

Compatibility of Bentonite and DNAPLs

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Abstract

The compatibility of dense nonaqueous phase liquids (DNAPLs), trichloroethylene (TCE), methylene chloride (MC), and creosote with commercially available sodium bentonite pellets was evaluated using stainless steel, double ring, falling head permeameters. The hydraulic conductivity (K) of the bentonite clay was measured under three experimental conditions: (1) water soluble constituents of the DNAPLs were used to hydrate and permeate the bentonite; (2) bentonite pellets were submersed in DNAPL prior to hydration and permeation with water; and (3) DNAPLs were pooled on water-hydrated bentonite. Further, the effect of hydraulic head (2.5, 145, and 710 cm) on water-hydrated bentonite permeated with TCE and the effects of TCE exposure time to mixtures of bentonite grout and sand were measured.

Solubility concentrations of DNAPL constituents did not effect the hydraulic conductivity of the bentonite pellets relative to baseline (water only) measurements; a competent hydraulic barrier was formed ($K < 5 \times 10^{-9}$ cm/s). Bentonite pellets submersed in DNAPLs retained their rigid shape, did not swell, and did not perform as a hydraulic barrier. However, when the DNAPL was removed and replaced with water, the DNAPL-wetted pellets imbibed water to swell and form an adequate hydraulic barrier ($K < 6 \times 10^{-9}$ cm/s). Competent hydraulic barriers constructed with bentonite pellets and hydrated with water were subsequently permeated with TCE, MC, or creosote DNAPLs developing desiccation cracks up to 5 mm wide. The intrinsic permeability of water-hydrated bentonite was 46 to 2640 times greater to DNAPLs relative to water, indicating that the desiccation cracks predominantly facilitated preferential DNAPL transport. The propagation rate of cracks was positively correlated to the hydraulic gradient, but the formation of cracks is chemically dependent on the contact time of DNAPL. Silica sand is expansively inert, yet 95, 90, 83, 75, and 50%

(wt sand/wt bentonite) mixtures with bentonite grout were insufficient to prevent desiccation cracks and hydraulic failure. The incompatibility between DNAPLs and bentonite observed in this study is important due to the numerous exploratory borings in DNAPL zones, the increasing dependency on hydraulic containment as a remedial alternative, and the fact that such remedial systems are often designed to be functional for many years.

Introduction

Bentonite clay has several environmental applications for hydraulic barriers. For example, bentonite can be used to construct slurry walls, annular seals in wells, liner and cap systems, and to backfill exploratory borings. Bentonite-based barriers are sometimes constructed at hazardous waste sites to separate DNAPLs from the surrounding ground water. However, DNAPLs and high concentrations of organic compounds may compromise the structural integrity of these systems and increase permeability (Anderson et al. 1985a; Mitchell and Madsen 1987; Abdul et al. 1990; Broderick and Daniel 1990; and Sai and Anderson 1992). Current guidelines for constructing wells (U.S. EPA 1992 and Aller et al. 1989) and slurry wall systems (Grube 1992) at hazardous waste sites may be inadequate with regard to deteriorating bentonite in the presence of DNAPLs.

The mechanisms by which DNAPLs effect the permeability of clay materials are related to the chemical and physical properties of the fluid used to hydrate the clay, the permeant fluid (i.e., DNAPL), and the clay. Two mechanisms—differential hydration and chemical desiccation—are affected by these properties. Differential hydration occurs while the clay is undergoing expansion (hydration) and results in unequal swelling by a clay mineral from the absorption of water relative to that by a different liquid, such as DNAPL, DNAPL/water mixtures, or water containing soluble-phase

organic compounds. Dry bentonite does not swell in non-polar DNAPLs (Graber and Mingelgrin 1994), and the swelling volume of clay decreases with an increasing concentration of organic compounds in water (Hettiaratchi and Hrudey 1987). Hydration of bentonite in the presence of either contaminated water or DNAPL may result in reduced or unequal swelling relative to bentonite hydrated with uncontaminated water. Under these conditions, zones of non- or poorly hydrated bentonite may result in a heterogeneous hydraulic barrier where its physical integrity is compromised.

Chemical desiccation occurs after the clay has initially expanded and involves the shrinkage of the soil fabric producing a similar affect as dehydration. For example, clays swell as water moves into the space between the mineral sheets, thereby forcing the layers apart. During dehydration, water is removed from the clay, the expansion process is reversed, and the clay volume decreases leaving cracks in the water-deficient clay. Similarly, organic chemicals (acetic acid, ethanolamine, heptane, methanol, and TCE) compress the diffuse double layer that surrounds clay particles, causing clay particles to flocculate, the soil fabric to shrink, and syneresis cracks to form (Mitchell and Madsen 1987; Broderick and Daniel 1990). Laboratory studies have observed the formation of syneresis cracks in the presence of xylene (Brown et al. 1986), TCE (Bowders 1985), methanol, acetone, and aniline (Anderson et al. 1985b). Hettiaratchi and Hrudey (1987) reported that high concentrations of water-miscible organic compounds (methanol and acetone) resulted in shrinkage close to that for the pure solvent. However, formation of syneresis cracks in clay material attributed to soluble-phase concentrations of polar organic compounds has not been reported.

