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Evaluation of Performance of Polyacrylamide-Modified Compacted Clay as a Gas Barrier: Water Retention and Gas Permeability and Diffusion Characteristics

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Abstract: In this paper, the performance of a gas barrier that consisted of polyacrylamide (PAM)-modified compacted clayey soil was experimentally explored. The moisture content and water loss characteristics of the tested soils were adopted as indicative indices of water retention capacity (WRC). The gas permeability (K_p) and gas diffusion coefficient (D_p) of the modified compacted clays were evaluated via gas permeability and gas diffusion tests. The test results showed that the moisture content of the modified compacted clay samples subjected to drying tests increased with increasing polyacrylamide content. K_p and D_p decreased with increasing PAM content. Compared with 0.2% PAM content, the K_p of the sample with 1.0% PAM was reduced by ten times, and the D_p was reduced to ~35%. Compared to the unmodified clay, the liquid limit of the PAM-modified clay increased by 45~55%. Comparison of the liquid limit tests between this study and previous studies revealed that the liquid limit ratio of the zwitterionic polyacrylamide (ZP)-modified soil was much higher than the other material-modified soils. The results of this study are useful to facilitate the application of modified compacted clays as gas barrier materials at industrial contaminated sites.

Keywords: compacted clay; polyacrylamide; gas barrier performance; gas permeability; gas diffusion coefficient

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1. Introduction

The compacted clay cover (CCC), as one of the main horizontal barriers, is widely applied in industrial organics contaminated sites to effectively control upward migration of volatile organic compound (VOC) and semi-volatile organic compound (SVOC) vapors or gases [1]. Studies reveal that gas migration through the CCC in landfills is predominated by diffusion [2]. Diffusion of VOC and SVOC gases through CCC may lead to the emission of toluene gas in landfills, migrating from pollution sources in deep soil to the air [3]. Upward migration of gas in clay occurs via advection [4] and diffusion [5]. Diffusion is the primary mechanism of VOC and SVOC gas migration in clayey soils on most occasions [6,7]. Advection can affect the migration of VOC or SVOC gas only when the temperature and vapor pressure in clays are relatively high, e.g., during the summer season [8,9]. In real projects, the CCC stays unsaturated on most occasions, except for relatively heavy rainfall infiltration. There are three indicators that quantify gas advection in clays when air pressure is high, gas permeability, air-water relative permeability, and moisture content [10]. A critical step in evaluating a CCC's performance against VOCs or SVOCs is to measure the permeation and diffusion of gas while they change with the moisture contents of CCC.

The influence of moisture content in clay is significant for gas migration. In recent years, a geosynthetic clay liner (GCL) has been extensively used as the VOC/SVOC gas

barrier in contaminated sites. However, the bentonite in GCL is usually sodium-activated calcium bentonite in China, and the barrier performance is not as good as sodium bentonite GCL. This is because the high-quality sodium bentonite resources in China are scarce. Previous studies [11,12] found that the gas permeability of the sodium bentonite GCL decreased with increasing moisture content under different pressures. Studies have shown that the gas permeability changes after hydration from 1.0×10^{-18} to 1.0×10^{-11} m^2 [13–15]. After drying, the gas permeability of the GCL can range between 0.03 and 0.21 m^2 [16]. The VOC/SVOC gas migration from contaminated soil through GCL into the air is mainly controlled by pressure and concentration gradients. The advection governs gas flow caused by differential pressures, and the gas advection indicator is reflected by the gas permeability [17]. Gas migration due to a concentration gradient is controlled by the gas diffusion coefficient [18]. Rouf et al. [19] demonstrated that when the apparent degree of saturation (ADOS) of the sodium bentonite GCL increased greater than approximately 65%, both the gas diffusion coefficient and gas permeability of the GCL were considerably reduced. The ADOS is defined as the gravimetric water content (w) of a GCL at a given time, divided by the maximum gravimetric water content (w_{ref}) that the same GCL reaches during hydration under the same applied stress conditions [19]. It can be anticipated that the gas diffusion and gas permeability of CCC increase significantly with the decrease in both gravimetric water content and ADOS [20]. Extremely low moisture content will lead to VOC gas migration into clay by diffusion and advection more easily, thus impairing the CCC gas barrier efficacy. Low moisture contents in compacted clay can cause fissures due to water loss [21]. Ultimately, a crack network may develop from the fissures, becoming the preferential and dominant pathway for the upward advection of VOC or SVOC gas released from the unsaturated contaminated soils. Through laboratory tests, Drumm et al. [22] found that the hydraulic conductivity near soil cracks increased sharply as compared to intact soil that is not intact, confirming the existence of dominant flow paths after the soil cracked.

Adopting modified materials in CCC is one potential approach to suppress cracking caused by water loss and improve the gas barrier performance. Super absorbent polymers (SAP) are a type of polymers with strong water-absorbing capability, composed of many hydrophilic functional groups, such as carbonyls, hydroxyls, and quaternary ammonium salts. One of the most commonly used SAPs is polyacrylamide (PAM), which is usually adopted as a water retention agent in agriculture, due to its long-term water retention capabilities [23,24]. Studies [25–27] have shown that polymers are adsorbed on the surface of soil particles through physicochemical reactions. A polymer is one of the promising materials recently applied to soil stabilization. It has a long chain of monomers connected to each other by sufficiently strong and flexible Van der Waals forces. The polymer can encapsulate the soil particles and connect them through polymer chain expansion, thereby improving the soil's water retention capacity (WRC). As a result, the hydraulic properties, erosion resistance, and gas impermeability of the modified soils can be improved. Qi et al. [28] researched the dried cracking of clay modified by PAM through a constant temperature evaporation test and image processing technology. They found that PAM is effective in mitigating soil cracking and even inhibiting crack formation. In addition, Yu et al. [29] conducted column tests to compare the cracking of the GCL before and after PAM modification at different temperatures. They demonstrated that the number of GCL cracks decreased after PAM modification at 40 °C. Therefore, using PAM to modify the CCC is promising, as it may improve the WRC and enhance the gas barrier performance. Nevertheless, previous studies mainly focused on polymer-modified clay's WRC and hydraulic properties. The barrier performance of GCLs/CCCs containing VOC/SVOC gases should be evaluated not only by gas permeability and WRC, but also by the gas diffusion coefficient.

