills, were measured after MFP tests. The MFP tests for PSB backfills were then conducted under various applied pressures to obtain the relationship between void ratio (e) and hydraulic conductivity of backfills. Finally, the flexible-wall permeability test (FWP test) under osmotic pressure 100 kPa was conducted to verify the effectiveness of the MFP test. The results indicate that slurry with 8% bentonite dosage is the reasonable choice in slurry wall construction. PSB has lower G_s and higher w_L compared to SB; increasing Pb concentration leads to G_s of PSB increased and w_L of PSB decreased. PSB with 0.6% PAC content is supposed as the optimum proportion of backfills when permeated with concentrated $\text{Pb}(\text{NO}_3)_2$ solution. PAC adsorbs large amount of bound water, which leads to higher water content (w) and e of PSB backfills, while lead ions (Pb) cause the diffuse double layer (DDL) of bentonite compressed and e of PSB backfills reduced. The k_c of PSB-0.6 remains lower than 10^{-9} m/s and increases less than 10 times though the Pb concentration was up to 500 mM, demonstrating that the hydraulic performance of backfills can be improved effectively in $\text{Pb}(\text{NO}_3)_2$ solution by the additive PAC. The comparison results between k from MFP tests and FWP tests show that the MFP test is an effective and easy evaluation of hydraulic conductivity of backfills.

1. Introduction

Sand-bentonite (SB) vertical cutoff walls are extensively employed as in situ vertical barriers to prevent pollutants migrating into groundwater [1–7]. The typical SB cutoff walls are constructed by first excavating a trench with 0.6 to 1.5 m in width while simultaneously filling the trench with bentonite-water slurry (typically 6–12% by dry weight of conventional bentonite) to maintain the trench stability. The

sand is mixed with bentonite and then combined with bentonite-water slurry satisfied rheological properties to prepare homogeneous backfills with optimum slump ($\sim 125 \pm 25$ mm). The backfills is then poured into the slurry trench, forming a barrier with low hydraulic conductivity, k (typically $k \leq 10^{-9}$ m/s).

The potential for chemical incompatibility between backfills and the contaminated groundwater is a crucial consideration for vertical cutoff walls, which results in an

increase in k . The k of the SB backfills increases obviously (typically greater than 10 times) when exposed to inorganic solution with ionic strength (SI) greater than 300 mM, resulting in the barriers performance destroyed [8–10].

Polymers as additives used in modifying bentonite have been investigated for improving the hydraulic performance of bentonite-rich barriers [11–16]. Several kinds of polymer-modified bentonite have been developed, including but not limited to HYPER-Clay, dense prehydrated GCLs (DPH-GCL), polymer-modified bentonite plays an important role in GCL), and BPC [12, 14, 17–20]. The hydraulic performance of polymer-modified bentonite has been largely improved compared to conventional bentonites. Nevertheless, the polymer content optimization of polymer-modified bentonite has not been reported in previous studies.

Generally, polymer with lower molecular weight (10^3 – 10^4) exhibits dispersibility, polymer with larger molecular weight (generally greater than 5×10^6) shows superior flocculability, and when the molecular weight of polymer is in the range of 10^4 to 5×10^6 , polymer is called super absorbent polymer (SAP) because of its excellent water absorbing capacity. As a result, PAC with molecular weight 1,730,000 (commercial products) is selected as the amended agent in this study. Polyanionic cellulose (PAC) is a kind of polymer, nontoxic and tasteless, which is a viscosity modifier and can improve bentonite-suspension viscosity. Additionally, PAC has been extensively used as thickener in petroleum drilling construction and emulsifier constitute in coating brushing [21, 22]. However, PAC-amended bentonite or sand-bentonite backfills used in hydraulic barrier applications has not been reported.

The objective of this study is to evaluate the potential use of SB backfills amended with polyanionic cellulose (PAC), and for cost effectiveness and low-carbon consideration, the PAC dosage for PAC-amended SB backfills (PSB) is optimized, which may be an alternative for conventional SB backfills to improve the hydraulic performance when exposed to contaminated solutions. In this study, powder PAC is directly mixed with dry bentonite and sand combined with bentonite slurry to prepare the PSB. The hydraulic conductivity to distilled water (k_w) and to $Pb(NO_3)_2$ solutions (k_c) of backfills are conducted by improved membrane filter press (MFP) tests. Index properties, including the specific gravity (G_s) and liquid limit (w_L) of PSB backfills, are measured after MFP tests. The optimum dosage of PAC (by dry mass) of PSB is obtained through the hydraulic performance of PSB with various dosages permeated to $Pb(NO_3)_2$ with concentration from 20 to 500 mM. The filter press tests for PSB backfills are then conducted under various applied pressures to obtain the relationship between void ratio (e) and hydraulic conductivity of backfills. Finally, the flexible-wall permeability test (FWP test) is conducted to verify the effectiveness of MFP test.

2. Materials and Methods

2.1. Constituent Soils and Polymer. The backfills comprised powered conventional bentonites (CB), fine sand, and PAC. The CB manufactured by Mu-Feng Co., Ltd was powdered

natural calcium bentonite activated with Na_2CO_3 treatment in order to obtain more superior swelling capacity and lower permeability. The physicochemical properties and mineralogical compositions of CB are summarized in Table 1. The X-ray diffraction phase identification is performed by China Petroleum and Chemical Corporation (Sinopec Corp.), Jiangsu Oilfield Branch. Based on the X-ray diffraction analysis, the dominant clay mineral of CB is found to be montmorillonite; the mineral constituent of CB is shown in Table 2. The properties of PAC provided by manufactures are shown in Table 3. The fine sand was chosen to model a typical in situ sandy aquifer, which was obtained from the floodplains of Yangzi River in China. The sand was washed by tap water and air dried and then screened with 1 mm sieve. The uniformity coefficient (C_u) is 3.66, and the curvature coefficient (C_c) is 0.76, indicating that the sand exhibits poor grain-size distribution.

2.2. Base Mixtures for Backfills. The base mixtures used to prepare the backfills included a conventional sand-bentonite mixture and PAC-amended sand-bentonite mixtures. The sand-bentonite mixture comprised 90% air dried sand mixed with 10% CB. The dosage of PAC in the PAC-amended SB mixtures was controlled at 0.3, 0.6, 0.9, and 1.2%, and the bentonite content was also designed as 10%. The PAC-amended SB mixtures were then made by mixing a certain mass of PAC with base mixture. The PAC-amended backfills with various PAC dosages were defined as PSB- i to present a base mixture for backfill with PAC content (PC) of $i\%$, bentonite content (BC) of 10%, and sand content (SC) of $(90-i)\%$. The designed proportions of each constituent for backfills are shown in Table 4.

