Pore Fluid Effects on the Fabric and Hydraulic Conductivity of Laboratory-Compacted Clay

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The effect of organic fluid permeation on the fabric of compacted clay was investigated in order to assess whether changes in hydraulic conductivity could be estimated from changes in fabric, pore fluid characteristics, and the characteristics of clay minerals. Pore size distribution analyses were first conducted to assess the magnitude of the effect of compactive effort and molding water content on the changes in fabric and hydraulic conductivity. Second, the effect of pore fluid characteristics on the consistency limits and free swell of kaolinite, Ca-montmorillonite, and Na-montmorillonite was investigated in an attempt to determine the effect of compositional variables. Finally, hydraulic conductivity tests were conducted with selected organic fluids and compacted kaolinite and Ca-montmorillonite specimens originally molded with water. Nitrobenzene, acetone, phenol, benzene, and p-dioxane were used for these permeation studies. Fabric of the specimens was quantified before and after permeation with the specific pore fluid. The results indicate that changes in hydraulic conductivity correlate well with the point changes in the fabric when the molding pore fluid and the permeation pore fluid are both water. A decrease of 20 percent in dry density at a fixed water content may lead to at least an order of magnitude increase in hydraulic conductivity. Tests with organic fluids indicate that changes in hydraulic conductivity are in response to changes in fabric as well as pore fluid characteristics, interaction with the clay mineral, and confining stress. Practical implications of the study are discussed.

Placement of wastes in shallow waste disposal facilities is the most common and economical method of disposal in the United States and around the world. Organic and inorganic pollutants, together with the infiltrating water, generate leachates that are transported through the liner under field gradients (1). To retard the movement of contaminants, waste disposal facilities are often located in areas having soil strata with a high amount of fine fraction. The disposal facilities are further secured using earthen barriers or artificial barriers.

In the design and analysis of the earthen barriers, the fundamental engineering parameter affecting the rate of transport of the solutes is hydraulic conductivity and the diffusion coefficient (2). The presence of organic compounds in the disposal facilities prompted the need to investigate the effect of these fluids on engineering properties of soils. A review of the data generated by recent studies in the last decade is given by Mitchell and Madsen (3).

The objective of this study is (a) to investigate the effect of selected organic fluid permeation on the fabric of compacted clay and (b) to investigate whether the changes in hydraulic conductivity could be predicted from changes in fabric, pore fluid characteristics, and characteristics of clay minerals.

The study was accomplished in three stages. First, an investigation was initiated to assess the effect of the mechanical variables of compaction on the fabric of laboratory-compacted specimens, using water as the molding pore fluid. This stage was designed to reevaluate whether changes in absolute hydraulic conductivity of compacted specimens using water as the molding fluid could be estimated from point changes of the fabric in the specimen. This stage was also designed to determine the magnitude of the effect of compaction effort and molding water content on the changes in the fabric and hydraulic conductivity. In the second stage, the effect of pore fluid characteristics on the consistency limits and free swell of three clay minerals was investigated in an attempt to determine the effect of compositional variables. In the third stage, hydraulic conductivity tests were conducted with selected organic fluids and compacted kaolinite and Ca-montmorillonite molded with water. Fabric of the specimens was quantified before and after permeation with the specific pore fluid.

PROCEDURE

Consistency Limits and Free-Swell Tests

The procedure and apparatus for the liquid limit and plastic limit tests are given by ASTM D-423 and ASTM D-424. Holtz and Gibbs (4) developed the free-swell test in the classification of soils for swelling potential. The test consists of pouring 10 cc of dry soil passing the No. 40 sieve into a 100-cc graduated cylinder and then filling it with water (or other fluids) and noting the free-swell volume of the soil after it comes to rest (24 hr). The free swell is calculated as the ratio of the swell amount to the original volume of dry soil.

Soil Mixing, Curing, and Compaction

The clay was mixed manually at a specific molding water content. The air-dried clay (as commercially available) was mixed with small increments of finely sprayed distilled water. The soil was then mixed manually, and the molding water amount was increased incrementally until the desired water

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content was reached. Care was exercised to avoid any likelihood of precompaction effects. After the final mixing, the mix was examined for its looseness. Manual mixing was chosen after an experience with mechanical mixing devices that created precompaction effects—especially at the wet side of optimum water content. A curing period of at least 48 hr was used to ensure uniform water content.

To establish the moisture density relationships, all cured samples were compacted using the same procedure presented in ASTM D698-70A, except that a miniature compaction mold was used, and test specimens were prepared by compacting the soil in approximately three equal layers.

Freeze Drying

The most important operation in the analysis of the fabric of soils at high water contents is sample preparation. Drying of the sample must not result in excessive swelling or shrinkage. The pore fluid was removed by freeze drying before scanning electron microscopy (SEM) and mercury intrusion tests. The procedure recommended by Zimmie and Almaleh (5) was used; details of the procedure were given by Olivieri (6).

Scanning Electron Microscopy

The freeze-dried samples were cut slightly to further expose the fresh faces. The specimen block was fixed on an aluminum stub by means of tube coat (silver paint). The sample was then coated with a layer of gold by a Hummer sputter coater under a vacuum of 70 to 80 mTorr. (This metal coating ensured sufficient electrical conductivity.) The sample coated with the conductor was then inserted into the sample chamber of the SEM operating at 25 kV.

Mercury Intrusion Test

A Micromeritics 9300 pore sizer was used in this study; the unit had a pressure range between 0.5 and 30,000 psia (0.0035 and 207 MPa). Two low-pressure stations and one high-pressure station accommodated sample filling, macropore, and micropore analyses. Both pressure and intrusion data were digitally displayed. The porosimeter measured volumetric increments of 0.001 ml. Consequently, it was possible to obtain the size and distribution of pores within a range of 0.008 micron (80 Å) to greater than 100 microns (1,000,000 Å). The detailed procedure for this test was given by Olivieri (6).

Hydraulic Conductivity Test

A detailed description of the apparatus, membrane compatibility, saturation procedure, and hydraulic conductivity testing procedures was provided by Hamidon (7), Rad and Acar (8), and Acar et al. (1).

Hydraulic conductivity testing of fine-grained soils with organic fluids required the testing to continue until the effluent concentration reached the influent level (100 percent breakthrough). Because the transport of the organic fluids was governed by advective-dispersive-reactive transport mechanisms (9), it was necessary to continue testing more than one pore volume in order to reach full breakthrough and assess the effect of the full-strength organic fluid. Unless the sample pore volume was decreased, testing could take several months—even at considerably high gradients. Consequently, sample dimensions were restricted to 3.55 cm in diameter by 3 to 5 cm in height.

Rad and Acar (8) determined that latex membranes were not compatible with organic fluids that had a dielectric constant less than 10. This problem was effectively remedied by wrapping the samples in two layers of Teflon sheet [0.03 mm (0.001 in.)]. Once the membranes had been placed, they were also coated with contaminant-resistant (silicon base) grease to decrease the possibility of chemical diffusion.

Backpressures of 60 to 70 psi (414 to 473 kPa) were used to saturate the samples, which had initial saturations of 88 percent or higher. The effective stress was increased to 8 psi (55 kPa) by incrementally raising the cell pressure and the backpressure after measurement of the B-value. To promote saturation, a slight gradient was applied during backpressuring.

Reference hydraulic conductivity was obtained after passing approximately 1 pore volume of 0.01 N $CaSO_4$ solution. It should be noted that it is not possible to achieve a complete substitution by permeating only 1 pore volume of any solution. Consequently, 0.01 N $CaSO_4$ solution was used both to achieve a relatively homogeneous initial pore fluid and to be able to compare the results with those from previous studies that used the same solution (10).

The influent was subsequently switched to organic fluids without any change in backpressure. The effluent was collected and continuously monitored for the organic influent concentration. Testing continued until the hydraulic conductivity or the organic effluent concentration, or both, was stabilized. Hamidon (7) demonstrated that the gradient effect on hydraulic conductivity of compacted soils may be significant for gradients of less than 100. Therefore, gradients of 100 were used during testing.

ANALYSIS OF RESULTS

The choice of clay minerals to be tested in the flexible wall permeameters was limited to two: a kaolinite and a Ca-montmorillonite. A Na-montmorillonite was added to the list in the survey of the effect of various organic fluids on the consistency limits and free swell of clay minerals.