The primary purpose of this study was to investigate the gas barrier performance of PAM-modified CCCs. A series of laboratory tests were conducted, which included liquid limit, water retention, gas permeability, and gas diffusion tests. The results are

useful in facilitating CCC design and its application as gas barriers in VOC and SVOC contaminated sites.

2. Materials and Methods

2.1. In-Site Clay

Sampling the in situ CCCs was based on ASTM D3441 [30], The *Geotechnical Engineering Investigation Handbook* [31] and other references [32,33]. The specific sampling procedure was displayed in the authors' previous study [18]. A total of 40 sampling points were set up. Sampling depth was one-half of the CCC thickness. The GXY-1 engineering driller was adopted for rotary drilling sampling. The methods of the drilling operation were employed as per the *Geotechnical Engineering Investigation Handbook* [34], Standard practice for Classification of Soils for Engineering Purposes [35], and Geotechnical design, Part 2: Ground investigation and testing [36]. Samples should be wrapped in an impermeable material (plastic sealing bag) and stored in a shockproof box (filled with foam buffer) to prevent transport disturbance. The soil's fundamental physical properties were tested based on the standards of GB/T 50145–2007 [37] and ASTM D2487 [38]. Test results were shown in Table 1. Figure 1 is the plasticity chart to identify the soil classification. As the organic content of the CCC sample is only 4.2%, the soil of the contaminated site can be classified as clay with low LL, based on Figure 1 and ASTM D2487.

Table 1. Basic physical indicators of the clay used in the test.

Parameters	Number of Samples	Mean	Test Method
Natural moisture content (%)	40	22.5	ASTM D2216 [31,39]
Specific gravity, G_s	40	2.72	ASTM D854 [40]
Liquid limit, LL (%)	40	38.14	ASTM D4318 [41]
Plastic limit, PI (%)	40	14.90	
Optimal moisture content (%)	6	25.6	ASTM D7382 [42]
Maximum dry density (g/cm^3)	6	1.78	ASTM D4253 [43]
Organic content, C_{oc} (%)	6	4.2	ASTM D2974 [44]

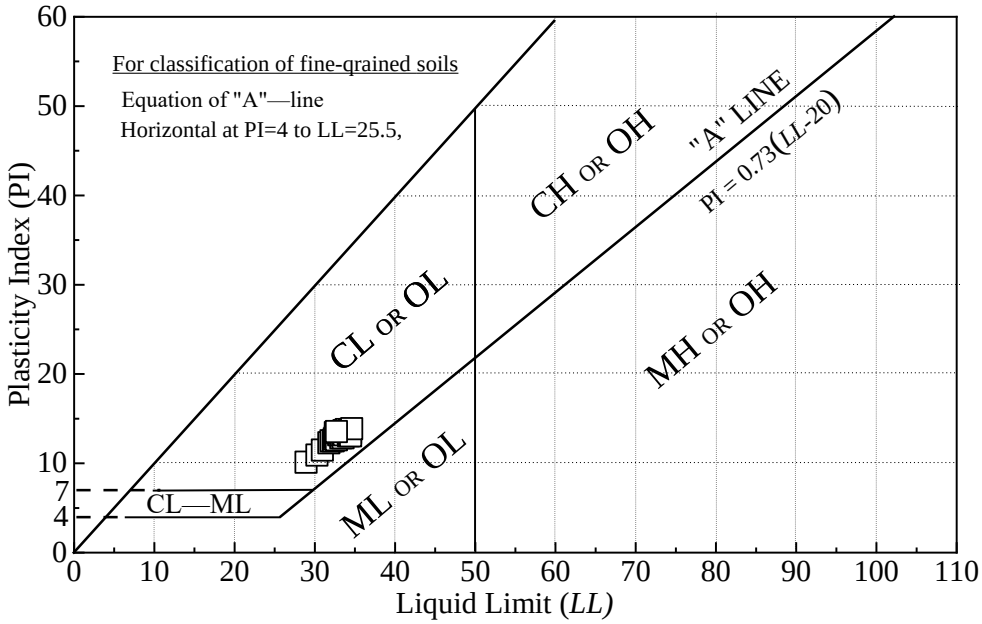

Figure 1. Plasticity chart for classification of fine-grained soils.

2.2. Polyacrylamide

There are four kinds of PAM in the market, cationic PAM (CP), anionic PAM (AP), nonionic PAM (NP), and zwitterion PAM (ZP). According to the authors' preliminary test

results (see Supplementary Materials), the zwitterionic PAM worked best in inhibiting the cracking of CCCs. The modified clay had a much lower gas permeability (K_p) and gas diffusion coefficient (D_p) with good gas barrier performance than that modified by cationic, anionic, and nonionic polyacrylamide. Hence, zwitterionic polyacrylamide was selected as the tested modifier in this research, which was provided by Henan Zhengzhou Lvjie Environmental Protection Material Co., Ltd. (Zhengzhou, China), with a molecular weight of 12 million and solid content no less than 90%. The parameters of PAM were shown in Table 2.

Table 2. Testing program and parameters of this study.

