PERMEABILITY OF AN ORGANO-MODIFIED BENTONITE TO ETHANOL-WATER SOLUTIONS

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Abstract—Permeability is often the limiting factor in clay-based barrier systems designed to attenuate miscible or immiscible contaminant transport. One critical aspect of barrier design is prediction of the effects of permeant conditions on physicochemical properties (*e.g* swelling) of the clay component and thus, ultimately, the permeability of the barrier. To this end, the permeability of an organically modified bentonite to ethanol-water solutions was determined to approximate the effects of organo sorption-induced swelling. The bentonite was modified with a substituted alkylammonium cation: benzyloctadecyl-dimethylammonium (BODMA). Powder X-ray diffraction (XRD) measurements were used to measure interlayer expansion and to estimate aggregate particle densities at any given ethanol concentration. Permeability measurements were conducted on samples under confining overburden stresses of 43 kPa (~2.5 m of saturated soil) using a hydraulic gradient of ~300. Sample thickness was continuously monitored during measurements of volumetric flow so that sample strain, void ratio and porosity could be calculated from changes in sample pore volumes. For calculations of porosity and void ratio, the swelling solid volume, determined from XRD, was assumed to include the sorbed layer (crystalline water/ethanol), the thickness of which is not normally considered in engineering applications. Exposure of the BODMA bentonite to increasing ethanol concentrations increased the swell volume of the clay. Measured coefficients of permeability for the BODMA bentonite decreased from $\sim 1 \times 10^{-7} \, \mathrm{m \, s^{-1}}$ for pure water to $\sim 8 \times 10^{-10} \, \mathrm{m \, s^{-1}}$ for pure ethanol. Exposure of the organo clay to ethanol-water solutions containing 0.2 M NaCl increased the effect of ethanol on clay swelling and permeability. Probable consequences of the effects of sorption-induced swelling on permeability and the performance of organo clay-based permeable reactive barriers are discussed.

Key Words—Intrinsic Permeability, Porosity, Reactive Barriers, Swell Volume, Viscosity.

INTRODUCTION

Clay liners are often called upon to contain organic liquid wastes from spills or leaks from storage facilities as well as those placed in landfills. A growing amount of organic liquid wastes that are disposed in landfills, or stockpiled for future treatment, are associated with materials removed from contaminated sites, including soils around leaking underground petrochemical storage tanks. Most clay-lined landfill or containment designs for storage facilities have proven unreliable in providing permanent containment of organic wastes. Causes of liner failure may include the effects of exchange reactions (Brown, 1988; Dobras and Elzea, 1993; Jo *et al.*, 2001), permeant permittivity (dielectric constant) and permeant viscosity (Petrov and Rowe 1997; Petrov *et al.*, 1997) on shrink-swell reactions in the liner. Shrink-swell reactions may adversely affect permeability.

Development of relatively inexpensive materials with large sorption capacities for organic contaminants remains one of the more intractable problems associated

with mitigating their transport into or through surface and groundwater systems. Recent research on the effectiveness of permeable reactive barriers in addressing these problems has focused on biomass-based sorbents (Guerin *et al.*, 2002), redox-reactive layer silicates (Nzengung *et al.*, 2002) or geosynthetic clay liners (Shackelford *et al.*, 2000; Egloffstein, 2001; Sangman and Rowe, 2001). Only a few studies incorporate the enhanced organophilic properties of organo clays (*e.g.* Brixie and Boyd, 1994; Lo, 1996; Gitipour *et al.*, 1997; Nzengung *et al.*, 1996, 1997) and the authors are aware of only one study (Rakhshandehroo *et al.*, 1998) demonstrating the feasibility of organo-clays in sorptive-zone applications. Organo-modified clays are effective sorbents of a wide range of organic contaminants from aqueous solution (Jaynes and Boyd, 1991; Xu and Boyd, 1995; Nzengung *et al.*, 1995, 1997; Koh and Dixon, 2001; Bonczek *et al.*, 2002). Alther (1995, 2002) has shown that organo-modified clays can also be cost-effective pre-treatments for conventional activated carbon-based sorbents in pump-and-treat remediation strategies. The improved cost efficiency is due to their greater sorptive capacity for a wide range of organic contaminants, and also to the longer lifetime associated with activated carbon sorbents, with which organo-modifed clay pre-treatments were used.

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The swelling of organo-modified clays in aqueous mixtures of miscible organic solvents has generally been under appreciated (Jordan, 1949; Jordan *et al.*, 1950; Lagaly *et al.*, 1983; Lagaly, 1984; Raussell-Colom and Serratosa, 1987; Moraru, 2001). Investigations of the swelling of organo-modified clays when exposed to pure hydrocarbon solvents (Nzengung *et al.*, 1996; Slade and Gates, 2004), aqueous miscible organic solvents (Gitipour *et al.*, 1997; Gates, 2004) or relatively insoluble organic compounds (Singh *et al.*, 2003) have been initiated recently with the aim of improving organo clay-based sorbents. Slade and Gates (2004) found that ethanol and toluene increased the unconfined basal spacings from 1.76 nm to ~4.60 nm in smectites and vermiculites exchanged with hexadecyltrimethylammonium (HDTMA). Singh *et al.* (2003) found that an HDTMA montmorillonite was able to sorb as much as 8 mass% fenamiphos (solubility in water of ~600 ppm) with corresponding increases in the basal spacing from ~1.8 to ~3.6 nm. Gates (2004) showed that clays exchanged with a substituted alkylammonium cation swelled substantially under unconfined conditions in mixed solutions of ethanol-water and in ethanol-water mixtures containing 0.2 M NaCl.

The ability of organo-modified clays to swell in hydrocarbon solvents is supposed to be related to the ability of the solvent to disrupt the attractive van der Waals forces operating between the aliphatic chains of adjacent organic cations arrayed within the interlayer space (Moraru, 2001; Gates, 2004; Slade and Gates, 2004). Disruption of van der Waals bonding apparently overcomes any enhanced electric double layer repulsion expected to form because of the lower dielectric constant of organic solvents compared to water. The presence of dissolved inorganic salts (*e.g.* NaCl) can moderate the influence of the solvent depending on the packing density of the organic cations (Lagaly and Witter, 1982). Regardless of the exact mechanism, these swelling-induced changes are expected to decrease the permeability of organo-modified clays to water containing organic compounds. In contrast, when exposed to organic solvents, clays, whose exchange capacities are satisfied with inorganic cations, often experience shrinkage or flocculation as compared to solvation in water (see *e.g.* Theng, 1974; Raussell-Colom and Serratosa, 1987; Shackelford, 1994; Anandarajah, 2003). Indeed, Petrov *et al.* (1997) found that the permeability of a geosynthetic liner, containing Na⁺-clay, to such solvents increased by more than two orders of magnitude due to this interlayer contraction.