The kaolinite used was Georgia kaolinite RC-32, furnished by the Thiele Kaolin Company. The Ca-montmorillonite used was the Southern bentonite/Panther Creek and the Na-montmorillonite was CS-200, both furnished by the American Colloid Company. Table 1 presents the composition and characteristics of the clay minerals used in this study.

It was postulated that the dielectric constant of the pore fluid would be one of the principal factors that controlled the interactions between the clay minerals and the pore fluid. Consequently, it was decided to use organic fluids with a wide range of dielectric constants. Table 2 presents various characteristics of these fluids. Among these, only benzene, nitrobenzene, phenol, acetone, and p-dioxane were used for permeation studies, whereas the consistency limits of the three clay minerals were determined using all the fluids on the list.

TABLE 1   COMPOSITION AND CHARACTERISTICS OF CLAYS USED

Characteristic	K	Ca-M	Na-M
Mineralogical Composition (% by weight)			
Kaolinite	96	–	–
Illite	4	1	–
Ca-montmorillonite	–	99	–
Na-montmorillonite	–	–	100
Index Properties (%)			
Liquid Limit	64	88	425
Plastic Limit	34	54	58
Plasticity Index	30	34	367
Specific Gravity	2.65	2.70	2.70
% Finer than 2 microns Size	90	12	80
Activity	0.32	2.80	4.50
Proctor Compaction Parameters			
Maximum Dry Density (t/m^3)	1.30	1.07	1.07
Optimum Water Content (%)	35.0	25.0	25.0

K – Georgia Kaolinite

Ca-M – Ca-montmorillonite

Na-M – Na-montmorillonite

Atterberg Limits and Free-Swell Tests

It is well established that the engineering properties of clays are dependent on the interaction of the clay particles with the pore fluid. The relative thickness of the diffuse double layer may be related to the square root of the dielectric constant. If the properties of the pore fluid in the diffuse double layer around the clay particle are different from those of water, and if the effective stresses do not restrict the variations in the fabric, the changes in the thickness of this layer will result in rearrangements in the effective pore space contributing to the total flow. Because the extent of repulsive forces is related to the thickness of the diffuse double layer (*11*) and the liquid-limit and free-swell tests present a good estimate of this thickness, it was decided to conduct such tests on the three clay minerals with organic molding fluids.

Figure 1 presents the results of the free-swell test, and Figures 2 and 3 present the results of consistency limits.

It was observed that the free swell and liquid limit of mont-

morillonitic clays displayed an increasing trend with an increase in dielectric constant. These clays became nonplastic for fluids with dielectric constants of less than 30. These results were anticipated from a review of the interactions between the pore fluid and the clay surfaces. On the other hand, it was observed that different organic fluids induced different responses in the liquid limit and free swell of kaolinite. This mineral was not plastic to acetone and to contaminants with a dielectric constant less than 3. Nitrobenzene, phenol, and carbon tetrachloride with low pH resulted in high liquid-limit values.

The Gouy-Chapman theory of double layers (*12*) assumes that the clay plates are infinitely long and negatively charged. The effects of positive charges at the ends are neglected. Consequently, the variable responses observed with kaolinite could be attributed mainly to the positive charges at the broken edges of this mineral. A low pH would tend to dissociate the OH⁻ groups on the edges of the particle, resulting in higher liquid limits (*13*). However, it should also be noted that the change (increase or decrease) in the index properties

TABLE 2 CHARACTERISTICS OF ORGANIC SOLVENTS USED

Compound	Formula	ε	μ	γ	DM	pH	Class	Max. Conc. (mg/1)	SBL (mg/1 at 25°C)
Water	H_2O	80.4	1.0	0.98	1.83	7.0			
Ethylene Glycol	$C_2H_6O_2$	38.66	21.0	1.11	2.2				∞
Nitrobenzene	$C_6H_5NO_2$	35.74	2.03	1.2	4.22	3.9	H,T,S,P	0.73	1.90
Ethanol	C_2H_6O	24.30	0.2	0.79	1.69	5.4			∞
Acetone	C_3H_6O	20.7	0.54	0.79	1.66	6.81	T	42.4	∞
Phenol	C_6H_5OH	13.13	12.7	1.06	1.45	3.50	H,T,S,P	17.0	86.34
Aniline	$C_6H_6NH_2$	6.9	4.4	1.02	1.55		T,S	1.9	34.0
Xylene	C_8H_{10}	2.50	0.81	0.87	0.40		T,S	60.0	.20
Tetrachloroethylene	Cl_2CCl_2	2.30	0.72	1.62	0	5.6	H,T,S,P		.02
Carbontetrachloride	CCl_4	2.24	1.50	0.97	0	4.0	H,S,T,P	25.0	.77
Benzene	C_6H_6	2.28	0.65	0.88	0	5.65	H,T,S,P	7.4	1.77
P-dioxane	$C_4H_8O_2$	2.21	1.44	1.03	0.45		H,T		∞
Heptane	C_7H_{16}	1.0	0.41	0.68	0				0.003

ε – dielectric constant (20°C)
γ – unit weight (gm/cm^3) (20°C)
μ – viscosity (centipoises) (20°C)
DM – dipole moment (debyes)
SBL – water solubility

Class – hazardous classification (EPA)
    H – hazardous   T – toxic
    S – section 311 compound   P – priority pollutant

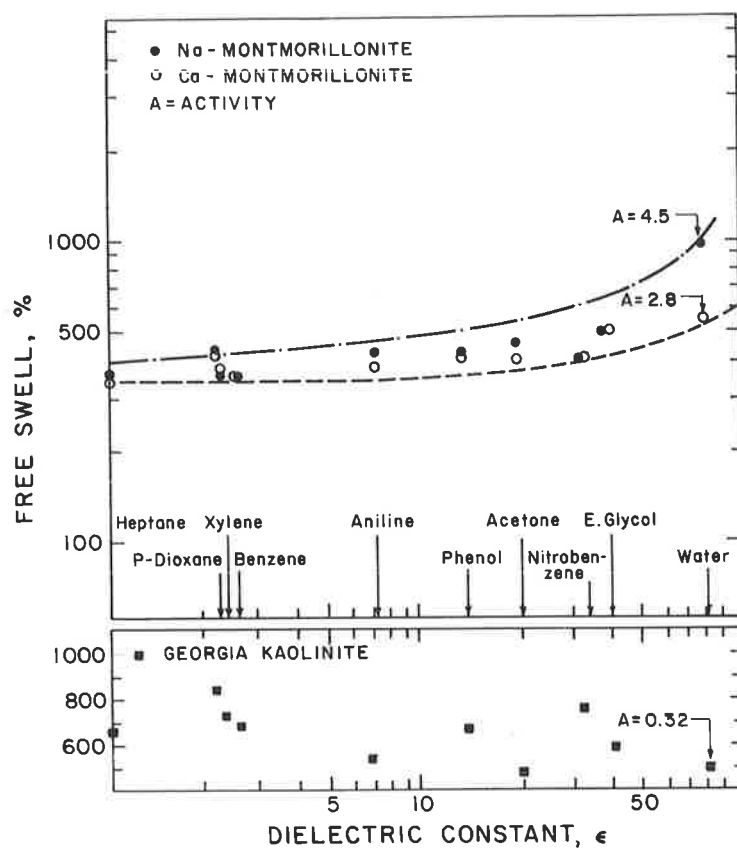Max. Conc. – maximum concentration reported in leachates

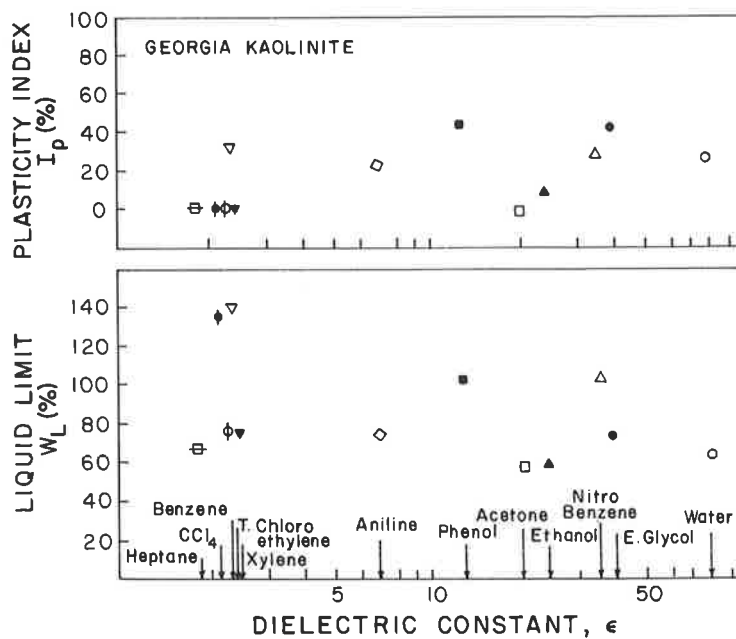FIGURE 1 Effect of organic fluids on free swell of clays.