Testing Parameters	Values
Polymer type	Zwitterionic polyacrylamide (ZP)
Molecular weight	12 million
Admixture amount (%)	0, 0.2, 0.4, 0.6, 0.8, 1.0
Drying time (h)	0, 3.5, 7, 10.5, 14, 17.5
Testing program	Moisture content, water loss, gas permeability, gas diffusion, liquid limit

2.3. CCC Sample Preparation

The compacted clay samples were prepared according to the w_{opt} and ρ_{dmax} of the clay materials. The soil can reach the maximum degree of compaction only when it satisfies the w_{opt} and ρ_{dmax}. This is because Ralph R. Proctor proposed a compaction test, where a soil sample is compacted by means of a set of blows of a hammer per lift, which prove that the maximum dry density (ρ_{dmax}) of soil is related to certain moisture, called the optimum moisture content (w_{opt}) [45]. The soil samples with the size of 61.8 × 20 mm were prepared by the static compression method. The dry density and moisture content of all the compacted clay samples were 1.78 and 25.6%, respectively. The moisture content was in accordance with the optimum water content (w_{opt}).

The degree of compaction was designed based on the authors' previous study [46], which proved that compacted clays with 90% degree of compaction had superior gas barrier performance than those with lower degrees of compaction. The specific ZP-modified compacted samples were prepared as follows: (1) thoroughly mix the air-dried in-situ soils with a certain amount of ZP powder. The ZP dosage is shown in Table 2 (2) distilled water was added until the moisture content reached 25.6%, and the soil–water mixture was thoroughly stirred using a glass rod until uniform; (3) the above soil–water mixture was added into a rigid mold with a size of 61.8 × 20 mm, and it was statically compacted using a hydraulic jack to the designed degree of compaction of 90%; (4) CCC samples were sealed with plastic bags and cured in the curing room for 14 days until the samples reached the moisture balance.

The CCC samples used in the gas permeability and gas diffusion tests were prepared with the same method with that used in the WRC tests samples. It is noted that the samples were subjected to drying at various times of 0 h, 3.5 h, 7 h, 10.5 h, 14 h, and 17.5 h, respectively, and the drying temperature was 100 °C (see Table 2).

2.4. Test Methods

2.4.1. WRC Tests

After soil sample preparation, the compacted clay samples were placed in aluminum boxes. The opening percentage of the aluminum box was greater than 85%. The opening percentage is the ratio of hole area to the total lid area. Studies [47] show that PAM solutions can maintain at least half their original viscosity for more than 8 years at 100 °C and for approximately 2 years at 120 °C. Its backbone can remain stable at high temperatures. So, the soil samples were dried in an oven with a temperature of 100 °C in order to save time. The quality changes in the samples were recorded every 3.5 h, and Equations (1) and (2) were used to calculate the moisture content and water loss rates after drying.

The water loss rates of the clay samples after drying were calculated as follows:

$$W_s = \frac{m_0 - m}{m_s \times 25.6\%} \times 100\% \quad (1)$$

where w is the moisture content; m_s is the sum of the mass of the clay and polyacrylamide (g); m_0 is the mass of a compacted clay sample before being baked (g); m_t is the mass of a compacted clay sample after drying for time t (g), and W_S is the water loss rate (%).

2.4.2. Clay Gas Permeability Tests

The CCC samples used in the gas permeability tests were prepared with the same method as those used in the WRC samples. It is noted that the samples were subjected to drying at various times of 0 h, 3.5 h, 7 h, 10.5 h, 14 h, and 17.5 h, respectively, and the drying temperature was 100 °C. Gas permeability is defined according to Darcy's equation as the factor of proportionality between the ratio of gas flow and the pressure gradient along the flow distance. The gas permeability of the CCC samples was measured immediately after drying for 10.5 h at 100 °C. The air permeability of soil was measured using the Eijkelkamp-type air permeability apparatus (model 08.07, Eijkelkamp Agrisearch Equipment, The Netherlands) with the following procedures: firstly, the instrument should be tested for tightness before the test. The preliminary test results revealed that it had good airtightness and no air leakage. Secondly, a thick rubber sealing ring (inside diameter: 50 mm, outside diameter: 70 mm, thickness: 10 mm), a perforated plate (diameter: 53 mm, thickness: 1 mm, the diameter of the hole: 1 mm), and a compacted soil sample were placed into a sample holder (inside diameter: 105 mm, outside diameter: 150 mm, height: 50 mm, material: stainless steel) in turn and fixed with a clamp for subsequent sealing. Finally, the flow meter (range: 0.1~10 L/min, accuracy: 1.25%) was switched on by turning the button counterclockwise to a vertical position to control the air pressure within an acceptable range for measurement. Each measurement was repeated for 5 replications within a max. of 10 min and enabled the quantification of pneumatic soil properties.

The testing time should be kept as short as possible during the experiments. This is because gas will dry out the soil sample. Three identical samples were prepared for testing. The air pressure was set as 10 kPa. It is noted that the gravimetric moisture content change in the samples before and after the tests was found to be insignificant, i.e., within 3%. This is attributed to the relatively low gas flow rate (0.5 L/min) and short testing time (10 min). Rouf et al. have proven that a maximum variation in gravimetric moisture content of ±5% was deemed acceptable during the gas permeability tests [48].

The gas permeability (Kp) of the compacted clay samples in the tests was derived in accordance with the published studies [49,50].

$$K_p = \frac{k \cdot \rho_1 \cdot g}{\mu} \quad (2)$$

$$Q = \frac{k \cdot A \cdot P}{\mu \cdot L} \quad (3)$$

$$Q = v \cdot A = \frac{v}{t \cdot A} \cdot A = \frac{v}{t} \quad (4)$$

$$K_p = \rho_1 \cdot g \cdot \frac{V \cdot L}{t \cdot P \cdot A} \quad (5)$$

where K_p is the gas permeability of a clay sample (m^2); k is the permeability coefficient (m/s); ρ_1 is the air density (kg/m^3); t is the test time (s); V is the amount of air passing through the sample within time t (m^3); L is the thickness of the compacted clay sample to be tested (m); p is the actual pressure value (MPa), and A is the bottom area of the sample (m^2).