The polarity of the permeant or a change in the dielectric constant (ϵ) of the permeant can affect the permeability of clay soils (Murray and Quirk 1982; Acar et al. 1985; Schramm et al. 1986; Brown and Thomas 1987). A lower dielectric constant in the liquid will reduce the repulsive force and the distance between two clay mineral plates. Consequently, interparticle (attractive) forces increase, flocculating conditions develop, shrinkage occurs, and ultimately cracks form (Hettiaratchi and Hrudey 1987). Chen et al. (1987) tested the effect of eight organic solutes on the dielectric constant of water and the swelling response of montmorillonite. They found that the effect was not consistent between organic solutes and, therefore, the dielectric constant of a solution is not the only control on swelling. Hettiaratchi and Hrudey (1987) reported that the shrinkage of montmorillonite soils was well explained by sorption characteristics and that the water-organic-clay interaction must be evaluated individually rather than depending solely on ϵ as a predictive indicator. Specifically, the competitive attraction of the exchange cations, water, and organic molecules to montmorillonite surfaces affects the size of the clay micelle and the net physio-chemical force between individual clay particles.

The compatibility between NAPLs and kaolinite or illite clays under compacted and optimum moisture con-

ditions has been evaluated. These evaluations are generally applicable to landfill liner materials and their compatibility with NAPLs. However, the influence of chemicals on the hydraulic conductivity (K) of high water content clays in slurry walls may be much greater than on lower water content compacted clays owing to the greater particle mobility and easier opportunity for fabric changes in the high water content system (Mitchell and Madsen 1987). Bentonite pellets and (grout) slurries commonly used to construct hydraulic barriers such as annular seals in wells and slurry walls have not been tested.

This study evaluated the compatibility between DNAPLs (TCE, MC, and creosote) and commercially available bentonite (pellets and grout) commonly used to construct hydraulic barriers. The dielectric constants for water, TCE, and MC (at 20°C) are 80.1 (Broderick and Daniel 1990), 3.42, and 9.14 (Lange 1985), respectively. The composition of creosote depends on the raw products and methods used during manufacture. The dielectric constant for creosote is assumed to be small (i.e., phenanthrene, 2.72; anthracene, 2.65; naphthalene, 2.54) (Chemical Rubber Co. 1996). The dielectric constants of these DNAPLs represent a significant departure from water and indicate their potential for incompatibility with an expansive clay. Since these DNAPLs are commonly found at hazardous waste sites and bentonite is commonly used to hydraulically isolate this type of waste, this study was undertaken to evaluate the potential limitations of bentonite as a hydraulic barrier in the presence of DNAPLs. Compatibility was evaluated via permeability changes in stainless steel double ring falling head permeameters and by visual observation of the bentonite material when DNAPL was present.

The different experimental conditions under which the hydraulic conductivity of bentonite was measured were: (1) water-soluble constituents of the DNAPLs were used to hydrate and permeate bentonite pellets; (2) dry pellets were submersed in DNAPL prior to water hydration and permeation; and (3) DNAPLs were pooled on water-hydrated bentonite. These conditions were intended to represent the following respective scenarios in which: (1) bentonite barriers are constructed in the presence of aqueous solutions of DNAPL constituents; (2) bentonite barriers are constructed in DNAPL-contaminated areas; and (3) a competent, water-hydrated bentonite barrier is exposed to DNAPLs. The expansion/shrinkage characteristic of clay results in its vulnerability to chemical desiccation and differential hydration. Since silica sand is expansively inert and more conductive than bentonite clay, it was postulated that mixtures of sand and bentonite would compromise hydraulic conductivity yet reduce the overall shrink/swell potential. In an effort to minimize chemical incompatibility, the hydraulic conductivity of TCE in mixtures of silica sand and bentonite grout was measured. The effect of hydraulic head and exposure time on DNAPL compatibility was evaluated by pooling TCE on water-hydrated bentonite barriers with 2.5 cm (1 inch), 145 cm (4.75 feet), and 710 cm (23.3 feet) of hydraulic pressure.

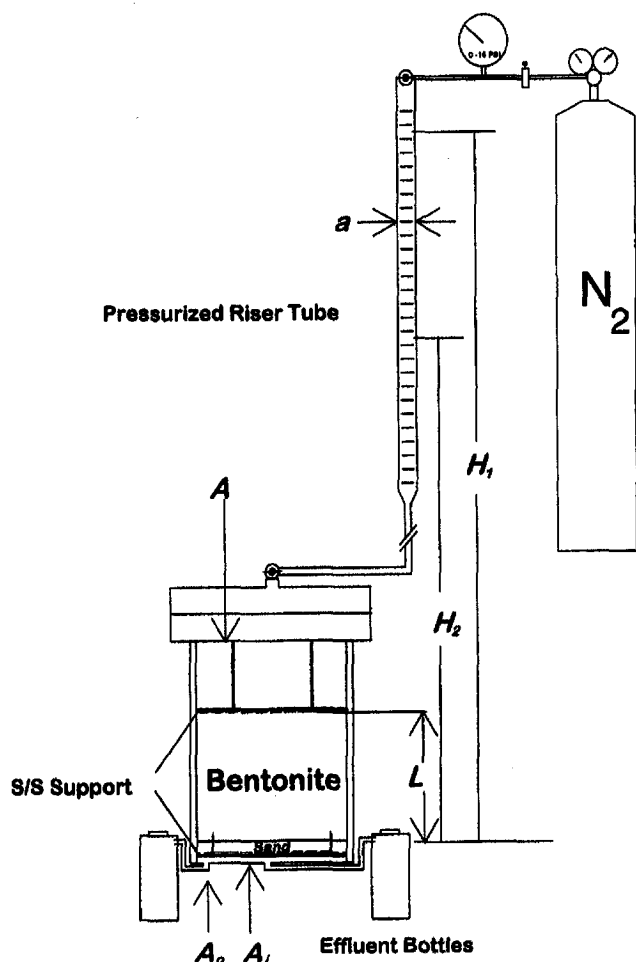


Figure 1. Schematic of pressurized, falling head permeameter; V_{effo} , V_{effi} volume of effluent in outer and inner rings (mL); A_o , A_i cross-sectional area of outer and inner rings (cm^2); A total cross-sectional area of permeameter (cm^2); a cross-sectional area of riser tube (cm^2); H_1 , H_2 initial and final height of water in riser tube.