Very few data exist detailing the permeability of organo-modified clays to water or organic liquids. The purpose of this study, therefore, was to show how swelling of organo clays under confining stresses affects their permeability to mixed permeant solutions. Ethanol-water mixtures were used as test solutions for safety considerations and due to the ease with which steady-state conditions could be met. The test conditions used in

this study included simulated hydraulic gradients and confining stresses typical to what would be encountered in sub-surface reactive barriers.

BACKGROUND AND THEORY

Permeability

Permeability is the capacity for a porous medium to allow fluid flow under an applied hydraulic pressure. Implicit is the assumption that viscous flow is laminar and not turbulent (Marshall *et al.*, 1996). Laminar flow through a capillary tube of radius r is given by the Hagen-Poiseuille equation:

$$q_e = \frac{\pi r^4}{8\eta} \cdot \frac{\Delta P}{L} \qquad (1)$$

where, q_e is the volumetric flow rate, ΔP is the pressure gradient, L is the length of the tube, and η is the dynamic viscosity of the fluid. For a column of porous media, Darcy's law states that the discharge velocity of a fluid is directly proportional to the pressure gradient ($\Delta P/L$) across the porous medium and inversely proportional to the dynamic viscosity (η) of the fluid viz:

$$v \propto \frac{\Delta P}{\eta L} \qquad (2)$$

Here L is the path length of the porous material. The discharge velocity can be replaced with an expression for the volumetric flow rate per unit of cross-sectional area (q_e/A) and the proportionality then becomes

$$\frac{q_e}{A} = K\frac{\Delta P}{\eta L} \qquad (3)$$

Here, the proportionality constant, K, is the intrinsic permeability and is expressed in units of m^2. Effectively, Darcy's law incorporates the effects of tortuous pathways and fluid-solid interactions in the form of equation 1. Equation 3 can be rearranged as

$$K = \frac{q_e \eta L}{\Delta P A} \qquad (4)$$

and ΔP is often expressed in terms of the piezometric head (Δh) occurring across the porous medium as

$$\Delta P = \Delta h \rho g \qquad (5)$$

In equation 5, Δh is the difference in hydraulic (or more generally piezometric) head at the entrance (h_i) and the exit (h_e), respectively, and g is the acceleration due to gravity. For a given solvent with known density (ρ_{solv}) and viscosity (η_{solv}) substitution of equation 5 into equation 4 yields

$$K = \frac{q_e \eta_{solv} L}{\Delta h \rho_{solv} g A} \qquad (6)$$

All terms on the right-hand side of equation 6 can be determined experimentally or obtained from literature sources. Thus, the intrinsic permeability of a material can be calculated for any permeating fluid of known density and viscosity. The intrinsic permeability (also called the 'absolute' or 'specific' permeability) is dependent on the porosity of the material, but is independent of the fluid (Klute and Dirksen, 1986; Marshall *et al.*, 1996). For porous materials whose porosity is affected by interaction with the permeating liquid (*i.e.* swelling clays), the intrinsic permeability is variable and is thus dependent on fluid properties such as permittivity, ionic strength and surface tension, all of which are, to varying degrees, measures of fluid-solid interactions.

The coefficient of permeability (k) is another widely used measure of permeability. Because fluid viscosity and density are constant at constant *T* and *P*, the coefficient of permeability can be related to the intrinsic permeability by the fluid's fluidity, *f*

$$f = \frac{k}{K} = \frac{\rho_{solv} g}{\eta_{solv}} \qquad (7)$$

Substitution of equation 7 into equation 6 leads to a working expression for the coefficient of permeability:

$$k = \frac{q_e L}{\Delta h A} \qquad (8)$$

and all terms on the right can be determined experimentally. The coefficient of permeability has SI units of m s^{-1}. If the fluid used is water, the coefficient of permeability is more commonly referred to as the hydraulic conductivity, and $f = 9.77 \times 10^6$. Table 1 shows experimental and literature values for viscosity, density and fluidity for the ethanol-water solutions, with and without 0.2 M NaCl, used in this study.

Porosity and equivalent pore radii

If pores within the material are considered to be tubes, then the rate of flow through a pore is q_e/A, where $A = \pi r^2$. The discharge velocity, *v*, through a material containing a tubular pore is then

$$v = \frac{\varepsilon q_e}{A} \qquad (9)$$

The porosity, ε, in equation 9 represents the cross-sectional area of a pore per unit of cross-sectional area of the material, *A*. Combining equations 1, 6 and 9 yields

$$K = \frac{\varepsilon r^2}{8} \qquad (10)$$

which, upon rearrangement

$$r = \left(\frac{8K}{\varepsilon}\right)^{\frac{1}{2}} \qquad (11)$$

Table 1. Measured densities (ρ), dynamic viscosities (η) and fluidities (*f*), and their respective literature values, for ethanol-water mixtures at 20°C and 1 atm.

EtOH content		Measured values[†]			Literature values[‡]		
		ρ	η	f	ρ	η	f
Vol.%	mass %	g cm^{-3}	mPa s	m^{-1} s^{-1} ($\times 10^6$)	g cm^{-3}	mPa s	m^{-1} s^{-1} ($\times 10^6$)
0.0 M NaCl							
0	0.00	0.998	1.0	9.878	0.99823	1.0022	9.768
10	8.06	0.986	1.4	6.928	0.98187	1.3891	6.932
20	16.5	0.974	1.9	4.999	0.96864	1.9212	4.944
30	25.3	0.960	2.4	3.897	0.95382	2.4371	3.838
40	34. 5	0.944	2.8	3.275	0.93518	2.7753	3.305
50	44.1	0.926	2.9	3.172	0.91384	2.8489	3.146
60	54.1	0.905	2.8	3.121	0.89113	2.7507	3.177
70	64.7	0.881	2.4	3.545	0.86766	2.3915	3.558
80	75.8	0.855	2.0	4.136	0.84344	2.0215	4.092
90	87. 5	0.826	1.6	5.063	0.81797	1.6250	4.936
100	99.7	0.796	1.2	6.456	0.78934	1.2136	6.379
0.2 M NaCl							
0	0.00	1.006	1.0	9.865	1.0065	1.0229	9.649
10	7.93	0.992	1.3	7.483	0.9919	1.3337	7.293
20	16.03	0.982	1.8	5.350	0.9819	1.7878	5.836
30	24.36	0.970	2.3	4.136	0.9694	2.2362	4.251
40	32.95	0.955	2.6	3.602	0.9553	2.5951	3.610
50	42.03	0.936	2.9	3.165	0.9363	2.8589	3.212
60	51.52	0.917	2.9	3.101	0.9166	2.9062	3.093
70	61.74	0.892	2.7	3.240	0.8922	2.7181	3.219

[†] Error (2σ) for density = ±0.005 g cm^{-3} and for viscosity = ±0.1 mPa s
[‡] Values for density from Kaye and Laby (1959). Values for viscosity from National Bureau of Standards

allows an equivalent pore radius to be determined experimentally for a material with known porosity and corresponding intrinsic permeability. The equivalent pore radius calculated in this fashion is effectively an average of multiple constricting pores with an unknown distribution of pore radii.

