

Hydraulic Conductivity of Organoclay and Organoclay-Sand Mixtures to Fuels and Organic Liquids

Craig H. Benson, F.ASCE¹; Ho Young Jo, A.M.ASCE²; and Telma Musso³

Abstract: Hydraulic conductivity, swelling, and liquid sorption capacity (i.e., maximum organic liquid mass bound per mass organoclay solid) were measured for an organoclay with dimethylammonium bound to the surface. Five fuels (No. 1 fuel oil, No. 2 fuel oil, diesel, jet fuel, and gasoline), four pure organic liquids (methanol, phenol, ethylbenzene, and dioctyl phthalate), ranging from hydrophilic to hydrophobic, and Type II deionized (DI) water were used as liquids for solvation and permeation. The more hydrophilic liquids (methanol and phenol) and DI water resulted in low swelling (≤ 6 mL/2 g) or liquid sorption capacity ($\leq 202\%$) and high hydraulic conductivity ($> 10^{-6}$ m/s). The term hydraulic herein refers to liquid and applies to all permeant liquids used. The less-refined fuels composed of heavier distillates (fuel oil and diesel) and the phthalate resulted in low swelling (10–12 mL/2 g) and liquid sorption capacity ($< 235\%$) and intermediate to low hydraulic conductivity (10^{-10} to 10^{-11} m/s). The highly refined fuels composed of lighter distillates and ethylbenzene resulted in higher swelling (> 20 mL/2 g), high liquid sorption capacity ($< 340\%$), and very low hydraulic conductivity (typically, $< 10^{-11}$ m/s). The swelling, liquid sorption capacity, and hydraulic conductivity of this organoclay are related systematically; however, none of these properties correlates systematically with the common parameters describing hydrophobicity, namely, solubility or the octanol-water partition coefficient. When the swell index is at least 10 mL/2 g, this organoclay has hydraulic conductivity of less than 10^{-10} m/s. Below 10 mL/2 g, the hydraulic conductivity increases rapidly as the swell index decreases. Sand-organoclay mixtures with uniform sand require more organoclay to achieve low hydraulic conductivity and are more sensitive to the swell index. For this organoclay, a mixture with at least 50% organoclay is recommended to ensure low hydraulic conductivity to gasoline and jet fuel. Diesel and fuel oil can require at least 75% of this organoclay to achieve low hydraulic conductivity. DOI: [10.1061/\(ASCE\)GT.1943-5606.0001194](https://doi.org/10.1061/(ASCE)GT.1943-5606.0001194). © 2014 American Society of Civil Engineers.

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Introduction

Organoclays are modified clays in which the hydrophilic mineral surface has been transformed to an organophilic and hydrophobic surface by replacing the cations natively bound to the mineral surface with organocations. Organoclays commonly are synthesized using sodium (Na) bentonite that has been exchanged with quaternary ammonium cations. Bentonite is used because the lamella of the primary mineral constituent (montmorillonite) can separate, which results in high surface area and large cation exchange capacity (Smith et al. 1990; de Paiva et al. 2008). Quaternary ammonium cations bound to the montmorillonite surfaces facilitate binding of organic molecules to the montmorillonite mineral via adsorption and

partitioning, which otherwise would be negligible for a conventional montmorillonite (Zhao and Burns 2012). The organocations provide a bridge between the charged clay surface and organic molecules in the pore space.

Organoclays are used as sorbents in industrial operations (e.g., oil absorbents in shops and bilge water treatment) or for hydraulic and sorptive barriers for organic compounds in geotechnical and geological engineering because of their capacity to bind organic compounds and their potential for low hydraulic conductivity when solvated by an organic liquid (Lo and Yang 2001; Smith et al. 2003; Lorenzetti et al. 2005; Lee et al. 2012). In this context and henceforth, hydraulic conductivity refers to liquid conduction in accordance with Darcy's law and applies to all permeant liquids used in this study. For example, Lee et al. (2012) described an application where organoclay is used as the reactive medium in a vertical variably permeable reactive barrier (VPRB) to block the flow of creosote non-aqueous-phase liquid (NAPL) but allow free flow of water while binding organic compounds dissolved in the water phase.

In the presence of organic liquids, organoclays can behave in a manner similar to Na bentonites contacted with water, i.e., exhibiting high plasticity, swelling, and low hydraulic conductivity (Lee et al. 2012). Swelling and hydraulic conductivity differ between organic compounds in contact with the organoclay and the type of organic cation bound to the mineral surface (Lee et al. 1989; Boldt-Leppin et al. 1996; Li et al. 1996; Lo et al. 1997; Smith et al. 2003; Groisman et al. 2004; Yang and Lo 2004; Reible 2005; Lee et al. 2012; Zhao and Burns 2012).

The literature provides examples suggesting that sorption of organic compounds onto the surface of organoclays from vapors or aqueous solutions can be related to chemical parameters indicative of hydrophobicity. Lee et al. (1989) evaluated the sorption of three

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organoclays exchanged with different organic cations and contacted with benzene, toluene, and ethylbenzene dissolved in water. They report that sorption increased as the water solubility of organic liquid decreased. Similarly, Groisman et al. (2004) show that sorption in organoclay was related to the octanol-water partition coefficient ($\log K_{ow}$) of six organic compounds dissolved in water with $\log K_{ow}$ ranging between 2.47 and 6.12. Lo et al. (1997) reported that the sorptive capacity of an organoclay contacted with benzene, toluene, ethylbenzene, *o*-xylene, phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol dissolved in leachate. Sorption of *o*-xylene (lowest water solubility, 0.152 g/L) was highest and phenol (highest water solubility, 93 g/L) was lowest.

The hydraulic conductivity of organoclays is influenced by the properties of the organic permanent liquid and is substantially lower than the hydraulic conductivity to water. Gates et al. (2004) reported hydraulic conductivities to ethanol on the order of 8×10^{-10} m/s, about three orders of magnitude lower than the hydraulic conductivity of organoclay to water. Reible (2005) reported hydraulic conductivities of two commercial granular organoclays to creosote NAPL ranging between 3.2×10^{-8} and 2.5×10^{-10} m/s. Lee et al. (2012) reported that the hydraulic conductivity of three granular organoclays to creosote ranged between 3.4×10^{-11} and 3.7×10^{-12} m/s, with lower hydraulic conductivities obtained with organoclays having higher organic carbon content. Lee et al. (2012) also indicated that the hydraulic conductivity to creosote diminishes over a period of several weeks, and that lower hydraulic conductivities would have been obtained by Reible (2005) if his tests had been conducted longer (the hydraulic conductivity was still decreasing when the tests were terminated). Lee et al. (2012) attributed the gradual reduction in hydraulic conductivity to interlayer swelling of the montmorillonite during solvation, which gradually reduces the pore space active in flow. Tests conducted by Smith et al. (2003) on organoclays with unleaded gasoline yielded hydraulic conductivities ranging from 1.7×10^{-8} to 7.4×10^{-8} m/s, depending on the organic cation on the mineral surface. Yang and Lo (2004) reported hydraulic conductivity of an organoclay to gasoline of 6.0×10^{-11} m/s, making it four orders of magnitude lower than the hydraulic conductivity of Na bentonite to gasoline. Lee et al. (2012) reported hydraulic conductivities of granular organoclay to water ranging from 0.0014 to 0.0039 m/s, which is consistent with the sand-size granules in the organoclays they evaluated.

The sorptive capacity, swelling, and hydraulic conductivity of organoclays are affected by the organic cation bound to the mineral surface (Lee et al. 1989, 2012; Li et al. 1996; Smith et al. 2003). Molecular dynamics simulations conducted by Zhao and Burns (2012) showed that binding mechanisms between the mineral surface of montmorillonite and the organic cation vary with the type of organic cation, and that the arrangement of the organic cation on the surface of montmorillonite affects the binding between organic molecules and organoclays. For example, benzene interacts directly with the montmorillonite surface for organoclays synthesized with tetramethylammonium (TMA); however, benzene interacts with the aliphatic chain in organoclays synthesized with hexadecyltrimethylammonium (HDTMA). A matrix composed of aliphatic chains forms in the interlayer of organoclays synthesized with HDTMA. This matrix acts as a solute that promotes partitioning of benzene, with greater partitioning capacity as the total organic carbon in the interlayer increases. In contrast, binding to TMA-synthesized clay is limited by the availability of surface sites (Zhao and Burns 2012).