2.3. Bentonite-Water Slurry. The bentonite-water slurries (4 to 10% dry bentonite by mass) were prepared in order to evaluate the optimum bentonite content for using in slurry vertical cutoff wall construction. The slurries were mixed in a high-speed blender for 10 min and then sealed in a beaker and allowed to hydrate for 24 h. The slurries were stirred again for 5 min before measuring their rheological properties. The desired rheological properties of slurry to prepare SB backfills (Bohnhoff and Shackelford, 2013) include Marsh viscosity, density, filtrate loss volume, and pH values; the target viscosity is approximately 40 s as measured with a Marsh funnel viscometer in accordance with American Petroleum Institute (API) recommended practice 13B-1; the desired filtrate loss should be less than 25 mL as measured through the fluid loss test following the API 13B-1 and ASTM D5891; the pH values of slurries are in the range from 6.5 to 10.5 determined by a Model 720A pH meter (Cole-Parmer Instrument Company, Vernon Hills, IL), and the densities of slurries are in the range from 1.02 to 1.08 g/cm³ as measured using a balance and a 1000 mL graduated cylinder. The rheological property results of slurry of bentonite-water slurries are shown in Figure 1, and the results indicated that slurries with 8% and 10% bentonite content could satisfy the desired rheological properties for SB backfills slurry wall constructions. For economic and

TABLE 1: Properties of CB used in this study.

Index	CB	Test method
Silt fraction (2–75 μm , %)	100	ASTM D 422
Clay fraction (<2 μm , %)	69.3	ASTM D 422
Classification	CH	ASTM D 2478
Liquid limit (%)	269	ASTM D 4318
Specific surface area (m^2/g)	252	EGME method
Swell index ($\text{mL}/2\text{g}$)	16.0	ASTM D 5890
pH (water)	10.33	ASTM D 4972
G _s	2.72	ASTM D 854
CEC (meq/100 g)	48.1	ASTM D 7503
Ca ²⁺ (meq/100 g)	14.5	ASTM D 7503
Mg ²⁺ (meq/100 g)	0.6	ASTM D 7503
Na ⁺ (meq/100 g)	32.7	ASTM D 7503
K ⁺ (meq/100 g)	0.3	ASTM D 7503

TABLE 2: The mineral fraction of CB based on X-ray diffraction analyses.

Minerals	Montmorillonite	Kaolinite	Quartz	Plagioclase feldspar	Calcite	Chlorite
Fraction (%)	66.9	1.0	18.1	11.7	1.7	0.6

TABLE 3: Properties of polymer used in this study (data from the manufacturer).

Index	PAC
pH	7.3
Particle size (mm)	<0.15
w (%)	5.7
Swell index ($\text{mL}/2\text{g}$)	152.0
G _s	1.26
Polymer charge	Anionic
Apparent viscosity (mPa·s)	35
Bulk density (g/cm^3)	0.4
Polydispersity index (PDI)	3.22
Weight (average molecular weight)	1730000

TABLE 4: The dosage of constituent soils and polymer in base mixtures.

Backfill ID	SC (%)	BC (%)	PC (%)
SB	90	10	0
PSB-0.3	89.7	10	0.3
PSB-0.6	89.4	10	0.6
PSB-0.9	89.1	10	0.9
PSB-1.2	88.8	10	1.2

low-carbon costs consideration, the slurry with 8% bentonite content was selected as the reasonable test slurry.

2.4. Backfill Slump Testing. The 8% bentonite-water slurry was thoroughly mixed with base mixture in various proportions to determine the amount of slurry, the mixing processes of which were carried out by using a paddle mixer, and the corresponding water content required to satisfy the workability of backfills with a measured slump of 125 ± 5 mm (ASTM C143). Three slump tests were performed for each specimen at any given water content to eliminate the variability in measured slumps, and the amount of added

slurry was varied to provide a range of slump values and a corresponding range in the backfill-slurry water content (w_{bs}). The measured slumps of SB and PSB with various polymer dosages are shown in Figure 2.

The total bentonite content (BC_{total}) in the backfill was calculated using the following equations:

$$BC_{\text{total}} = \frac{(m_{\text{ben}} + m_{\text{ben,s}})}{m_{\text{total}} * 100\%}, \quad (1)$$

$$m_{\text{ben}} = (m_{\text{total}} - m_{\text{ben,s}}) * c_{\text{b}}, \quad (2)$$

$$m_{\text{ben,s}} = \frac{(m_{\text{total}} * w_{\text{bm}})}{(1 - c_{\text{b,s}}) * c_{\text{b,s}}}, \quad (3)$$

where m_{ben} is the mass of dry bentonite in the base mixture, $m_{\text{ben,s}}$ is the mass of dry bentonite from bentonite-water slurry, m_{total} is the mass of backfill dry mass, c_{b} is bentonite dosage of base mixture (i. e., 10% in this study), and $c_{\text{b,s}}$ is the bentonite contents of slurry (i. e., 8% in this study). The total bentonite contents of backfills with water contents of w_{bs} were calculated, and the results are plotted in Table 5.

2.5. Permeate Liquids. Lead (Pb) was selected as a target contaminant as it was the most common contaminant found in subsurface soils and groundwater. To simulate Pb exposure, distilled water (DW) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$) solutions were selected at various concentrations. The $\text{Pb}(\text{NO}_3)_2$ solutions were prepared by dissolving a certain mass of $\text{Pb}(\text{NO}_3)_2$ powder (chemical analytical reagent) in a known volume of distilled water to yield solutions with the designed concentrations (c_{d}) of Pb (20, 50, 100, 200, and 500 mM). These concentrations are similar with the concentrations of heavy metal used in the previous studies [10, 14, 23]. The Pb concentration (c_{m}) was measured by an atomic absorption spectrometer (ICE 3300, Thermo Fisher Scientific Inc.). Triplicate samples are tested, and the average

