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# Permeability of Clays under Organic Permeants

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# PERMEABILITY OF CLAYS UNDER ORGANIC PERMEANTS

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**ABSTRACT:** A magnesium montmorillonite and a kaolinite clay are subjected to organic and inorganic permeants to study the changes in permeability caused by the reaction between clays and permeants. The permeants are acetic acid, aniline, methanol, and xylene. Tests are conducted in specially designed and constructed flexible wall permeameters that provide precise measurements of pressures and flows. Increases in clay permeability due to clay-permeant chemical reactions are measured to be on the order of two to three times the original permeability. This is in contrast to the 100 tò 1,000 times increases reported by others. The writers believe that the large increases reported by others is probably due to the use of fixed-wall permeameters. The writers' results show that methanol doubles the permeability of montmorillonite. Acetic acid reacts with the carbonates in montmorillonite and liberated carbon dioxide. The resulting loss of mass triples the clay's permeability. Aniline and xylene will not flow through saturated montmorillonite but will flow through saturated kaolinite at reduced flow rates. Hydraulic fracturing of the montmorillonite occurred when methanol passed through it under a high gradient and low confining pressure.

## INTRODUCTION

Until recently, the problem of permeability of a natural or compacted clay soil was viewed only in terms of the flow of water. Compacted clay soils were generally considered "impervious." As a result, even with the advent of hazardous waste disposal and the attendant problems of groundwater pollution by toxic leachates, clays are being accepted as barriers to protect the environment from leachates that are coming from hazardous waste management facilities. Therefore, hazardous leachate permeants, such as organic aqueous and nonaqueous fluids, are being contained by clay soil liners at these facilities.

The object of the investigation was to study the change in clay permeability brought about by the chemical reactions between a clay and a permeant. Any change induced by such a reaction in the microstructure (microfabric) of the clay was studied by scanning electron microscope.

### Permeability and Hydraulic Conductivity

Hydraulic conductivity defines the capacity of a porous medium to conduct a particular fluid, and is a function of both the medium and the fluid.

Permeability (American Society for Testing and Materials 1981), also known as the intrinsic or absolute permeability, expresses the capacity of flow in terms of the properties of the porous medium only. The intrinsic permeability ($K$, in square centimeters) and the coefficient of hydraulic conductivity (permeability) ($k$, in centimeters per second) are related by the following equation:

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$$k = \frac{Kv}{\rho} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

in which $v$ = the absolute viscosity of the permeant, in poise (g/cm-s); $\rho$ = the mass density of the permeant (g/cm$^3$), and $g$ = the acceleration of gravity (cm/s$^3$).

In this investigation, the hydraulic conductivity value, $k$, which was obtained using the standard permeant, was taken as the base (reference) permeability, $k$, with units of centimeters per second. By using all other permeants, the hydraulic conductivity values were converted into relative permeability values denoted by $k$. By using the relative viscosities and relative densities of the permeants, these values were converted to that of the standard permeant at 25° C, as shown by the following equation:

$$k = \frac{Kv_r}{\rho_r} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

in which $v_r$ = the relative viscosity of the permeant; and $\rho_r$ = the relative density of the permeant.

## TESTING EQUIPMENT AND PROCEDURE

### The Triaxial Flexible Wall (TXFW) Permeameter

It is the writers' belief that the most suitable equipment for determining the permeability of fine grained soils in the laboratory is the triaxial flexible wall (TXFW) permeameter. The key feature of the triaxial permeability permeameter is that the specimen is surrounded by a thin flexible membrane, which is pressed tightly against the specimen walls, preventing flow along the sides of the specimen. Another advantage of the triaxial method is that the specimen may be back pressure saturated and that saturation may be checked before permeation. Further, the external stress state on the soil sample can be both measured and controlled during testing.

Carpenter and Stephenson (1985), after extensive permeability testing, developed equipment and techniques for measuring permeability of fine-grained soils with permeabilities as low as $10^{-11}$ cm/s.

The triaxial cell permeameter used in this investigation was designed for precise permeability measurements using organic solvents. The setup, shown in Fig. 1, consists of a measuring and control panel, a triaxial cell, a volume-change indicator and an air-water interface. The main objectives of the design were: (1) Precision in the measurements of pressures and flows; (2) independent measurement of volume change of the sample during testing; (3) use of larger-diameter [6.35 cm (2.5 in.)] samples; (4) elimination of air from the lines; (5) chemical resistance to the organic solvents to be used; and (6) facility of safe and easy handling of the toxic permeants. All system controls and measurement devices for pressures and flows are located on a single panel. Gages on the panel roughly monitor the pressures, which are precisely measured by a calibrated pressure transducer. All permeant lines are of Teflon and all valves and fittings are of brass.