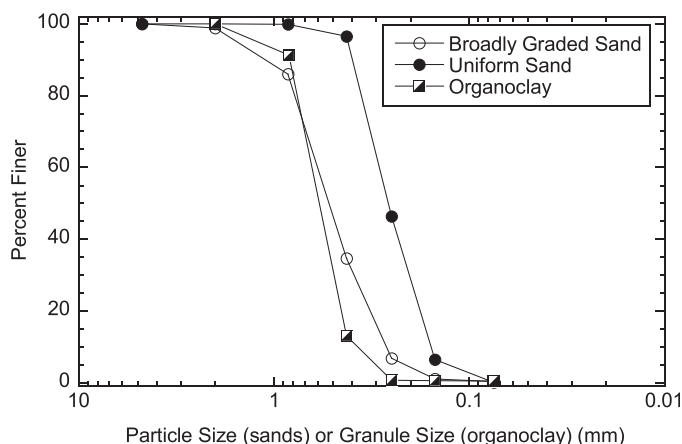
This study explored the liquid sorption capacity, swelling, and hydraulic conductivity of a commercially available organoclay and organoclay-sand mixtures permeated with five common fuels and four pure organic liquids varying in hydrophobicity. The term liquid sorption capacity is used herein to quantify the ability of solvated

organoclay to retain organic liquid on the organoclay surface and within the matrix. This usage is different from the other common use of sorption (and sorptive capacity), which typically describes binding of organic molecules dissolved in the aqueous phase to the organoclay solid via adsorption and absorption. For organoclays alone, the primary objective of the study was to determine if the hydraulic conductivity can be related directly to readily obtainable properties of organic liquids (e.g., the water solubility, S , and octanol-water partition coefficient, K_{ow}) or to easily measured parameters such as the liquid sorption capacity measured in a centrifuge sorption test or the swell index determined using the procedures in ASTM D5891 (ASTM 2013b). For the organoclay-sand mixtures, the objective was to determine how the hydraulic conductivity varied with the fraction of organoclay in the mixture, the gradation of the sand, and the effect of the permanent liquid on the organoclay fraction.

Materials

Organoclay

Organoclay PM-199 obtained from CETCO (Hoffman Estates, Illinois) was used in this study. The organoclay is synthesized by treating Na bentonite with bis(hydrogenated tallow alkyl) dimethyl ammonium chloride, which results in the organic cation dimethylammonium exchanged on the bentonite surface (Lee et al. 2012). Organoclay PM-199 consists of uniform sand-sized granules of organoclay ranging in size from 2 to 0.25 mm (Fig. 1) that are composed of agglomerated particles. The specific gravity of solids is 1.75 ± 0.02 (three tests), which is lower than the specific gravity of Na bentonite because of the organic cations bound to the mineral surface (Soule and Burns 2001; Burns et al. 2006; Lee et al. 2012). The results of X-ray diffraction indicate that the bentonite fraction of the organoclay consists of 62% smectite, 14% quartz, 12% plagioclase feldspar, 5% halite, and 2% potassium feldspar (Lee et al. 2012). The total organic treat loading on the clay is 33% [ASTM D7626 (ASTM 2013f)] and the total organic carbon is 21.7% (combustion with CO_2 measurement) (Schumacher 2002). The saturated hydraulic conductivity of the organoclay to deionized (DI) water was determined using ASTM D2434 (ASTM 2013d) and was found to be 6.8×10^{-4} m/s, which is similar to the hydraulic conductivities reported by Lee et al. (2012) and is consistent with the sand-sized granules in the organoclay.



Sands

Two natural quartz sands from southern Wisconsin with subrounded particles were used to prepare the organoclay-sand mixtures. The particle-size distributions for these sands, referred to herein as uniform and broadly graded sands, are shown in Fig. 1. The broadly graded nomenclature is used because this sand has a broader particle-size distribution compared with uniform sand, but does not meet the definition of well graded in the Unified Soil Classification System. The saturated hydraulic conductivity of each sand was measured at 90% relative density using the procedure in ASTM D2434 (ASTM 2013d) (uniform: 3.8×10^{-4} m/s; broadly graded: 6.4×10^{-4} m/s).

Fuels and Pure Organic Liquids

Five fuels were used in this study to investigate how fuel type affects the swelling, liquid sorption capacity, and hydraulic conductivity of the organoclay: No. 1 fuel oil, No. 2 fuel oil, winter blend diesel fuel, aviation jet fuel, and unleaded gasoline. All fuels were obtained from Zurbuchen Oil (Verona, Wisconsin), except for the jet fuel, which was obtained from the Wisconsin Air National Guard (Truax Field, Madison, Wisconsin). Four organic liquids were chosen to provide a wide range of hydrophobicity ($\log K_{ow} = -0.9$ – 8.1): methanol, phenol, ethylbenzene, and dioctyl phthalate. Ethylbenzene was selected because it is a common antiknock additive in gasoline. All four organic liquids were obtained from Sigma-Aldrich (St. Louis, Missouri).

The chemical and hydrodynamic properties of the fuels and the pure organic liquids are shown in Table 1. For the fuels, $\log K_{ow}$ was approximated based on an assumed blend of constituent compounds using the ranges in the Agency for Toxic Substances and Disease Registry (ATSDR 1995). The properties of the pure organic liquids were obtained from The U.S. EPA (USEPA 2010), and DI water meeting the Type II criteria in ASTM D1193 (ASTM 2013a) was used as a reference liquid.

Methods

Swell Index

Swell tests were conducted following the methods in ASTM D5890 (ASTM 2013e) using DI water, fuel, or a pure organic liquid for solvation. Organoclay was air-dried and ground using a mortar and pestle until the clay passed the No. 200 sieve. A clean 100-mL graduated cylinder was filled with 90 mL of liquid followed by addition of 2 g of dry powdered organoclay in 0.1-g increments.

Liquid was then added to the cylinder until the 100-mL mark was reached. The volume of swollen organoclay was measured (in milliliters) after 24 h of exposure.

Liquid Sorption Tests

Liquid sorption tests were conducted following the centrifuge sorption procedure developed by CETCO (2010) (see the draft test method in the supplemental data). Approximately 20 g of granular organoclay was thoroughly blended with 120 g of test liquid using a spatula in a 250-mL centrifuge bottle. After 24 h, the mixture was centrifuged at 3,500 rpm for 10 min (Model J2-21, Beckman Coulter, Brea, California). The supernatant was decanted and the masses of the organoclay and bound test liquid were measured. The liquid sorption capacity was computed as the ratio of the mass of bound liquid to the mass of dry organoclay multiplied by 100 and reported as percent.

Hydraulic Conductivity Tests

The hydraulic conductivity of the organoclays to the fuels and organic liquids was measured in cylindrical stainless steel columns with a diameter of 60 mm and a height of 52 mm following the procedure described in Lee et al. (2012) and in general accordance with the procedures in ASTM D5856 (ASTM 2013c). Duplicate hydraulic conductivity tests were conducted for each permeant liquid. Stainless steel plates with a polytetrafluoroethylene (PTFE) O-ring were placed on both ends of the column.

All specimens were prepared in three layers, with each layer compacted using 25 tamps of a rubber-tipped wooden rod. This process resulted in organoclay specimens with a dry density of 0.88 ± 0.02 Mg/m³. The sand-organoclay mixtures were prepared by blending air-dry sand and organoclay by hand using a spatula. The air-dry mixture was then placed into the column using the same procedure used for the pure organoclay specimens.

The test specimens were hydrated in the permeant liquid for 48 h without application of hydraulic gradient (effluent line closed). The hydraulic conductivity tests were then initiated using the falling headwater-constant tailwater method with an average hydraulic gradient of 30. The gradient was chosen using the guidelines in ASTM D5856 (ASTM 2013c) and was intended to preclude excessive stress within the test specimen while ensuring that data collection was practical. Testing continued until the hydraulic conductivity was steady (no temporal trend upward or downward), the incremental inflow equaled the incremental outflow within 25%, and at least four consecutive measurements of hydraulic conductivity were within 25% of the mean (per ASTM D5856) (ASTM 2013c). All tests were conducted for at least 2 pore volumes of flow.