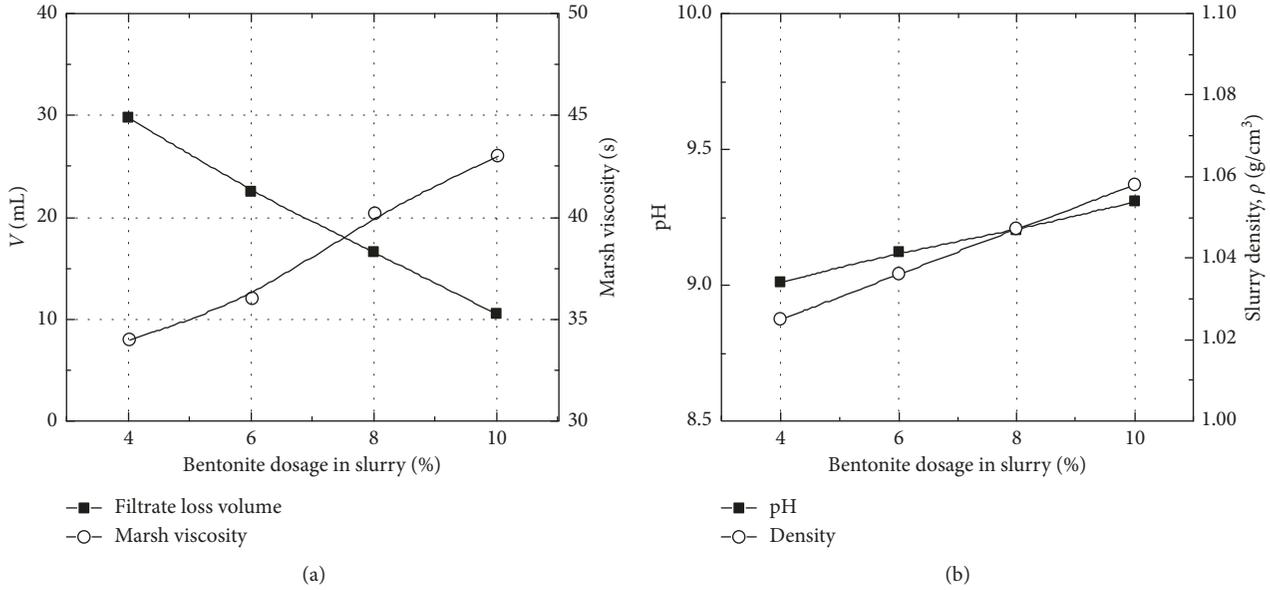


FIGURE 1: The rheological properties of bentonite-water slurries.

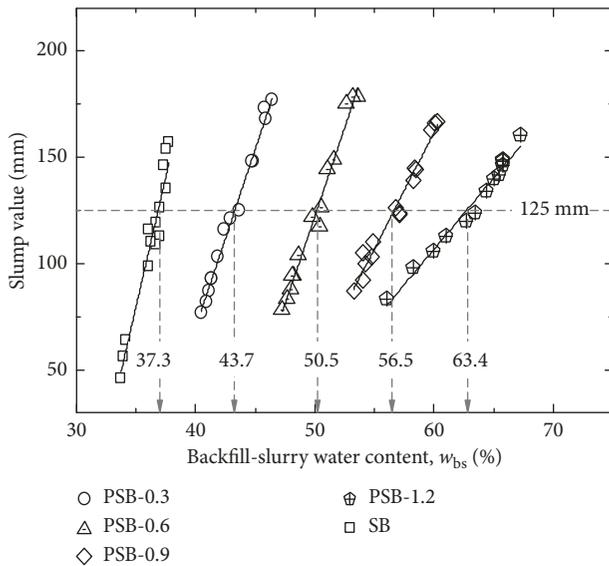


FIGURE 2: The slump values of SB and PSB with various polymer dosages.

values are calculated. The density (ρ) of solutions was measured by a hydrometer 151H, and the absolute viscosity (μ) of solutions was tested by using a rotational Brookfield viscometer DV2T. The EC was tested through an electrical conductivity probe (150A conductivity meter, Thermo Orion, Beverly, Massachusetts). The solution pH was conducted by a HORIBA D-54 pH meter as per ASTM D 4972. The index property results of $Pb(NO_3)_2$ solutions are shown in Table 6.

2.6. Modified Filter Press Test. The test process was originated with ASTM D5891 [24] and the API 131B, and hydraulic conductivity tests of backfills with API filter press

apparatus (the inner diameter is 76.2 mm) are conducted. Firstly, the cell was upside down on the test platform, and then the petrolatum was lightly greased on sidewall to avoid sidewall leakage. The polyethylene (PE) backing ring, saturated porous stone, and filter paper were successively placed in the bottom of the cell. The aged saturated backfills with calculated mass was then poured into the cell, and it was compacted with an earth knife until it reached the designed thickness (i. e., 2.5 cm in this study). The backfills were covered by another saturated filter paper and porous stone successively, and then the bottom cap of the cell was hermetically closed and turned over to keep it upright. Finally, the 120 mL test liquid was filled into the cell through inlet hole by a Pasteur pipette, and air pressure was applied on the top of the material through the inlet hole.

In order to obtain a relationship between hydraulic conductivity and stress, tests were performed under several different applied pressures ranging from 50 kPa to 400 kPa, which could be representative of stress conditions in site. The pressures induced by liquid self-weight and soil self-weight were negligible compared to air pressure, which had very limited influence on consolidation and effective pressure of specimens. Therefore, the liquid self-weight and soil self-weight could be ignored when the total applied pressure was calculated.

The typical termination criteria usually used during the test were (1) a steady hydraulic conductivity value for at least 4 consecutive measurements, (2) the hydraulic conductivity test should be performed for more than 24 h, (3) the ratio of pH, electric conductivity (EC), and the Pb concentrations between the effluents and influents are within 1.0 ± 0.1 [25–27]. At the end of the test, the effluent leachate volume and elapsed time were measured; the cell was disassembled immediately, and the properties of backfills (height, weight, and moisture content) were measured. The height of the specimen was measured five points on the surface with a

TABLE 5: The initial index properties of backfills before modified filter press test.

Samples	BC _{total} (%)	w _{bs} (%)	Initial height, L ₀ (mm)	Density, ρ ₀ (g/cm ³)	Specific gravity, G _s	Degree of saturation, Sr (%)	Initial void ratio e ₀
SB	12.9	37.3	20	1.77	2.69	92.90	1.08
PSB-0.3	13.4	43.7	20	1.73	2.68	96.03	1.22
PSB-0.6	13.9	50.5	20	1.67	2.66	93.28	1.40
PSB-0.9	14.4	56.5	20	1.59	2.67	93.02	1.62
PSB-1.2	14.9	63.4	20	1.54	2.66	92.63	1.82

TABLE 6: The index properties of the Pb(NO₃)₂ solutions.

Target concentration (mM)	Measured concentration (mM)	Density (g/cm ³)	Absolute viscosity, μ (mPa·s)	EC (μS/cm)	pH
0	0	1.00	1.13	724	4.99
20	19.9	1.01	1.14	2481	4.92
50	50.1	1.02	1.23	5425	4.87
100	99.8	1.04	1.33	9040	4.62
200	199.7	1.07	1.58	16931	4.12
500	500.2	1.17	1.64	31022	3.78

digital slide caliper. The void ratio of backfills specimens was calculated from specific gravity, dry density, and water content of backfills specimens. The hydraulic conductivity of backfills was obtained from the following equations:

$$k_{MFP} = \frac{V}{Ait}, \quad (4)$$

$$i = \frac{H_0}{L} = \frac{P_0}{\gamma_w L}, \quad (5)$$

where V is the leachate volume (m³), t is the elapsed time (s), A is the cross section area of backfill specimens (m²), i is the hydraulic gradient, H_0 is the headwater value, L is the length of backfills specimens, and γ_w is the gravity of water.