### The Triaxial Permeability Cell

The triaxial permeability cell is an acrylic cylinder with an internal diameter of 12.70 cm (5 in.) and a height of 17.78 cm (7 in.). The base and
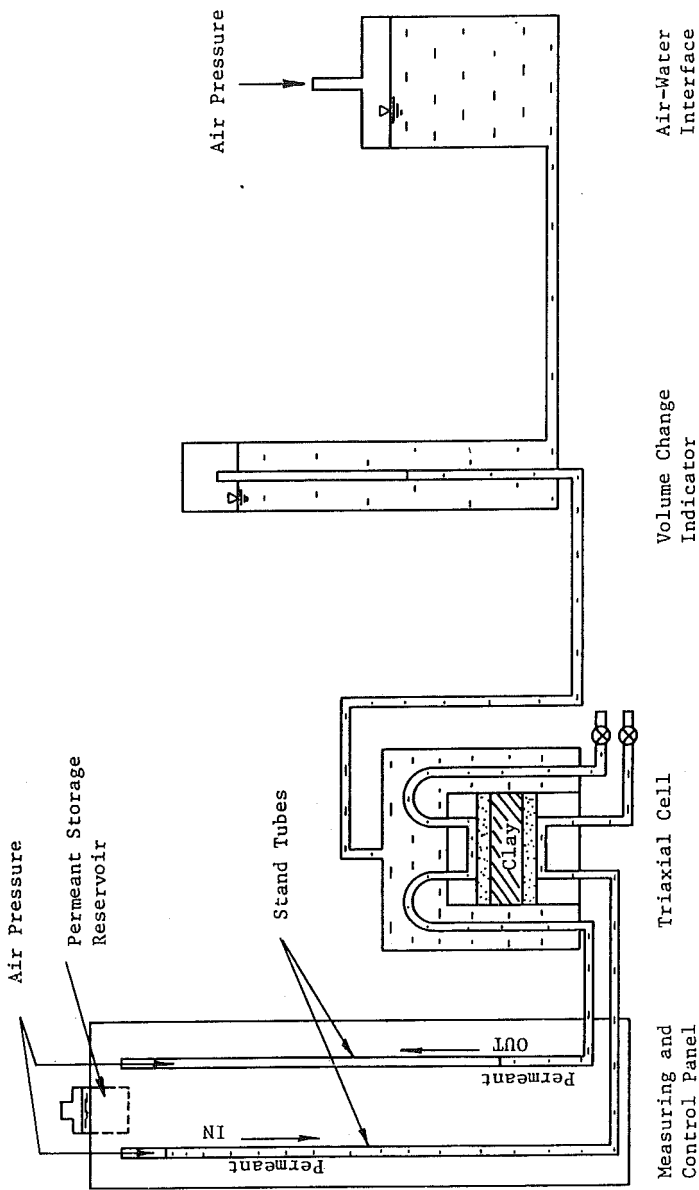
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**FIG. 1. Schematic of Triaxial Cell Permeability Test Setup**

the top cap of the cell are made of either aluminum or Teflon. Soil samples, 6.35 cm (2.5 in.) in diameter and up to a maximum of 5.08 cm (2 in.) in height, can be tested in the cell.

There are two permeant lines both at the base (the pedestal) and on the top cap of the specimen. One of these from the base and from the top cap is connected to the inflow and outflow lines coming from the control panel, respectively. The second line from the base and the top cap are brought outside the cell. These dual lines facilitate the flushing of air from the system and also make it possible to replace one permeant by another in both the inflow and outflow lines. Samples of the effluent can be obtained from the outflow side during a test.

Since latex membranes are not chemically resistant to the organic solvents used, a lining of Teflon film is used inside the outer latex membrane. The latex membrane provides elasticity to the confinement of the specimen. It was found that a commercial plastic wrap would also resist attack by the organic solvents used in this investigation.

### The Volume-Change Indicator

A double-tube volume-change indicator (VCI) was modified by replacing the inner tube by a 0.635-cm (0.25-in.) tube to increase its precision. Despite all the factors that affect the VCI readings, it was found that the VCI was capable of registering small volume changes due to clay-permeant reactions that occur within as short a time as is required for one pore volume flow and could also measure large volume changes that occur during several pore volumes of flow. However, small volume changes that occur over several pore volumes of flow are not easily detectable by the VCI.

### Clays and Permeants

Two clays were tested with six organic permeants and the standard permeant. A description of the clays and permeants follows.

### The Clays

A kaolinite and a montmorillonite clay were used in this investigation. These were selected because they represent the two extremes in clay structure. Kaolinite is a two-sheet mineral with a nonexpanding lattice and a low cation exchange capacity. Montmorillonite is a three-sheet mineral with an expanding lattice and high cation exchange capacity.

The kaolinite was Kentucky ball clay, available commercially. X-ray diffraction tests on the material indicated that its clay mineral part is composed of approximately 90% kaolinite and 10% illite.

The montmorillonite was obtained from an operating clay mine in Bloomfield, Missouri. X-ray diffraction tests on the material indicated that its clay mineral part is composed of approximately 75% montmorillonite, 15% kaolinite, and 10% illite. The clay also contained significant amount of carbonates. Chemical analysis of the clay (Carpenter 1982) indicated the major exchangeable cation in the montmorillonite to be magnesium, and hence it is hereafter called magnesium montmorillonite in this report. The physical and index properties of the clays are given in Table 1.