FIGURE 2 Effect of organic fluids on the consistency limits of Georgia kaolinite.
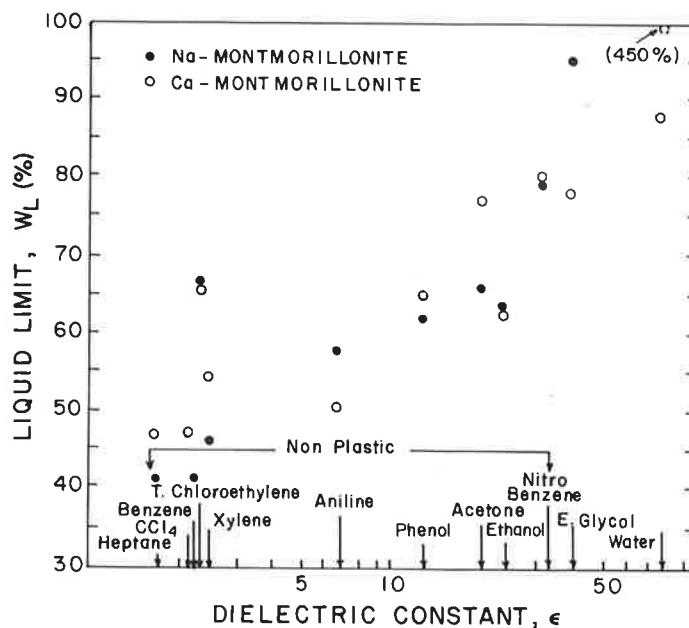
FIGURE 3   Effect of organic fluids on the consistency limits of montmorillonites.

and free-swell values of this mineral with the organic contaminants when compared with those of water was not as drastic as with the highly active montmorillonites.

There are several implications of the observed decreases in the consistency limits and free-swell values of the active clay minerals (montmorillonites) with organic contaminants that have low dielectric constants. Currently, soils of high activity are used to ascertain the low permeability of the compacted soil liners. Fine-grained soils with high activities are associated with lower water permeability (*11*). However, the initial structure of these soils is more sensitive to postconstruction changes in the pore fluid chemistry. Decreases in the dielectric constant of the pore fluid with the transport of organic contaminants depresses the thickness of the diffuse double layer, resulting in a decrease in the forces of repulsion in the system (*9*). As a consequence, a restructuring of the fabric occurs, leading to shrinkage (*14*), increase in hydraulic conductivity (*1,10,15*), decrease in compressibility (*16*), and an increase or decrease in shear strength depending on the dielectric constant of the medium (*17,18*). The free-swell and consistency limit tests present an indirect and conservative indication of the expected fabric changes in the soil when the effective stresses on the soil particles are negligible. High effective stresses on soil specimens always tend to restrict further reorientation of the particles.

Effect of Compaction Effort and Molding Water Content on the Fabric of Compacted Clay

Compaction curves for kaolinite and Ca-montmorillonite were generated with three compactive efforts—one, two, and four times the standard compaction effort (10, 20, and 40 blows per layer in the miniature compaction mold). The moisture-density curves for kaolinite and Ca-montmorillonite are shown in Figure 4.

Two sets of compacted specimens of Ca-montmorillonite were prepared for SEM observation. One set was prepared at dry of optimum water content (w = 10 percent, γ = 129
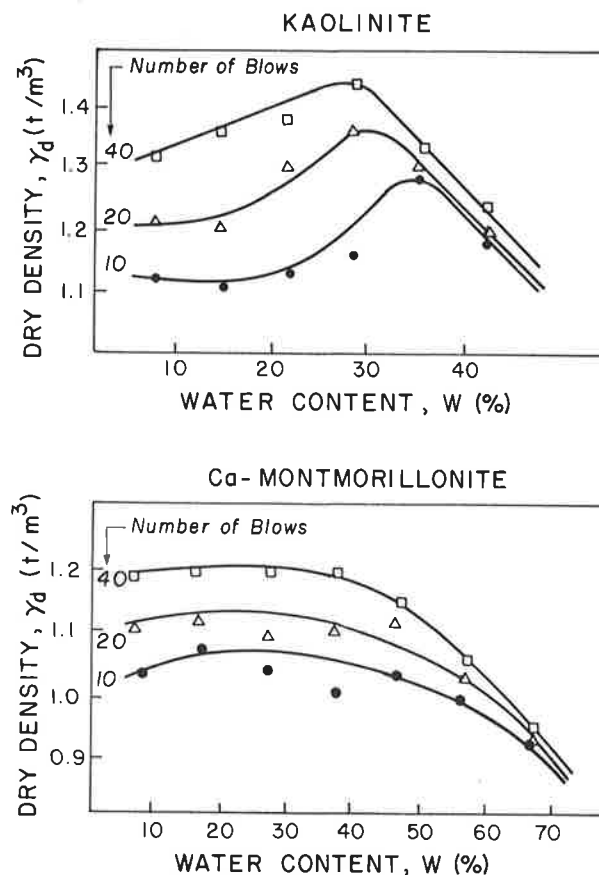

FIGURE 4   Moisture density curves for Georgia kaolinite and Ca-montmorillonite (Southern bentonite).

pcf), and the other set was prepared at wet of optimum water content (w = 45 percent, γ = 129 pcf). The detailed results of the SEM studies were presented by Olivieri (*6*).

It was determined that the surface texture at dry of optimum was rough because of resistant micropeds. At wet of optimum, the surface was smoother because the micropeds progressively

lose their shear strength. At higher magnification, the sample compacted at dry of optimum showed development of the edge-to-face flocculated fabric, whereas the sample at wet of optimum showed a smoother surface and a dominantly face-to-face dispersed fabric (the Ca-montmorillonite particles lie flat on top of each other). At even higher magnification, individual flakes of clay showed somewhat random orientation and stood resistant to the compaction stress. Individual flakes showed a dominantly face-to-face association at wet of optimum. Higher magnification of the sample at wet of optimum showed a very typical dispersed fabric.

Figure 5 presents a pore size distribution analysis from SEM studies. It was observed that pore diameters in samples compacted at dry and wet of optimum water content range from about 0.01 to 10 microns (100 to 100,000 Å). The pore size frequency distribution in compacted clay was bimodal at dry of optimum water content and was unimodal at wet of optimum water content. The limiting diameter for the small mode was found to range between 0.01 and 0.1 micron (100 to 1,000 Å) and for the large pore mode between 1 and 10 microns (10,000 to 100,000 Å).

The foregoing study on the fabric of compacted clay using SEM reassessed the fact that the fabric of compacted clay at wet of optimum is dispersed and the pore size frequency distribution unimodal, whereas a flocculated structure with a bimodal pore size distribution is observed at dry of optimum water content.

As a consequence of these two observations, absolute hydraulic conductivity was lower at the wet side of the optimum water content. Similar results were then expected with the pore size distribution analysis conducted by the mercury intrusion technique. It was also anticipated that the pore size parameter that reflected the fabric and was calculated from the frequency distribution data would correlate with the changes in the hydraulic conductivity.

Mercury intrusion porosimetry tests were performed on samples at three compactive efforts (10, 20, and 40 blows)

and six molding water contents (7, 14, 21, 28, 35, and 42 percent).

