Organic liquids and the hydraulic conductivity of barrier clays

Hydrocarbures liquides et la conductivité hydraulique des argiles

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SYNOPSIS: The effects of ethanol, xylene and cyclohexane in pure and mixed forms on the hydraulic conductivity, k, of permeant compacted and water compacted barrier clays are discussed in this paper. Permeant compacted clays demonstrate **k** values as high as 10^{-4} cm/s for xylene compared to 5×10^{-9} cm/s for water at e = 0.8. Water compacted clays experience no increase in **k** for water insoluble xylene unless ethanol is present in the pore fluid, the ethanol acting as an association liquid. Mixed ethanol and cyclohexane permeants form both two-phase and single phase liquids, depending on their relative proportions, greatly complicating **k** studies since the measured **k** will depend on which of the two phases passes through the soil first.

INTRODUCTION

Extensive research is continuing on the damaging effects that liquid hydrocarbons may have on the hydraulic conductivity of clay barriers or liners, both natural or compacted. Major fundamental work dates back to Michaels and Lin (1954), Mesri and Olson (1971) with a great increase in interest in the 1980s as a result of groundwater contamination by liquid organics. Some of the more recent works include Anderson et al (1982), Foreman and Daniel (1986), Fernandez and Quigley (1985), Mitchell and Madsen (1987), Acar et al (1985), and Fernandez and Quigley (1988).

This paper describes the hydraulic conductivity, k, of a silty clay exposed to water, ethanol, xylene and cyclohexane. Table 1 contains a description of these liquids and sketches showing their chemical structure. Table 2 summarizes the soil composition.

The paper is presented in three parts: part 1 describing **k** of permeant compacted clay; part 2 describing **k** of pure organic liquids forced through water compacted clay; and part 3 describing **k** of ethanol/cyclohexane mixtures forced through water compacted clay.

HYDRAULIC CONDUCTIVITY OF PERMEANT

A very clear picture of the transmissive properties of dry clay mixed with pure liquids was presented by Mesri and Olson (1971). At a given void ratio, smectite demonstrates enormous increases in **k** as the dielectric constant, ε, of the liquid hydrocarbons decreases from 80 for water to ε = 2 for materials like benzene or carbon tetrachloride. Illite is less reactive and kaolin is only slightly reactive.

Work by Michaels and Lin (1954) for kaolinite is replotted in Figure 1 to show intrinsic permeability, K, versus void ratio. Although

Table 1. Description of Permeant Liquids

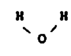
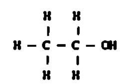
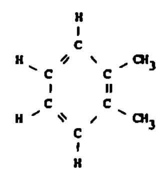
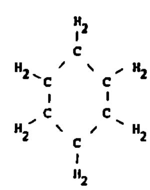
Liquid	Molecular Formula	Dielectric Constant, ε (20°)	Structural Formula
Water	H_2O	80.4	
Ethanol	C_2H_6O	25.0	
o-xylene	C_8H_{10}	2.47	
Cyclohexane	C_6H_{12}	2.02	

Table 2. Test Soil

Clay size (< 2μm)	~ 57%
Quartz + feldspar	~ 20%
Carbonates	~ 6%
Illite	~ 50%
Chlorite	~ 8%
Smectite	~ 15%
CEC	~ 30 meq/100 g

the increases are only by a factor of 2 to 8, the trend of increasing K with decreasing ε is very clear. These increases in **k** (and K) are caused by a combination of double layer collapse due to low ε and an aggregated ped-like structure related to flocculation during mixing of the low ε liquids. The authors referred to decreasing particle dispersion in the presence of reduced polarity.

Measured values of **k** obtained on dry natural clay samples mixed as a slurry then consolidated (k_{consol}) or mixed at the required void ratio and then permeameter tested at a constant flow rate (k_{direct}) are presented in Fig. 2 for water, ethanol and xylene. For ethanol, the two methods yield quite similar **k** values. For xylene, k_{direct} is considerably higher that k_{consol} at a given void ratio, a feature believed to reflect a relatively strong xylene flocculated structure that resists consolidation. For water, the samples were prepared by kneading compaction (Harvard miniature) and k_{direct} was less than k_{consol}. This reflects the greater compressibility of the more dispersed soil/water system.