Table 1. Hydrodynamic and Partitioning Properties of Permeant Liquids (Data from Green and Perry 2007)

Liquid	Density (kg/L) at 20°C	Kinematic viscosity (m ² /s) $\times 10^6$ at 20°C	Water solubility (g/L)	Log octanol-water partition coefficient
Pure organic compound				
Methanol	0.78	0.7	1,000	−0.9
Phenol	1.04	11.3	82.8	1.5
Ethylbenzene	0.85	0.8	0.2	3.2
Dioctyl phthalate	0.97	81.6	2.0×10^{-5}	8.1
Fuel				
Fuel oil (No. 1)	0.82	1.3–2.4	—	3.3–7.1
Fuel oil (No. 2)	0.84	1.9–4.1	—	3.3–7.1
Winter blend diesel fuel	0.84	6.8	—	3.3–7.1
Aviation jet fuel	0.70	1.3–2.0	—	2.1–4.9
Unleaded gasoline	0.80	0.4–0.5	—	3.6–8.1

The hydraulic conductivity of the organoclays and sand-organoclay mixtures gradually diminished over time as the fuel or organic liquid solvated the organoclay in the same manner that the hydraulic conductivity of Na bentonite diminishes as it hydrates and swells when permeated with DI water (e.g., Bradshaw and Benson 2014). As noted previously, Lee et al. (2012) attributed the gradual reduction in hydraulic conductivity to interlayer swelling of the montmorillonite during solvation, which gradually reduces the pore space active in flow. A typical graph of hydraulic conductivity versus time is shown in Fig. 2. When the organoclay was less permeable (10^{-10} m/s), testing normally required at least 90 days to reach the aforementioned equilibrium criteria. Lee et al. (2012) showed similar gradual reductions in hydraulic conductivity with time. Thus, when testing organoclays, care should be used to ensure that the test has reached equilibrium before the test is terminated and the hydraulic conductivity is reported.

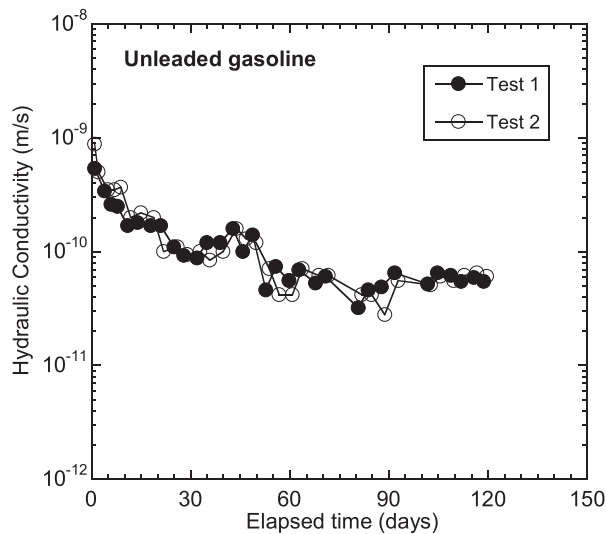


Fig. 2. Hydraulic conductivity versus time of duplicate organoclay specimens permeated with unleaded gasoline

Table 2. Swell Index and Liquid Sorption Capacity of Organoclay Contacted with Fuels and Pure Organic Liquids

Liquid	Swell index ^a (mL/2 g)	Liquid sorption capacity ^b (%)
Pure organic compound		
Methanol	5.3 ± 0.3	143.3 ± 1.7
Phenol	6.0 ± 0.0	202.3 ± 1.9
Ethylbenzene	24.8 ± 0.3	571.7 ± 7.2
Diocetyl phthalate	8.0 ± 0.0	223.4 ± 1.7
Fuel		
Fuel oil (No. 1)	10.8 ± 0.2	235.1 ± 4.8
Fuel oil (No. 2)	11.0 ± 0.0	233.4 ± 2.5
Winter diesel	10.2 ± 0.2	223.5 ± 1.1
Aviation jet fuel	20.3 ± 0.3	339.7 ± 5.9
Unleaded gasoline	24.7 ± 0.3	445.1 ± 4.7
DI water		
Type II	6.0 ± 0.2	178.1 ± 2.8

^aMean ± standard error (SE) for three replicates per ASTM D5890-11 (ASTM 2013e).

^bMean ± SE for three replicates per CETCO (2010) organoclay-NAPL liquid sorption capacity test procedure.

Results and Discussion

Swell Index and Liquid Sorption Capacity

The swell index and sorption capacity of the organoclay for each of the fuels and pure organic liquids are summarized in Table 2. To evaluate the influence of hydrophobicity, graphs were prepared of the swell index and liquid sorption capacity (the physical parameters describing liquid uptake) as a function of $\log K_{ow}$ (Fig. 3) and solubility (Fig. 4) of the liquid. No systematic relationship exists between either the physical parameter and $\log K_{ow}$ or solubility when considered over the entire range, suggesting that neither chemical parameter is a direct indicator of the affinity of the organoclay to bind organic liquids. However, a trend between the swell index (and liquid sorption capacity) and $\log K_{ow}$ or solubility does exist for lighter distillates comprised primarily of shorter hydrocarbon chains (e.g., gasoline versus jet fuel versus diesel), and the highest swell index and largest sorption capacity were obtained with ethylbenzene,

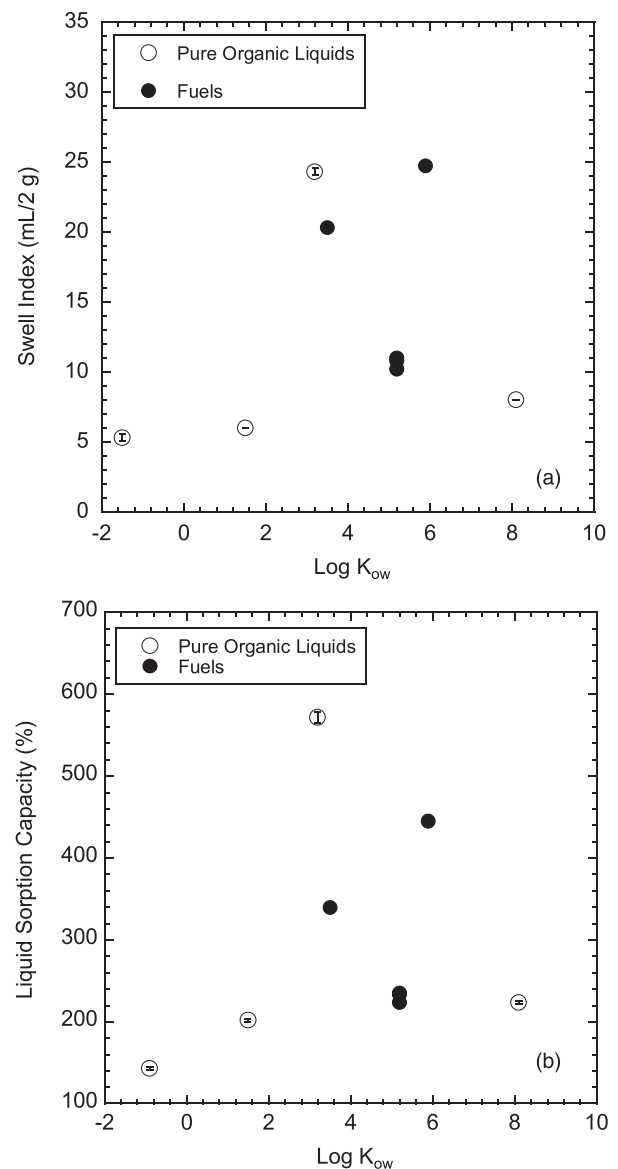


Fig. 3. (a) Swell index and (b) centrifuge sorption capacity as a function of $\log K_{ow}$ for fuels and organic liquids

which has the lowest boiling point of the pure organic liquids that were tested and is a constituent in gasoline. A strong relationship was observed between the swell index and liquid sorption capacity (Fig. 5), indicating that either can be used as an index of the binding capacity of the organoclay for organic liquids.