MATERIALS AND METHODS

The commercial bentonite (Miles, Queensland, Australia) used is predominantly smectite (montmorillonite), but contains ~29% non-swelling components, including quartz, feldspar and opal-CT (Gates *et al.*, 2002). The Na^+-bentonite was modified by exchange with benzyloctadecyldimethylammonium (BODMA) chloride (Gates, 2004). Volumetric ratios of ethanol:water mixtures were prepared from deionized water and technical grade ethanol. Technical grade NaCl was used to create 0.2 M NaCl in ethanol-water mixtures.

Solution density measurements

Solution densities (ρ_{solv}) were determined on outgassed ethanol-water solutions using calibrated quartz pycnometers at 20±0.25ºC. Reference ethanol-water series were prepared with ethanol concentrations ranging from 0 to 100 vol.%, and for solutions containing 0.2 M NaCl, ethanol concentrations of 0 to 70 vol.% were used in increments of 10 vol.%. For the latter series, >70 vol.% ethanol concentrations were avoided due to the insolubility of NaCl. The densities of the permeating solutions were determined when 100 mL of the permeant had passed through the sample during hydraulic conductivity measurements, to ensure that steady-state conditions had occurred, and to estimate the amount of ethanol in the ethanol-water solutions.

Viscosity measurements

Viscosities of ethanol-water solutions were measured using a Brookfield rotational viscometer fitted with an ultra-low viscosity sample device. The sample cell was kept at 20±0.25ºC by passing iced water through a thermal-coupled constant-temperature water bath. Measurements were conducted on ~5 mL of test solution using a shear rate of 223.2 s^{-1} for 5 min to minimize any torsional variations due to change in shear rate.

Free (unconfined) swell tests

Free swell tests (ASTM D5890-95) were conducted to estimate the bulk (3-dimensional) swelling of BODMA bentonite in ethanol-water solutions. Approximately 4 g (weighed accurately) of oven-dried, powdered sample were packed uniformly into 10 mL graduated cylinders and the initial solid volumes measured. 5 mL of ethanol-water solutions were added, the cylinders capped and the contents shaken vigorously for 1 min. To wash down the sides of the cylinders, 5 mL of the same ethanol-water solutions were added and the samples were then evacuated to remove entrapped air, sealed and allowed to stand for 1 week. The free swell volume ($V_{f\text{-tot}}$) was determined by recording the volume of the solvated material.

Crystalline (1-dimensional) swelling was recorded by powder XRD on oriented films of BODMA bentonite bathed in ethanol-water solutions. The basal spacings, determined by XRD, measure directly the volume change of swelling components only. Approximately 60 mg of BODMA bentonite, suspended in ethanol, were vacuum-deposited onto ceramic tiles. Once deposited, 10 mL aliquots of ethanol-water solutions, with successively decreasing ethanol contents to pure water, were vacuum-filtered through the samples. Prior to each XRD measurement, the samples were re-washed with 10 mL of ethanol-water solutions and were allowed to stand for up to 60 min in ~5 mL of the same solution. The samples were wrapped in Mylar to prevent evaporation. See Gates (2004) for further details.

Particle densities

If the interaction of ethanol-water solutions with BODMA smectites results in crystalline swelling of the organo clay, then the particulate densities of the swelling components should decrease as a function of increasing ethanol content. However, the bentonite used also contains considerable non-swelling minerals (Table 2 and Gates *et al.*, 2002). Thus, an accurate measure of the aggregate particle density is needed.

Table 2. Mean particle density (ρ_{ns}^{ave}) of the non-swelling components of Miles bentonite (Queensland) calculated using equation 12.

Mineral component[†] Mass %	Mass fraction y_i	ρ_i g cm^{-3}	y_i/ρ_i cm^{-3}	ρ_{ns}^{ave} g cm^{-3}
Smectite 71				
Quartz 14	0.483	2.65	0.182	
Opal CT 4	0.138	2.65	0.052	
Feldspar 6	0.207	2.3	0.090	2.497
Zeolite 4	0.138	2.2	0.063	
Illite 0.5	0.017	2.76	0.006	
Gypsum 0.5	0.017	2.32	0.007	

[†] Mineralogy from Gates *et al.* (2002)

The mean particle density of the non-swelling components, ρ_{ns}^{ave}, was calculated from the relation

$$\rho_{ns}^{ave} = \frac{1}{\sum \left(\frac{y_i}{\rho_i}\right)} \qquad (12)$$

by determining the mass fraction, y_i, and using known particle densities, ρ_i of each non-swelling impurity component (i). Values determined for the Miles (Queensland) bentonite are listed in Table 2.

Swelling-particle densities (ρ_{sw}) at various ethanol contents in ethanol-water mixtures were calculated from XRD measurements, assuming that sorption of the solutes accounted for all crystalline swelling observed. The unit-cell volume of the BODMA Miles bentonite was calculated from the area of a unit-cell of the montmorillonitic component (45.52 Å^2) and the basal spacing produced by solvation with any given ethanol-water mixture. The mass of the organo clay was determined from the chemistry and structural formulae of the organo clay, and from the mass of the sorbed ethanol-water mixtures. The mass of water and/or ethanol sorbed during solvation and swelling was assumed to be equal to the product of the increase in unit-cell volume and density ρ_{solv} of the ethanol-water mixture used. Aggregate particle densities $\rho_{s\text{-}tot}^{ave}$ were then determined from the mass fraction and densities of swelling and non-swelling components in the organo clay. Swelling-particle densities determined in this fashion account for the portion of the total pore volume that is occupied by the sorbed layer. Thus, the sorbed layer is assumed to be part of the crystal structure. Note that this differs from conventional engineering considerations, where the volume change is generally not considered to be associated with the solid phase (Anandarajah, 2003; Jo *et al.*, 2001; Petrov and Rowe, 1997; Petrov *et al.*, 1997).

All measurements were referenced to the oven-dry state (105ºC, for 4 h). Oven-dry mass was determined on duplicate samples in titanium vessels that allowed for gas purge and sealing. The vessels were then placed within a manifold and heated at 105ºC for 4 h under dry N_2 purge. Vessels were sealed, allowed to cool and reweighed.