During the MFP test, the backfills were compressed by the applied pressure, P_0 (i. e., air pressure), and the average effective pressures ($P_{e,ave}$) of various backfills positions were different, which could be calculated from the following equations [27]:

$$P_{e,ave} = \frac{P_0}{L * \int_0^L \left(1 - \frac{x}{L}\right)} = \frac{P_0}{L * \left(L - \frac{L^2}{2L}\right)} = 0.5P_0, \quad (6)$$

where x is the distance between the calculated position to the bottom of backfills specimen.

After the MFP test, the specific gravity (G_s) and liquid limits (w_L) of backfill specimens were evaluated following the ASTM standards.

2.7. Flexible-Wall Permeability Test. The flexible-wall permeability test (FWP test) with the constant headwater method was conducted to verify the effectiveness of the MFP test. SB and PSB-0.6 backfills were used in comparison; the Pb(NO₃)₂ solutions with various concentrations (0–500 mM) were used as the permeant liquid. A rigid acrylic cylinder with inside diameter of 50 mm and height of 50 mm was placed around the flexible membrane to support the soft specimens during preparation of specimens, setting up into

the testing cell, and permeation periods. After the specimens were prepared, they were placed into the vacuum saturation chamber for the purpose of specimen saturation, the air within cylinder was extracted for 2 h, then the influent valve of chamber was opened, and clean tap water was passed into the chamber under the air pressure until the liquid level higher than the specimens; the influent valve was then turned off, the influent tube moved out of the tap water surface, then influent valve was then turned on again for at least 4 h, and the specimens were saturated under the air pressure applied. After the specimen saturation was completed, the triaxial cell was assembled and a nominal confining pressure was applied. The average effective confining stress was maintained at 100 kPa, and the corresponding hydraulic gradient was 200. During the permeation period, the effectiveness stress was realized by setting cell pressure, bottom pressure, and top pressure as plotted in Table 7, respectively. The effluent bottle was connected with atmosphere, and hence the top pressure was 0 kPa. According to the ASTM D7100 standard [28], the permeation for each specimen was continued until at least four values of hydraulic conductivity are obtained over an interval of time and all of the following criteria are satisfied: (1) the ratio of outflow to inflow (Q_{out}/Q_{in}) shall be between 0.75 and 1.25; (2) the hydraulic conductivity shall be considered steady if four or more consecutive hydraulic conductivity determinations fall within $\pm 25\%$ or better of the mean value for $k \geq 1 \times 10^{-10}$ m/s or within $\pm 50\%$ or better for $k < 1 \times 10^{-10}$ m/s (3) at least 2 pore volumes of flow (PVF) shall occur through the specimen; (4) the ratio of pH, electric conductivity (EC), and Pb concentrations between the effluents and influents is within 1.0 ± 0.1 . Then, the permeated solution was replaced by Pb(NO₃)₂ solution with higher concentration, and permeation was conducted continually similar with the previous stage.

3. Results and Analysis

3.1. Index Properties of Backfills. The specific gravity (G_s) results of both SB and PSB are shown in Figure 3(a). In

TABLE 7: The pressure used in flexible-wall permeability test.

Hydraulic gradient, i	Bottom pressure, P_B (kPa)	Top pressure, P_T (kPa)	Cell pressure, P_C (kPa)	Effectiveness stress, P_e (kPa)
200	100	0	105	38.3

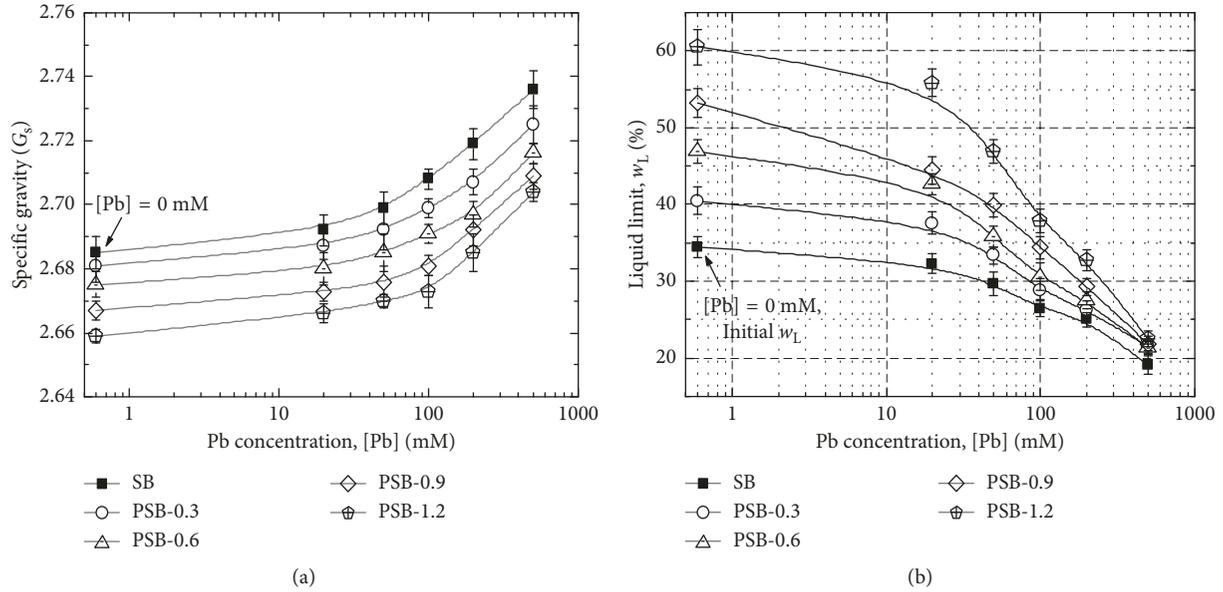


FIGURE 3: (a) The relationship between specific gravity of backfills and Pb concentrations (number of replicates = 3; coefficient of variation ≤ 0.01) and (b) the relationship between liquid limits of backfills and Pb concentrations (number of replicates = 3; coefficient of variation ≤ 0.04).

general, the G_s of PSB decrease with the increase of PAC dosage in backfills and the G_s both SB and PSB increase with the increase of Pb concentration. With PAC content from 0 up to 1.2%, the G_s of backfills decrease from 2.69 to 2.66. With Pb concentration increasing from 0 to 500 mM, the G_s of SB increases from 2.69 to 2.73 and the G_s of PSB-1.2 increases from 2.68 to 2.72. The reasons for these phenomena can be attributed to the lower G_s of PAC ($G_s = 1.26$) compared to SB ($G_s = 2.69$), and the elevated G_s with respect to the Pb concentration is attributed to the higher G_s of Pb ($G_s = 4.53$) compared to SB [29, 30].