Hydraulic Conductivity of Organoclay

The hydraulic conductivity and intrinsic permeability of the organoclays to the fuels and organic liquids are summarized in Table 3. The intrinsic permeability (k) and hydraulic conductivity (K) of a porous medium are related by (Fernandez and Quigley 1988)

$$K = k \frac{g}{\nu} \quad (1)$$

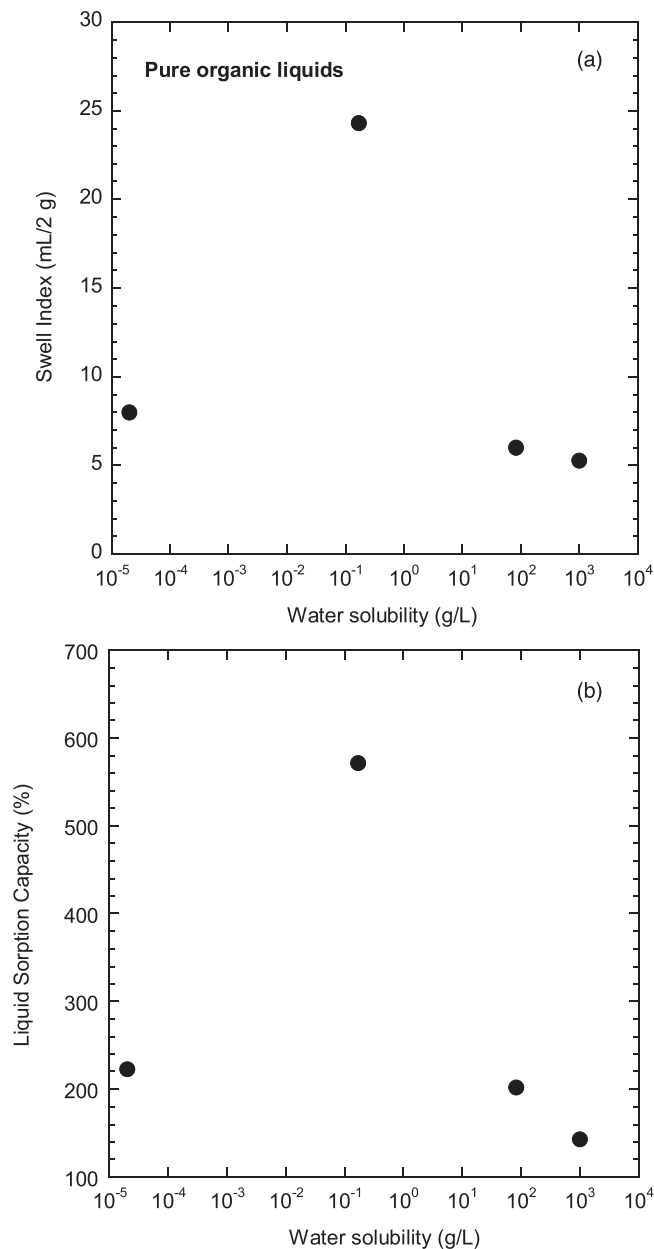


Fig. 4. (a) Swell index and (b) liquid sorption capacity as a function of aqueous solubility for organic liquids

where ν = kinematic viscosity of the permeant liquid; and g = gravitational acceleration. The intrinsic permeability reflects the influence of the geometry of the pore space (i.e., size, shape, and connectivity of the pores) on the rate of fluid flow through a porous material, whereas the hydraulic conductivity accounts for the geometry of the pore space and the hydrodynamic properties of the fluid flowing in the pores (ν). Liquids that alter the intrinsic permeability alter the pore network in a soil (Fernandez and Quigley 1988). For organoclays, the alteration is caused by swelling because the organoclay solvates in the same manner that occurs when a Na bentonite is hydrated during permeation with water (Lee et al. 2012).

Hydraulic conductivity and intrinsic permeability are shown as a function of $\log K_{ow}$ in Fig. 6. The hydraulic conductivities and intrinsic permeabilities vary by approximately six orders of magnitude depending on the liquid used for permeation. Considerably

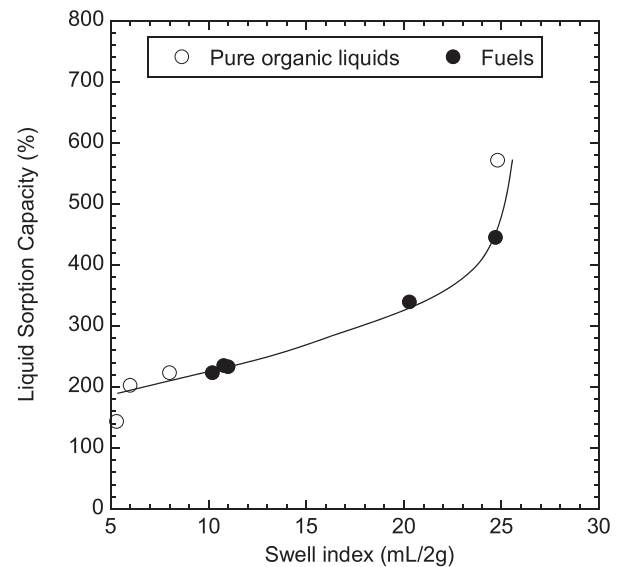


Fig. 5. Liquid sorption capacity versus swell index for organoclay in fuels and pure organic liquids with the trend line drawn subjectively

Table 3. Hydraulic Conductivity and Intrinsic Permeability of Organoclay to Fuels and Pure Organic Liquids from Duplicate Hydraulic Conductivity Tests

Liquid	Hydraulic conductivity (m/s)		Intrinsic permeability (m ²)	
	Low	High	Low	High
Pure organic compound				
Methanol	9.7×10^{-6}	1.2×10^{-5}	7.3×10^{-13}	9.2×10^{-13}
Phenol	1.7×10^{-6}	1.4×10^{-6}	1.9×10^{-12}	1.6×10^{-11}
Ethylbenzene	5.4×10^{-11}	1.4×10^{-10}	4.0×10^{-18}	1.1×10^{-17}
Diocetyl phthalate	2.6×10^{-10}	—	2.2×10^{-15}	—
Fuel				
Fuel oil (No. 1)	2.1×10^{-11}	5.5×10^{-11}	4.0×10^{-18}	1.0×10^{-17}
Fuel oil (No. 2)	3.2×10^{-11}	3.7×10^{-11}	9.7×10^{-18}	1.1×10^{-17}
Winter diesel	1.4×10^{-11}	3.4×10^{-11}	9.6×10^{-18}	2.4×10^{-17}
Aviation jet fuel	4.5×10^{-11}	5.9×10^{-11}	1.9×10^{-18}	2.4×10^{-18}
Unleaded gasoline	1.6×10^{-11}	4.3×10^{-11}	2.9×10^{-18}	7.7×10^{-18}
DI water				
Type II	6.8×10^{-4}	6.9×10^{-4}	7.0×10^{-11}	7.0×10^{-11}

higher hydraulic conductivities and intrinsic permeabilities were obtained with the more hydrophilic compounds (methanol and phenol), which also had minimal swell (≤ 6 mL/2 g) and liquid sorption capacity ($\leq 202\%$). In fact, the hydraulic conductivity to methanol was much closer to the hydraulic conductivity to DI water than to the hydraulic conductivity to the fuels or hydrophobic liquids. In contrast, the hydrophobic compounds all had much lower hydraulic conductivity, with most being below 1×10^{-10} m/s. The lowest hydraulic conductivities and intrinsic permeabilities were obtained with the fuels, with hydraulic conductivities ranging from 1.4 to 5.9×10^{-11} m/s.