Selected distributions (presented in Figure 6) showing the dry of optimum (*left*) and wet of optimum (*right*) specimens indicate that the results replicated those previously obtained with SEM (Figure 5). It was noted that with increased compactive effort, the compaction curve for the same clay was higher and displaced to the left—indicating a lower optimum water content. Figure 6 further shows that as the compactive effort was doubled (20 blows), the water content of 28 percent (which was at dry of optimum for 10 blows) corresponded to almost the optimum, and a decrease in the large mode was observed. As the compactive effort was further increased (40 blows), the water content of 28 percent corresponded to optimum water content and the large pore mode practically disappeared. Increasing the water content beyond optimum developed discontinuities in the air voids, making it more difficult to reduce the large pore mode; thus, the large pore mode developed again.

Hydraulic conductivity tests were conducted on kaolinite samples compacted at four molding water contents (14, 21, 28, and 35 percent) and at the three compactive efforts. Figure 7 compares the changes in absolute hydraulic conductivity with variations in molding water content and compactive effort and presents the change in pore size parameters [Marshall and hydraulic radius (*19*)] with respect to water content. As previously indicated by the size and frequency distribution of the pores, the hydraulic conductivity decreased toward the optimum molding water content but subsequently displayed an increasing trend.

It is interesting to note that the change in pore size parameters displayed an almost identical pattern to the changes in hydraulic conductivity with the molding water content. This implies that the pore size parameters do in fact correctly reflect the changes in fabric and hence the engineering parameter, hydraulic conductivity.

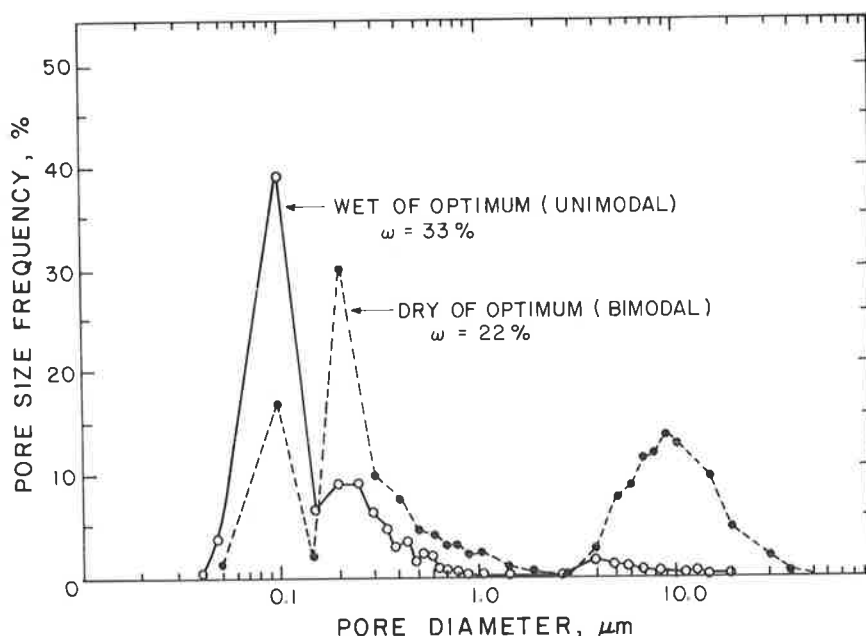Figure 8 presents a comparative plot of the pore size param-

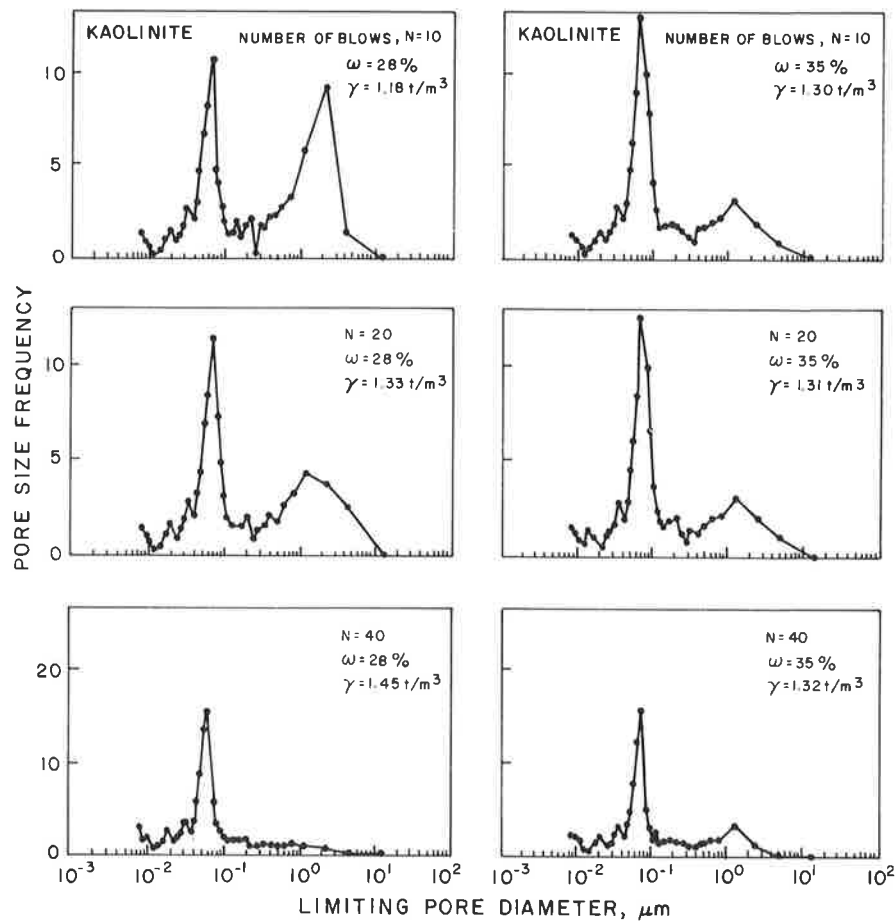**FIGURE 5 Pore size and frequency distribution of compacted kaolinite with a scanning electron microscope.**

FIGURE 6 Selected distributions showing dry of optimum (*left*) and wet of optimum (*right*) specimens.
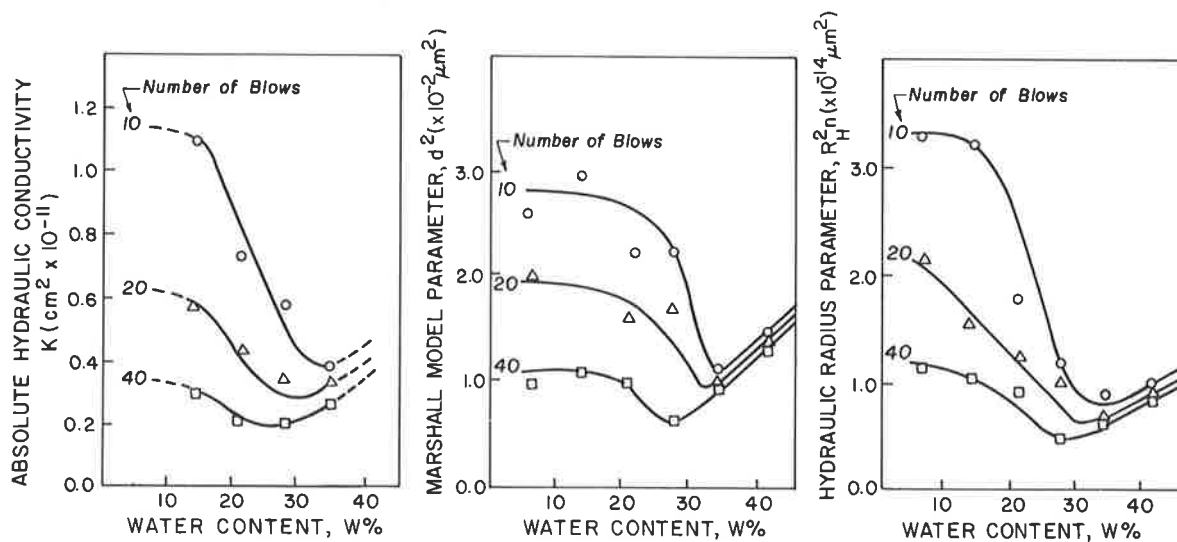