Projections of bench-scale results to actual field conditions are beyond the objectives of this investigation, which was limited to the proof-of-concept determination of whether incompatibility exists between DNAPLs and bentonite.

Method and Materials

Bentonite pellets (1/4-inch diameter) from Baroid Drilling Fluids Inc., Houston, Texas, were composed of 85% sodium montmorillonite, 5% quartz, 5% feldspar, 2% cristobalite, 2% illite, and 1% gypsum. The specific gravity is 2.5 to 2.6 with a compacted dry bulk density of 1.17 g/cm^3 and 8% moisture content by weight. This manufactured product was selected because of its availability and its similarity to other commercial bentonite products. Water used in this study consisted of a 0.01 N CaSO_4 solution and represents the ionic strength of natural water (Shackelford 1994).

MC and TCE were liquid chromatography grade solvents (Fisher Scientific). Coal tar-based creosote was obtained from the Mississippi Forest Products Laboratory (Mississippi State). The creosote composition,

described in Davis (1993), includes 21% phenanthrene, 10% fluoranthene, 10% fluorene-related compounds, 9% acenaphthene, 9% pyrene, and unknown hydrocarbons. Soluble concentrations of DNAPL constituents were prepared by mixing water (0.01 N CaSO_4) with an excess of DNAPL in a closed flask (20°C) for seven days. Water soluble constituents of MC and TCE were measured by analyzing headspace concentrations with a gas chromatographer/mass spectrometer (GC/MS) using a Saturn II ion trap detector. Water soluble constituents of creosote were extracted (U.S. EPA method 3510) and analyzed using GC/MS analysis (U.S. EPA method 8270A).

Hydraulic conductivity measurements were made using stainless steel, pressurized, falling head permeameters with a combined water head (145 cm) and N_2 gas pressure (8.0 psi) equal to approximately 710 cm (23 feet) of water on the bentonite barrier (Figure 1). Measurements involved placing bentonite pellets into the permeameter containing the hydration solution to swell without confinement for 48 hours. An excess amount of hydration solution was applied to the bottom and top of the permeameter during the 48 hours, after which the top of the bentonite was trimmed and confined against further swelling using a rigid stainless steel screen placed on top of the bentonite. Prior to pooling DNAPL, water permeated the bentonite until the hydraulic conductivity stabilized. Compatibility testing involved different experimental conditions: (1) a solution of water soluble constituents of the DNAPLs were used to hydrate and permeate bentonite pellets; (2) pellets were submersed in DNAPL for 24 hours, drained, placed in the permeameter, and hydrated and permeated with water; and (3) 360 mL of DNAPL was pooled on water-hydrated barriers after a stable hydraulic conductivity measurement with water was achieved. The influence of hydraulic head on DNAPL-bentonite compatibility was evaluated using replicate permeameters with TCE pooled on top of water-hydrated bentonite and exposed to 2.5, 145, and 710 cm of hydraulic head. The effect of long-term DNAPL exposure was evaluated by pooling TCE as described previously for 162 days at hydrostatic pressure (2.5 cm of TCE), then performing the permeability test with 710 cm of hydraulic head. Barriers of #60 silica sand (Cisco) and AquaGuardTM bentonite grout (Baroid Inc.) were pre-mixed (wt/wt mixtures, 95%, 90%, 83%, 75%, and 50%) and allowed to equilibrate with water in the permeameter for 48 hours prior to permeating with water at 710 cm of head. TCE was pooled on the sand/bentonite barrier after the hydraulic conductivity measurements stabilized.

The hydrated bentonite was 10.2 cm (4 inches) thick and approximately 12.4 cm (4.75 inches) in diameter. The area of the inner and outer rings were approximately equal, 59 and 52 cm^2 , respectively. Permeameters were filled with the permeant solution and connected to a water-filled, pressurized riser tube. Periodic measurements were taken by weighing the effluent bottles and measuring the height of water in the riser tube. Methods for the falling head permeameter experiments followed the standard methods described by Klute and Dirksen

Table 1
Experimental Conditions and Results of Permeability Measurements

Hydration Fluid	Permeant Fluid	Average Hydraulic Conductivity (K) ($\times 10^{-9}$ cm/s)	Average Intrinsic Permeability (k) ($\times 10^{-6}$ darcy)	Number of Experiments
Baseline				
Water ¹	Water ¹	2.75	2.80	4
Hydrated and Permeated with Soluble Constituents of DNAPLs				
TCE/Water ²	TCE/Water ²	4.95	5.05	2
MC/Water ²	MC/Water ²	2.25	2.30	2
Creosote/Water ²	Creosote/Water ²	2.35	2.40	2
DNAPL-Wet. Hydrated and Permeated with Water				
TCE	Water ¹	3.25	3.31	2
MC	Water ¹	2.80	2.85	2
Creosote	Water ¹	5.25	5.30	2
Water Hydrated, Permeated with DNAPL				
Water ¹	TCE	414	161	3
Water ¹	MC	398	130	2
Water ¹	Creosote	475	7390	1

¹Standard water 0.01 N CaSO₄.