The hydraulic conductivity of the organoclay appears to be related to hydrophobicity of the liquid [see $\log K_{ow}$ in Fig. 6(a); a similar relationship was obtained for solubility with the organic liquids]. However, this relationship is spurious because low hydraulic conductivity to the most hydrophobic liquid used in the study (dioctyl phthalate) is a result of high viscosity (Table 1) rather than blockage of pore space as a result of swelling organoclay. The intrinsic permeability of organoclay solvated with dioctyl phthalate was at least two orders of magnitude higher than the intrinsic permeability obtained with the fuels or ethylbenzene, which are less hydrophobic than dioctyl phthalate. These findings are consistent

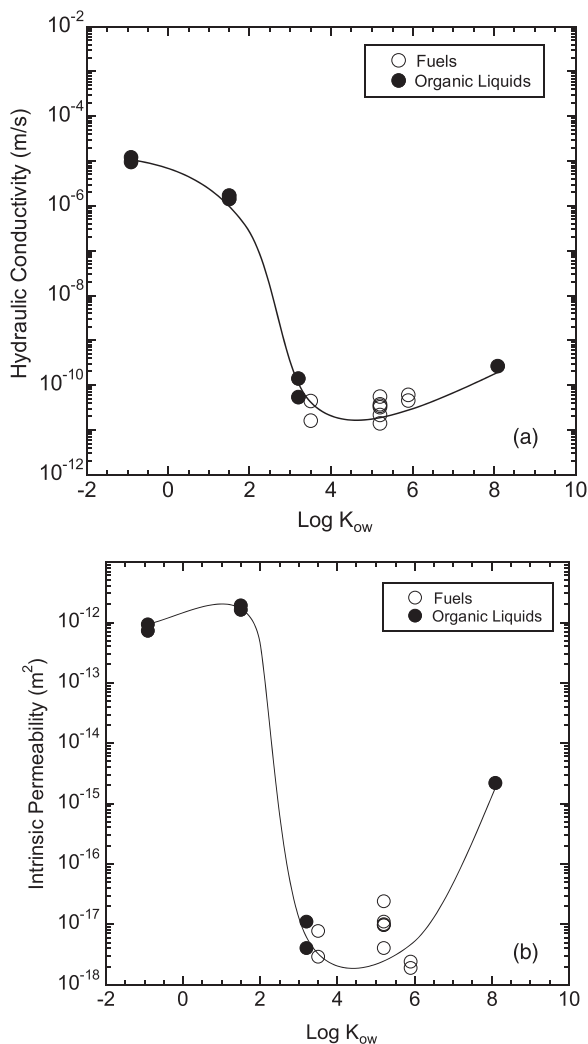


Fig. 6. (a) Hydraulic conductivity and (b) intrinsic permeability as a function of $\log K_{ow}$ for fuels and organic liquids with trend lines drawn subjectively

with the swell index data (Table 2). Swelling in dioctyl phthalate was similar to swelling in phenol and methanol (much less hydrophobic liquids), and much lower than the swell index for the hydrophobic jet fuel, gasoline, and ethylbenzene. Because solvation with dioctyl phthalate results in less swelling of organoclay granules, intergranule pore spaces in the organoclay are not filled as efficiently, which leads to higher hydraulic conductivity.

Fig. 7 illustrates how swelling associated with solvation of the organoclay affects the pore structure and network. Organoclay specimens permeated with hydrophobic jet fuel (swell index = 20.3 mL/2 g) and hydrophilic methanol (swell index = 5.3 mL/2 g) are shown in Fig. 7(a). The specimen permeated with jet fuel has a homogeneous and monolithic appearance with no visible pores, and very low hydraulic conductivity (4.5 – 5.9×10^{-11} m/s, Table 3). In contrast, the specimen permeated with methanol appears granular, has large visible pores, and has much higher hydraulic conductivity (9.7×10^{-6} to 1.2×10^{-5} m/s, Table 3).

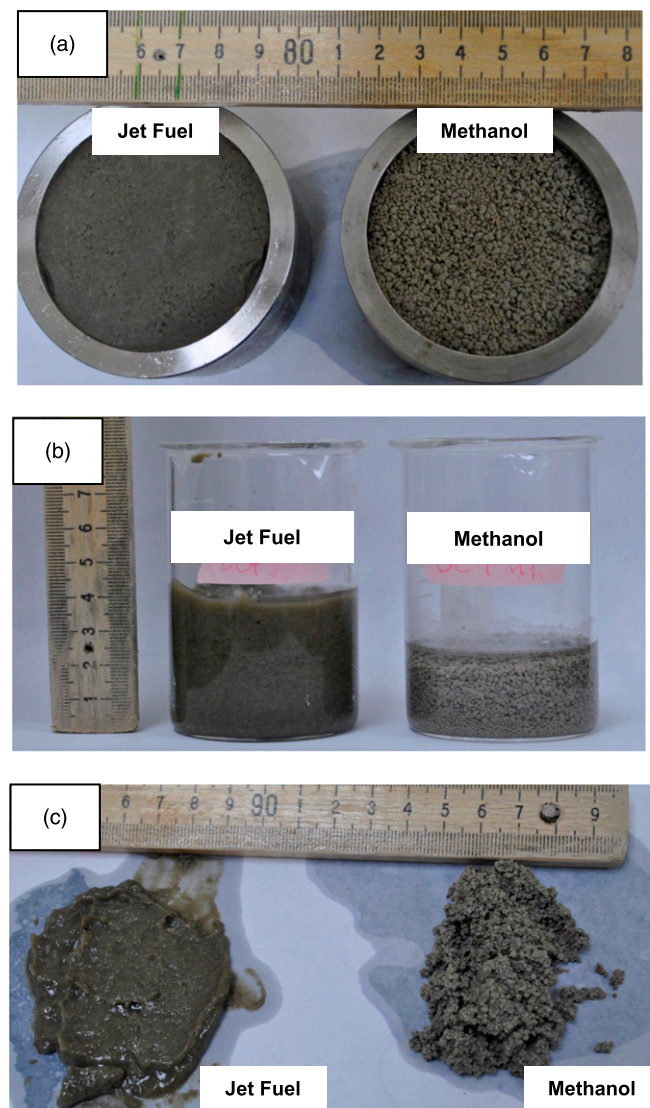


Fig. 7. (Color) Organoclay specimens permeated or contacted with jet fuel or methanol: (a) influent end of hydraulic conductivity test specimens; (b) beakers containing 25 g of organoclay inundated with liquid; (c) organoclay solvated with organic liquids in a beaker and placed on a sheet with a spatula

The structural differences are a result of swelling of the bentonite granules resulting from solvation of the organoclay (or lack thereof), as illustrated by the beakers containing 25 g of organoclay shown in Fig. 7(b), where organoclay in each beaker was inundated with jet fuel or methanol. The organoclay inundated with jet fuel swelled to approximately three times its original volume and formed a gel structure, whereas the organoclay in methanol did not swell and retained a granular appearance. The gel obtained by solvation with jet fuel was plastic and smeared, whereas the granular organoclay in methanol was friable and nonplastic [Fig. 7(c)].

Hydraulic Conductivity and Swelling

The hydraulic conductivity of Na bentonite is known to be strongly related to swelling of the bentonite, and inverse monotonic relationships have been reported between the hydraulic conductivity and swell index for Na bentonites permeated with simple salt solutions prepared in DI water as well as inorganic solutions encountered in industry (Jo et al. 2001; Kolstad et al. 2004; Katsumi et al. 2008). Solutions that promote swelling of Na-bentonite granules correspond to small and tortuous pore spaces in hydrated bentonite

and low hydraulic conductivity (Kolstad et al. 2004). Based on Fig. 7, a similar correspondence should exist between the hydraulic conductivity (or intrinsic permeability) to fuels and organic liquids and the swell index.

The hydraulic conductivity and intrinsic permeability of the organoclays are shown in Fig. 8. Both the hydraulic conductivity and intrinsic permeability decrease by approximately six orders of magnitude as the swell index increases from approximately 5 to 11 mL/2 g. For swell indexes greater than 20 mL/2 g, the hydraulic conductivity increases slightly as the swell index increases, whereas the intrinsic permeability remains essentially unchanged or diminishes slightly when the swell index exceeds 10 mL/2 g. The slight rise in hydraulic conductivity at higher swell indexes is associated with changes in the hydrodynamic properties of the liquid rather than a change in the pore space of the organoclay. For example, ethylbenzene is less viscous than jet fuel, making the hydraulic conductivity higher for ethylbenzene even if the pore structure is identical. A similar relationship exists between the hydraulic conductivity (or intrinsic permeability) and the liquid sorption capacity, as shown in Fig. 9. When the liquid sorption capacity exceeds 220%, the hydraulic conductivity is less than