Permeability measurements

Permeability measurements of BODMA Miles bentonite to ethanol-water solutions were determined on a fixed-wall odometer (Churchman *et al.*, 2002). The odometer allowed direct and precise measurement of sample thickness changes under applied hydraulic heads and vertical stresses, with minimal edge effects. It was modified (Figure 1) from Churchman *et al.* (2002) so that the minimum sample thickness could be reduced to ~5 mm. This modification allowed for quicker equili-
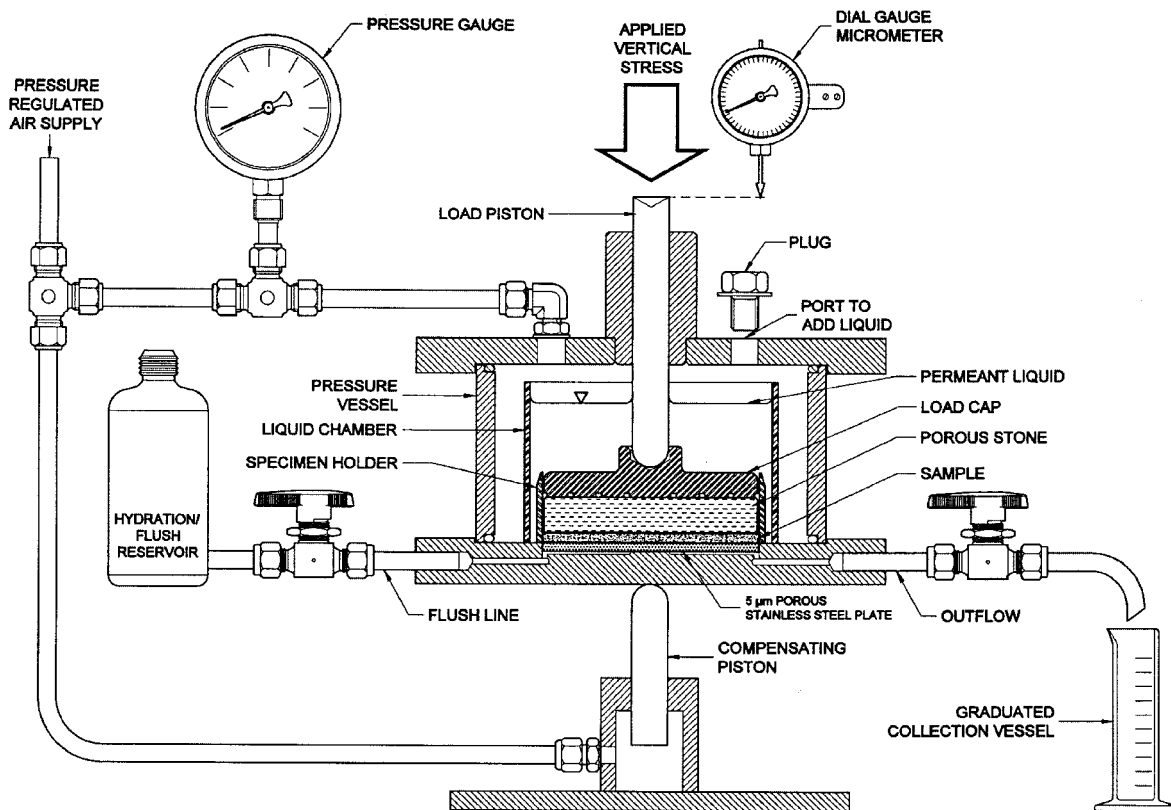

Figure 1. Diagram detailing the modified permeameter.

brium of the sample to the permeant, a greater reservoir volume for the permeant and, ultimately, the passage of greater pore volumes of permeant through the organo clay during the tests. Experiments were conducted at 20±0.25ºC using ethanol-water solutions with 0, 10, 50, 90 and 100 vol.% ethanol, as well as 0, 10, 30, 50, 70 vol.% ethanol in solutions containing 0.2 M NaCl.

Approximately 20 g of oven-dried, ground (to pass 200 µm sieve) BODMA-bentonite were lightly and uniformly packed onto a stainless steel filter within a 76 mm diameter ring housed within the pressure cell. The initial thickness of the sample was determined and the sample was capped with a top-plate consisting of porous sandstone. The permeability of the sandstone had been shown previously (Peter, unpublished data) to have a permeability several orders of magnitude greater than the organo clay, and thus was unlikely to impact on the results. The entire pressure cell was placed within a loading frame to exert a simulated confining stress of 43 kPa (~2.5 m). Micrometers were affixed to enable continual measurement of changes in sample thickness during tests. Two such cells were prepared. A 50 vol.% solution of ethanol in water was initially allowed to wet the sample passively from beneath over a period of 10 days, under a slight (0.005−0.01 m) hydraulic head, to ensure degassing of the sample void space and to induce sample consolidation during wetting. Sample thickness changes indicated that the sample had obtained steady-state with the initial wetting solution under the over-burden stresses applied. At this time ~125 mL of test solution were added to the reservoir above the sample, and after sealing the cell, hydraulic conductivity tests were conducted by applying air pressure above the solution in the reservoir. Prior to changing test solutions, excess solution from previous tests were siphoned from the reservoir to hasten establishment of steady-state conditions to the new test solutions. The samples were not allowed to de-saturate at any time when exchanging solutions during the ensuing tests.

Permeability tests were conducted at a constant applied pressure of 15 kPa and hydraulic pressure of 15 kPa. Thus, for a sample thickness of 0.005 m, a hydraulic gradient of ~300 was established. As much as 300 mL of each ethanol-water solution was expressed through the sample to allow the swelling organo clay to reach steady-state with sufficient pore volumes of the permeating solution. Changes in sample thickness were monitored to follow sample-volume change in response to ethanol-water solutions and to determine sample parameters, e.g. pore volumes, void ratio and volume of solids. Permeant density was also monitored to ensure that steady-state had occurred when ethanol-water solutions were changed.

The intrinsic permeabilities and coefficients of permeability for ethanol-water solutions were determined using equations 6 and 8, respectively. Equivalent pore radii were estimated by applying equation 11. Resulting estimated errors are 0.05×10^{-8} for k and 0.05×10^{-15} for K.

RESULTS AND DISCUSSION

Effect of ethanol-induced swelling on physical parameters

The basal spacings determined from XRD revealed an increase in the crystalline (1-dimensional) swell volume (V_{sw}) of ~50% in pure ethanol relative to pure water for the BODMA bentonite (Table 3). Bathing the BODMA bentonite in ethanol-water solutions containing 0.2 M NaCl also resulted in crystalline swelling. In comparison, the bulk (3-dimensional) swell volume (V_{f-tot}) of the BODMA bentonite increased by ~230% with respect to the oven-dried state when bathed in 100% ethanol, or 70% ethanol containing 0.2 M NaCl.