HYDRAULIC CONDUCTIVITY OF WATER COMPACTED CLAY

Tests run on initially water saturated clays are complex because both the clay minerals and their adsorbed cations strongly adsorb polar water molecules preferentially over less polar, water soluble liquid hydrocarbons. As a result the organics seem excluded from the double layers of water and increases in **k** do not occur until the percentage of organic liquid approaches 70% (Mitchell and Madsen, 1987, Fernandez and Quigley, 1988).

When water insoluble xylene is forced through water saturated compacted clay (Figure 3) no change in **k** is observed even though the effluent is 100% xylene. At the end of testing, xylene occupied only 11% of the pore space which probably represented macropores and compaction induced fractures. Early arrival of the 50% xylene concentration at 0.28 pore volumes supports the interpretation of fracture flow. Work by some authors showing huge increases in **k** for insoluble organics appears related to high gradients and fracture opening.

Permeation with water soluble ethanol causes a slow increase in **k** to a value 8 to 10 times that for water permeation (Figure 4). If xylene (alcohol soluble but water insoluble) is then forced through the sample, an enormous increasein **k** is observed to a $k_f = 10^{-4}$ cm/s about 1000 and 10000 times greater than for alcohol and water, respectively). At the end of testing, the pore fluid in the soil sample consisted of approximately 35% water, 20 to 35% ethanol and 30 to 45% xylene. The 65% ethanol in the pore fluid at the end of ethanol permeation was about half removed by xylene permeation.

The large increases in **k** are interpreted to result from double layer contraction by the low ε xylene which entered the double layers only because ethanol was already present. Thus insoluble liquid hydrocarbons which normally

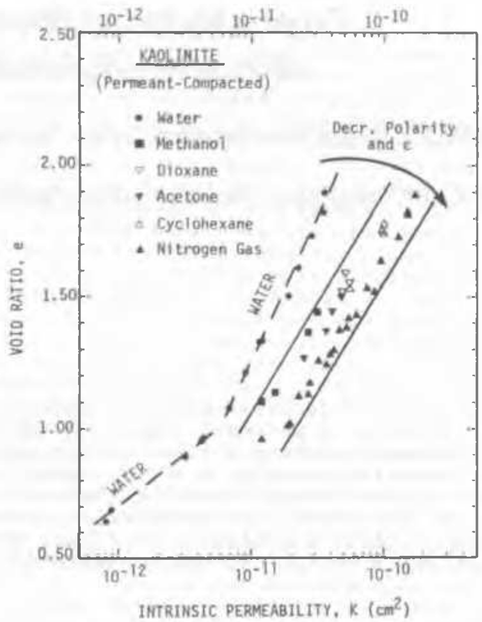


Figure 1. Intrinsic permeability vs void ratio for kaolinite; moulded, compacted and permeated with the fluid indicated. (Adapted from Michaels and Lin, 1954; ε = dielectric constant)

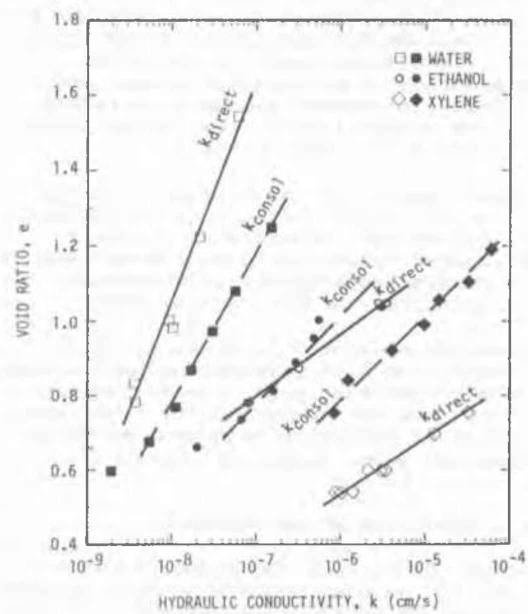


Figure 2. Hydraulic conductivity from direct measurements and consolidation tests at various void ratios