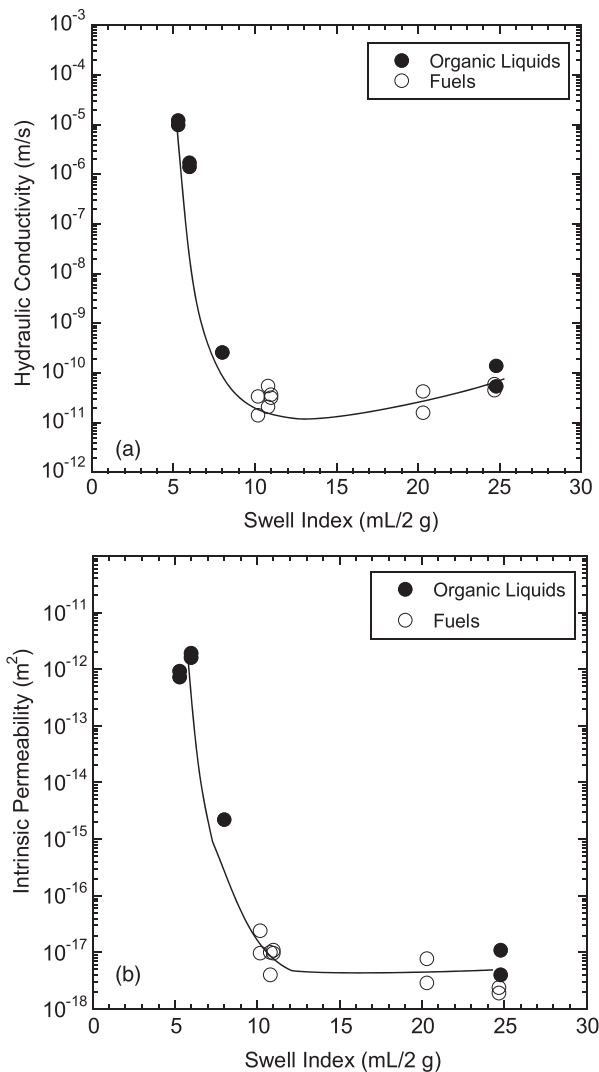


Fig. 8. (a) Hydraulic conductivity and (b) intrinsic permeability as a function of swell index for fuels and organic liquids with trend lines drawn subjectively

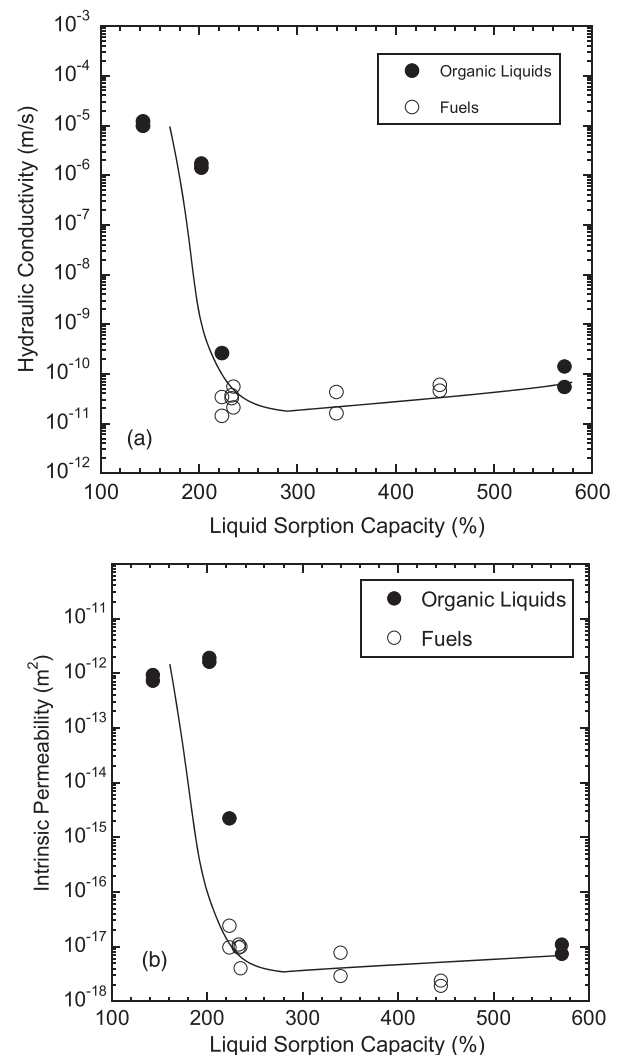


Fig. 9. (a) Hydraulic conductivity and (b) intrinsic permeability as a function of liquid sorption capacity for fuels and organic liquids with trend lines drawn subjectively

1×10^{-10} m/s. Much higher hydraulic conductivities are realized when the liquid sorption capacity is less than 220%.

Hydraulic Conductivity of Sand-Organoclay Mixtures to Fuels

The hydraulic conductivities of the sand-organoclay mixtures are shown as a function of organoclay content in Fig. 10 for mixtures prepared with the uniform and broadly graded sands and permeated with the fuels and ethylbenzene. The hydraulic conductivities shown in Fig. 10 are geometric means of duplicate tests. All of the hydraulic conductivities are summarized in Tables 4 and 5. For the mixtures, tests with No. 1 fuel oil were not conducted because of the similarity in behavior observed in the previous experiments for Nos. 1 and 2 fuel oils.

For both sands, the hydraulic conductivity of the mixtures decreased as the organoclay content increased, which was anticipated because solvating organoclay granules fill pores conducting flow in sand. However, the hydraulic conductivity of mixtures prepared with the uniform sand was more sensitive over a broader range of organoclay content and to the type of permeant liquid. For example,

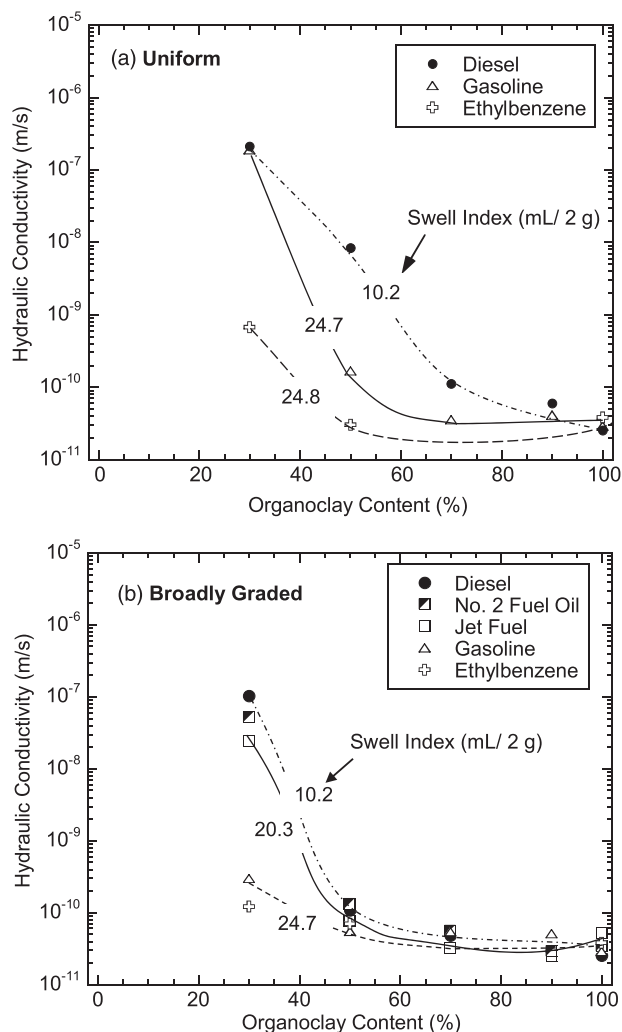


Fig. 10. (a) Hydraulic conductivity versus organoclay content for mixtures prepared with uniform sand; (b) broadly graded sand for fuels and organic liquids; trend lines drawn subjectively

mixtures prepared with the broadly graded sand had low hydraulic conductivity ($<10^{-10}$ m/s) when the organoclay content exceeded 50% regardless of the permeant liquid, whereas mixtures prepared with the uniform sand and 50% organoclay had hydraulic conductivities ranging from 2.8×10^{-11} m/s (ethylbenzene) to 8.4×10^{-8} m/s (diesel). The hydraulic conductivity of mixtures prepared with the uniform sand was also more sensitive to the swell index of the organoclay in the permeant liquid, with lower hydraulic conductivities obtained for most organoclay contents with permeant liquids having a higher swell index. The greater sensitivity for the fine uniform sand reflects the more uniform pore sizes in a uniformly graded material, which are known to require more clogging material (swollen organoclay) to block pathways conducting flow (Abichou et al. 2004).