Table 3. Unconfined sample volumes of the swelling components (V_{sw}) determined from XRD and total free swelling volume (V_{f-tot}) determined from free swell tests on BODMA bentonite (Miles, Queensland) in ethanol-water solutions, with and without 0.2 M NaCl.

ETOH:H$_2$O (vol.%:vol.%)	0.0 M NaCl				0.2 M NaCl			
	d_{001}[†] nm	V_{sw} % [‡]	V_{f-tot} cm^3	%	d_{001} nm	V_{sw} %	V_{f-tot} cm^3	%
0:100	2.25	114	2.41	117	2.22	113	2.30	112
10:90	2.34	119			2.34	119	2.44	118
20:80	2.41	122	2.56	124	2.50	127		
30:70	2.53	128			2.68	136	3.19	155
40:60	2.60	132			2.87	146		
50:50	2.71	138	3.23	157	3.11	159	4.48	217
60:40	2.99	152			3.30	168		
70:30	3.13	159			3.45	175	4.66	226
80:20	3.20	162						
90:10	3.33	169	4.60	223				
100:0	3.42	174	4.74	230				

[†] Error estimates on XRD data = ±0.01 nm (Gates, 2004). Oven-dry d_{001} = 1.97 nm. Error on free swell ±0.01 cm^{-3}
[‡] % relative to the oven-dried state

Table 4. Particle densities (ρ_{sw}) and volumes of the swelling component (V_{sw}) determined from XRD and resulting aggregate densities ($\rho_{s\text{-}tot}$) and volumes ($V_{s\text{-}tot}$) calculated by incorporation of non-swelling components of BODMA-bentonite (Miles, Queensland) in ethanol-water mixtures, with and without 0.2 M NaCl.

ETOH:H$_2$0	0.0 M NaCl				0.2 M NaCl			
	ρ_{sw}	$\rho_{s\text{-}tot}$	V_{sw}	$V_{s\text{-}tot}$	ρ_{sw}	$\rho_{s\text{-}tot}$	V_{sw}	$V_{s\text{-}tot}$
	g cm^{-3}		cm^3 g^{-1}		g cm^{-3}		cm^3 g^{-1}	
Oven-dried	1.79	1.94	0.562	0.515				
Air-dried	1.63	1.81	0.614	0.552				
0:100	1.55	1.74	0.644	0.574	1.58	1.77	0.634	0.566
10:90	1.50	1.69	0.668	0.591	1.50	1.69	0.669	0.591
20:80	1.45	1.65	0.688	0.605	1.40	1.60	0.715	0.624
30:70	1.38	1.59	0.723	0.629	1.30	1.51	0.766	0.660
40:60	1.35	1.56	0.742	0.643	1.22	1.43	0.818	0.697
50:50	1.29	1.50	0.775	0.667	1.13	1.34	0.887	0.746
60:40	1.17	1.38	0.855	0.723	1.06	1.27	0.941	0.784
70:30	1.12	1.33	0.895	0.751	1.02	1.23	0.984	0.815
80:20	1.09	1.31	0.914	0.765				
90:10	1.05	1.26	0.952	0.792				
100:0	1.02	1.23	0.977	0.810				

Errors associated with particle density measurements: ±0.01 g cm^{-3}

The presence of 0.2 M NaCl in ethanol-water solutions enhanced the swelling of the BODMA clay. For example, the free swell volume for the organo clay in 50 vol.% ethanol with 0.2 M NaCl was comparable to that observed for 90 vol.% ethanol without salt. The cause of this effect is likely due to the decreased activity of water in 0.2 M NaCl ethanol-water solutions (Gates, 2004).

Particle densities of the swelling components (π_{sw}) and of the aggregate materials $\rho_{s\text{-}tot}^{ave}$ and their corresponding volumes (V_{sw}, $V_{s\text{-}tot}$), calculated from XRD and mineralogy (Tables 2 and 3), are shown in Table 4. Increased ethanol concentration in the ethanol-water solutions resulted in increased sample volume and correspondingly lower swelling particle densities. The presence of 0.2 M NaCl in 70 vol.% ethanol caused the aggregate particle densities to decrease by the same magnitude as for 100 vol.% ethanol without added salt.

In the permeability tests, vertical strain (Figure 2), sample volume (Figure 3a) and porosity (Figure 4) changed predictably with increasing ethanol concentrations. While the total sample volume changes under the conditions of this study were small compared to those measured for free swelling (conducted under no overburden pressure), significant changes did occur. Decreasing ethanol concentrations caused both bulk and crystalline shrinkage: the sample thickness and volume decreased, but the porosity increased. In contrast, with increasing ethanol concentration, sample thickness and volume increased.

Permeability of BODMA-clay to 0.2 M NaCl in ethanol-water

Figure 5 shows that a substantial number of pore volumes of flow were necessary for the permeant density to approach its initial value at an applied hydraulic

pressure of 15 kPa. For tests with sequentially increasing ethanol concentrations, the approach to steady-state required more than 30–40 pore volumes (Figure 5a). At higher ethanol concentrations, while the measured densities were within 1–2% of the initial permeant values after 50 pore volumes (30 and 50 vol.%), steady-state with the initial permeant density was apparently not attained. These results may indicate that during confined swelling, the organo clay preferentially retains ethanol. Preferential sorption of one component from binary solvents by organo clays has been observed previously (Lagaly *et al.*, 1983; Regdon *et al.*, 1998). For tests with sequentially decreasing ethanol concentrations (Figure 5b), steady-state was achieved for all ethanol concentrations within 40 to 50 pore volumes. These results probably reflect the counteracting effect of the
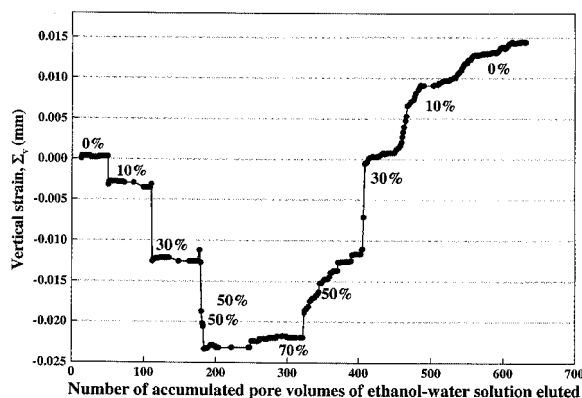

Figure 2. Effect of accumulated pore volumes of test permeant on the vertical strain experienced by BODMA bentonite (Miles, Queensland). Negative strain indicates sample swelling. Numbers correspond to the vol.% of ethanol in ethanol-water solution, containing 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.

confining stresses on the swelling forces of the organo clay.