FIGURE 7 Variation of the absolute hydraulic conductivity and Marshall and hydraulic radius pore size parameters with compactive effort and molding water content.
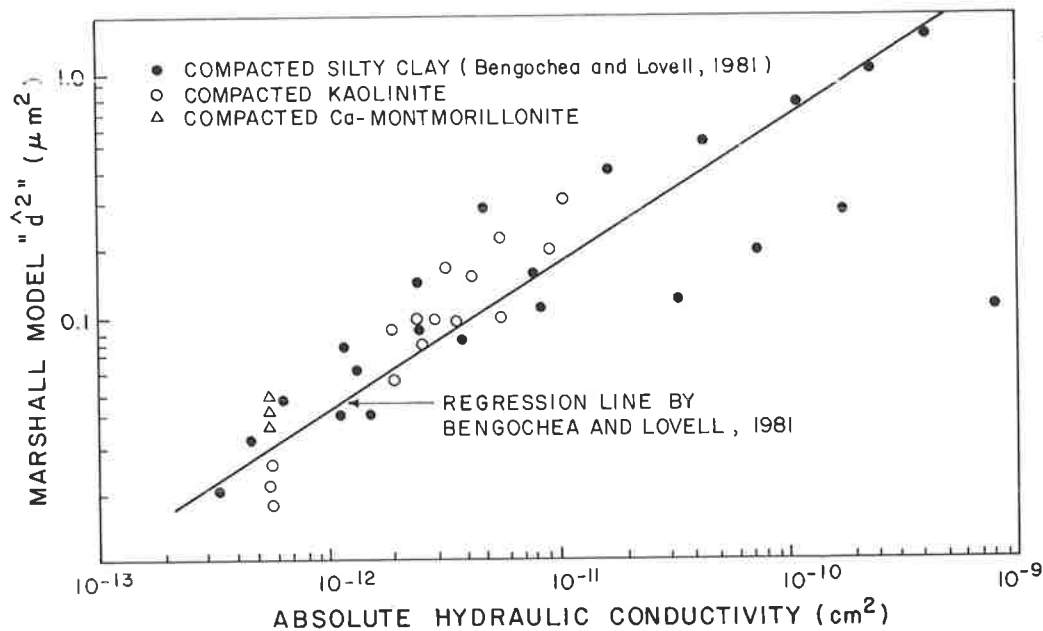
FIGURE 8   Absolute hydraulic conductivity versus the Marshall pore size parameter.
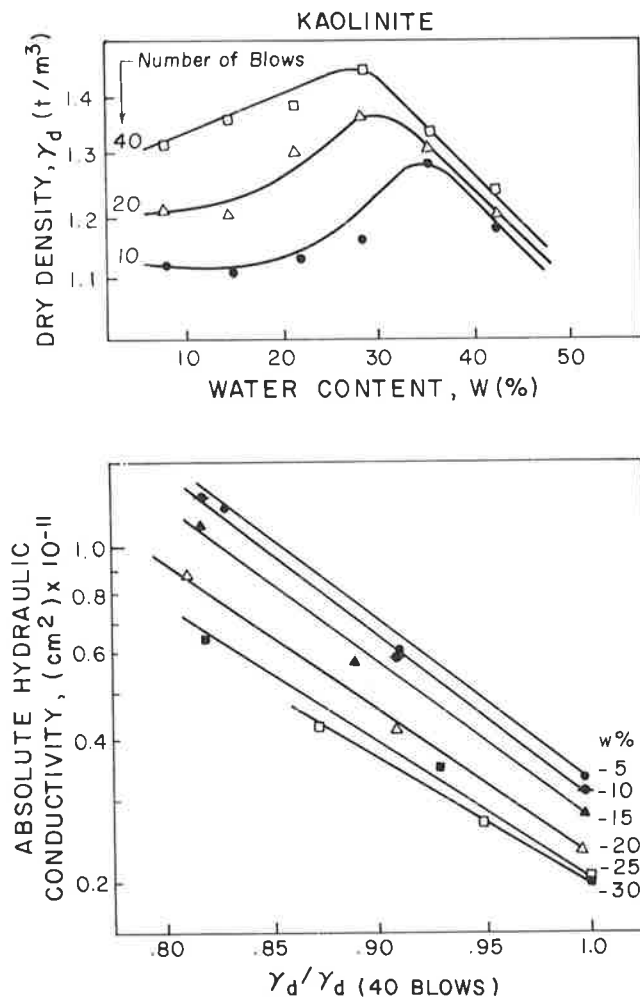

FIGURE 9   Sensitivity of the hydraulic conductivity to variation in dry density and molding water content.

eter with respect to the experimental values of hydraulic conductivity. The results of this study were also compared with the data previously reported by Bengochea (*19*). Changes in fabric quantification or pore size distribution parameters correlated quite well with the changes in absolute values of hydraulic conductivity for kaolinite and Ca-montmorillonite used in this study and the regression line given by Bengochea and Lovell for compacted silty clay.

Figure 9 presents the sensitivity of the hydraulic conductivity to variations in dry density and molding water content. It is interesting to note that compacting a kaolinite sample to 80 percent of a specified density would lead to approximately one order of magnitude increase in hydraulic conductivity above that for 100 percent compaction. This is also valid for samples compacted at or slightly above optimum water content. These results emphasize the fact that the detrimental effect of undercompaction should not be underestimated by a practicing engineer who intends to design a low-permeability barrier.

Effect of Organic Fluid Permeation on the Fabric of Compacted Clay

Five samples of kaolinite compacted at the Standard Proctor effort and at a water content of 38 percent and a dry density of 76 pcf (1.21 t/m³) were identically prepared and tested. Consequently, the initial fabric of these samples was identical. The permeation fluids were acetone, phenol, nitrobenzene, benzene, and a 0.01 N CaSO$_4$ solution.

Six samples of Ca-montmorillonite compacted at the Standard Proctor effort and molding water content of 60 percent and a dry density of 62.4 pcf (1.00 t/m³) were also identically prepared and tested. Table 3 reports the initial and final values of hydraulic conductivity and their ratios.

The tests indicated that hydraulic conductivity for kaolinite slightly increased with acetone and phenol but decreased almost

TABLE 3   RESULTS OF HYDRAULIC CONDUCTIVITY TESTS

Permeant	Hydraulic Conductivity		k_f/k_i
	Relative $\times 10^{-8}$ cm/sec		
	k_i *	k_f	
Compacted Kaolinite			
**Nitrobenzene 1	5.60	<0.025	<0.005
**Nitrobenzene 2	5.20	<0.015	<0.005
Acetone 1	5.60	6.00	1.07
Acetone 2	5.00	11.00	2.00
Phenol	6.00	14.00	2.33
**Benzene	5.10	<0.010	<0.0005
Compacted Ca-montmorillonite			
Nitrobenzene 1	0.55	0.45	0.82
Nitrobenzene 2	0.72	0.45	0.63
**Acetone 1	0.72	0.01	<0.01
**Acetone 2	0.70	0.01	<0.01
Phenol 1	0.77	0.21	0.27
Phenol 2	0.48	0.14	0.08
P-Dioxane 1	0.84	0.73	0.87
P-Dioxane 2	0.63	0.52	0.83
**Benzene 1	0.74	stop	<0.01

*initial permeabilities with 0.01 N $CaSO_4$.

**full breakthrough was not achieved due to decrease in hydraulic conductivity to less than 1×10^{-10} cm/sec.

three orders of magnitude with benzene and nitrobenzene. Results of the tests for Ca-montmorillonite indicated that the hydraulic conductivity decreased slightly with nitrobenzene p-dioxane and phenol. The decrease in hydraulic conductivity of Ca-montmorillonite with acetone was almost two orders of magnitude. Full breakthrough was not achieved with acetone, because it took about 20 days to permeate only 0.1 pore volume at such a low hydraulic conductivity. Similarly, the hydraulic conductivity of Ca-montmorillonite permeated with benzene first decreased to less than 1×10^{-10} cm/sec. Subsequently, it was not possible to detect any changes in effluent levels for almost 2 months. Consequently, full breakthrough was again not achieved in these tests.

The hydraulic conductivity experiments were duplicated with the specific organic fluids except benzene. Figures 10 through 12 present the results of hydraulic conductivity tests on compacted Ca-montmorillonite; the results of hydraulic conductivity tests with kaolinite were presented by Acar et al. (1).

From the results of only the hydraulic conductivity tests, it was concluded that a specific trend was not observable between the absolute hydraulic conductivity of the compacted soils and the dielectric constant of the organic fluids used in this study. Other factors such as fluid immiscibility, pH, and effective stress should then be considered.