2.4.3. Gas Diffusion Tests

The CCC samples used in the gas permeability tests were prepared with the same method as that used in the WRC tests samples. It is noted that the samples were subjected to drying at various times of 0 h, 3.5 h, 7 h, 10.5 h, 14 h, and 17.5 h, respectively, and the drying temperature was 100 °C. The testing apparatus used for this study is schematically shown in Figure 2. The apparatus consisted of a 3D printing gas diffusion chamber, an oxygen sensor (KE-25, Figaro Inc., Tokyo, Japan) with the accuracy of ±1%, and a data-logger (CR1000, Campbell Scientific, Inc., Logan, UT, USA), and a computer. The oxygen sensor was used to measure the concentration of oxygen with a unit of % (the concentration defined based on the content of oxygen in the atmosphere, 21%). The location of this oxygen sensor is in the bottom of the diffusion chamber. The size of the diffusion chamber is shown in Figure 2. The soil sample is placed at the top of the diffusion chamber; thus, the oxygen gas can only migrate into the chamber through the soil sample. A soil sample can be rapidly inserted into the apparatus and sealed to prevent the loss of gases and water and can be removed without further soil disturbance. The steps of gas tightness self-tests were conducted as follows: (1) an air-tight PVC lib was covered on the top of the chamber, and (2) the nitrogen gaseous were released to fill the chamber. The oxygen concentration should be decreased to the threshold of 0.3~0.6%. (3) It can be considered that the chamber has good air tightness when the variation range of oxygen concentration is less than 0.3%. The specific practical steps were listed as follows: (1) the samples were placed at the top of the diffusion chamber; (2) the silicon grease was evenly applied to the contact part between the samples and the inner wall of the diffusion chamber. Applying the silicon grease was found to be effective in preventing gas migration through the gap in the contact part; (3) the air inlet and outlet valves were opened, and the nitrogen gas container was opened to introduce nitrogen into the diffusion chamber through the inlet. Furthermore, we adjusted the flow control valve to make nitrogen enter the diffusion chamber evenly and steadily through the inlet. The oxygen sensor was installed to monitor the oxygen concentration change in the diffusion chamber until all the oxygen was discharged, and (4) the oxygen was released when the oxygen concentration decreased to the threshold of 0.3–0.6%. The inlet was closed after injecting nitrogen for 5~15 s.

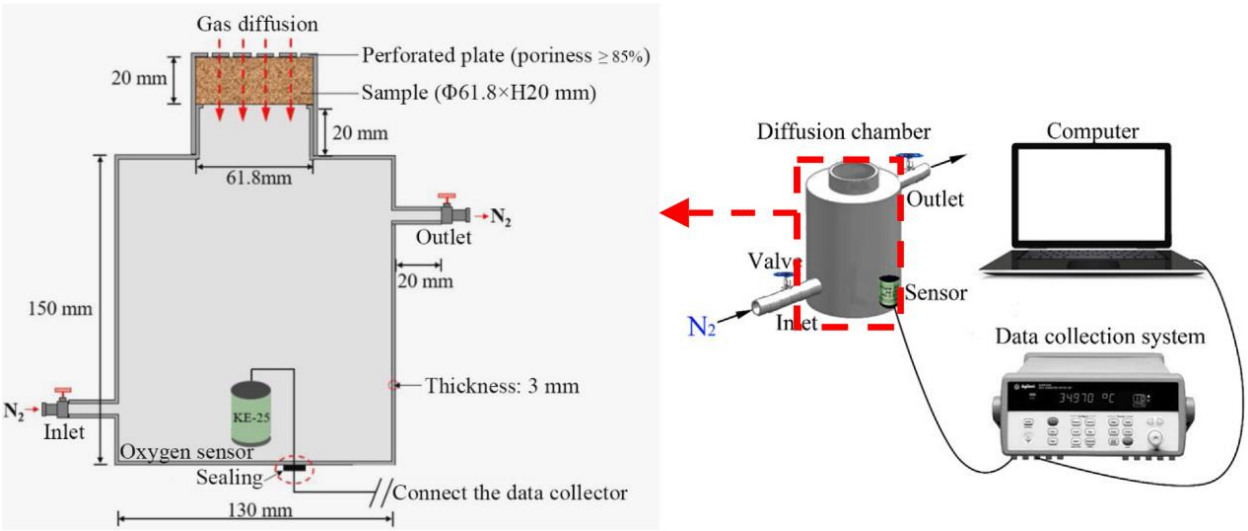

Figure 2. The 3D printing gas diffusion chamber.

In this research, a data acquisition instrument was applied to record the oxygen concentration in the diffusion chamber (C_t) every 5 min until the concentration was equal to the oxygen in the atmosphere (C_0), i.e., a steady state was reached.