The effect of swelling of the organoclay was evident when the specimens were disassembled. Mixtures with 30% organoclay permeated with liquids that induce less swelling were friable and crumbled readily [e.g., No. 2 fuel oil specimen, Fig. 11(a)], whereas similar specimens permeated with liquids yielding a large swell index were cohesive, plastic, and could be smeared [e.g., jet fuel specimen, Fig. 11(b)]. This difference in texture reflects the greater propensity for some organic liquids to solvate the organoclay and to induce swelling of the montmorillonite interlayer in a manner similar to the sensitivity of hydration and swelling of Na bentonite in different salt solutions (Jo et al. 2001; Kolstad et al. 2004).

The data in Fig. 10 suggest that sand-organoclay mixtures prepared with this organoclay generally should have at least 50% organoclay in order to have low hydraulic conductivity, and that a higher organoclay content may be necessary if the sand is more uniformly graded, or the liquid to be contained yields a lower swell index. This percentage is higher than recommended by Lee et al. (2012), who reported that sand-organoclay mixtures permeated with coal tar creosote had hydraulic conductivities of less than 10^{-10} m/s when the organoclay fraction was at least 25%. However, coal tar creosotes readily solvated the organoclay and induced considerable swelling of the organoclay evaluated by Lee et al. (2012), whereas the data in the current study suggest that higher organoclay contents can be necessary for other organic liquids.

Sand-organoclay mixtures with approximately 30% organoclay are used in practice, and in some cases these mixtures have not performed effectively as hydraulic barriers (e.g., Benson et al. 2008). This observation is consistent with the data in Fig. 10. Depending on the type of sand and the swell index associated with the liquid and organoclay, the hydraulic conductivity with 30% organoclay can vary by as much as four orders of magnitude.

The hydraulic conductivities of the sand-organoclay mixtures containing 30% organoclay are shown in Fig. 12 for each of the permeant liquids. All of the hydraulic conductivities are shown in Fig. 12, rather than the geometric means reported in Fig. 10, to illustrate the variability in hydraulic conductivity obtained with each liquid. The hydraulic conductivities obtained with the broadly graded sand are consistently lower than those obtained with the uniform sand because a swelling material is more effective in filling the broader distribution of flow paths in a broadly graded sand relative to uniform sand (Abichou et al. 2004). The lowest hydraulic conductivities correspond to gasoline and ethylbenzene as permeant liquids (liquids yielding the highest swell indexes).

The difference in hydraulic conductivity between the mixtures with uniform and broadly graded sands varied with the organic liquid used for permeation. Hydraulic conductivities of the mixtures with the two sands were more similar when permeated with organic liquids that induce low swelling of the organoclay (and high hydraulic conductivity of the fuel oils and diesel) or the highest swelling of the organoclay (and lowest hydraulic conductivity of

Table 4. Hydraulic Conductivity and Intrinsic Permeability of Sand-Organoclay Mixtures Prepared with Broadly Graded Sand and Permeated with Fuels and Ethylbenzene from Duplicate Hydraulic Conductivity Tests

Liquid	Organoclay content (%)	Hydraulic conductivity (m/s)		Intrinsic permeability (m ²)	
		Low	High	Low	High
Fuel oil (No. 2)	30	1.3×10^{-8a}	1.2×10^{-7}	7.0×10^{-15}	6.5×10^{-14}
	50	3.9×10^{-11}	2.2×10^{-10}	2.1×10^{-17}	1.2×10^{-16}
	70	3.5×10^{-11}	7.8×10^{-11}	1.8×10^{-17}	1.2×10^{-17}
	90	1.2×10^{-11}	4.5×10^{-11}	6.5×10^{-18}	2.4×10^{-17}
Winter diesel	30	7.7×10^{-8}	1.4×10^{-7}	5.3×10^{-14}	9.5×10^{-14}
	50	9.5×10^{-11}	1.2×10^{-10}	6.6×10^{-17}	8.4×10^{-17}
	70	3.6×10^{-11}	6.1×10^{-11}	2.5×10^{-17}	4.2×10^{-17}
	90	1.8×10^{-11}	4.1×10^{-11}	1.2×10^{-17}	2.9×10^{-17}
Jet fuel	30	2.1×10^{-9b}	1.2×10^{-7}	6.5×10^{-16}	3.7×10^{-14}
	50	6.8×10^{-11}	8.6×10^{-11}	2.1×10^{-17}	2.6×10^{-17}
	70	1.4×10^{-11}	4.9×10^{-11}	4.4×10^{-18}	1.5×10^{-17}
	90	1.8×10^{-11}	3.2×10^{-11}	5.5×10^{-18}	9.8×10^{-18}
Unleaded gasoline	30	2.6×10^{-10}	3.4×10^{-10}	1.1×10^{-17}	1.4×10^{-17}
	50	3.3×10^{-11}	4.1×10^{-11}	1.3×10^{-18}	1.7×10^{-18}
	70	2.2×10^{-11}	3.1×10^{-11}	9.1×10^{-19}	1.3×10^{-18}
	90	8.1×10^{-12}	4.4×10^{-11}	3.3×10^{-19}	2.1×10^{-18}
Ethylbenzene	30	3.7×10^{-11}	1.5×10^{-10}	3.0×10^{-18}	1.3×10^{-17}
	50	2.5×10^{-11}	3.5×10^{-11}	2.0×10^{-18}	2.8×10^{-18}

^aFour specimens tested; other specimens had hydraulic conductivities of 6.8 and 7.1×10^{-8} m/s.

^bFour specimens tested; other specimens had hydraulic conductivities of 1.6 and 8.6×10^{-8} m/s.

Table 5. Hydraulic Conductivity and Intrinsic Permeability of Sand-Organoclay Mixtures from Duplicate Hydraulic Conductivity Tests on Mixtures Prepared with Uniform Sand and Permeated with Fuels and Ethylbenzene

Liquid	Organoclay content (%)	Hydraulic conductivity (m/s)		Intrinsic permeability (m ²)	
		Low	High	Low	High
Winter diesel	30	1.8×10^{-7}	2.5×10^{-7}	1.2×10^{-13}	1.7×10^{-13}
	50	8.0×10^{-9}	8.8×10^{-9}	5.5×10^{-15}	6.1×10^{-15}
	70	6.8×10^{-11}	1.5×10^{-10}	4.7×10^{-17}	1.1×10^{-16}
	90	4.6×10^{-11}	7.3×10^{-11}	3.2×10^{-17}	5.0×10^{-17}
Jet fuel	30	1.3×10^{-7a}	1.6×10^{-7}	4.0×10^{-17}	4.9×10^{-17}
Unleaded gasoline	30	1.4×10^{-7b}	2.4×10^{-7}	5.7×10^{-15}	1.0×10^{-14}
	50	1.6×10^{-11}	2.3×10^{-10}	6.5×10^{-19}	1.3×10^{-17}
	70	2.4×10^{-11}	2.6×10^{-11}	1.4×10^{-18}	1.5×10^{-18}
	90	2.4×10^{-11}	3.6×10^{-11}	9.7×10^{-19}	2.4×10^{-18}
Ethylbenzene	30	5.8×10^{-10}	8.0×10^{-10}	4.7×10^{-17}	6.5×10^{-17}
	50	1.9×10^{-11}	3.7×10^{-11}	1.5×10^{-18}	3.0×10^{-18}

^aThree specimens tested; the other specimen had hydraulic conductivity of 1.4×10^{-7} m/s.

^bThree specimens tested; the other specimen had hydraulic conductivity of 1.8×10^{-7} m/s.

ethylbenzene). For the liquids causing moderate-to-high swelling (jet fuel and unleaded gasoline), the hydraulic conductivity varied significantly between the two sands because swelling of the organoclay is more effective in filling the more irregular flow paths in broadly graded sand than the uniform flow paths in the uniform sand. However, when swelling of the organoclay is sufficiently high, as with ethylbenzene, the swollen organoclay effectively fills the flow paths in both uniform and broadly graded sands, resulting in both having low hydraulic conductivity.

For the liquids that induce moderate or low swelling, the hydraulic conductivities can be highly variable for some of the fuels, notably No. 2 fuel oil and jet fuel, which have low or moderate swell indexes (11.0 mL/2 g for No. 2 fuel oil and 20.3 mL/2 g for jet fuel). For these mixtures, the organoclay content is at a transition point, with lower hydraulic conductivity obtained when swelling of the organoclay blocks more permeable flow paths, and high hydraulic conductivity obtained when some of the permeable flow paths are

unblocked. Heterogeneities in the distribution of the organoclay likely contribute to variation in filling of pore spaces during swelling and differences in hydraulic conductivity (i.e., a perfectly distributed organoclay would fill pores equally, whereas in an actual mixture some regions inevitably have a higher or lower fraction of organoclay and are more or less effective at filling pores).