²Solubility concentrations in water.

(1986) and those described for double ring permeameters by Daniel (1994). All reported values of hydraulic conductivity are the weighted average hydraulic conductivity calculated separately from the inner ring and outer ring effluent measurements for the last three measurements (Table 1). Intrinsic permeability (k) can be used to compare the properties of bentonite permeated with dissimilar fluids (i.e., water and DNAPL). Intrinsic permeability (k) can be related to hydraulic conductivity using the following equation:

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

where:

k = intrinsic permeability (darcy, 9.87×10^{-9} cm²)
K = weighted average hydraulic conductivity (cm/s)
μ = fluid dynamic viscosity (centipoise)
ρ = fluid density (g/cm³)
g = gravity (9.81 m/s²).

The values of density and dynamic viscosity used in calculations for water, TCE, MC, and creosote are 0.997, 1.462, 1.325, and 1.1 g/cm³ and 1.0, 0.57, 0.43, and 17.0 centipoise, respectively.

Results

Four replicate baseline experiments with water-hydrated bentonite pellets resulted in an average hydraulic conductivity of 2.7×10^{-9} cm/s (95% confidence interval [CI] 2.2×10^{-9} - 3.2×10^{-9} cm/s) and an average intrinsic permeability of 2.8×10^{-6} darcy (95% CI

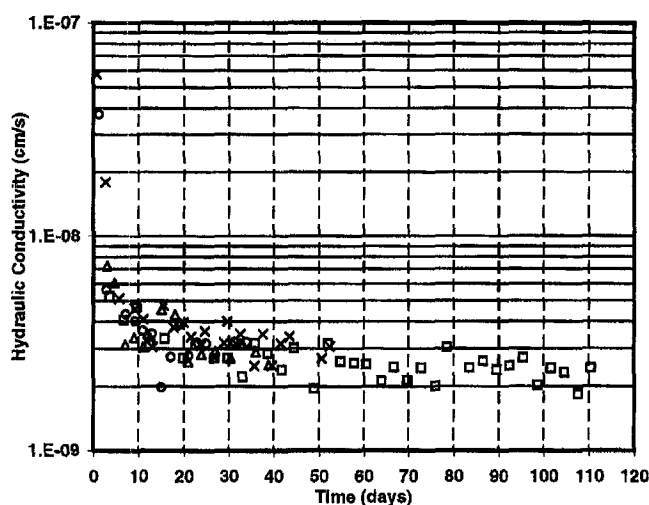


Figure 2. Baseline hydraulic conductivity of bentonite pellets hydrated with water (0.01 N CaSO₄). The average hydraulic conductivity was 2.68×10^{-9} cm/s (95% confidence interval 2.2×10^{-9} - 3.2×10^{-9} cm/s, n = 4).

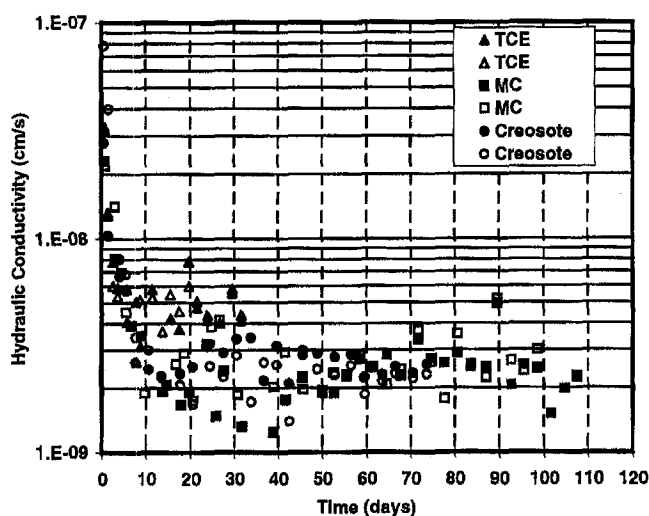


Figure 3. Hydraulic conductivity of bentonite pellets hydrated and permeated with water containing 0.01 N CaSO₄ and solubility concentrations of TCE, MC, or creosote.

2.2×10^{-6} - 3.4×10^{-6} darcy) (Table 1 and Figure 2). The solids content (by weight) of the water-hydrated barriers averaged 41.5% over the top 1.5 cm, 50% for the 1.5 to 3.5 cm interval, and 56% for the 3.5 to 10 cm interval. The weighted average solids content was 52%. The increasing density with depth was due to bentonite confinement at the bottom and on the sides of the permeameter during the initial hydration period.

Permeability of Water Containing Soluble Concentrations of TCE, MC, and Creosote

The average (supersaturated) concentrations (n=2) of TCE and MC in water were 1190 mg/L and 19,550 mg/L, respectively. The average concentrations (n=2) of the soluble constituents of creosote were phenanthrene (46.3 mg/L), acenaphthene (30 mg/L), naphthalene (30 mg/L), fluoranthene (28.2 mg/L), and fluorene (27.6 mg/L). There were other unidentified hydrocarbons