Volume Changes in Freeze Drying

Samples that were permeated with organic fluids were removed from the permeameter and subjected to freeze drying for SEM
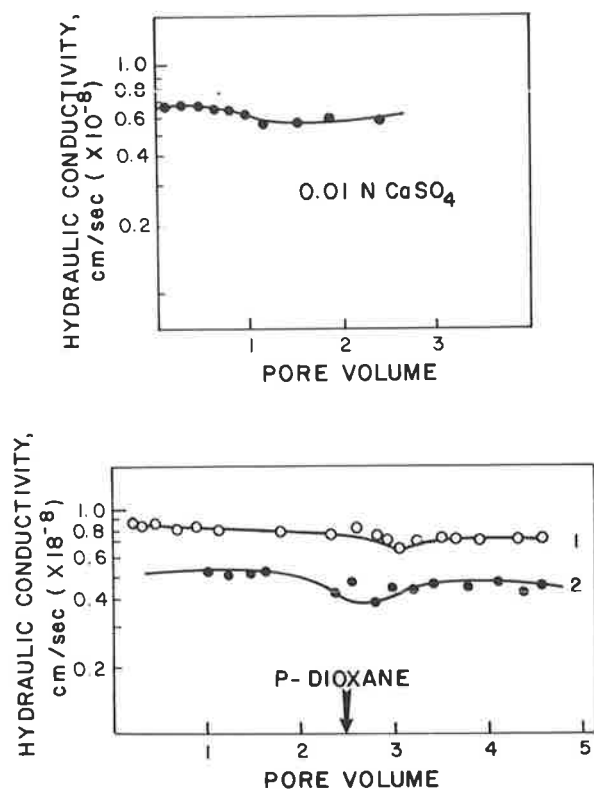
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FIGURE 10 Hydraulic conductivity of compacted Ca-montmorillonite to 0.01 N CaSO₄ solution and p-dioxane.

FIGURE 12 Hydraulic conductivity of compacted Ca-montmorillonite to nitrobenzene and phenol.

and porosimetry tests. It was necessary to assess the effect of freeze drying on samples with organic pore fluids. There seemed to be no information available on the subject. However, it was believed that the triple point of such organic fluids was higher than that of water, and freeze-drying such samples would induce lower strains than those of an identical sample with water-filled pores. Consequently, the shrinkage or swelling of the samples during freeze drying was monitored following the procedure used by Zimmie and Almaleh (5).
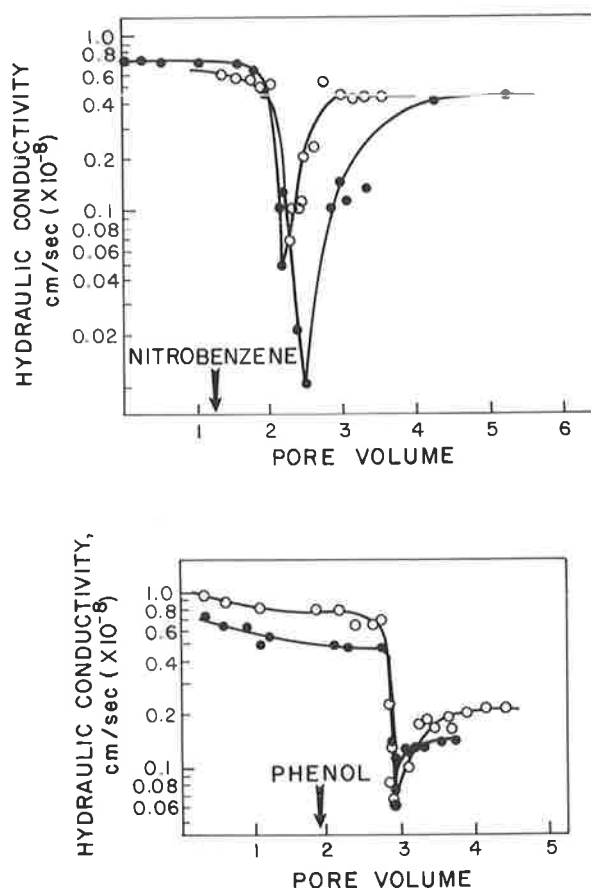
Table 4 presents the volume changes due to freeze drying of samples permeated with different organic fluids. The results indicate that the volume change experienced in the specimens permeated with 0.01 N CaSO₄ (control) was comparable with that in other studies (5,19). The volume change in the samples permeated with organic fluids was found to be less than that
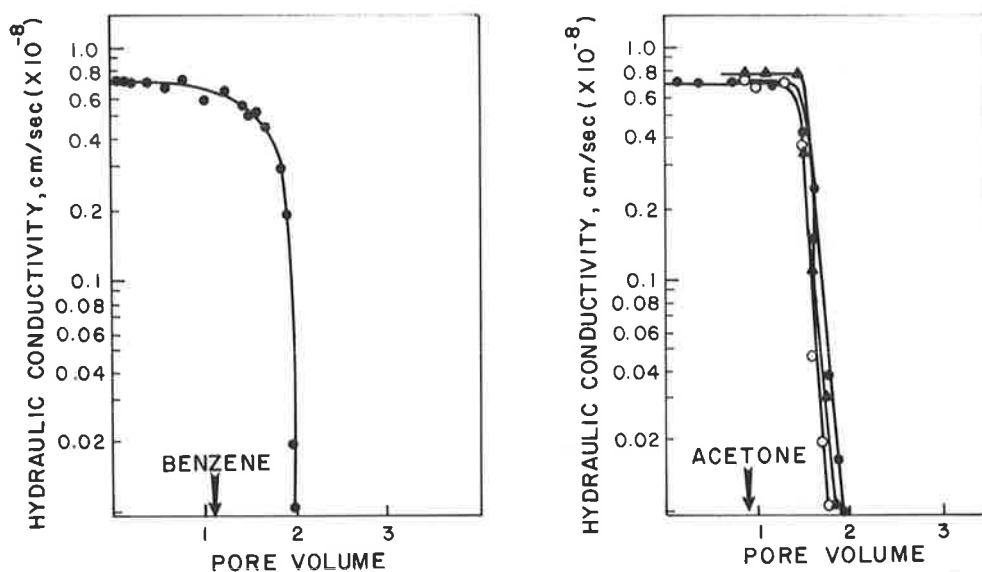
FIGURE 11 Hydraulic conductivity of compacted Ca-montmorillonite to benzene and acetone.

TABLE 4   VOLUMETRIC CHANGE IN CLAY SAMPLES DUE TO FREEZE DRYING

Pore Fluid	Dielectric Constant	Swell (+) Shrinkage (−)	
		Mean*	Variance*
Compacted Kaolinite			
0.01 N CaSO$_4$	84	+5.2	0.3
Nitrobenzene	35.7	+4.8	0.1
Acteone	20.7	+0.8	0.1
Phenol	13.1	+2.3	0.2
Benzene	2.3	+1.2	0.1
Compacted Ca-montmorillonite			
0.1 N CaSO$_4$	84	+3.9	0.9
Nitrobenzene	35.7	−2.2	0.2
Acetone	20.7	−5.3	0.3
Phenol	13.1	−1.7	0.1
Benzene	2.3	−2.0	0.3
P-Dioxane	2.0	−1.1	0.1

*Mean and variance are for three specimens.

of the control specimens, with the exception of the acetone-permeated Ca-montmorillonite sample. However, even in this sample, the shrinkage experienced (5.3 percent) was found to be within the limits presented in other studies (5,20).

Pore Size Distribution Analyses

The reliability and reproducibility of pore size distribution measurements were addressed in this study. Several precautions were taken to ensure homogeneity in compacted samples. Three pore size distribution measurements were taken from each sample after permeation. Overall, the replication of the pore size distribution measurements was excellent (6).

The pore size distribution curves of compacted kaolinite samples permeated with benzene, nitrobenzene, phenol, and benzene were compared with the pore size distribution of the 0.1 N CaSO$_4$-permeated sample (21). The study indicated that major changes in the pore size distribution were not observed. Table 5 compares the pore size parameters and hydraulic conductivity values obtained in that study with the Ca-montmorillonite specimens used in this study. Changes in kaolinite hydraulic conductivity with benzene and nitrobenzene and in

Ca-montmorillonite hydraulic conductivity with acetone and benzene resulted in a decrease of two to three orders of magnitude. Similarly, phenol led to a slight (within an order of magnitude) decrease, whereas the pore size frequency did not significantly change for these three chemicals.