The gas diffusion coefficients D_p of the compacted clay samples were calculated based on the previous studies [51,52] and combined with Fick's first law.

$$D_p' = h_s \cdot h_c \cdot k \quad (6)$$

$$\ln\left(\frac{\Delta C_t}{\Delta C_0}\right) = k \cdot t \quad (7)$$

$$K_j = \frac{D_p}{D_p'} = \frac{\varepsilon}{\alpha_1^2} \cdot \frac{1}{h_s \cdot h_c} \quad (8)$$

$$\varepsilon = 1 - \frac{\rho_b}{\rho_s} - \theta_V \quad (9)$$

where D_p is the correction gas diffusion coefficient (m^2/s); D_p' is the gas diffusion coefficient before calibration (m^2/s); h_s is the height of the compacted clay sample (m); h_C is the height of the diffusion chamber (m); k is the slope of the straight line in the scatter diagram of $\ln(\Delta C_t/\Delta C_0)$ (dimensionless); ΔC_t is the difference between OC at both ends of the clay sample at time t (g/cm^3); ΔC_0 is the difference between OC at both ends of the clay sample at time t_0 (t_0 means initial stage); K_j is the corrected coefficient introduced with changes in the storage capacity of OC; α_1 is the first solution of the equation $(\alpha \times h_S)\tan(\alpha \times h_S) = (h_S \times \varepsilon)/h_C$ greater than 0; ε is the gas-filled porosity [53]; ρ_b is the bulk density of the soil sample (g/cm^3); ρ_s is the particle density of the clay (g/cm^3); and θ_v is the volumetric moisture content of the clay sample.

2.4.4. Liquid Limit Test

The liquid limit test was conducted according to ASTM D4318 [39]. The liquid limit and plastic limit data were obtained from a liquid–plastic combined tester according to the standard test method SL237-007-1999 [54].

3. Results and Discussion

3.1. Liquid Limit

Figure 3 shows the relationship between the liquid limit of the modified compacted clay and the content of ZP. The liquid limit increases with the increasing ZP, which is higher than the unmodified clay (in Table 1). The liquid limits of the compacted clay were 45%, 49%, 52%, 54%, and 55%, when the corresponding ZP content ranged from 0.2 to 1%. Previous studies have demonstrated [55–57] that the WRC of clay increases with LL values. This is because clay with high LL can retain more content of water in the soil pore, which in turn can reduce gas permeability.

To compare the effects of different modification materials on LL, a dimensionless parameter, LL_d, is proposed, which was defined as the ratio of LL to LL_{ck}, where LLck is the liquid limit of un-treated clay. The comparison results of LL_d are shown in Figure 3b. The results show that the ZP-modified soil has higher LL_d values when compared with other modifiers.

3.2. WRC

The evolution of the moisture content with various ZP contents is shown in Figure 4. For the untreated samples, the initial moisture content was 25.6%. It decreased significantly with the increase in drying time from 0 h to 7 h; the moisture significantly decreased from 9% to 13%. After 17.5 h of drying, the moisture content of the compacted clay mixed with ZP of 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% were 4%, 7%, 8%, 9%, and 12%, respectively. The moisture of the soil treated with 1.0% ZP content was 193% higher as compared to the soil with 0.2% ZP. Studies have proven [37] that ZP has a large specific surface area with many hydrophilic groups. Due to the electrostatic attraction between the anions and the penetration disparity induced by the differing concentrations of cations inside and outside, PAM expands linearly to form a three-dimensional network structure [25,26]. Thus, the polymer network of ZP

has a strong physical adsorption effect on water molecules. Accordingly, ZP can effectively improve the WRC of compacted clay and inhibit the evaporation of clay moisture during the drying process. After drying, the moisture content of the clay increased with increasing ZP content, and the modification was the most prominent when the ZP content was 1%.

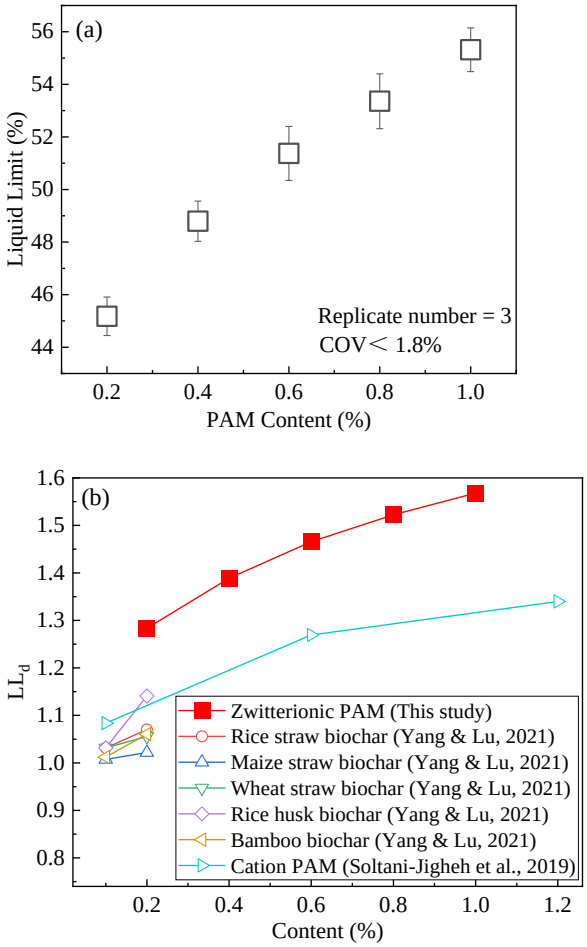

Figure 3. Liquid limit of CCC mixed with ZP. (**a**) Influence of PAM content on the LL of the compacted clay; (**b**) effect of different materials mixed with clay on LL/LL_{ck} of the compacted clay [58,59].