Fig. 13(a) corresponds to the effluent end of a specimen prepared with broadly graded sand and 30% organoclay that had lower hydraulic conductivity to jet fuel (2.1×10^{-9} m/s). The specimen in Fig. 13(b) was prepared similarly and permeated with jet fuel; however, it had much higher hydraulic conductivity (1.2×10^{-7} m/s). The cross section in Fig. 13(a) has uniform color and appearance, which is indicative of a uniform distribution of organoclay. In contrast, Fig. 13(b) has a more heterogeneous appearance corresponding to zones with greater (dark regions) or lesser (light regions) organoclay. At higher organoclay contents, heterogeneity in organoclay content within the specimen becomes less important

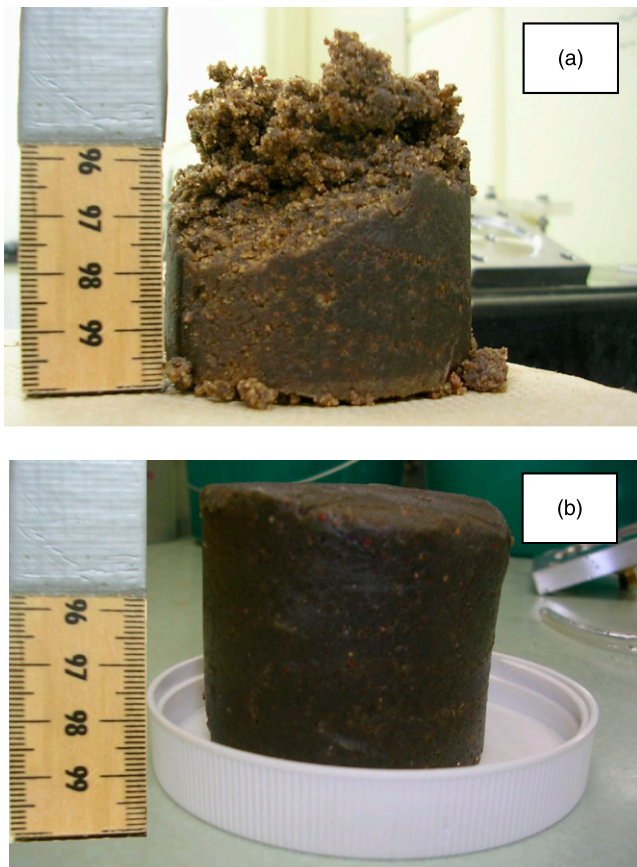


Fig. 11. (Color) Specimens prepared with mixtures of broadly graded sand and 30% organoclay by mass and permeated with (a) No. 2 fuel oil and (b) jet fuel

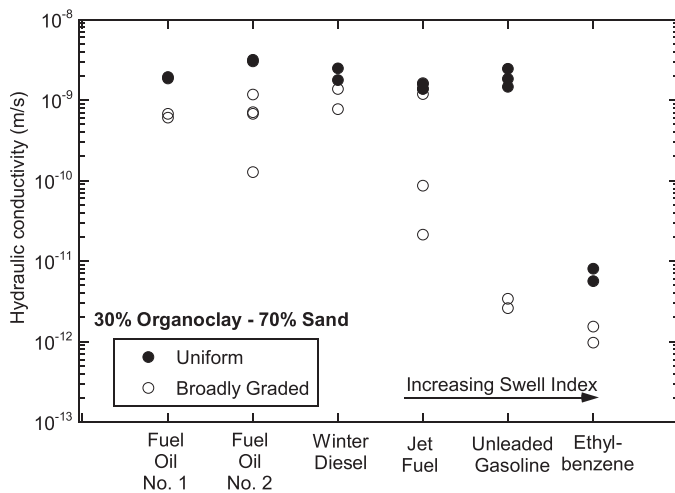


Fig. 12. Hydraulic conductivity of sand-organoclay mixtures with 30% organoclay by mass

because there is sufficient organoclay to block all of the permeable flow paths.

Summary and Conclusions

The hydraulic conductivity of an organoclay with dimethylammonium bound to the bentonite surface was evaluated using five commercially

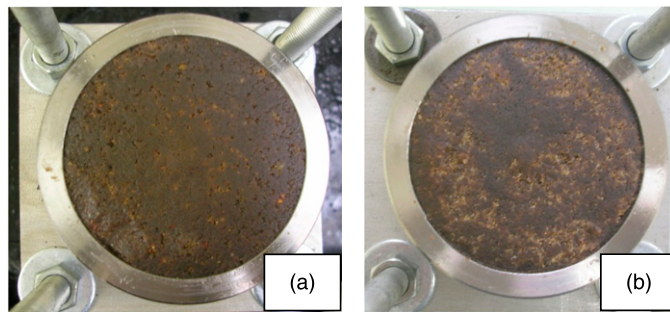


Fig. 13. (Color) Specimens of mixtures of uniform sand and 30% organoclay permeated with jet fuel and having (a) lower and (b) higher hydraulic conductivities (light-colored particles in the cross section are sand; dark material is organoclay)

available fuels (No. 1 fuel oil, No. 2 fuel oil, winter blend diesel fuel, aviation jet fuel, and unleaded gasoline) and four pure organic liquids (methanol, phenol, ethylbenzene, and dioctyl phthalate) ranging from hydrophilic (methanol) to strongly hydrophobic (dioctyl phthalate). Swell index and liquid sorption tests were conducted on the organoclay using each fuel and organic liquid. Control tests were also conducted with Type II DI water.

Swelling of the organoclay and the liquid sorption capacity for the organic liquids varied widely, with little to no swelling or liquid sorption in hydrophilic liquids (methanol and phenol) and DI water; low-to-moderate swelling and liquid sorption capacity in less-refined fuels composed of heavier distillates (fuel oils and diesel) and the phthalate; and high swelling in the more highly refined fuels comprised of lighter distillates (jet fuel and gasoline) and ethylbenzene. However, the swelling and the liquid sorption capacity were not related monotonically to the typical parameters used to describe hydrophobicity (i.e., the solubility and octanol-water partition coefficient). A strong direct relationship was found between the swell index and the liquid sorption capacity, indicating that either parameter can be used as an indicator of solvation potential for an organoclay and organic liquid.

The hydraulic conductivity of this organoclay varied by approximately six orders of magnitude depending on the organic liquid used for permeation, with the lowest hydraulic conductivities associated with the more highly refined fuels composed of lighter distillates and ethylbenzene that induce the greatest swell, and the highest hydraulic conductivities with the hydrophilic liquids that induce the least swell (or no swell). The hydrodynamic properties of the permeant liquid also affect the hydraulic conductivity of the organoclay in a systematic manner. A strong correlation was obtained between the hydraulic conductivity and the swell index that is analogous to hydraulic conductivity-swell index relationships reported for Na bentonite permeated with salt solutions having varying compositions and ionic strengths. When the swell index is at least 10 mL/2 g, the organoclay has hydraulic conductivity less than 10⁻¹⁰ m/s. Below 10 mL/2 g, the hydraulic conductivity increases dramatically as the swell index decreases. This threshold in the swell index can be used as an indicator for the propensity of this organoclay to transmit or block flow. Similar thresholds may exist for other organoclays.

The hydraulic conductivity tests conducted on the sand-organoclay mixtures with the organic liquids showed that the hydraulic conductivity is sensitive to the organoclay content, the gradation of the sand, and the swell index associated with the permeant liquid. Mixtures prepared with broadly graded sand require less organoclay and are less sensitive to the swell index. For the fuels that

were tested, mixtures prepared with this organoclay should have at least 50% organoclay to ensure low hydraulic conductivity. For fuels such as diesel and fuel oil, mixtures prepared with this organoclay should have at least 75% organoclay unless the sand is broadly graded. Testing with sands having a broader range of particle size and gradation and with other organoclays is recommended to generalize these findings.

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Supplemental Data

Supplemental data are available online in the ASCE Library (www.ascelibrary.org).

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