Benzene, nitrobenzene, and phenol have low solubilities in water. It was then expected that these fluids would not be able to displace the water in the smaller pores because of higher flow-initiation pressures required to overcome the surface tension at the interface of the two fluids. Consequently, the resulting decrease in flow volume would lead to lower hydraulic conductivity. The pore size distribution results indicate that there were no significant fabric changes in amounts that may have diffused into the specimen, possibly below the solubility limit of these chemicals.

Acetone is infinitely soluble in water. This chemical was fully displaced in the pores in these tests. Table 5 indicates that the final hydraulic conductivity increased slightly in the tests with kaolinite (6 to 10 as compared with 1). Pore size distributions indicate that the fabric of the specimens before and after permeation with acetone was comparable—also verifying the slight change in absolute hydraulic conductivity (21). However, Figure 3 indicates that this liquid

TABLE 5   CORRELATION OF PORE SIZE PARAMETERS AND ABSOLUTE HYDRAULIC CONDUCTIVITY

Sample Type	Hydraulic Radius Model $R_h^2 \times n \times 10^{-5} \ \mu m^2$		Marshall Model $d^2 \times 10^{-2} \ \mu m^2$		Final Hydraulic Conductivity $\times 10^{-8} \ cm/sec$
(*)	σ	σ_n	σ	σ_n	
COMPACTED KAOLINITE					
Dry of Optimum					
0.01 N CaSO$_4$	14.75	0.22	4.75	0.18	10
Wet of Optimum					
0.01 N CaSO$_4$	8.01	0.35	2.10	0.30	1
*Nitrobenzene	7.25	0.22	1.78	0.05	<0.02
Acetone	8.66	0.70	2.25	0.15	6-10
Phenol	8.69	0.60	2.27	0.25	14
*Benzene	9.66	0.78	1.87	0.07	<0.01
CA-MONTMORILLONITE					
Wet of Optimum					
0.01 N CaSO$_4$	5.20	0.10	4.80	0.55	0.96
Nitrobenzene 1	10.60	0.27	5.00	0.26	0.45
Nitrobenzene 2	7.0	0.07	5.50	0.13	0.45
*Acetone	2.40	0.02	1.90	0.13	<0.01
Phenol 1	6.80	0.11	2.70	0.37	0.21
Phenol 2	8.00	0.12	3.80	0.26	0.14
P-Dioxane 1	7.80	0.09	2.30	0.28	0.73
P-Dioxane 2	5.10	0.06	1.80	0.24	0.53
*Benzene	9.80	0.29	6.00	0.40	stop

*full breakthrough is not achieved

σ = mean

σ_n = standard deviation

(*) means and standard deviations are for three samples

makes the soil nonplastic, implying a flocculated fabric and higher absolute hydraulic conductivity. Drastic changes were restricted, possibly due to high confining stresses (8 psi).

For the Ca-montmorillonite specimens, Figure 13 compares the fabric of benzene-permeated specimens. The flow practically stopped (less than 1×10^{-10} cm/sec) upon switching to benzene. This fluid has a very low solubility in water. Hence, it was expected that hydraulic conductivity would decrease upon switching to this fluid, and pore size distribution was not significantly changed. However, during testing, it was observed that the specimen swelled during permeation. This is also shown from the cumulative porosity in Figure 13. The reason for this swell was not explainable from consistency limits with Ca-montmorillonite. It is possible that this organic fluid leads to interlayer swelling in the mineral and changes the d-spacing.

Figure 14 compares the pore size distributions of the nitrobenzene-permeated specimen. Breakthrough was achieved in this specimen because of the larger pore mode. A significant change was not observed in either hydraulic conductivity or pore size parameters. It was hypothesized that the immiscibility of this fluid resulted in its flow through the larger pores without a significant effect on the pore size distribution.

Figure 15 presents the fabric of the acetone-permeated specimen. This experiment was terminated at 70 percent breakthrough when hydraulic conductivity reached a minimum (1×10^{-9} cm/sec). Because of the prolonged testing times (200 to 300 days/pore volume), full breakthrough was not achieved. Figure 15 indicates that although the total porosity of the specimen was identical to that before permeation, the large pore mode had shifted to the smaller mode and was distributed over a wider band of pore diameters. One would
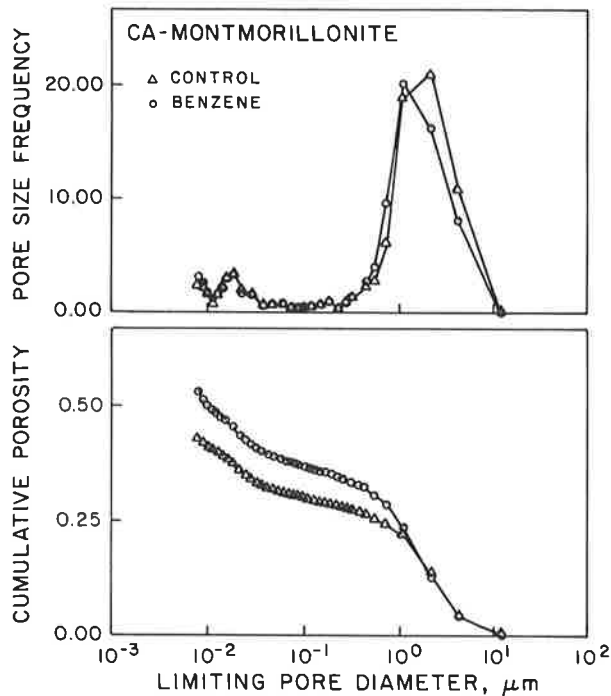
FIGURE 13 Comparison of pore size distributions in benzene-permeated specimen.
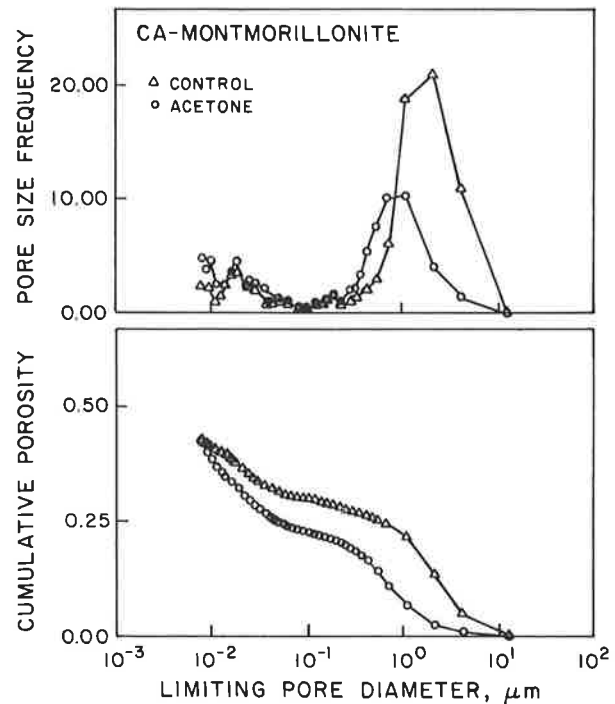

FIGURE 15 Comparison of pore size distributions in acetone-permeated specimen.
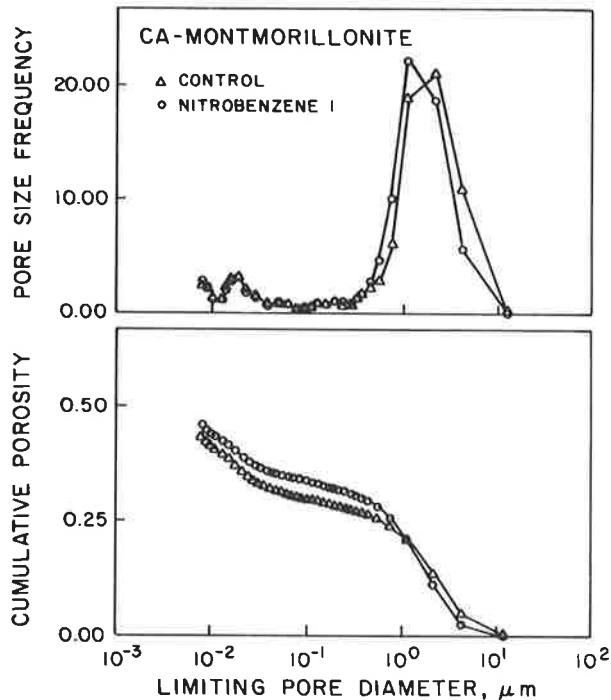