The results of liquid limits of both SB and PSB are presented in Figure 3(b). When exposed to DW, the w_L of PSB increases with the dosage of PAC. With PAC content from 0 up to 1.2%, the w_L of PSB increases from 34.5 to 60.5, which is almost twice of conventional backfills (i. e., SB). However, when exposed to $Pb(NO_3)_2$ solutions, the w_L of both SB and PSB decreases with the increasing Pb concentration. With the Pb concentration increasing from 0 (DW) to 500 mM, the w_L of SB backfills decreases from 34.5 to 19.1 and the w_L of PSB-1.2 decreases from 60.5 to 22.5. The water absorbing capacity of PAC improves the w_L of PSB, while the increasing predominance of lead ions (Pb) result from cation exchange with sodium ions (Na^+) and potassium ions (K^+) between bentonite interlayers, which causes stronger net interparticle forces and leads to a lower w_L of bentonite [31, 32].

3.2. Assessment of Chemical Equilibrium Conditions. The chemical equilibrium is verified after the MFP test; the

electrical conductivity (EC), pH, Pb concentrations of influent solution (i.e., initial test solutions), and effluent leachate are measured as a supplemental criterion. Figure 4 shows the properties of effluent solution from SB and PSB specimens under 100 kPa overall stress at chemical equilibrium. The ratio of EC in effluent solution to EC in influent solution (EC_{out}/EC_{in}) is within 1.0 ± 0.1 , the ratio of pH in effluent solution to pH in influent solution (pH_{out}/pH_{in}) is within 1.0 ± 0.1 , and the Pb concentrations in effluent solution is within 1.0 ± 0.1 of the influent solution ($0.9 \leq c_{out}/c_{in} \leq 1.1$). The results indicate that chemical equilibrium has been established in accordance with ASTM D7100.

3.3. The Optimum Polymer Dosage. The k_c of backfills permeated with $Pb(NO_3)_2$ solutions is shown in Figure 5, for a certain Pb concentration; the k_c of backfills decreases with the increasing PAC content of backfills; and for a given PAC content, the k_c of backfills increases with Pb concentration. Under applied pressure 100 kPa, the k_c of PSB-0.6 was maintained lower than 10^{-9} m/s, regardless the Pb concentration variation, which is below the limit designed value of hydraulic conductivity for typical sand-bentonite backfills in vertical cutoff walls [1, 33]. The k_c/k_w of PSB-0.6 is lower than 10 permeated with concentrated $Pb(NO_3)_2$ solution (100–500 mM), indicating that the k_c of PSB-0.6 has no obvious increase. The results indicate that the additive PAC can improve the hydraulic performance and chemical compatibility of backfills when exposed to $Pb(NO_3)_2$ solutions.

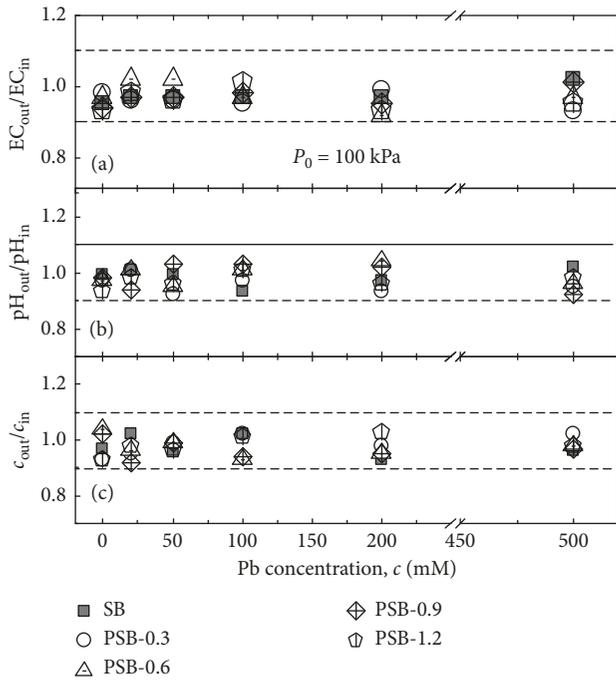


FIGURE 4: The properties of effluent leachate: (a) EC_{out}/EC_{in} , (b) pH_{out}/pH_{in} , and (c) c_{out}/c_{in} .

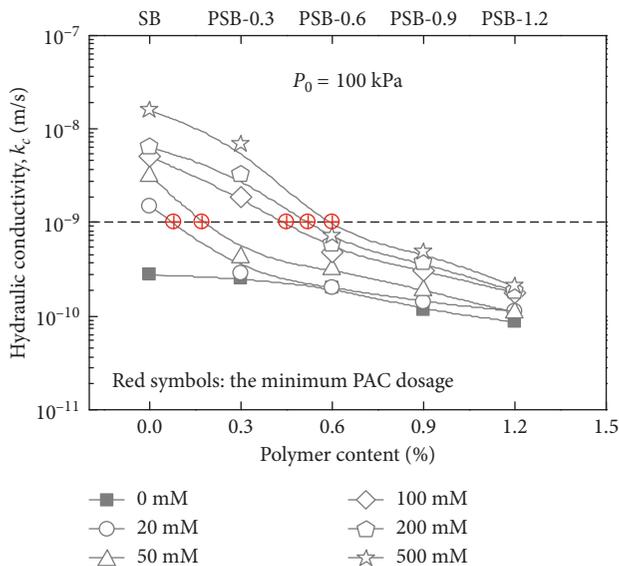


FIGURE 5: The correlation of k_c -polymer content of backfills permeated with $Pb(NO_3)_2$ solutions.

Figure 6(a) presents the minimum PAC dosage of backfills (obtained from Figure 5) that satisfy requirements of hydraulic performance, when permeated with various $Pb(NO_3)_2$ solutions under 100 kPa. When permeated with concentrated $Pb(NO_3)_2$ solutions (100–500 mM), PSB with PAC dosage less than 0.6, the backfills exhibit $k_c > 10^{-9}$ m/s and $k_c/k_w > 10$. Therefore, the minimum PAC dosage of backfills that satisfy requirements of hydraulic performance is 0.6. Figure 6(b) shows the minimum PAC dosage of backfills exposed to 500 mM $Pb(NO_3)_2$ solutions under