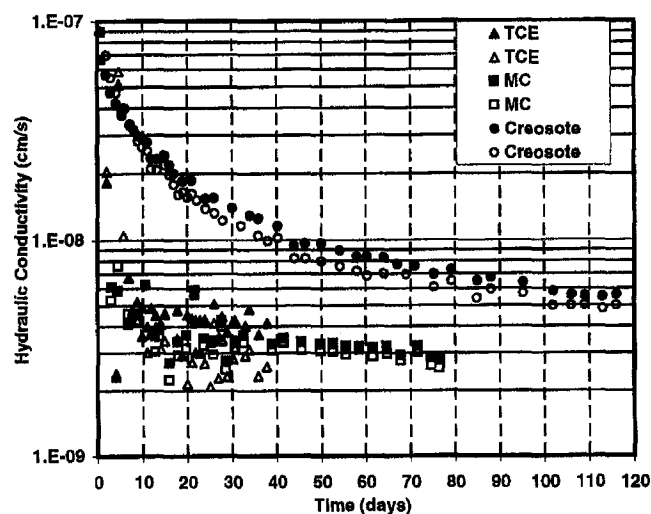


Figure 4. Hydraulic conductivity of bentonite pellets initially saturated with TCE, MC, or creosote, and subsequently hydrated and permeated with water containing 0.01 N CaSO_4 .

present in the solution. Bentonite pellets were hydrated and permeated with water contaminated with soluble constituents of TCE, MC, and creosote (Table 1 and Figure 3). The hydraulic conductivity and intrinsic permeability of MC- and creosote-contaminated water were within the 95% CI of the baseline K. The hydraulic conductivity of TCE-contaminated water was greater than the 95% CI of the baseline K. Tests for replicate permeameters involving TCE, MC, and creosote were conducted for 32, 107, and 74 days, respectively. Since K decreased (asymptotically) with time in all experiments, it is reasonable that K of TCE-contaminated water would have decreased further and converged with values observed for MC and creosote (Figure 3). These data indicate that soluble component(s) of DNAPLs in solution had no significant effect on the hydraulic conductivity of bentonite.

DNAPL-Immersed Bentonite Pellets and Subsequent Water Hydration/Permeation

TCE, MC, and creosote inhibited swelling of the bentonite pellets which retained their rigid shape while immersed in the DNAPL. Permeability tests were conducted in which bentonite pellets were placed in permeameters containing TCE. The bentonite did not swell, causing unrestricted flow of TCE from the permeameters when the effluent valve was opened. In subsequent tests, bentonite pellets immersed in DNAPL were drained and placed in water-filled permeameters. The water permeated the pellets as indicated by the hydration and swelling of the bentonite. The hydraulic conductivity of MC and TCE was at or within the 95% CI of the baseline, indicating a competent hydraulic barrier (2.5×10^{-9} to 3.5×10^{-9} cm/s) (Table 1 and Figure 4). A downward trend in K for creosote was observed when the test was terminated. Although k and K for creosote were approximately two times greater than baseline, a competent hydraulic barrier was formed (5.3×10^{-9} cm/s) (Table 1).

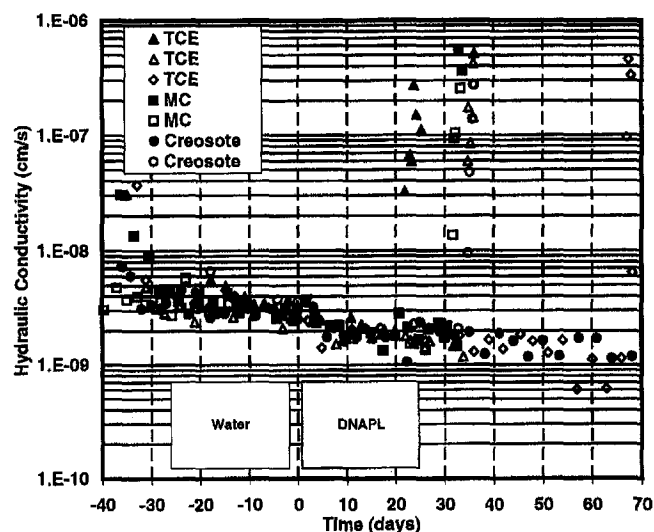


Figure 5. Hydraulic conductivity of bentonite pellets hydrated with water containing 0.01 N CaSO_4 and permeated with TCE, MC, or creosote DNAPL.

Cores removed from each of the permeameters had visible DNAPL zones indicated by changes in the clay texture. For example, where DNAPL was present in the hydrated bentonite core, the bentonite retained the grainy texture of an unhydrated pellet. This suggests that barriers constructed by hydrating bentonite pellets in the presence of DNAPL may form discrete zones where DNAPL remains after the bentonite pellets swell.

Water-Hydrated Bentonite Permeated with DNAPL

Prior to pooling the DNAPL, water permeated the hydrated bentonite until the hydraulic conductivity stabilized ($< 3 \times 10^{-9}$ cm/s), which required 24 to 53 days (Figure 5). The hydraulic conductivity trended downward with time similar to the baseline experiments until dramatic breakthrough of the DNAPL occurred. Breakthrough of TCE occurred 22, 35, and 67 days after the initial pooling of TCE in three replicate permeameters. Breakthrough of MC occurred 32 and 33 days after the initial pooling of MC in two replicate permeameters. Breakthrough of creosote occurred 35 days after pooling creosote in only one of two replicate permeameters. Breakthrough of creosote in the second permeameter had not occurred at 150 days when the permeameter was dismantled.

The volume of influent to the permeameter between the time when TCE was initially pooled and when breakthrough occurred was used to calculate the fraction of pore volume (F_{PV}) occupied by TCE when TCE breakthrough occurred, i.e., influent volume/pore volume. Based on coring and oven drying results, the porosity (weighted average over four discrete depths) and pore volume were estimated to be 0.63 and 773 mL, respectively. In the three replicate permeameters, F_{PV} was estimated as 0.024, 0.033, and 0.060. These values clearly indicate that deterioration of the bentonite by TCE facilitated the preferential TCE transport rather than Darcian flow.