### The Permeants

**Standard Permeant.** The standard permeant used in this investigation was a 0.004-N (1 g/l) solution of magnesium sulphate heptahydrate (Epsom

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**TABLE 1. Physical and Index Properties of Test Clays**

| Properties (1) | Kaolinite (2) | Magnesium montmorillonite (3) |
|---|---|---|
| Liquid limit | 66 | 102 |
| Plastic limit | 31 | 59 |
| Plasticity index | 35 | 43 |
| Percent finer than 2 μ | 83% | 46% |
| Activity | 0.35 | 0.80 |
| Specific gravity | 2.62 | 2.65 |
| Cation exchange capacity | 12 meq/100 g | 72 meq/100 g |

salt) in distilled water. Because of the very low concentration of the salt, the density and viscosity of this permeant were measured to be equal to those for the distilled water. This permeant was selected because it is compatible with the test soils and would not cause any significant change in the clay-permeant chemical makeup.

**Organic Permeants.** Four organic fluids, representing acidic, basic, neutral polar, and neutral nonpolar were selected as organic permeants (Table 2). They are commonly found to be constituents of leachates in hazardous waste landfills and have a wide range of dielectric constants.

## Procedure

*Sample Preparation*

The samples for the permeability testing were consolidated from slurry as follows: 500 g of the air-dried clay was mixed with sufficient deaired standard permeant to make a thick slurry. The slurry was stirred for about 10 min by an electric agitator, covered, and kept for hydration in a moist room for at least 48 hours. After this, the slurry was taken out, stirred again for about 10 min, and poured into the mold of the slurry consolidation apparatus. A mechanical rod vibrator was inserted into the slurry and vibrated for about 5 min in order to remove entrapped air. A total vertical pressure of 172 kPa (25 psi) was applied in 34-kPa (5-psi) increments to the slurry and allowed to consolidate. At the completion of consolidation, the soil sam-

**TABLE 2. Relevant Physical and Chemical Properties of Organic Fluids Used in Test**

| Organic fluid name (1) | Density at 25° C (g/cm) (2) | Viscosity at 25° C (centipoise) (3) | Dielectric constant at 25° C (g/L) (4) | Water solubility at 25° C (5) |
|---|---|---|---|---|
| Acid, acetic acid miscible | 1.05 | 1.28 | 6.2 | — |
| Base, aniline | 1.02 | 4.40 | 6.9 | 34 |
| Natural polar, methanol miscible | 0.79 | 0.54 | 31.2 | — |
| Neutral nonpolar, xylene | 0.87 | 0.81 | 2.4 | 0.20 |
| Water | 0.98 | 1.0 | 80.4 | — |

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ples were carefully extruded, wrapped, and stored until testing. The samples prepared this way were found to be uniform and homogeneous. No significant water content variation was observed between the top and bottom of the consolidated sample.

Although this method of specimen preparation does not model field compaction procedures, it does produce test specimens with relatively little variation between specimen as verified by X-ray analysis. Because this was an investigation into the physical-chemical behavior of the permeation, sample structure variations were to be avoided. For this reason these specimen were ideal.

*Permeability Testing*

In order to establish a proper hydraulic gradient for testing, the first series of triaxial permeability tests were performed on the magnesium montmorillonite and the kaolinite using the standard permeant under different gradients. The gradients were 60, 277, 554, and 831. The permeability was found to be independent of gradient between the values of 277 and 831. The slight expansion (indicated by the VCI) at the inflow end of the sample did not significantly affect the permeability.

Only four tests were performed on the magnesium montmorillonite with a lower gradient of 60 since the time necessary for the passage of one pore volume was about three days. Two of these tests showed no change in permeability, whereas the other two showed an increase of about two times in the permeability. Hence the results were not conclusive. Further study of the permeability at low gradients is needed.

Based on the results of these tests, a gradient of 831 [103 kPa (15 psi) of differential pressure between the inflow and the outflow sides on 1.27-cm- (0.5-in.-) long sample] was selected. A few tests were conducted using a gradient of 277 as discussed later. The testing procedure was as follows.

A 1.27-cm- (0.5-in.-) long sample was trimmed with a wire saw from the slurry consolidated sample and the initial pore volume of the sample was computed. The sample was then mounted in the triaxial cell and wrapped by the appropriate membrane.

The cell was then filled with deaired tap water. The specimen was then back pressure saturated and simultaneously consolidated to an effective consolidation pressure of 138 kPa (20 psi).

The back pressure and the cell pressure were chosen for the following reasons. The sample consolidated from slurry was calculated to have a degree of saturation of above 99%; therefore a 69 kPa (10 psi) of back pressure was sufficient to cause saturation. During specimen preparation, the sample had been consolidated to a vertical pressure of 172 (25 psi). Hence, the isotropic consolidation pressure in the cell of 138 kPa (20 psi) would not cause a large volume change in the sample.

After 24 hours of consolidation, back-pressure saturation and initial readings were recorded the sample was then ready for permeation. Two pore volumes of the standard permeant were passed through the sample in order to establish a base permeability. The gradient across the sample was created by increasing the air pressure in the inflow stand tube to 172 kPa (25 psi), while maintaining the outflow line pressure at 69 kPa (10 psi) and the cell pressure at 207 kPa (30 psi). Inflow and outflow stand-tube permeant level

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and elapsed time readings were taken initially and approximately at the end of each pore volume of flow.