Table 5 shows that sample parameters varied proportionately with increasing ethanol concentration in the ethanol-water solutions containing 0.2 M NaCl. Negative strain values imply sample swelling, and positive values imply sample compression or consolidation. Void ratios decreased substantially when the ethanol concentration was increased, as did the equivalent pore radii. The net effect of ethanol concentration on these sample parameters caused a decrease in both the coefficient of permeability and intrinsic permeability with increasing ethanol concentration. Permeability of the organo clay to various ethanol-water solutions ranged from $1.3 \times 10^{-7} \, \text{m s}^{-1}$ for water to $7.3 \times 10^{-10} \, \text{m s}^{-1}$ for ethanol, nearly 3 orders of magnitude.

Figure 6a displays the averaged results from one test cell of the coefficient of permeability for the organo clay calculated using equation 8 for ethanol-water solutions with and without 0.2 M NaCl. Increasing ethanol concentration caused k to decrease. For the ethanol-

Figure 4. Effect of accumulated pore volumes of test permeant expressed through BODMA bentonite (Miles Queensland) on sample porosity. Numbers correspond to the vol.% of ethanol in ethanol-water solution, containing 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.

water solutions without NaCl, k decreased linearly until 90 vol.% ethanol, but k measured for the 100 vol.% ethanol solution was substantially lower. When 0.2 M
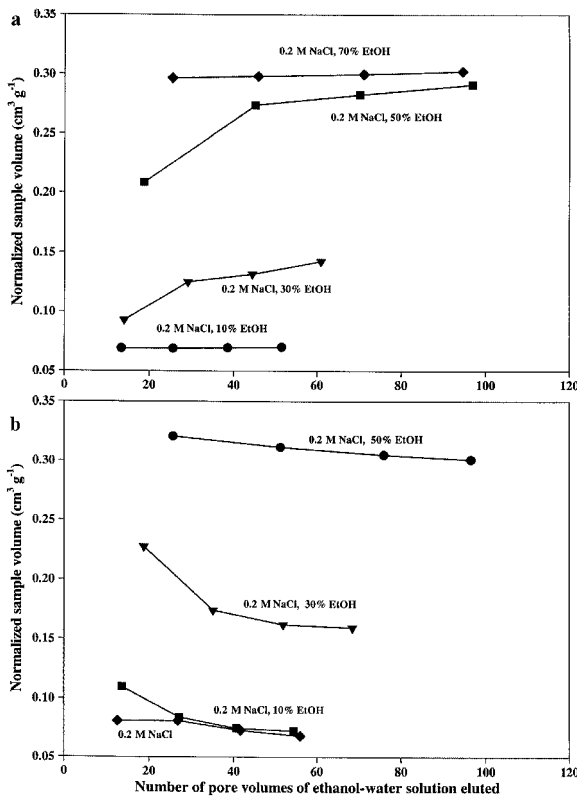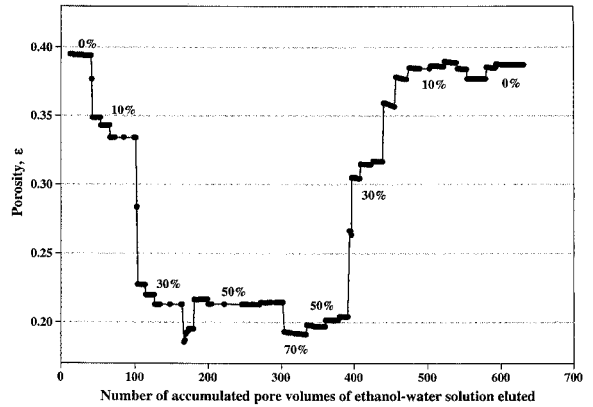

Figure 3. Swelling of BODMA bentonite (Miles, Queensland) as evidenced by the gram-normalized volume changes as a function of permeant ethanol concentrations and cumulative pore volumes eluted. (a) Series of increasing ethanol concentration (vol.%); (b) series of decreasing ethanol concentrations (vol.%). Ethanol-water solutions containing 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.
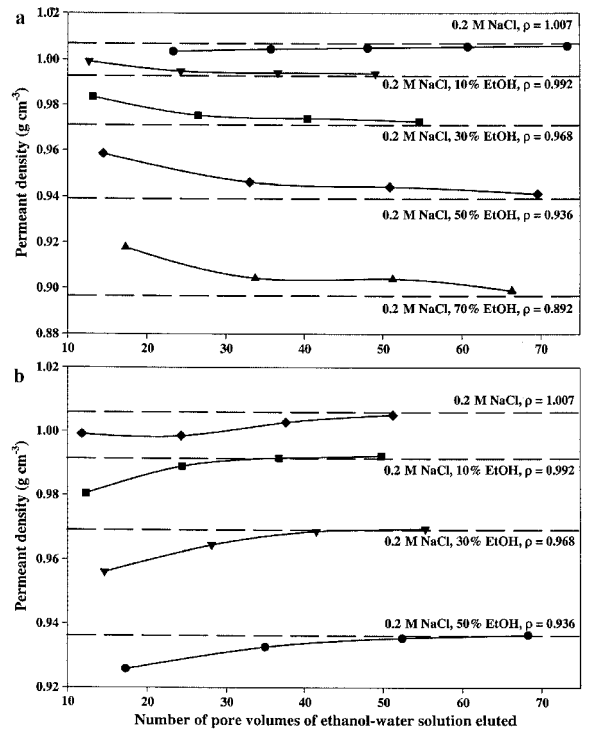

Figure 5. The number of pore volumes of ethanol-water solutions necessary to achieve steady-state conditions as a function of pore volumes eluted through BODMA bentonite (Miles, Queensland), as evidenced by the permeant density with different ethanol concentrations. (a) Series of increasing ethanol concentration (vol.%); (b) series of decreasing ethanol concentrations (vol.%). Ethanol-water solutions containing 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.

Table 5. Effect of ethanol concentration in ethanol-water solutions on solvent density (ρ_{solv}), average changes in vertical strain Σ_v void ratio (e), porosity (ε), pore radius (r) and coefficient of permeability (k) and intrinsic permeability (K) determined for BSDMA-bentonite (Miles, Queensland) saturated with ethanol-water solutions. Values averaged over 100 mL of ethanol-water solutions.