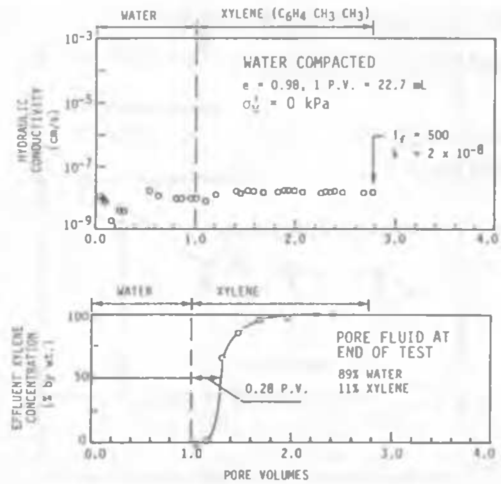


Figure 3. Hydraulic conductivity and effluent concentration vs pore volumes.

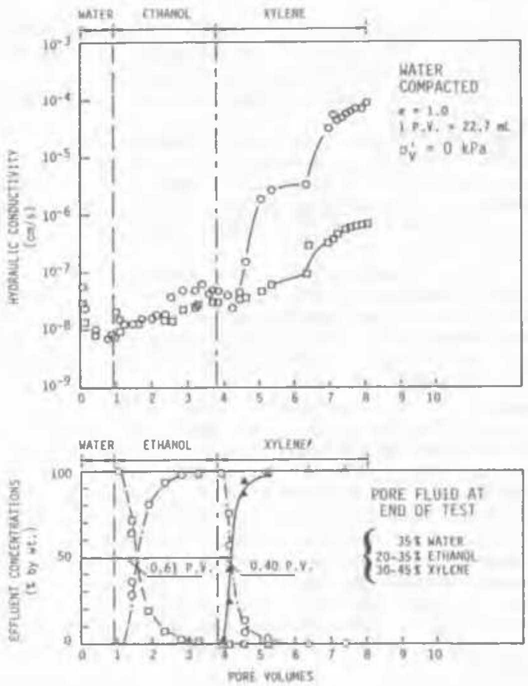


Figure 4. Hydraulic conductivity and effluent composition vs pore volumes. (Sequential permeation of ethanol and xylene through water saturated clay)

would not represent a danger may destroy a clay barrier if mutually soluble association liquids such as alcohols, acetone, etc. are present.

Figure 5 illustrates the sequential permeation of a xylene compacted sample by xylene, ethanol and water. The polar permeants efficiently displace xylene from the soil causing rapid decreases in **k** from 10^{-4} to 10^{-7} cm/s. This final **k** is larger than the 10^{-8} for water moulded clay (Figure 4) due to moulding fabric effects.

These data confirm the work on benzene reported in detail by Fernandez and Quigley (1985).

MIXED LIQUID HYDROCARBON PERMEANTS

The results of **k** tests on water compacted clays permeated with mixtures of ethanol and cyclohexane are summarized in Figure. 6. Pure cyclohexane produces little increase in **k**. In fact, breakthrough gradients of 175 were required to initiate flow. At gradients > 175, the values of **k** increase with gradient. Similar resistance to flow was reported for benzene and nitrobenzene (Acar et al, 1985) and heptane (Foreman and Daniel, 1986) on water compacted kaolinite.

The mixtures of ethanol and cyclohexane exhibit increases in **k** that become more pronounced with increasing alcohol content. This trend seems compatible with the acetone/xylene mixtures of Brown et al (1984) who obtained higher **k** values for acetone than for xylene/acetone mixtures. Interpretation of our results is greatly complicated by phase separation. After mixing, two of the permeants with ethanol:cyclohexane ratios of 20:80 and 40:60 separated into two phases: an upper, low density, cyclohexane-rich phase and a lower, high density, ethanol-rich phase (Table 3). In both cases the ethanol-rich phase permeated through the sample first (top to bottom flow). All ethanol/cyclohexane mixtures probably further re-arranged into different phases as they entered the aqueous pore fluid. The importance of cyclohexane in the ethanol is clearly indicated by a companion curve for