The permeant in the reservoir and the in and out stand tubes was then replaced with the new test permeant in such a manner that there was no change in the effective stresses on the sample. As the flow continued, readings were taken at intervals of every half pore volume of flow initially, and at approximately every one pore volume afterwards. The test was continued until the permeability stabilized (4–9 pore volumes of flow). Some tests with a single permeant (aniline and xylene), were terminated after about 12 hours of testing because there was no or very little flow. Volume change was monitored during the test by the VCI as well as by the difference between the inflow and outflow stand tube readings. At the end of the test, the sample was removed, wrapped, and preserved for later scanning electron microscope studies.

### Other Tests

Other tests performed were scanning electron microscope photography, x-ray diffraction, index property tests, cation exchange capacity, gas chromatography (for the analysis of cell water for the presence of the permeant diffused through the membrane from the sample), and density and viscosity measurements of permeants.

## RESULTS

### Permeability Change Due to Organic Permeants

#### Acetic acid

Fig. 2 shows that after a very slight decrease during the first one and a half pore volumes of flow the permeability of magnesium montmorillonite increased to about three times its base value. Carbon dioxide was evolved, accompanied by an approximately 2.5% decrease in the volume of the sample. No significant change in permeability occurred for the kaolinite sample.

It is known that strongly acidic and strongly basic liquids can dissolve clay minerals. Loss of mass through dissolution of clay mineral particles by a permeant increases the effective pore space and thus increases the permeability. Carbonates in the clay can react with acidic permeants, generating carbon dioxide gas, which escapes. The solid product of the reaction may go into solution in the permeant. The resulting loss of mass will increase the permeability.

It is believed that the threefold increase in permeability of the magnesium montmorillonite observed in these tests was mainly occasioned by the loss of mass produced by the reaction between the acetic acid and the calcium carbonate in the clay. There was no dissolution of the kaolinite, which did not contain calcium carbonate, therefore the permeability did not change. Acetic acid (50% solution) is weak and the contact time was too short to cause significant dissolution.

Another significant finding of the test was the decrease in volume of the sample that accompanied the reaction which resulted in a loss of mass. The 2.5% decrease in volume of the sample indicated that the loss of mass induced a partial collapse of the more porous structure of the sample. The collapse was partial, in that despite the collapse there was a threefold in-
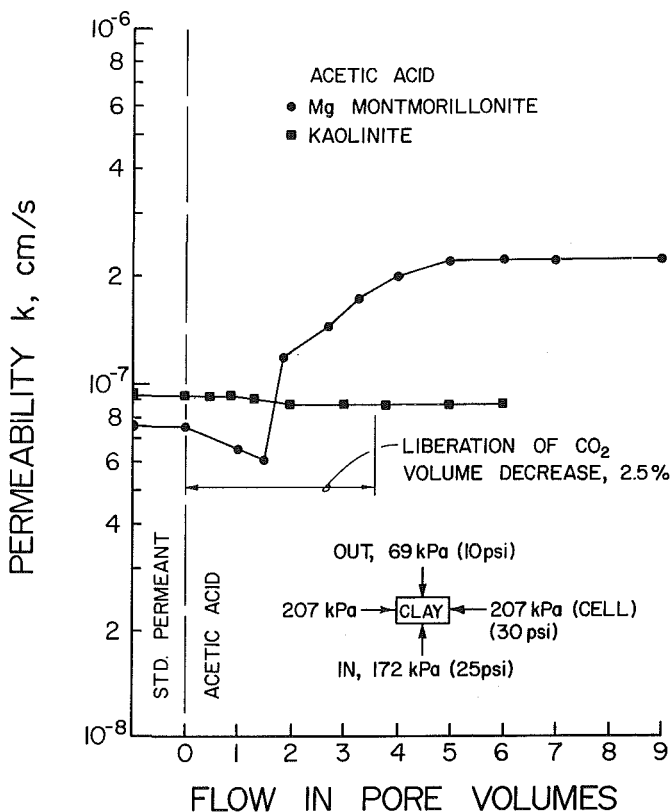
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**FIG. 2. Change in Permeability Due to Acetic Acid Flow**

crease in permeability. It could be inferred that in a situation where the confining pressure is less than that applied during this test, there would be little or no collapse and a greater increase in permeability. It could also be inferred that with stronger and more concentrated acids passing for a longer time through the clay, the reaction with the carbonates would be more complete and there might also be dissolution of clay minerals, resulting in greater loss of mass and greater increases in permeability.

Kaolinite, illite, noncalcareous smectite, and calcareous smectite were tested for permeability by Brown and Anderson (1984) at Texas A&M University. The permeants tested were acetic acid, aniline, methanol, acetone, ethylene glycol, heptane, and xylene. Compacted samples were tested in a fixed-wall permeameter, with surcharge pressure applied in the stand tube to increase the gradient.

In Brown and Anderson's (1984) acetic acid tests, the main phenomenon observed by the authors was dissolution and piping. According to Brown and Anderson, dissolution resulted in smaller particles. As particles were transported by the permeant, they clogged the pores downstream. This caused an initial decrease in permeability. But, as dissolution progressed in the zones

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of clogging, particles were removed by piping and the permeability tended to increase.