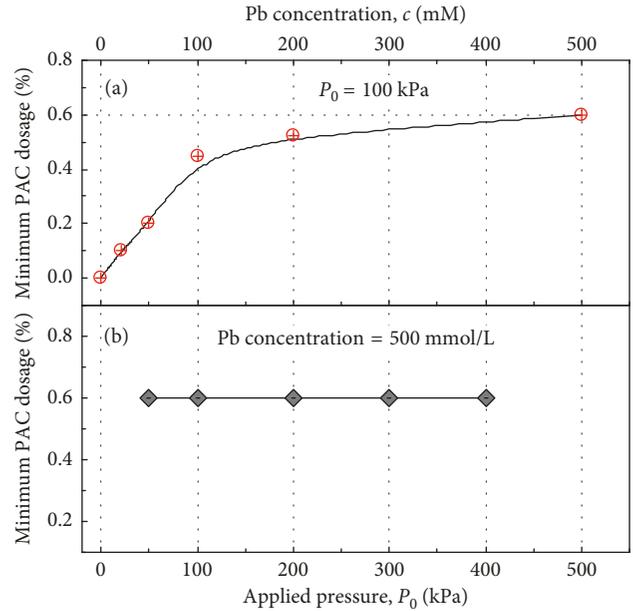


FIGURE 6: (a) The minimum PAC dosage of backfills when exposed to $Pb(NO_3)_2$ solutions with various concentrations, and (b) the minimum PAC dosage of backfills permeated with 500 mM Pb under various pressures.

various pressures, which is a constant value 0.6, regardless the pressure variation; the result demonstrates that the minimum PAC dosage is independent on pressure. Based on the above analysis, the PAC content 0.6% is supposed as the optimum PAC dosage of backfills. In the following tests, the conventional backfills (SB) and PSB-0.6 were used in the MFP test under various pressures and the flexible-wall permeability test.

3.4. Void Ratios of Backfills. The correlation between void ratio (e) of SB and PSB-0.6 backfills under average effective pressure is presented in Figure 7. Generally, PSB-0.6 backfills have greater e value than SB backfills, and the e values of both backfills decrease with increasing $P_{e,ave}$ and Pb concentration. The results can be attributed to the following: the additive PAC in PSB-0.6 adsorbs more water and exhibits superior swell capacity, which also contributes to the higher water content of PSB-0.6, resulting in higher void ratio of PSB-0.6 compared to conventional backfills SB. Additionally, the lead ions (Pb) of liquids exchange the sodium ions (Na^+) and potassium ions (K^+) between bentonite interlayers, which causes the diffuse double layer (DDL) of bentonite compressed, and results in void ratio reduced.

3.5. Hydraulic Conductivities of Backfills. The relationship between k_c of backfills and the average effective pressure ($P_{e,ave}$) is shown in Figure 8. The k_c of PSB-0.6 is lower than k_c of SB; the k_c of both SB and PSB-0.6 backfills decreases with increasing $P_{e,ave}$ and increases with Pb concentration. The results indicate PSB-0.6 has superior hydraulic performance compared to conventional backfills (SB), and

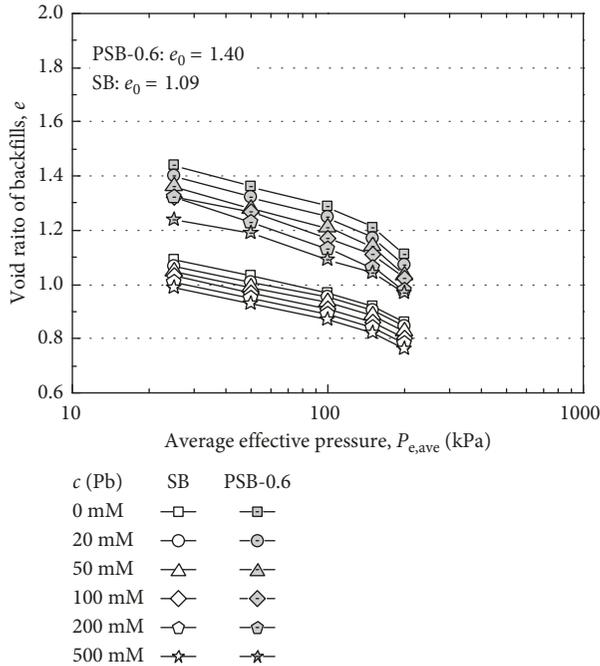


FIGURE 7: The void ratio (e) of backfills and applied pressure.

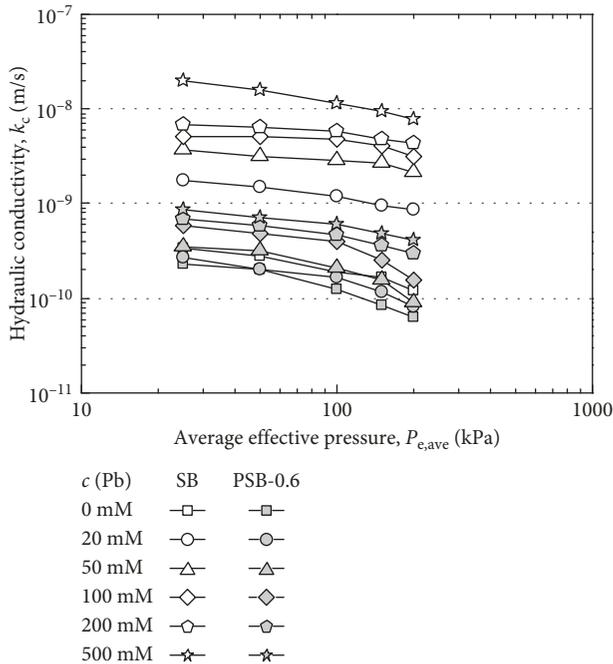


FIGURE 8: The relationship between hydraulic conductivity (k_c) of backfills and the average effective pressure ($P_{e,ave}$).

higher $P_{e,ave}$ results in smaller e value of backfills, which leads to lower k_c for a certain Pb concentration.

3.6. Relationship between Hydraulic Conductivities and Pb Concentrations. Figure 9(a) shows the relationship between k_c of backfills and Pb concentration (c), and Figure 9(b) displays the correlation between k_c/k_w and c . Generally, the

k_c of SB and PSB-0.6 increases with Pb concentration, and k_c of SB is greater than that of PSB-0.6. When Pb concentration is equal to 20 mM, the k_c of SB backfills exhibits greater than 10^{-9} m/s and the k_c/k_w of SB greater than 10 under the applied pressure 100 kPa, while the k_c of PSB-0.6 remains lower than 10^{-9} m/s and the k_c/k_w of PSB-0.6 is less than 10 though the Pb concentration up to 500 mM. The results demonstrate that SB would have a significant increase once permeated with Pb concentration over 20 mM, whereas the PSB-0.6 could maintain low hydraulic conductivity ($<10^{-9}$ m/s) in the Pb concentration range from 0 to 500 mM. The hydraulic performance of backfills can be improved effectively when exposed to $Pb(NO_3)_2$ solution by the additive PAC.