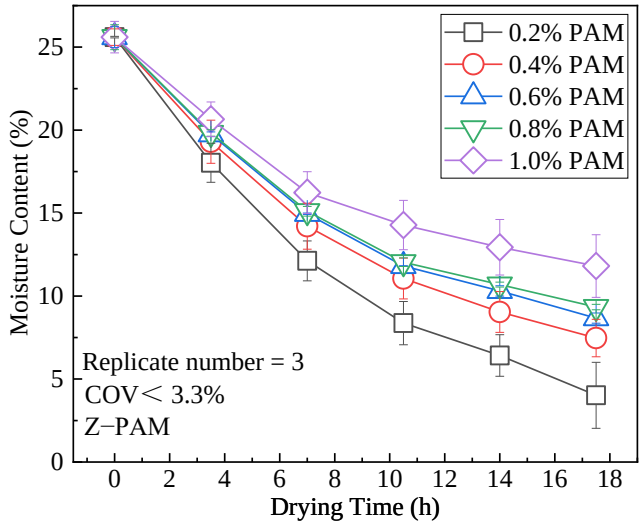

Figure 4. The moisture content of the compacted clay mixed with different PAM contents.

Figure 5 reflects the influence of ZP content on the water loss of the compacted clay after drying. After 17.5 h of drying at 100 °C, the water loss rates of the compacted clay mixed with different contents of ZP were 84%, 71%, 66%, 64%, and 54%, as the ZP content ranged from 0.2% to 1.0%. Therefore, increasing the content of modifier ZP can effectively reduce the water loss rate of clay and improve its WRC. Studies have indicated that the water loss of the clay mixed with various ordinary agricultural and forestry water-retaining agents varies from 55% to 63%, after they are dried for 360 min with a temperature of 60 °C [53]. However, when our research used 0.8% and 1.0% ZP for modification, the water loss rates of the clay after drying at 100 °C for 17.5 h were 64% and 54%. Furthermore, field monitoring results in the Changzhou contaminated site showed that [18] the highest atmospheric temperature was 45 °C, which was much lower than the test temperature of 100 °C in this paper. As a result, ZP plays a more prominent role in enhancing the WRC of CCC under low temperatures of 45 °C rather than 100 °C.

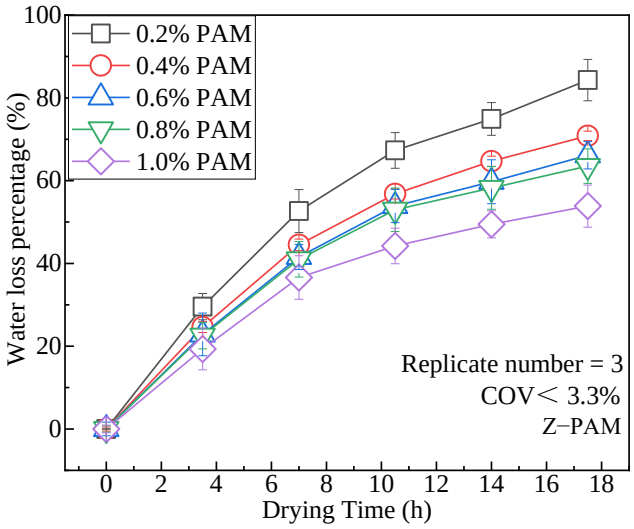

Figure 5. Water loss percentage of the compacted clay mixed with different contents of ZP.

Based on the preliminary test results, when the ZP content was than 1%, the clay with the same initial moisture content was too viscous to be blended homogeneously. Therefore, we did not test the soils with ZP content higher than 1.0%.

3.3. Gas Permeability

Figure 6 shows the relationship between the gas permeability and moisture content. It is noted that the gas permeability of the soils was measured immediately after drying for various times. It is observed the gas permeability of compacted clay increased with the rise in moisture. The relationship of GCL K_p and moisture content can be reflected in three stages in Figure 6. The first trend in stage I represents K_p decreasing sharply with increasing moisture content ranging from 4% to 30%. The second trend in stage II shows K_p very slightly decreasing with the increasing moisture content of 30~50%. The third trend in stage III represents K_p decreasing sharply with the increasing moisture content of 50~100%. According to the comparison between this study and geosynthetic clay liners in previous studies, as shown in Figure 6, the gas permeability of both CCC and GCL decreases with the rise in moisture content. In addition, the test results of Rouf et al. [11] showed that when the moisture content of the GCL was 5~100%, the gas permeability at 20 kPa overburden pressure varied from 10^{-13} m^2 to 10^{-16} m^2, much lower than that of compacted clay. Only when the ZP content reached 1.0% was the gas permeability of ZP-modified compacted clay lower than that of the GCL, with moisture content in the range of 20% to 28%.

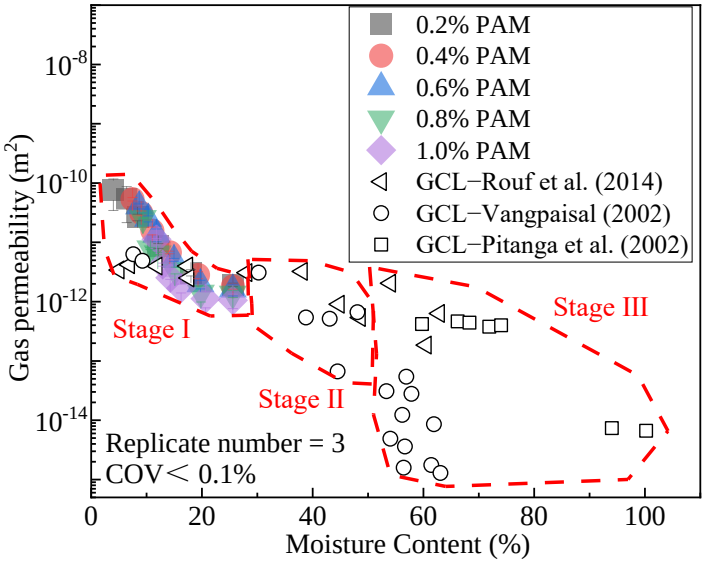

Figure 6. Relationship between the gas permeability and moisture content of compacted clay after ZP modification [11,13,60].