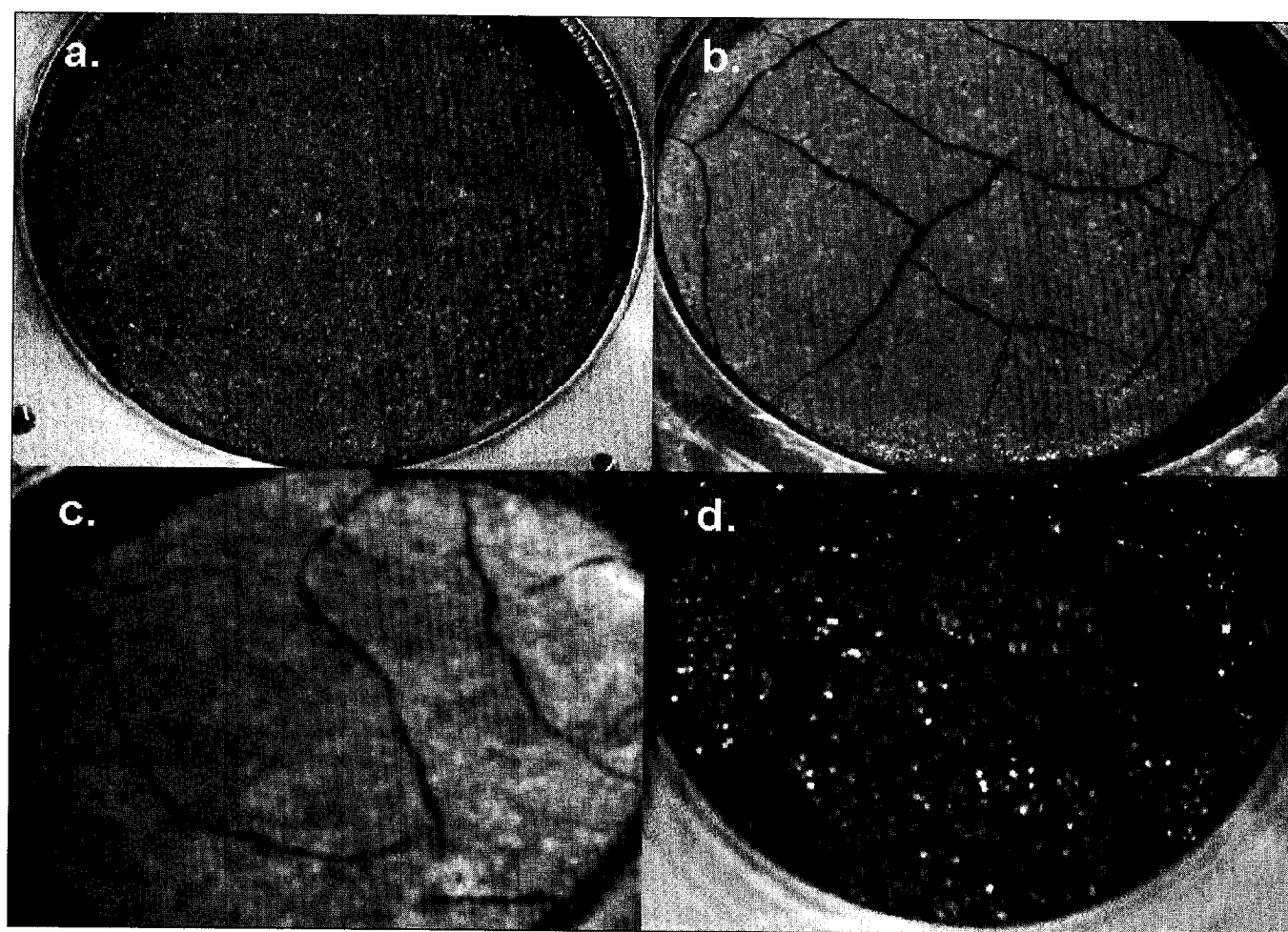


Figure 6. Photographs of water-hydrated bentonite and the associated desiccation cracks attributed to DNAPL. The bentonite hydraulic barriers were permeated with: (a) water; (b) TCE; (c) MC; and (d) creosote.

Sudden breakthrough of the DNAPLs indicated a large increase in hydraulic conductivity and a significant compromise in the physical integrity of the bentonite hydraulic barrier. The average intrinsic permeability of TCE, MC, and creosote was 57, 46, and 2640 times greater than baseline values, respectively (Table 1). The permeability measurements during breakthrough periods were dependent on the volume of DNAPL placed in the permeameter. For example, during breakthrough, DNAPL passed through the permeameter and was replaced by the water from the riser tube (Figure 1). As water replaced the DNAPL in the desiccation cracks, the bentonite rehydrated and swelled, reducing the permeability to the pre-breakthrough value (Figure 5). Assuming the permeameters had been designed with a large reservoir of DNAPL, the final permeability measurement would have been greater. Therefore, values (k , K) reported in Table 1 represent minimum values, and would have increased assuming a larger volume of DNAPL was present.