In order to investigate the impact of Pb concentrations on hydraulic conductivity of conventional backfills SB, the MFP tests on SB specimens permeated with $Pb(NO_3)_2$ solution with 0 to 50 mM (0, 5, 10, 15, 20, 30, 40, and 50 mM) were conducted, and the applied pressure was 100 kPa. The k_c and k_c/k_w of SB backfills exposed to $Pb(NO_3)_2$ solution with 0 to 50 mM are presented in Figure 10. When Pb concentration is lower than 5 mM, the k_c of SB increases slightly and the k_c/k_w of SB is approximately equal to 1 time; with Pb concentration higher than 5 mM, the k_c and k_c/k_w of SB exhibit obvious increase. When Pb concentration is equal to 15 mM, the k_c of SB is 9×10^{-9} m/s, which is almost equal to the limited value of hydraulic conductivity in hydraulic barriers (1×10^{-9} m/s). With Pb concentration growing up to 45 mM, the k_c/k_w of SB is about 10 times, indicating that the k_c of SB increases one order of magnitude and the hydraulic performance of SB backfills is significantly destroyed when exposed to Pb concentration higher than 45 mM. The reason for the increase of hydraulic conductivity of SB might be attributed to the diffuse double layer compression of bentonite; when exposed to divalent cations solutions (i. e., Pb^{2+} in this study), divalent cations replace monovalent cations (i. e., Na^+ , K^+) originally in the exchange complex, thereby reducing or eliminating the osmotic swell of bentonite [17, 32], resulting in flow paths more open and unimpeded and higher k_c of SB.

3.7. The Validity of the Present Study. The chemical equilibrium is evaluated during the flexible-wall permeability (FWP) test. As shown in Figure 11, the ratio of outflow to inflow (Q_{out}/Q_{in}) are within 1.0 ± 0.25 and the pore volumes of flow (PVF) are greater than 4 at each stage; the ratio of pH, electric conductivity (EC), and Pb concentrations between the effluents and influents are within 1.0 ± 0.1 . The results demonstrate that chemical equilibrium between $Pb(NO_3)_2$ solution and backfills has been established as per ASTM D7100 [28].

Hydraulic conductivity values of backfills from MFP tests (k_{MFP}) and flexible-wall permeability tests (k_{FWP}) are plotted in Figure 12. By comparison, k_{MFP} values are 4 to 6 times greater compared to the k_{FWP} value when permeated with DW. However, k_{MFP} values are less than 4 times greater compared to the k_{FWP} value when exposed to $Pb(NO_3)_2$

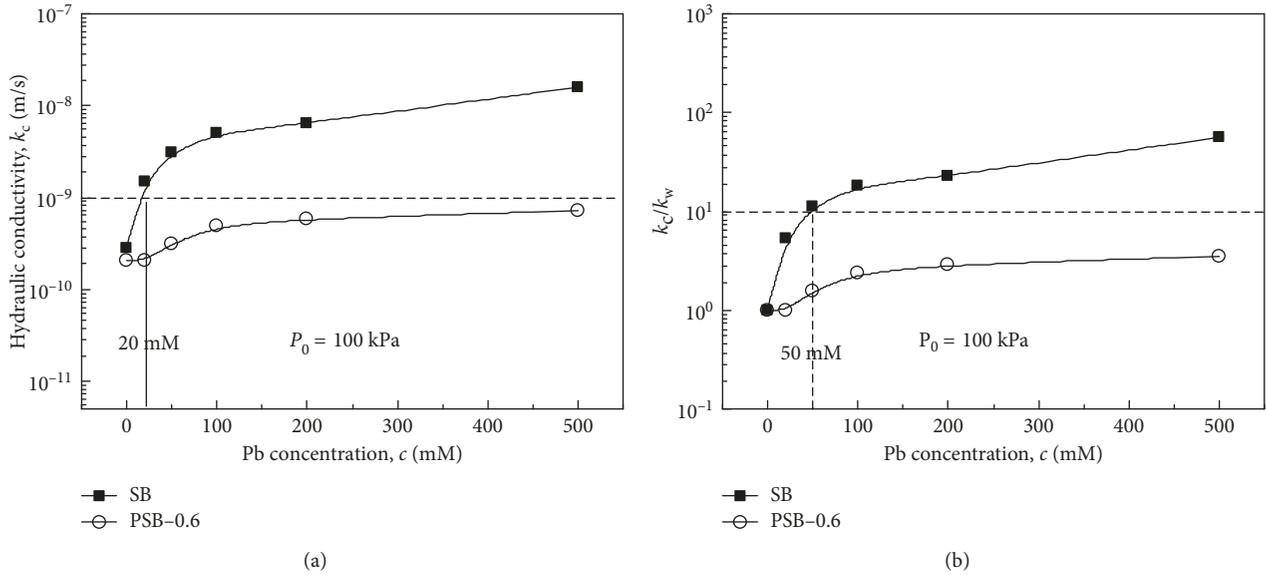


FIGURE 9: The relationship between (a) hydraulic conductivity of (k_c) of backfills and Pb concentration (c), and (b) hydraulic conductivity ratio (k_c/k_w) of backfills and c .

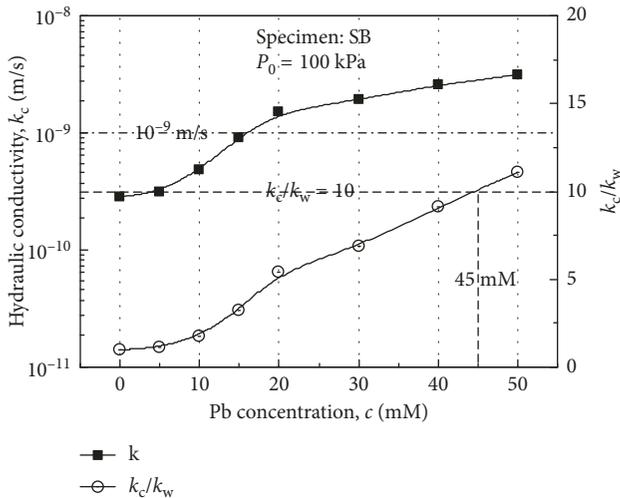


FIGURE 10: The hydraulic conductivity of (k_c) of SB backfills when exposed to $Pb(NO_3)_2$ solution with 0 to 50 mM.

solutions (20–500 mM), It should be noted that the k_{MFP} of SB are approximately equal to k_{FWP} of SB when permeated with $Pb(NO_3)_2$ solutions. These results suggest that k_{MFP} values and k_{FWP} value of backfills are within the same order of magnitude, which demonstrate that the modified filter press test is an effective and easy evaluation of hydraulic conductivity of backfills.