FIGURE 14 Comparison of pore size distributions in nitrobenzene-permeated specimen.
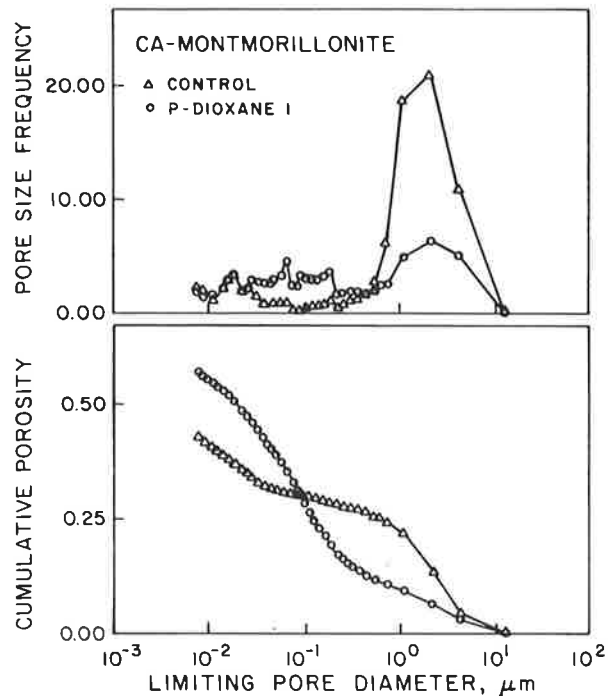

FIGURE 16 Comparison of pore size distributions in p-dioxane-permeated specimen.

then expect lower hydraulic conductivity from a scrutiny of Figure 15. It was hypothesized that introduction of miscible acetone into the pores led to a decrease in the thickness of the double layer and to variations in the forces of interaction. This resulted in a major reorientation of the particles, during which time the hydraulic conductivity decreased. Further permeation led to further reorientation until a stable, flocculated

fabric was achieved and hydraulic conductivity attained the higher terminal values. The pore size distributions referred to the time when the reorientation of fabric occurred and flow decreased.

Figure 16 compares the pore size distribution of samples permeated with p-dioxane and 0.01 N $CaSO_4$. Full breakthrough was achieved with this miscible organic fluid. P-diox-
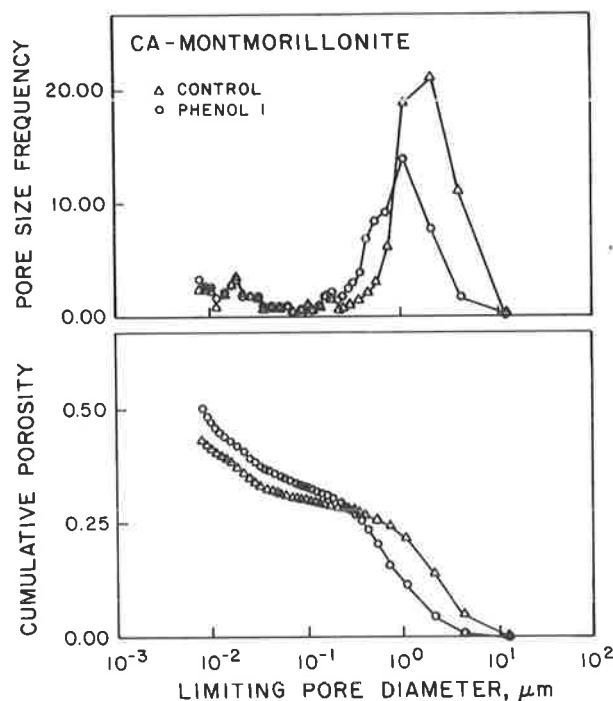
FIGURE 17 Comparison of pore size distributions in phenol-permeated specimen.

ane has a very low dielectric constant (2.0) and is fully miscible. It was specifically chosen to assess the effect of such an extreme variation in dielectric constant of the pore fluid on the hydraulic conductivity and pore size distribution. Figure 16 indicates that, although the peak value decreased in the large pore mode, a corresponding increase in the small pore mode increased the cumulative porosity. Table 5 indicates comparable pore size parameters in p-dioxane and 0.01 N CaSO$_4$-permeated samples. As a consequence, the hydraulic conductivity with p-dioxane was almost identical to the absolute hydraulic conductivity with 0.01 N CaSO$_4$ solution. The cumulative pore size distributions indicated approximately a 20 percent increase in the volume of the sample, which implies that the area of the gross sample was increased by 20 percent. This was, in fact, detectable during testing.

The results with phenol are presented in Figure 17. The specimen swelled slightly after permeation, and the frequency of the large pore mode decreased. The fabric changes indicate a decrease in hydraulic conductivity. Figure 12 indicates that the hydraulic conductivity decreased with phenol permeation. It should be noted that the solubility of phenol is low, and hence some of the decrease may be due to this low solubility of the organic fluid.

CONCLUSIONS

The results of this study on the effects of organic fluids on the fabric and hydraulic conductivity of kaolinite and Ca-montmorillonite indicate the following:

1. As previously detected with compacted silty clays (19), compacted kaolinite and Ca-montmorillonite also display bimodal to unimodal distributions with increases in the molding water content. The pore size parameters (hydraulic radius and Marshall) reflecting these changes correlate well with experimental values of hydraulic conductivity with 0.01 N CaSO$_4$ solution.

2. Hydraulic conductivity tests on kaolinite compacted at variable molding water contents and compaction efforts indicate that a decrease of 20 percent in the intended compaction dry density leads to an increase of about one order of magnitude in the hydraulic conductivity of the compacted soil.

3. Consistency limit and free-swell tests on kaolinite, Ca-montmorillonite, and Na-montmorillonite with organic molding fluids indicate that the dielectric constant and the pH of the pore fluid strongly influence their interaction in these clay minerals. Index properties and free swell of active montmorillonitic clays are observed to be highly affected by the variations in the dielectric constant of the pore fluid, whereas kaolinite does not indicate such a trend. The pH of the solution is observed to be dominant on the properties of this mineral.

4. The results of the study indicate that changes in hydraulic conductivity in compacted soil when organic fluids are permeated through them are in response to fabric changes, pore fluid characteristics, and interactions with the clay mineral. A knowledge of consistency limits with the pore fluid would not necessarily indicate changes in hydraulic conductivity. Pore fluid characteristics, type of clay mineral, and confining stresses significantly influence the final results.

5. The low solubility of the organic fluids used in this study resulted in a significant decrease in hydraulic conductivity of kaolinite and Ca-montmorillonite originally molded with water.

This study has the following practical implications:

1. In constructing low-permeability earthen barriers, it is essential to control both the molding water content and the dry density strictly. A decrease in the specified dry density may lead to at least an order of magnitude increase in hydraulic conductivity.

2. Pure organic fluids may increase or decrease the hydraulic conductivity of water-molded earthen barriers. Consistency limits with such fluids indicate that they may lead to shrinkage and subsequent tension cracks when in contact with high activity soils. However, high confining stresses and immiscible fluids may mitigate drastic changes. This implies that surface impoundments will be more susceptible to fabric changes than barriers confined under an overburden.

3. Porosimetry may be used as a fast and reliable way to estimate hydraulic conductivity of water-molded compacted specimens. However, porosimetry provides only a point estimate of the microfabric, and field values of hydraulic conductivity may be greater due to macrofabric features.

4. The one order of magnitude increase in hydraulic conductivity of compacted soils when permeated with miscible organic fluids at confining stresses of 2 to 10 psi suggests that field macrofabric resulting from compaction effort, clod size, compaction scheme, lift thickness, and desiccation cracks may overshadow any anticipated microfabric changes due to transport of organic contaminants. Therefore, construction quality assurance and improvement of field methods of assessing hydraulic conductivity with water are of utmost importance in constructing a low-permeability barrier.

ACKNOWLEDGMENTS

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