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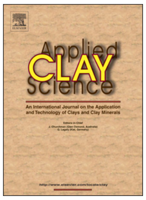

Research paper

Advection and retardation of non-polar contaminants in compacted clay barrier material with organoclay amendment

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ABSTRACT

Compacted clay liners (CCLs) are widely used as hydraulic barriers in landfills, underground storage tanks, vertical cutoff walls and surface impoundments. Most commonly, the breakthrough of contaminant flows in CCLs takes a long time due to the reduced advection rate; however, the attenuation of non-polar fluid or organic contaminants in CCLs is relatively low because of the non-reactive nature of most CCL materials. Surfactant-modified bentonites are promising barrier amendments as they are coated with organic surfactant and are capable of uptaking the non-polar species from the aqueous phase. In this study, laboratory tests were carried out to evaluate the swelling, permeability and contaminant retention of compacted silty clay amended with an organoclay (hexadecyltrimethylammonium (HDTMA) modified bentonite) against both gasoline and organic solution. The swelling properties and the hydraulic conductivities of compacted soils with varying liquids were evaluated and the transport of naphthalene, a representative of polycyclic aromatic hydrocarbons (PAHs) and a possible component of NAPLs, in organobentonite-amended silty clay was examined through batch sorption and column tests. The results indicated that the addition of 10% HDTMA bentonite to compacted silty clay slightly increased the permeability of the mixture to water. However, higher swelling tendency and lower permeability to gasoline were also observed. With 5% of HDTMA bentonite amendment, the compacted silty clay soil had a much stronger retardation capacity for naphthalene.

1. Introduction

Organic pollutants such as petroleum-related products and non-aqueous-phase liquids (NAPLs) pose serious risks to the public health and ecosystems (Fels, 1999; Pawełczyk et al., 2016). Polycyclic aromatic hydrocarbons (PAHs) and fuels are common organic pollutants in the subsurface due to inappropriate waste disposal practices, gas station operations and industrial activities (Samanta et al., 2002). Most commonly, geosynthetics and engineered earthen materials are used in liner barriers to reduce advection and the mass transport of the contaminant flow. The low hydraulic conductivities, reliable performance and low cost of compacted clay liners (CCLs) (Boynton and Daniel, 1985; Rowe et al., 2004) make CCLs ideal in applications for engineered barriers. Typically, the advection rate in CCLs is so low that the molecular diffusion governs the contaminant migration (Shackelford, 2014). However, previous field applications raised several concerns regarding the chemical compatibility between CCL soils and certain contaminants: (1) pure phase organic compounds or petroleum-related products can cause the soil to shrink and crack with an increase in hydraulic conductivity (Broderick and Daniel, 1990; Fernandez and Quigley, 1985; Bowders and Daniel, 1987; Hamdi and Srasra, 2013; Lake and Rowe, 2005), and (2) the mass flux of contaminants can be significant even if the flow rate is low due to the non-interactive nature of conventional clay and clay-type materials used in CCLs (Brown and Burris, 1996; Bright et al., 2000; Francisca and Glatstein, 2010). This is of significant concern where low concentration of organic pollutants in the groundwater can cause problems in the long term (Ma et al., 2015). Therefore, improvement of the barrier performance of CCLs against certain contaminant flows still merits further examination.

For CCLs with non-interactive components against the contaminants, mass transport is controlled by advection-dispersion because no chemical or biochemical reactions reduce the contaminant concentration in the pore volumes (Shackelford, 1994; Lu et al., 2010; Francisca and Glatstein, 2010; Du et al., 2009). Recently, a “new” concept of an active material amended low permeability-reactive barrier, in which the soil matrix or soil amendments in the barrier are capable

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of uptaking, immobilizing and/or degrading the pollutants actively while maintaining a satisfactory hydraulic performance (Wagner et al., 1994; Crocker et al., 1995; Lo and Yang, 2001), was proposed (Wiles et al., 2005; Lo et al., 1997; Bartelt-Hunt et al., 2005; Lu et al., 2015). The reduced release rate of the contaminant mass due to contaminant/soil reactions is commonly referred to as retardation and a retardation factor (R) (Freez and Cherry, 1979) is typically used to quantify the pace of the slow release. It is important to note that the flow rate does impact the apparent or measured retardation factor significantly. Shackelford (1994) demonstrated that for fast flow rate scenarios, the retardation factor could be estimated from the distribution coefficient (or partitioning coefficient, K_d). However, the application of the same equation tends to yield an overestimated retardation factor for low flow rate scenarios (Peclet number < 1) (Shackelford, 1994). Nonetheless, the mass flux through the porous media is significantly reduced if a reactive soil amendment is present and the retarded transport of contaminants occurs (Gullick and Weber, 2001; Varank et al., 2011a, 2011b).

Many different types of natural or engineered materials have been suggested as clay liner amendments to both enhance the reactivity of the liners and provide low hydraulic conductivity (LaGrega et al., 1994; Bartelt-Hunt et al., 2005). Most commonly, fly ash, zeolite, organo-zeolite, coated sand and organoclays have been suggested as potential reactive amendments to enhance the effectiveness of CCLs (Lo and Liljestrand, 1996; Prasad et al., 2012; Varank et al., 2011a, 2011b; Younus and Sreedeep, 2012). Among the suggested additives, organoclays have been proven to be effective sorbents for organic pollutants (Benson et al., 2015; De Paiva et al., 2008; Gates et al., 2004; Soule and Burns, 2001). Organoclays are aluminosilicates/organic surfactant hybrids that have high organophilic phase to uptake nonpolar or low-polarity species from aqueous phase. When in contact with organic liquids, organoclays exhibit low conductivity, high swelling tendency and high plasticity. The organic surfactants in organoclays provide partitioning media to the organic molecules in the interlayer spaces (Lee et al., 2012; Zhao and Burns, 2012). Consequently, organoclays can be used as a secondary compound liner barrier in industrial activities such as petroleum sewage refinement and the treatment of waste water due to their ability to bind with organic compounds (De Paiva et al., 2008; Lo and Yang, 2001; Seung and Tiwari, 2012).