4. Discussion

The results indicate that PAC-amended sand-bentonite backfills have superior hydraulic performance and chemical compatibility compared to conventional backfills, when exposed to $Pb(NO_3)_2$ solutions. The underlying mechanism of PAC-amended bentonite may include the following: (1) polymer intercalation between bentonite interlayers, which

increases the space between platelets and activate osmotic swell [34]. (2) Polymer adsorption to bentonite surface through exchangeable cation bridging [35]. In general, the extent of adsorption depends on the molecular weight and number of hydrophilic functional groups [36]; PAC has a large amount of carboxyl and hydroxyl groups and an enough molecular weight (1,730,000), which can adsorb many bentonite surfaces with a single polymer molecule by exchangeable cation bridging. (3) Polymer chains remove the intergranular porosity and stitch the granules together [14].

Previous studies [14, 37] indicate that a polymer can adsorb large amount of water molecules and then forms swellable hydrogels at the macroscale, which forms a three-dimensional net structure between bentonite granules. The water molecules in the hydrogel polymer are immobile compared to free water in the pore space. Therefore, the hydrogel polymer clogs larger pores that can conduct flow of water and solutes in backfills.

Moreover, the modified methods of bentonite may have an important impact on the chemical compatibility of polymer-amended bentonites and backfills; previous studies have conducted several modified methods: (1) polymer is directly mixed with dry bentonite [15, 27, 38]; (2) polymer solution is blended with bentonite slurries [13, 20]; and (3) monomer solution polymerization in bentonite slurry [14, 34]. The difference between several methods for PAC-amended bentonite and backfills should be investigated in the next study.

Additional research is warranted to investigate the adsorption property, membrane behavior, and microscopic mechanism of the PAC-amended sand-bentonite backfills under lead ion contaminated conditions.

5. Conclusions

A series of basic properties tests of slurry and backfills and MFP tests were conducted to investigate the effects of PAC

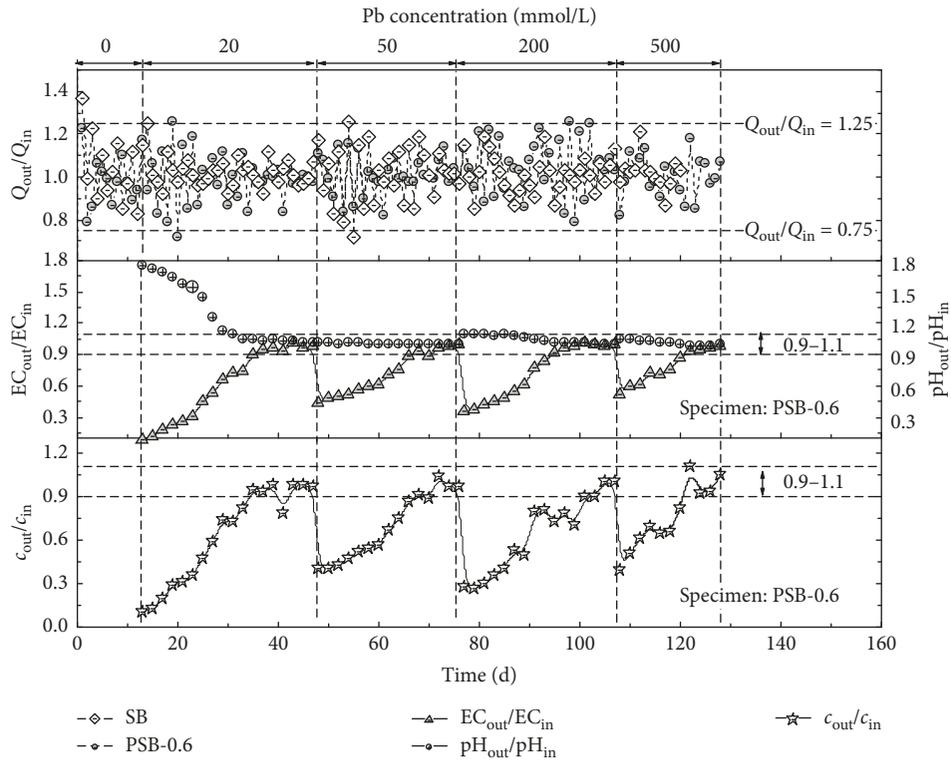


FIGURE 11: The chemical equilibrium condition of the flexible-wall permeability test.

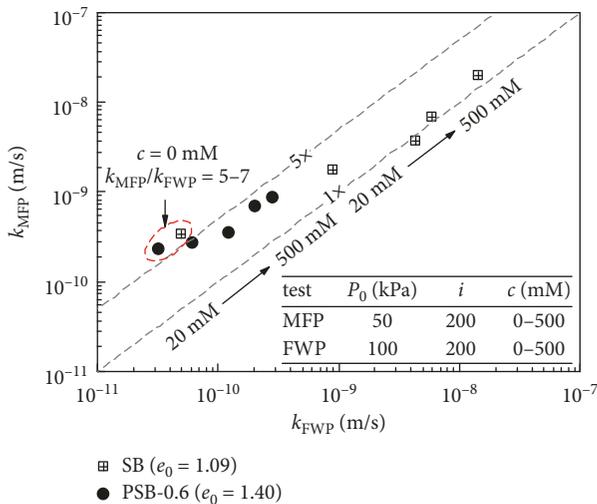


FIGURE 12: Comparison of hydraulic conductivity calculated from modified filter press tests (k_{MFP}) and measured by flexible-wall permeability tests (k_{FWP}).

amendment on the hydraulic conductivity and compressibility of sand-bentonite backfills for slurry trench walls, and FWP tests were conducted to verify the effectiveness of the MFP test on backfills. The following conclusions can be drawn:

- (1) PSB has lower G_S and higher w_L compared to SB; increasing Pb concentration leads to G_S of PSB increased and w_L of PSB decreased.
- (2) The k_c of PSB-0.6 remains lower than 10^{-9} m/s and increases slightly ($k_c/k_w < 10$) compared to PSB and

SB permeated $Pb(NO_3)_2$ solution over 100 mM. Therefore, PSB with 0.6% PAC content is supposed as the optimum proportion for PSB backfills when permeated with $Pb(NO_3)_2$ solution.

- (3) PAC adsorbs large amount of bound water, which leads to higher water content (w) and e value of PSB backfills, while lead ions (Pb) cause the diffuse double layer (DDL) of bentonite compressed and e value of PSB backfills reduced.
- (4) The k_c of SB backfills exhibits greater than 10^{-9} m/s and increases obviously ($k_c/k_w > 10$) when exposed to $Pb(NO_3)_2$ solution with concentration greater than 45 mM, while the k_c of PSB-0.6 remains lower than 10^{-9} m/s and increases slightly ($k_c/k_w < 10$) though the Pb concentration up to 500 mM. The hydraulic performance of backfills can be improved effectively by the additive PAC when exposed to $Pb(NO_3)_2$ solution.
- (5) The k_{MFP} values and k_{FWP} values of backfills are within the same order of magnitude, which demonstrate that the modified filter press test is an effective and easy evaluation of hydraulic conductivity of backfills.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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