Upon completion of compatibility testing, the permeameters were dismantled and the bentonite was photographed and excavated. A network of desiccation cracks developed in the bentonite (Figure 6). Some crack apertures measured more than 5 mm. Desiccation cracks

were largest at the top of the barrier and decreased with depth. Although cracks formed at the stainless steel/bentonite interface, they did not appear to be preferentially located; some of the largest cracks formed through the middle of the barrier. Vertical cracks that began at the surface intersected with other near horizontal cracks that appeared to connect to other vertical cracks below. The permeameter containing creosote, which did not break through, developed similar desiccation cracks as the permeameter in which breakthrough did occur, and creosote-contaminated water eluted from the permeameter within 41 days. In the replicate creosote permeameter, black stains were observed at or near the surface of the desiccation cracks, but not in between the cracks, indicating that creosote transport was limited to the network of cracks and did not move through the clay matrix.

Hydraulic Head Effect on Permeability

TCE eluted through three permeameters containing water-hydrated bentonite barriers with 710 cm of total head. However, breakthrough did not occur in replicate permeameters under 145 cm and 2.5 cm of total head. Desiccation cracking was observed in all barriers (Figure 7). Visible cracks formed in less than one week at 710 cm total head, approximately one month at 145 cm of

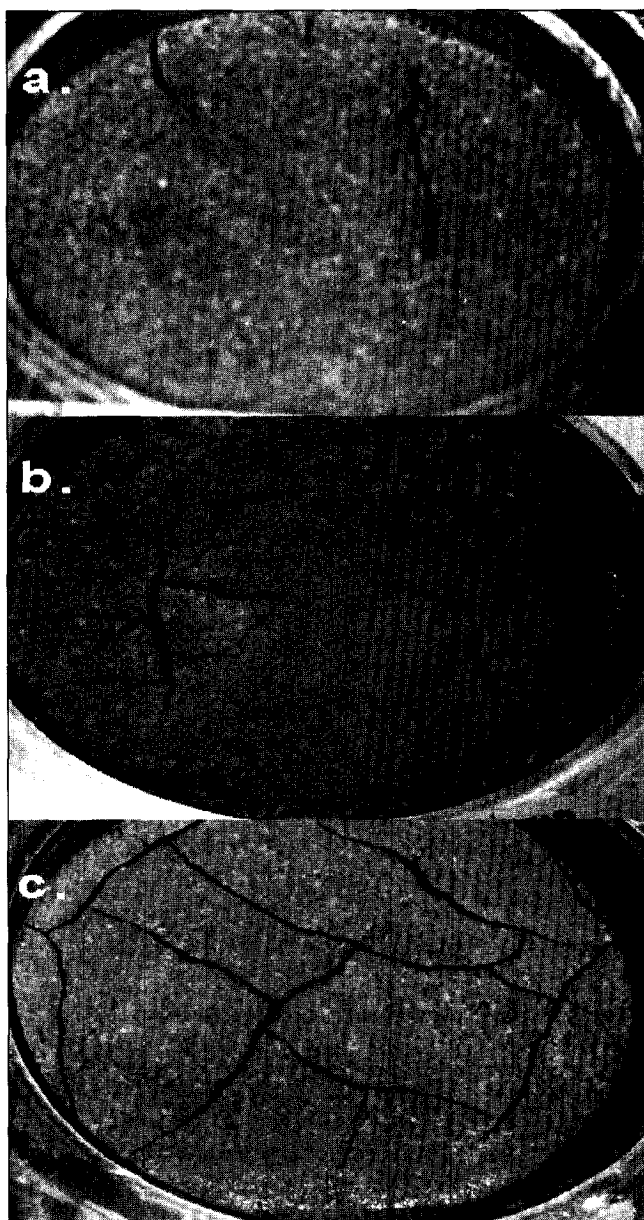


Figure 7. Photographs of water-hydrated bentonite and desiccation cracks attributed to TCE under: (a) 2.5 cm; (b) 145 cm; and (c) 710 cm of hydraulic pressure.

total head, and in three months under hydrostatic conditions (2.5 cm head), indicating that the rate of desiccation crack propagation was positively correlated with pressure. However, formation of desiccation cracks under hydrostatic conditions indicates that processes initiating chemical desiccation are not dependent on hydraulic pressure.

Prolonged Exposure to TCE Effect on Permeability

One bentonite barrier constructed and permeated with water was exposed to a 2.5 cm pool of TCE under hydrostatic conditions for 162 days prior to TCE-permeability testing under 710 cm of head. TCE eluted from the permeameter in 12 days, which was two to five times faster than TCE breakthrough in three water-hydrated bentonite barriers without prior TCE expo-

sure (22, 35, and 67 days). These data confirm the chemical dependency of incompatibility that indicates prolonged exposure of TCE to water-hydrated bentonite diminishes the structural integrity of the barrier.

TCE Permeability of Bentonite Grout and Sand Mixtures

The hydraulic conductivity of water to silica sand and bentonite grout mixtures of 90% and 95% sand (1.8×10^{-5} and 1×10^{-4} cm/s, respectively) exceeded the desired hydraulic conductivity for barriers (1×10^{-7} cm/s). Mixtures of 83%, 75%, and 50% sand and bentonite permeated with water at 710 cm of total head resulted in hydraulic conductivity measurements of 7.5×10^{-8} , 2.0×10^{-8} , and 1.7×10^{-8} cm/s, respectively. TCE was subsequently pooled on water-hydrated bentonite seal as previously described. TCE breakthrough occurred in replicate 83% sand/bentonite barriers in less than one day. TCE transport occurred along the sides of the stainless steel/grout sidewall interface, indicating preferential flow that was not observed with water. TCE breakthrough occurred in replicate 75% sand/bentonite barriers in two and 10 days, respectively. Similar transport in preferential pathways was also observed along the sidewall interface and desiccation cracks were observed in the bentonite. TCE breakthrough occurred within 29 days in the 50% sand/bentonite barrier. A network of desiccation cracks was observed deep within the bentonite and no indication of preferential pathways along the sidewall interface was observed. These results indicate that the addition of expansively inert sand to bentonite decreases the resistance to water flow and the bentonite remains vulnerable to chemical incompatibility mechanisms.