Bowders and Daniel (1987) noticed a relatively slight decrease in the hydraulic conductivity of kaolinite permeated with different concentrations of acetic acid. The decrease was less than one-half an order of magnitude.

*Aniline*

There was no measurable flow of aniline through the montmorillonite sample during an entire 12-hour testing period. The sample virtually behaved as an impervious barrier.

The flow of aniline through the kaolinite sample decreased significantly at the beginning. At the end of 12 hours, the permeability was about 400 times less than the base permeability.

Inspection of the samples after the test revealed that aniline did not penetrate the montmorillonite sample. There was about 3 mm of penetration of aniline in the kaolinite sample. Because the flow through the sample was negligible, it is believed that no reaction took place between the permeant and the clay during this test, although aniline, an organic base, is positively charged and is capable of being adsorbed on the negatively charged clay surface, displacing the adsorbed water.

In a saturated porous medium, when one liquid replaces another with which it is immiscible, energy is expended. This is defined as the interfacial energy. Apart from the properties of the two liquids, such as the viscosity and density, the energy required depends on the pore size: the larger the pore size the smaller the energy required. Thus, a liquid may be able to displace water from a porous stone and flow through the stone, but may fail to flow through a saturated clay adjacent to the stone. In this case, the interfacial energy is provided by the pressure gradient.

Aniline is more than four times more viscous than water and is of very low water solubility. The aniline flowed through the porous stone, flowed with difficulty through the kaolinite and did not flow (during the time of the test) through the montmorillonite clay due to its small pore size.

In the Brown and Anderson (1983) study, aniline permeants caused permeability increases in the various clays of between 10 and 100 times the base value. The increases occurred before the passage of one pore volume. The largest increase was in the sample of noncalcareous smectite, the smallest increase was in the kaolinite sample. Brown and Anderson (1983) did not observe evidence of dissolution or piping when aniline was the permeant. They attributed the increase in permeability to alteration of the massive structure of the clays into an aggregated structure, characterized by visible pores and cracks in the surface of the samples.

This discrepancy between the Brown and Anderson study and this work could possibly come from two sources. The first and perhaps most important is the fact that the Brown and Anderson study was conducted using a fixed-wall permeameter. It is difficult to insure against permeant short circuiting around the specimen with this type of equipment. The continuity of contact between the soil specimen and the specimen container cannot be verified or observed during fixed wall permeameter testing. Any imposed alterations on the stress state of the specimen either from a change in effective stresses or an alteration in pore fluid chemistry could cause a volumetric decrease in the specimen and a concomitant creation of a short circuiting of the flow
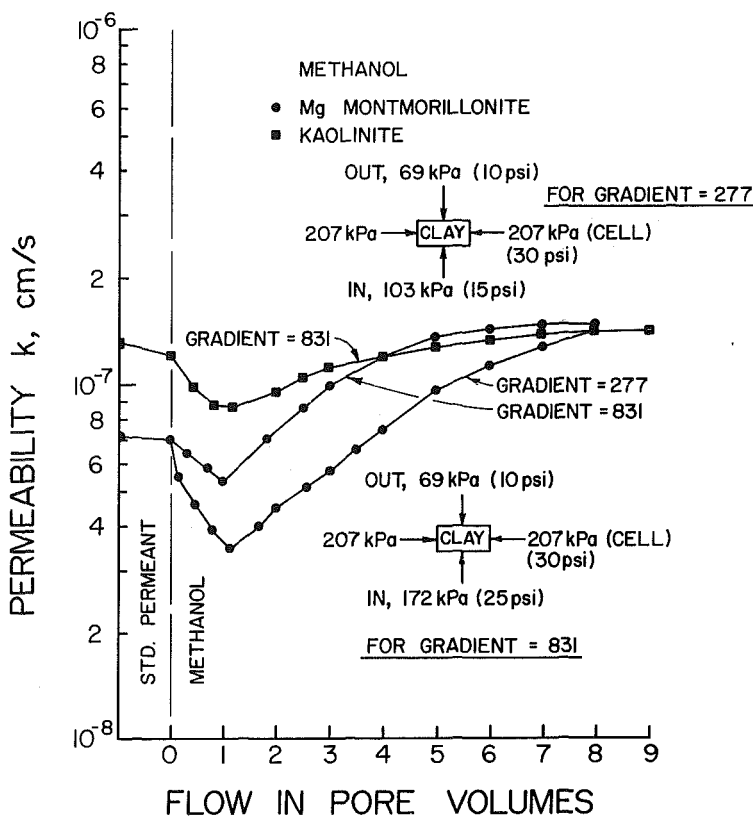
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**FIG. 3. Change in Permeability Due to Methanol Flow**

around the specimen between the soil and the rigid container wall. Acar et al. (1985) found that the permeability of kaolinite was measured to be approximately two orders of magnitude larger when tested in a rigid-wall permeameter than when it was tested in a flexible-wall permeameter.