Previous studies show that organoclay amendments may improve the efficiency of the clay barrier when facing organic liquids or petroleum products (Lo and Yang, 2001; Moon et al., 2007; Smith et al., 2003; Yang and Lo, 2004). The permeability of organoclays for gasoline was demonstrated to decrease two to four orders of magnitude compared to that for water (Smith et al., 2003; Moon et al., 2007). Although organoclays may have higher permeability for water, their impact on the overall conductivities of compacted soils might be negligible due to low dosage (Yang and Lo, 2004; Ghavami et al., 2016). Additionally, the beneficial attenuation capability of non-polar species in the soil may be greatly enhanced by the organoclay additives (Seliem et al., 2011; Liu et al., 2014; Li and Denham, 2000). This is because engineered organoclays, especially engineered organophilic clays, are extremely effective in terms of sorbing low or non-polar organics, chlorinated organics, polycyclic hydrocarbons and pesticides from aqueous phase (Boyd et al., 1988; Jaynes and Boyd, 1990, 1991; Larsen et al., 1992; Montgomery et al., 1991; Owabor et al., 2010; Qu et al., 2008; Smith et al., 1990; Katsumi et al., 2008; Seung and Tiwari, 2012; Zhu et al., 2015). The sorption of organic contaminants onto organo-carbon rich clays (organophilic clays), whose distribution coefficients can be hundreds of thousands of times higher than those of non-sorptive soils, is typically through partitioning (Redding et al., 2002; Nzengung, 1996; Shu et al., 2010). In addition, kinetic studies of hydrophobic organic materials (e.g. naphthalene and diuron) sorption onto organoclays reveal that sorption happened very fast and sorption equilibrium was often reached when the flow rate was low (Nzengung et al., 1997). Extensive laboratory column tests were conducted to assess the barrier performance of conventional CCLs against contaminants and to derive transport parameters (Acar and Haider, 1990; Crooks and Quigley, 1984). However, relatively few studies explored the applicability of using organoclays as CCL amendment for waste containment and pollutant attenuation (Lo and Mak, 1998). This is due to the difficulty of controlling and comparing soil components/properties and the long duration of breakthrough tests in compacted soils.

The objectives of this study are to quantify the free-swelling behavior of organobentonite in varying liquids and its permeability to varying liquids and to evaluate the NAPL attenuation capacity as additives in a silty clay. Hexadecyltrimethylammonium ($HDTMA^+$) surfactant modified bentonite was chosen as a representative CCL amendment with engineered high-organic carbon content and organophilicity. The barrier performance of silty clay/HDTMA bentonite against gasoline (representative of petroleum products) and PAH (common components in NAPLs) transport was assessed. Permeability tests on saturated specimens of compacted silty clay with HDTMA bentonite amendment were conducted in the flexible wall permeameter. Free swelling tests of the silty clay/HDTMA bentonite in water and gasoline were performed. Batch sorption tests and low-flow rate column tests were carried out to quantify the retardation coefficient and diffusion coefficient of naphthalene transport in compacted silty clay/HDTMA bentonite soil.

2. Materials

Three different types of soils such as (silty clay, Ca-bentonite and HDTMA modified bentonite) were used in this study. The natural low-plasticity silty clay soil (Nugent Sand Company) contained 1% gravel, 12% sand, and 87% fine particles (ASTM D422). Ca-bentonite soil had approximately 85% calcium montmorillonite (American Colloid Company). HDTMA bentonite was synthesized from the calcium bentonite by exchanging Ca^{2+} cation with hexadecyltrimethylammonium cation ($HDTMA^+$), following the method described in a previous study (Lorenzetti et al., 2005). The synthesized HDTMA bentonite had a total organic carbon of 21.44%, according to a carbon analyzer. The basal spacing of the base bentonite and HDTMA bentonite was determined by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded between 2° and 20° (2θ) using CuKa radiation ($n = 1.5406$ Å) at a scanning speed of 2°/min. The basal spacing of the base bentonite was observed to increase from 15.06 Å to 19.44 Å after intercalation of HDTMA cations (Fig. 1). Methylene blue absorption technique was used to determine the specific surface area of each studied soil (Santamarina et al., 2002). The SEM photo of Ca-bentonite and HDTMA bentonite was recorded using a FEI Nova NanoSEM 600 with a working distance of 5–6 mm (Fig. 2). Ca-bentonite was observed to have large aggregates and curvy edges, and after the surfactant intercalation, the particles showed less foliated structure with rough edges.

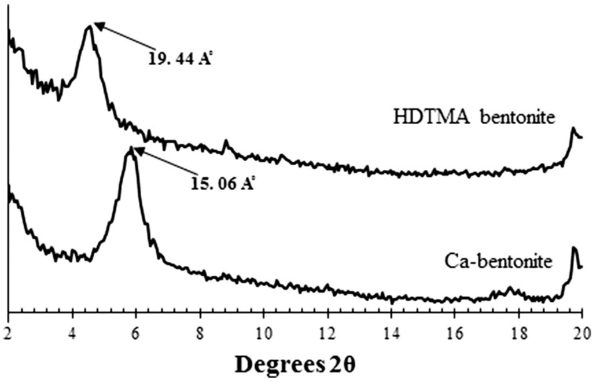

Fig. 1. XRD results of Ca-bentonite and HDTMA bentonite.

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