Discussion

The hydraulic conductivity of bentonite pellets hydrated and permeated with uncontaminated water was similar to the manufacturer's specifications and below the generally accepted hydraulic conductivity (1×10^{-7} cm/s) for hydraulic barriers. These results agree with other reported values using similar materials (Edil et al. 1992 and Lutenegeger and DeGroot 1994). Solubility concentrations of TCE, MC, and creosote constituents did not significantly affect the hydraulic conductivity of the bentonite over the duration of the test. Although the swelling response was not measured, measurements indicate that if any reduction in swelling did occur, it did not significantly affect the hydraulic conductivity. These results also indicate that a bentonite-based hydraulic barrier constructed under non-DNAPL conditions, yet heavily contaminated, would result in a competent hydraulic barrier.

TCE, MC, and creosote DNAPLs inhibited the swelling of bentonite pellets. DNAPL-wetted bentonite pellets may behave as a preferential pathway that facilitates the transport of DNAPL. It is recommended that conditions in which the direct placement of bentonite pellets into DNAPL be avoided. DNAPL-wetted bentonite pellets that subsequently contact water also imbibe the

water, hydrate, swell, and form an adequate hydraulic barrier ($< 6 \times 10^{-9}$ cm/s). Although visual inspection of bentonite under these experimental conditions indicated the formation of discontinuous pockets of unhydrated bentonite (due to discrete zones of DNAPL), the hydraulic integrity of the barrier was maintained. However, trapped DNAPLs in a water-hydrated barrier may be a long-term source of dissolved phase contaminants.

Water-hydrated, competent bentonite barriers impacted by pooling DNAPLs resulted in hydraulic failures. The intrinsic permeability of these barriers were 46 to 2640 times greater with DNAPLs than with water. All barriers developed large desiccation cracks, indicating incompatibility with TCE, MC, and creosote. Under such conditions, the hydraulic conductivity depends on flow through preferential pathways. On a large scale, there may be microfabric that contains cracks, fissures, root holes, laminations, etc., where the flow rate is so great as to totally obscure flow through the other pore space types (Mitchell and Madsen 1987). Correspondingly, the network of desiccation cracks in DNAPL-impacted bentonite barriers could ultimately lead to a hydraulic failure. Unfortunately, hydraulic failure attributed to DNAPL-clay incompatibility would most likely occur in source areas where the greatest contamination exists and where hydraulic containment is generally mostly desired.

Increasing the hydraulic pressure of TCE on bentonite increased the rate of desiccation crack propagation and decreased the time to hydraulic failure. The influence of hydraulic head on the transport of TCE into previously unaffected areas, and its subsequent deterioration of the bentonite barrier, provides the physical basis for the correlation. While the gradient used in laboratory testing devices does not accurately reflect field conditions, the results illustrate the incompatibility between DNAPL and bentonite clay. Two observations were made indicating that chemical compatibility is not wholly dependent on hydraulic pressure. First, desiccation cracks formed in bentonite with 2.5 cm of pooled TCE at hydrostatic conditions in a few months. Second, bentonite in extended contact (162 days) with TCE (hydrostatic conditions) broke through two to five times faster than continuously pressurized permeameters. This suggests that the mere presence of DNAPLs will deteriorate bentonite barriers and lead to hydraulic failure.

An increase in the silica sand content of the bentonite barrier increased the hydraulic conductivity but did not eliminate deterioration of bentonite by DNAPL. The incompatibility between DNAPLs and bentonite observed in this study is important due to the numerous exploratory borings in DNAPL zones which are commonly backfilled with bentonite, the increasing dependency on hydraulic containment as a remedial alternative, and the fact that construction of such remedial systems is often designed to be functional for many years. Additional research is warranted to mitigate DNAPL-induced mechanisms which result in the formation of preferential pathways in bentonite-based hydraulic barriers.

Conclusions

Bentonite pellets hydrated and permeated with water at solubility concentrations of TCE, MC, and creosote resulted in competent hydraulic barriers since the measured hydraulic conductivity was similar to baseline measurements using uncontaminated water. Bentonite pellets do not swell in the presence of DNAPL. However, when subsequently exposed to water, the DNAPL-wetted pellets imbibe water and hydrate and swell, forming a hydraulically competent barrier. Competent hydraulic barriers constructed with bentonite pellets and water physically deteriorate when in contact with liquid TCE, MC, and creosote. This results in the formation of desiccation cracks which lead to a significant increase in the hydraulic conductivity. In theory, DNAPLs generally have a lower dielectric constant than water, which reduces both the repulsive force and distance between clay particles leading to flocculating conditions, clay shrinkage, and the formation of desiccation cracks. The rate of desiccation crack propagation was positively correlated to the hydraulic gradient, but their formation was chemically dependent on the presence and contact time of DNAPL. The transport of DNAPL through a water-hydrated bentonite barrier is not limited to multiphase Darcian flow through porous media. Rather, the network of cracks facilitated the rapid, non-Darcian preferential flow of DNAPL through the clay. The addition of expansively inert silica sand to bentonite increased the hydraulic conductivity and did not mitigate the formation of desiccation cracks.

Disclaimer

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