A second cause of the differences in the two studies is the fact that the Brown and Anderson study was conducted on compacted soil specimens. These specimens probably were not fully saturated during testing. This would allow aniline to permeate through the air voids within the nonsaturated specimen and, possibly, cause chemical reactions, including particle aggregation, to take place. This flow could not take place if the specimen were fully saturated due to the immiscibility of the two fluids.

*Methanol*

The relationships between flow and permeability for magnesium montmorillonite and kaolinite with methanol are shown in Fig. 3. The permeability of the magnesium montmorillonite sample decreased initially and then increased to approximately twice the base permeability. Two tests at gradients of 831 and 277 were performed, and in each case the final permeability increase was the same. However, the initial decrease at the end of

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TABLE 3.   Atterberg Limit Tests on Methanol Treated Clays

| Stage of test (1) | Liquid limit (2) | Plastic limit (3) |
|---|---|---|
| (a) Magnesium montmorillonite | | |
| Before the test (using water) | 102 | 59 |
| After the test (using methanol) | 78 | 68 |
| After the test (using water) | 102 | 56 |
| (b) Kaolinite | | |
| Before the test (using water) | 66 | 31 |
| After the test (using methanol) | 80 | 46 |
| After the test (using water) | 69 | 33 |

the first pore volume was different for the two gradients. For the higher gradient of 831, the permeability decreased to about 70% of the base value. For the lower gradient of 277, permeability decreased to about 50% of the base value before increasing.

Only a slight trend towards increase was observed for the kaolinite sample. However, as seen with montmorillonite, there was an initial decrease in permeability to about 70% of the base permeability during the first pore volume flow under a gradient of 831. No volume change during the permeation was detected for either of the clay samples.

Visual inspection of both samples after the test revealed that they had become dehydrated and had lost much of their plasticity. Atterberg limit tests were conducted on the samples after the test, using methanol as well as water. The results are given in Table 3.

Photomicrographs of magnesium montmorillonite and kaolinite samples were taken before and after the permeation. The structure of magnesium montmorillonite after the test appeared to be more aggregated. The kaolinite structure appeared to be the same before and after the test.

A few methanol tests were also performed under a cell pressure of 186 kPa (27 psi) and a gradient of 831. This decrease in effective pressure produced a rapid increase in permeability of the montmorillonite sample, as shown in Fig. 4. The sample behaved as if a breakthrough of the permeant had occurred. The increase in permeability was between four and five times for the samples tested. On inspection after the test, it was observed that the samples were visibly cracked, indicating a probable hydraulic fracture. Because the flexible wall and the confining pressure kept the crack closed, the magnitude of the flow was not as great as it would have been in a rigid wall permeameter that does not have the ability to compensate for volume decreases in the test specimen. The kaolinite sample did not show any hydraulic fracture and the permeability variation was the same as had been measured under the lower pressure.

Ion exchange reactions with inorganic and organic cations in the new permeant, as well as adsorption of organic cations and neutral organic polar molecules in place of previously adsorbed water molecules, will change the thickness and composition of the adsorbed layer (Mitchell 1976). Influx of nonionic water might leach the existing cations, decrease the ionic strength of the pore fluid and swell the double layer. For clay minerals with an ex-
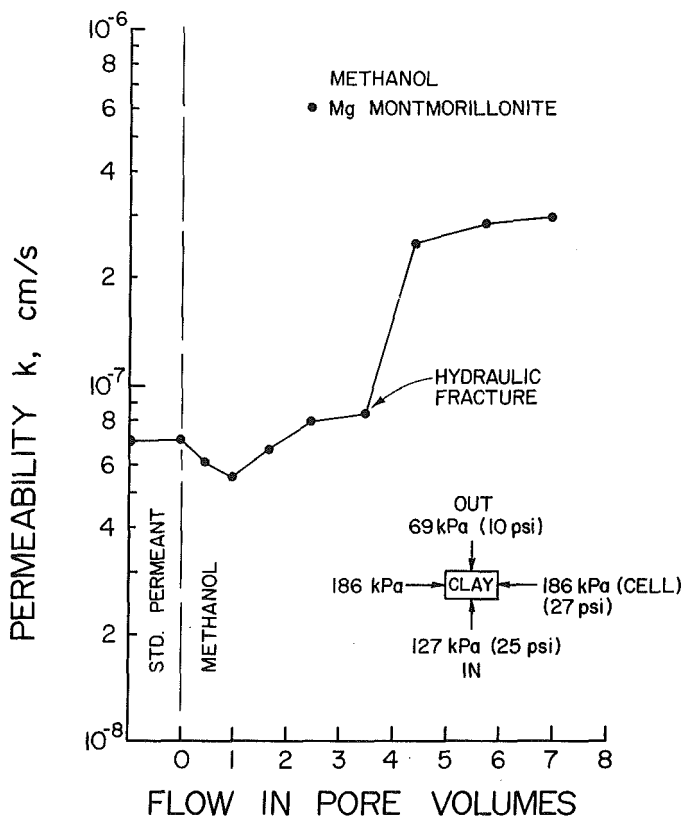
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**FIG. 4. Hydraulic Fracturing Due to Methanol Flow**

panding lattice, such as montmorillonite, these reactions will also take place in the interlayer spaces and cause the individual particles to swell or shrink.