The CCC sample total drying time is 17.5 h. The CCC's final state after drying can be compared to unveil the barrier performance under different ZP contents. Figure 7 shows the influence of ZP content on the gas permeability of the compacted clay after 17.5 h of drying. It can be observed that the moisture content of the clay enhanced as the content of ZP increased, while the gas permeability K_p gradually decreased. The moisture content and gas permeability showed an apparent negative correlation, meaning that gas permeability decreased with the rise in moisture content [11–13]. When the ZP content was 1.0%, the gas permeability of the clay after drying was 1.12×10^{-11} m^2, which was 97% lower than that of the ZP admixture content of 0.2%. As proved, ZP can increase the moisture content of clay after drying, thereby reducing its gas permeability. When the PAM content is 1%, the gas barrier performance of clay can be effectively improved by about one order of magnitude.

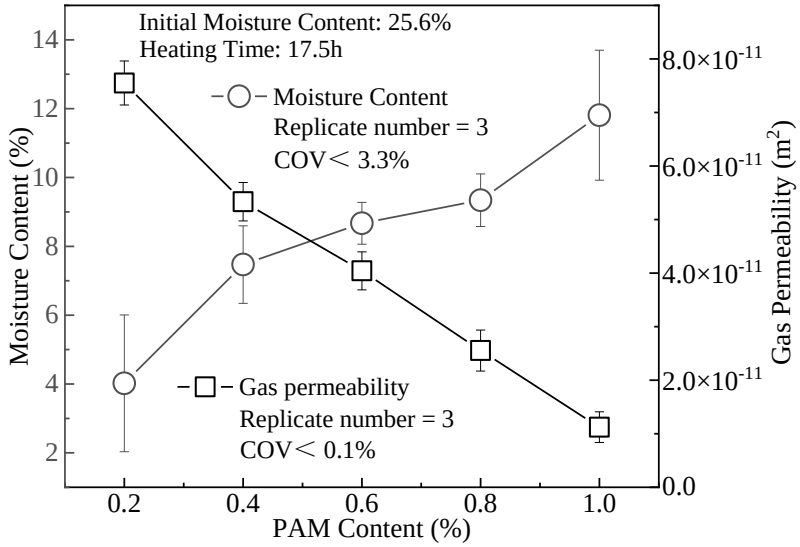

Figure 7. Influence of ZP content on gas permeability of the compacted clay.

3.4. Gas Diffusion Coefficient

Figure 8 displays the relationship between the gas diffusion coefficient and moisture content (after different times of drying with the initial moisture content of 25.6%) of the compacted clay after ZP modification. The relationship of GCL D_p and moisture content can be divided into two stages in Figure 8. The first trend in stage I represents D_p, which has no changes with the increasing moisture content, ranging from 8% to 42%. The second trend in stage II shows D_p, which decreases sharply with the increasing moisture content of 58~100%. The relationship between CCC D_p and moisture content follows the linear decreasing law; D_p decreases sharply with the increasing moisture content of 0~25.6%.

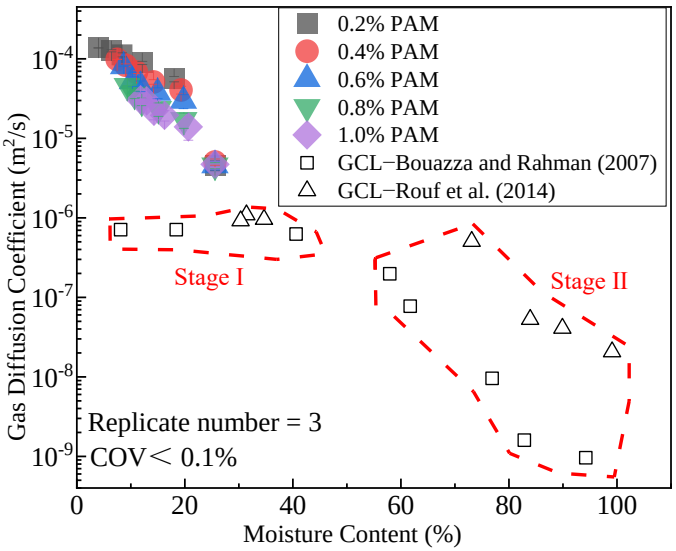

Figure 8. Relationship between the gas diffusion coefficient and moisture content of the compacted clay after PAM modification [11,57].

As the content of ZP ranged from 0.2% to 1.0%, the gas diffusion coefficient decreased with the rise in moisture. According to the analyses of the gas diffusion test results of Rouf and Bouazza [19,56] on the GCL, when the moisture content of the GCL was 8~100%, the gas diffusion coefficient was between 10^{-6} and 10^{-9} m^2/s, much smaller than that of compacted clay with the same moisture content.

As shown in Figure 8, when the moisture content was 25.6%, the gas diffusion coefficients of clay mixed with ZP at the contents of 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% remained in the same order of magnitude, which was 4.56×10^{-6} m^2/s, 5.05×10^{-6} m^2/s, 4.72×10^{-6} m^2/s, 4.56×10^{-6} m^2/s, and 4.51×10^{-6} m^2/s, respectively. When the drying starts, the CCC samples present different gas barrier properties. The D_p of the CCC sample with 0.2% ZP content after 17.5 h drying is 1.37×10^{-4} m^2/s, while the D_p of the 1.0% ZP content sample is 3.06×10^{-5} m^2/s. This is because the CCC samples mixed with high content ZP have high WRC, which can reduce the microstructure of clay particles and enhance the barrier property of CCC.