EtOH:H$_2$O	Cell	ρ_{solv} g cm^{-3}	Σ_v[†] mm	e[‡]	ε	r nm	k m s^{-1} ($\times 10^{-8}$)	K m^2 ($\times 10^{-15}$)
0.0 M NaCl								
00:100	17	0.997	§	1.012	0.503	462	13.1	13.4
	18	0.998		0.783	0.439	533	15.2	15.6
10:90	17	0.992	nil	0.996	0.499	492	9.73	15.1
	18	0.988	nil	0.744	0.427	553	10.5	16.3
50:50	17	0.942	−0.0148	0.816	0.449	298	1.63	4.99
	18	0.940	−0.0196	0.610	0.379	338	1.77	5.40
90:10	17	0.897	−0.0300	0.787	0.440	151	0.711	1.25
	18	0.881	−0.0490	0.494	0.331	192	0.854	1.53
100:00	17	0.878	−0.0779	0.684	0.406	63	0.073	0.20
	18	0.852	−0.0796	0.430	0.301	72	0.134	0.19
0.2 M NaCl								
00:100	17	1.006	§	0.867	0.464	376	7.90	8.21
	18	1.005		0.593	0.372	617	15.5	17.7
10:90	17	0.994	nil	0.895	0.472	341	5.07	6.87
	18	0.994	nil	0.591	0.372	462	9.96	9.92
30:70	17	0.973	−0.0032	0.734	0.423	282	1.85	4.20
	18	0.973	−0.0043	0.464	0.317	346	3.07	4.73
50:50	17	0.941	−0.0089	0.512	0.339	159	0.367	1.07
	18	0.941	−0.0134	0.247	0.198	196	0.452	0.95
70:30	17	0.899	−0.0186	0.487	0.328	83	0.102	0.29
	18	0.904	−0.0229	0.244	0.196	94	0.085	0.22

[†] $\Sigma = (T - T_i)/T_i$. Negative values imply swelling, positive values imply compression. Error estimates ±0.0001 mm
[‡] e = fluid (liquid and gas) volume/solid volume, estimate of error ±0.001
[§] T_i values: 0 M NaCl, cell 17 = 4.327; cell 18 = 5.451; 0.2 M NaCl cell 17 = 4.035; cell 18 = 4.837

NaCl was present in the ethanol-water solutions, k appeared to follow two linear relationships, from 0 to 30 vol.% ethanol and from 30 to 70 vol.% ethanol. The changes in k observed here reflect substantial interaction between the ethanol-water solutions and the organo clay, as can be seen by the intrinsic permeability values (Table 5). The fluidity of the ethanol-water solutions, with and without 0.2 M NaCl, is displayed in Figure 6b. The fluidity of the ethanol-water solutions, with and without 0.2 M NaCl, are the same until the solutions are composed of >50 vol.% ethanol. At >50 vol.% ethanol, the solutions containing 0.2 M NaCl have substantially lower fluidity values than corresponding solutions of ethanol-water without salt.

Figure 7 displays the hysteretic effect of changing ethanol concentrations on the coefficient of permeability of the organo clay to ethanol-water solutions. As the proportion of ethanol in the permeating solutions increased, k decreased; decreasing ethanol concentration resulted in increased values of k. However the coefficient of permeability did not return to original values when ethanol was replaced by water, whether 0.2 M NaCl was present or not. The presence of NaCl in the permeant caused k to be depressed at lower ethanol concentrations compared to ethanol-water solutions without salt. Thus, solutions of 70 vol.% ethanol

containing 0.2 M NaCl had values of k nearly identical to those obtained on solutions containing 90 or 100 vol.% ethanol.

Gates (2004) showed that unconfined crystalline swelling of BODMA montmorillonite in ethanol-water solutions occurred essentially without hysteresis, but Figure 7 shows that the permeability displays considerable hysteresis. Permeability measured for decreasing ethanol concentrations were all lower than those measured for increasing ethanol concentrations. The hysteresis observed here is probably the result of sample consolidation during fluid flow under confining stresses. Consolidation is a textural effect caused by particle rearrangement and porosity changes (generally lowering) due to the effect of the permeant on shrink/swell under overburden stresses. Measured vertical strain, sample volume, porosity and equivalent pore radii were also lower (Figures 2, 3 and 4, Table 5, respectively) following a complete cycle of increasing, then decreasing, ethanol concentrations. As the samples were continuously saturated during the tests, these results imply that repeated shrink/swell cycles, due to changing permeant properties, can cause considerable consolidation of organo clays, even when continuously saturated.

Yong (1999) and Anandarajah (2003) recently discussed possible mechanisms responsible for differ-
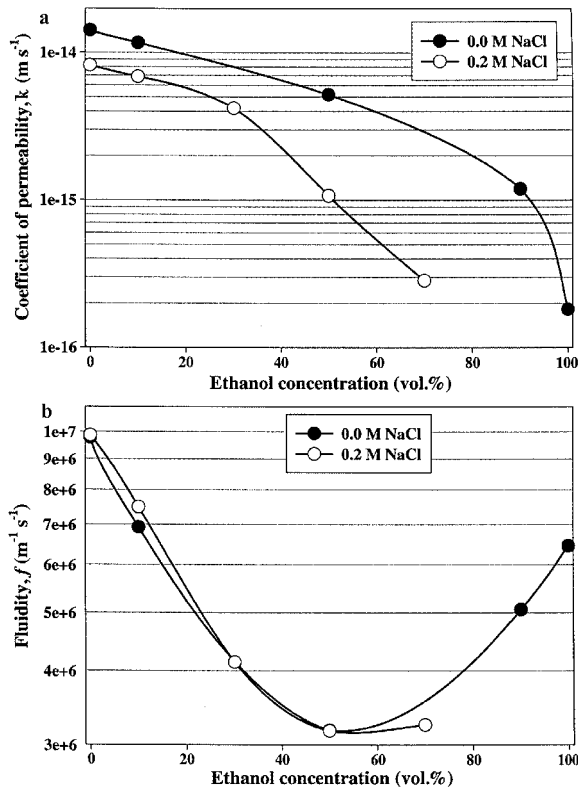
Figure 6. Experimentally determined values of (a) coefficient of permeability (equation 8) and (b) solution fluidity (equation 7) of BODMA bentonite (Miles, Queensland) as a function of ethanol concentration in ethanol-water solutions with, and without, 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.
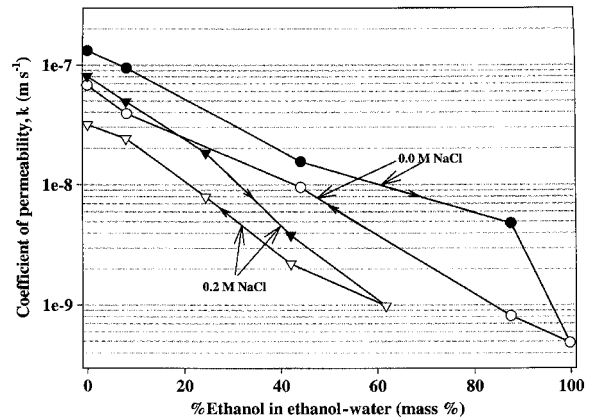