A change in the thickness of the adsorbed layer and its composition in the clay, may bring about: (1) A change in the effective pore space causing a change in permeability; (2) a change in the fabric of the clay and cause a change in the pore system so that permeability is changed; (3) a swelling, which, if confined, will decrease the permeability; (4) a shrinking and cracking that will greatly increase in permeability; and (5) a loss in plasticity. Under high gradients and low effective stresses, hydraulic fracture could occur in the clay and the permeant would break through.

According to Guoy-Chapman theory, the diffuse double layer thickness with methanol will be smaller than that with water. This change will increase the effective pore space, thus increasing permeability. The magnesium montmorillonite, with a cation exchange capacity of 72 meq/100 g has a much greater double layer thickness than that of kaolinite, which has a cation exchange capacity of 12 meq/100 g. The water in the interlayer spaces of the montmorillonite particles can be replaced by methanol, reducing the effective size of the particle and thus increasing the pore space. Interlayer space

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of the kaolinite particles cannot be changed. The effect of this difference is that, for the magnesium montmorillonite, the intrusion of methanol will produce an appreciable increase in the effective pore space. For kaolinite, the increase will be much less.

The hydraulic fracture in the montmorillonite samples under low effective pressure and high gradient was caused by the reduction in plasticity that occurred due to the reduction in double layer thickness during flow (Table 3). This loss in plasticity results in a loss of interparticle bonding, and thereby makes it easier for the permeant pressure to separate the particles. In the case of the kaolinite sample, which did not show hydraulic fracture under the same pressure and gradieint, the liquid limit increased from 66 to 80 and the change in the plasticity index was insignificant. The fact that the liquid and plastic limits of both the methanol-treated clays returned to their original values when retreated with water indicates that the adsorption reaction is completely reversible.

It is believed that the decrease in permeability for both the clays during the first pore volume of flow with methanol is caused by the energy spent in replacing water by methanol in the adsorbed layer. It is significant that this phenomenon was not observed for the clays when the permeant was acetic acid, which is not adsorbed on the clay surface.

In the tests by Brown and Anderson (1983), the neutral polar fluids, ethylene glycol, acetone, and methanol caused continuous permeability increases in the various samples with no apparent tendency to stabilize. Increases in permeability from 50 to more than 1,000 times were observed by these authors before the passage of two pore volumes. The increase in permeability was believed to have been brought about by structural changes in the clay produced by reaction between the permeant and the clay.

Permeability in montmorillonitic ranger shale, kosse kaolin, and fire clay was studied by Green et al. (1981). The organic solvents used as permeants were benzene, xylene, carbon tetrachloride, trichloroethylene, acetone, methanol, and glycerol. It was found that the permeability of all clays decreased under the flow of all organic solvents. In most samples, the permeability stabilized after 14–25 days. However, in several other samples, a solvent breakthrough phenomenon was observed, mainly in the case of fire clay with xylene, and the ranger shale with carbon tetrachloride and benzene. In these cases, the permeability increased sharply after having decreased and stabilized.

Green et al. (1981) attributed the difference in permeability for various fluids to their dielectric constants. According to these authors, there was a good relationship between permeability and the dielectric constant of the permeant: the greater the dielectric constant, the greater the permeability. Not all the results agreed with this relationship.

The breakthrough and sharp increase in permeability of the shale and clay after permeability had decreased and stabilized was explained as the result of shrinkage of the specimen caused by reaction between the permeant and the clay.

The neutral polar fluids, ethylene glycol, acetone, and methanol caused continuous permeability increases in the various samples with no apparent tendency to stabilize. Increases in permeability from 50 to more than 1,000 times were observed by the authors before the passage of two pore volumes. The increase in permeability was believed to have been brought about by

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structural changes in the clay produced by reaction between the permeant and the clay. Again, the use of rigid-wall permeameters and specimen not fully saturated prior to testing could contribute to the inconsistency of these results with the results reported in this research.

*Xylene*

There was no measurable flow of xylene through the magnesium montmorillonite sample. The permeability for the kaolinite sample decreased from $9*10^{-7}$ to $2*10^{-9}$ cm/s after one pore volume of flow. The test was terminated at this point.

Xylene is a neutral, nonpolar organic fluid, 0.8 times as viscous and 0.9 times as dense as water. It is practically immiscible with water, and the only way it could pass through a water-filled porous media is by physically displacing the water from the pores, unlike miscible liquids that can diffuse through the water. Being nonpolar, it has no net charge and little if any dipole moment. Therefore, xylene cannot displace water and be adsorbed on the clay surface.

The behavior of the sample clays was similar in respect to permeability with aniline and xylene permeants. Neither permeant could generate measurable flow through the magnesium montmorillonite during the testing period of 12 hours. Both fluids reduced permeabilities while flowing through the kaolinite samples, although xylene could flow faster than aniline.

The interfacial energy relationship between two immiscible liquids, used to explain the behavior in permeability of both clays to aniline, can also be applied to xylene. Xylene flowed faster than aniline through the kaolinite, as it is much less viscous and less dense than aniline. Because it is nonpolar, there was no adsorption reaction between the clay and xylene. A study of the clay samples before and after the test with xylene, using a scanning electron microscope, did not reveal any change in structure.