The CCC sample's total drying time is 17.5 h. After drying, the CCC's final state can be compared to unveil the barrier performance under different ZP contents. Figure 9 presents the relationship between the gas diffusion coefficient and moisture content of the compacted clay after drying for 17.5 h with the change in ZP content. It can be observed that the D_p decreased with increasing moisture content. When the ZP content was 1%, the gas diffusion coefficient of the clay was 3.06×10^{-5} m^2/s, which was only 35% of that at the ZP content of 0.2%. Hence, ZP can effectively improve compacted clay's gas-barrier and anti-diffusion performance, and its modification effect increases with the rise in ZP admixture content.

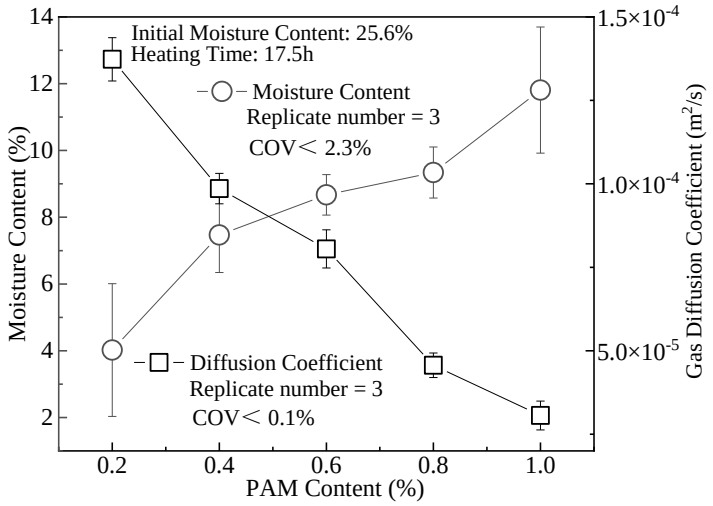

Figure 9. Influence of ZP content on the gas diffusion coefficient of the compacted clay.

4. Conclusions

This study investigated the gas barrier performance of CCC of an industrial contaminated site that was modified by zwitterion polyacrylamide (ZP). The water retention capacity (WRC) test, liquid limit (LL) test, gas permeability test, and gas diffusion test were conducted to unveil the barrier mechanism. Based on the results, the following conclusions can be drawn:

(1) ZP could increase the moisture content of the compacted clay. The WRC is related to the linear expansion of polymer molecules after water adsorption. The moisture content of the clay after drying increases with the rise in the ZP admixture content. The modification had a prominent effect at a ZP content of 1%, and the moisture content after drying increased by 193% more than at the ZP content of 0.2%.

(2) The WRC of compacted clay significantly improves after adding ZP. When the admixture content is 0.8% and 1.0%, the water loss rate after the clay is dried for 17.5 h at 100 °C is 64% and 54%. Its WRC is better than ordinary water-retention agents for agriculture and forestry.

(3) The effects of ZP, i.e., reducing the clay gas permeability K_p and gas diffusion coefficient D_p, are not obvious. When the content is 1.0%, the K_p of CCC is about one order of magnitude lower than that at the ZP content of 0.2%. Its D_p is only 35% at the admixture content of 0.2%. For CCC with the same moisture content, the K_p and D_p decrease with the rise in ZP content.

(4) The reasons for the slight improvement in the gas barrier performance of modified clay are as follows. ZP modification enhances the WRC of CCC after drying, thereby reducing the K_p and D_p.

(5) ZP can increase the LL of compacted clay. When the admixture content varies from 0.2 to 1.0%, LL increases by 45~55% more than unmodified clay.

Further studies are warranted to explore the economic efficiency and long-term stability of ZP-modified CCCs. The data in this study offer modified materials as gas barriers in applying geotechnical engineering.

Supplementary Materials: The supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12168379/s1. Figure S1: Clay cracking with different PAMs. Figure S2: Gas permeability and gas diffusion coefficient of clay under different PAMs. Table S1: The results of each sample.

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Nomenclature

WRC	Water retention capacity
LL	Liquid limit
LL_d	The dimensionless results of LL
LL_{ck}	The LL of soil without any additive
CCC	Compacted clay cover
ADOS	Apparent degree of saturation
I_p	Plasticity index
CL	Clay with low LL
CH	Clay with high LL
ML	Silt with low LL
MH	Silt with high LL
OL	Low liquid limit organic clay or silt
OH	High liquid limit organic clay or silt
VOC	Volatile organic compound
PAM	Polyacrylamide
ZP	Zwitterion polyacrylamide
GCL	Geosynthetic clay liner
CK	Control blank
COV	Covariance (it is a measure of the joint variability of two random variables)
OC	Oxygen concentration
m_s	Sum of the mass of the clay and polyacrylamide (g)
m_0	The mass of a compacted clay sample before drying (g)
m_t	The mass of a compacted clay sample after drying for time t (g)
W_S	The water loss rate (%)
K_p	The gas permeability of a clay sample
k	The permeability coefficient (m^2)
ρ_l	The air density (kg/m^3)
t	The test time (s)
V	The amount of air passing through the sample within time t (m^3)
L	The thickness of the compacted clay sample to be tested (m)
p	The actual pressure value (hPa)
A	The bottom area of the sample (m^2)
D_p	The correction gas diffusion coefficient (m^2/s)
D_p'	The gas diffusion coefficient before calibration (m^2/s)
h_s	The height of the compacted clay sample
h_C	The height of the diffusion chamber (cm)

k	The slope of the straight line in the scatter diagram of $\ln(\triangle C_t / \triangle C_0)$ (t)
ΔC_t	The difference between OC at both ends of the clay sample at time t
ΔC_0	The difference between OC at both ends of the clay sample at time t_0
FP	Filter paper
SSSM	Saturated salt solution method
RH	Relative humidity

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