Table 3. Two Phase Cyclohexane/Ethanol Mixtures

Intended Permeant (wt %)	
20% Ethanol 80% Cyclohexane	40% Ethanol 60% Cyclohexane
Actual Permeant	
Two Phases	Two Phases
Upper (80% by vol) 10% Ethanol 90% Cyclohexane	Upper (36% by vol) 20% Ethanol 80% Cyclohexane
Lower (20% by vol) 75% Ethanol 25% Cyclohexane	Lower (64% by vol) 52% Ethanol 48% Cyclohexane

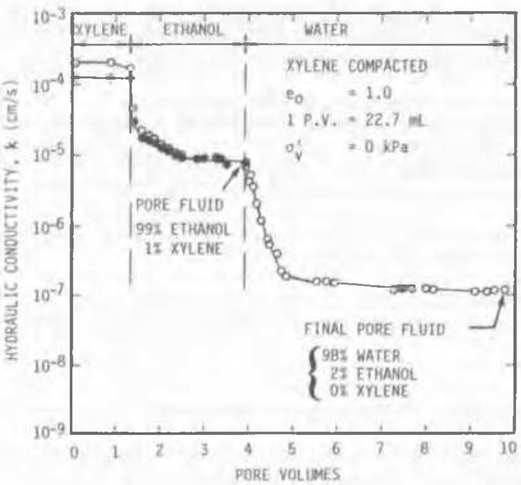


Figure 5. Hydraulic conductivity vs pore volumes. (Sequential permeation of ethanol and water through xylene saturated clay)

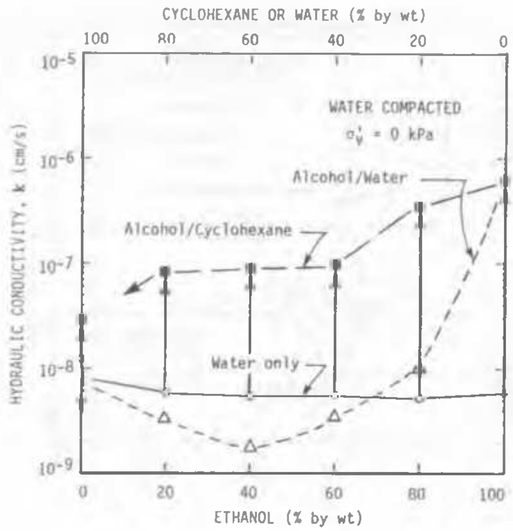


Figure 6. Hydraulic conductivity of water saturated clay permeated with liquid mixtures.

ethanol/water mixtures which demonstrates decreases in **k** due to viscosity effects (Fernandez and Quigley, 1988).

Chemical analyses of the pore fluid at the end of testing confirm the exclusion of cyclohexane. The sample permeated with 80% ethanol/ 20% cyclohexane yielded a maximum cyclohexane value of 11% in the pore fluid, reflecting entry associated with ethanol which itself seemed preferentially adsorbed.

CONCLUSIONS

1. Dry clay mixed with pure liquid hydrocarbons develops a flocculated soil structure and hydraulic conductivity values inversely related to dielectric constant. Values range from 10^{-8} cm/s for water (ε = 80) to 10^{-4} cm/s for xylene (ε = 2).

2. Water compacted and saturated clays are remarkably resistant to penetration by insoluble liquid hydrocarbons, yielding **k** values similar to or less than water except at large gradients that may cause fracture flow.

3. Water soluble liquid hydrocarbons such as alcohol may displace much of the water from the pore space of soils during permeation causing an increase in **k**. Once present in the double layer position, insolubles such as xylene may effect huge increases in **k** using alcohol as an "association" liquid.

4. Mixtures of mutually soluble hydrocarbon liquids may cause increases in **k** similar to those displayed by sequential permeation. Separation of the permeant into phases during testing greatly complicates interpretation. The presence of ethanol enhances entry of cyclohexane, resulting in much larger values of **k** than observed for water/ethanol mixtures.

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