Brown and Anderson's (1983) tests using the neutral nonpolar fluids xylene and heptane caused initial permeability increases in all of the samples of approximately 100 times, even before the passage of half a pore volume, and tended to reach a relatively constant permeability at that point. The authors believed that structural changes brought about by the reaction between the nonpolar organic fluid and the clay caused the increase in permeability. Since steady permeability values were reached within a short time (unlike the continuous permeability increases experienced with neutral polar fluids), they believed that the reactions were limited.

Brown et al. (1984) found that the permeability of micaceous soil liners compacted in rigid wall permeameters increased by four orders of magnitude when subjected to a pure xylene permeant. As acetone is mixed with the xylene, the relative increase in permeability was reduced.

The results of Brown and Anderson (1983) and Anderson et al. (1984) can be compared to those obtained for similar clays and permeants by Green et al. (1981) to note the contradictions.

Green et al. (1981) show a continuous decrease in permeability to about eight times for the montmorillonitic ranger shale, whereas Brown and Anderson (1983) report a sharp increase in permeability of about 1,000 times on the passage of half a pore volume of permeant for the smectite sample. Green et al. report a continuous decrease in permeability to xylene by about 20 times, followed by stabilization and finally, for the montmorillonitic fire

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clay sample, a sharp increase by about 50 times. Brown and Anderson, on the other hand, report an increase of about 100 times at the passage of one pore volume for the smectite. The permeability of to the montmorillonitic ranger shale to methanol decreased by more than two times in the work of Green et al. However, in the work by Brown and Anderson, permeability increased by about 1,000 times at the passage of half a pore volume for the smectite sample. Similar permeability increases were reported in the Brown et al. (1984) study. All three of the studies compared here were performed on compacted samples using fixed-wall permeameters.

## SUMMARY OF RESULTS AND CONCLUSIONS

It was observed during this investigation that the permeability of clays changes when fluids other than water flow through the clay. However, the increase is not on the order of 100 to 1,000 times as has been reported in the literature, but rather on the order of two to three times. It is the writers' opinion that the use of a fixed-wall permeameter introduces significant potential for high measurements of permeability in laboratory tests due to the limitations of the equipment itself. Any physical-chemical reaction that causes even a slight volumetric reduction in the soil specimen will decrease the boundary stress conditions on the specimen contained within a rigid confining chamber or ring. This decrease in boundary stress will increase the potential for permeant to pass between the specimen and the rigid cell wall. The amount of this short circuiting is difficult if not impossible to determine or quantify with normal rigid wall permeameters. In addition, although back pressure may be applied to the test specimen, there is no way to measure the effectiveness of the backpressure in saturating the specimen. If the specimen is not saturated during permeation then immiscible fluids can permeate through the air voids in the specimen perhaps generating chemical reactions within the specimen.

Changes in clay permeability are due to clay-permeant chemical reactions. No significant change in permeability due to cation exchange between magnesium and sodium was observed for the magnesium montmorillonite or the kaolinite samples. However, when distilled water was passed through a sodium-saturated magnesium montmorillonite, there was a fifteenfold decrease in permeability and a 13% swelling of the sample. When distilled water was passed through a magnesium saturated montmorillonite sample, there was no decrease in permeability nor did the volume of the sample change. The conclusion is that sodium, which is a very mobile ion, can be removed and replaced by water molecules in the double layer, resulting in an increase in double layer thickness which causes the clay to expand and reduces the permeability. If the swelling had been inhibited (as in a fixed-ring permeameter), the permeability decrease would have been much greater. Subsequent passage of a magnesium permeant through the same clay approximately doubled its permeability and decreased its volume by 9%. This indicates that magnesium had been reintroduced into the double layer with concomitant reduction in the double layer thickness. Kaolinite did not show a similar behavior because of its low cation exchange capacity.

Adsorption of methanol on the clay surface was observed. This permeant approximately doubled the permeability of magnesium montmorillonite. The kaolinite, because of its low cation exchange capacity, did not show any

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significant change in permeability. Methanol also reduced the plasticity of the montmorillonite which, under low effective pressure and high gradient, caused hydraulic fracture of the sample during flow. Because of the flexible wall confinement, the fracture did not open to the extent that it would have with a rigid confining wall.

The magnesium montmorillonite virtually acted as an impervious barrier to aniline and xylene. The fluids did flow through kaolinite, but at significantly reduced permeabilities.

Permeabilities increased due to loss of mass from gas-forming reactions when acidic permeants passed through magnesium montmorillonite. The increase in permeability was about three times for the acetic acid. As the pore volume increased due to the reaction, there was a partial collapse or consolidation of the montmorillonite structure, caused by the effects of the confining pressure, which partially offset the effect of the increase in pore volume. If the confining pressure had been less, the collapse would have been smaller or nonexistent and the permeability increase would have been greater than observed.

Scanning electron photomicrographs did not reveal any significant change in the structure of the clay after leaching with the organic fluids, although minor changes in fabric, induced by acetic acid and methanol, were observed.

## ACKNOWLEDGMENTS

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