Figure 7. Hysteretic effect of changing permeant ethanol concentration on the coefficient of permeability through BODMA bentonite (Miles, Queensland) determined for ethanol-water solutions with, and without, 0.2 M NaCl. Tests were conducted at 15 kPa applied hydraulic pressure and 43 kPa overburden stress.

ences observed in the permeability of clay liners to various organic liquid solvents. The relative amounts of anisotropy or isotropy in clay swelling, under confinement, were determined experimentally by Michel *et al.* (2000) on a variety of clay-rich soils. For systems in which the bulk volume is constrained, crystalline swelling decreases permeability, while shrinking increases permeability. Thus, increasing the proportion of ethanol in aqueous solution resulted in several simultaneous changes in the organo clay, including increased sample volume with concomitant decreased particulate density, decreased void ratio, pore volume and equivalent pore radii, all of which are a direct result of the enhanced swelling of the organo clay in ethanol as compared to water, and which decrease the permeability of the material. In contrast, for systems in which the bulk volume is unconstrained and allowed to change, the proportion of the bulk volume change associated with crystalline shrink/swell processes dictates whether permeability is enhanced or diminished.

Possible consequences for permeable reactive barriers

The ability of organically modified clays to swell upon sorption and retention of organic compounds has

consequences for the permeability of that organo clay to aqueous solutions. It has been shown that swelling has predictable affects on the permeability of confined BODMA bentonites to mixtures of ethanol and water. Changing the ethanol concentration in the ethanol-water solutions, whether salt is present or not, simultaneously causes bulk (3-dimensional) swelling and expansion of the interlayer space (1-dimensional swelling) of the clay. The opposite effect is true as well: decreasing ethanol concentration in the aqueous solution causes a bulk shrinkage and a collapse of the interlayer space (to the extent possible) to occur simultaneously. How such shrinking or swelling effects the porosity of the material depends upon whether bulk or crystalline shrink/swell dominates. If bulk shrink/swell dominates, then, in the most extreme case, the porosity may be unaffected. Alternatively, if crystalline shrink/swell dominates with little or no bulk shrink/swell, then the porosity will be significantly decreased, resulting in lower porosity. This is the expected case for organo clay barriers, under significant overburden stress, when exposed to waters contaminated with hydrocarbons. It follows then, that engineering practices that maximize compaction during installation of organically modified bentonite barriers would result in a lower total porosity, and, therefore, a lower permeability when exposed to hydrocarbons.

The permeability of such barriers to waters containing low levels of hydrocarbons (*e.g.* BTEX compounds, solvents) is expected to be quite high initially, because swelling of the organo clay in water would be low. The organo clay, however, would readily preferentially sorb any hydrocarbon present thereby inhibiting their transport. Upon prolonged exposure to hydrocarbons, the organo clay would swell as it sorbs sufficient organic contaminants from water. Once swelling takes place under overburden pressures, the void volume is expected to decrease and the permeability of the barrier to the

contaminated water should decrease as demonstrated. The sorption and retention of poorly miscible contaminants, such as benzene, toluene, ethylbenzene and xylene (BTEX compounds), or pesticides (Singh *et al.*, 2003), are expected to result eventually in irreversible swelling and thus irreversibly decreased permeability of the organo clay.

The presence of soluble salts in ethanol-water solutions increases the ability of the organic contaminants to cause clay swelling, and thus decreases permeability to saline solutions. A similar effect can be expected for systems designed to treat saline waters contaminated with hydrocarbons, especially at low contaminant levels. In practical terms, the presence of dissolved salts is also expected to enhance the affinity of hydrocarbons with the organo clay.

CONCLUSIONS

Ethanol-water solutions were used to demonstrate the effect of solvent-induced swelling on the permeability of organically modified clay. Sorbed water and ethanol solutions in the interlayer were assumed to be part of the solid volume and were therefore included in the calculations of void ratio and porosity. Under an overburden pressure of 43 kPa (~2.5 m), increasing the ethanol concentration increased sample volume and decreased the pore volume, void ratio, porosity and permeability. The presence of 0.2 M NaCl enhanced the effect of ethanol, even under constraining conditions, thus pore volume, void ratio, porosity and permeability measured for solutions of 0.2 M NaCl in 70 vol.% ethanol were as low as those in 100 vol.% ethanol without salt.

Based on these results, the efficacy of permeable reactive barriers, composed of organically modified clays, can be modeled when exposed to solutions containing low levels of dissolved hydrocarbons. Extension of these studies to other solvent-water systems or to systems containing small amounts of poorly miscible organic compounds would be necessary to demonstrate further the generality of these findings.

ACKNOWLEDGMENTS

DEFINITIONS

A = cross-sectional area (cm^2)

e = void ratio = void volume/solid volume (dimensionless)

f = fluidity ($m^{-1} s^{-1}$)

g = acceleration due to gravity ($m s^{-1} s^{-1}$)

Δh = piezometric (hydraulic) head difference (m)

h_i = entrance hydraulic head (m)

h_e = exit hydraulic head (m)

k = coefficient of permeability or hydraulic conductivity ($m s^{-1}$)

K = intrinsic permeability (m^2)

L = path length (m)

ΔP = hydraulic pressure difference (kPa)

q_e = volumetric flow rate ($m^3 s^{-1}$)

r = equivalent pore radius (nm)

$V_{f\text{-tot}}$ = total free (bulk, 3-dimensional) swelling volume (cm^3)

$V_{s\text{-tot}}$ = average total volume of solids in porous medium (cm^3)

V_{sw} = crystalline (1-dimensional) swell volume; volume of swelling solids (cm^3)

ε = porosity (dimensionless)

η = viscosity (mPa s)

η_{solv} = solvent viscosity (mPa s)

ν = discharge velocity ($m^3 s^{-1}$)

ρ = particle or solids density ($g cm^{-3}$)

ρ_{ns} = density of non swelling solids ($g cm^{-3}$)

ρ_{solv} = density of solvent ($g cm^{-3}$)

ρ_{sw} = density of swelling solids ($g cm^{-3}$)

$\rho_{s\text{-tot}}$ = average density of all solids ($g cm^{-3}$)

Σ_v = vertical strain = change in sample thickness with respect to initial thickness (dimensionless)

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