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CHARACTERIZATION OF HYDRAULIC PROPERTIES OF BATCH ORGANOMODIFIED INITIALLY DISPERSED AQUIFER TYPE SOILS FOR SORPTIVE ZONE APPLICATIONS

By

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ABSTRACT

CHARACTERIZATION OF HYDRAULIC PROPERTIES OF BATCH ORGANOMODIFIED INITIALLY DISPERSED AQUIFER TYPE SOILS FOR SORPTIVE ZONE APPLICATIONS

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The hydraulic feasibility of organomodified soils for potential use in sorptive zone applications was studied by measuring hydraulic conductivity and porosity of treated and untreated soils of 1) a natural sandy loam and 2) a reconstituted soil with different clay contents as a function of effective stress. The reconstituted soil samples with 6, 12, 18, and 24% fine material were employed. Organomodification of all soil samples was conducted in a batch process with hexadecyltrimethyl ammonium (HDTMA) to different levels of their cation exchange capacities. Treated and untreated samples of the natural soil were permeated with water and a pure organic liquid (Soltrol). Those of the reconstituted soil were only permeated with water. Upon initial packing all untreated soils (natural and reconstituted) were more porous than treated ones. In natural soils permeated with water, untreated soil retained its higher porosity at early loads and equaled the treated one at higher loads. Its conductivity was higher than the treated soil at early loads and lower at high loads. In the natural soils permeated with Soltrol, untreated soil retained its higher porosity and exhibited a higher conductivity, compared to treated soil, throughout the loading sequence. In reconstituted soils, with application of the first load (0.25 tsf) all untreated soils became equal or less porous than the treated soils and

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exhibited lower conductivities. Higher loads decreased the difference in porosity between treated and untreated soils while increasing the difference between their conductivities. At the highest load (8 tsf), treated soils were 5 to 129 times more conductive than untreated ones depending on their clay contents and treatment level. Observed differences in conductivities were explained in terms of the role of treated and untreated clays in controlling initial effective pore size and its change during consolidation. Creation of organomodified sorptive zones by batch process is shown to be hydraulically feasible as evidenced by similar or higher conductivities of treated soils compared to untreated ones. In addition, an increase in the sorptive capacity of the zone could potentially be achieved, without experiencing a loss in conductivity, by increasing the clay content during modification.

To the one who showed me the path

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INTRODUCTION

BACKGROUND

The study of clay mineral-organic reactions was initiated in the early 1930s (Evans and Pancoski, 1989). In 1934, Smith reacted organic compounds with clays and presented evidence that the reaction was ion exchange in nature (Grim, 1968). Jordan (1949) was one of the early investigators studying clay-organic interactions who found that organophilic bentonites swell and disperse in organic fluids. Since that time clay-organic interactions have been studied by a number of authors and proven to be effective in transforming a naturally hydrophilic clay into an organophilic clay (Grim, 1968; Mortland, 1970; Raussell-Colom and Serratosa, 1987; Boyd *et al.*, 1988). However, the use of organically modified clays in hazardous waste management applications is a relatively new technology (Evans *et al.*, 1989).

The enhanced sorption characteristics of modified clays could be managed to intercept and retard a migrating contaminant plume and thus, serve as a useful tool for many different remedial or containment applications such as containment barriers (Alther *et al.*, 1990; Boyd *et al.*, 1991); *in-situ* sorptive zones (Boyd *et al.*, 1991; Burris and Antworth, 1992), for stabilization of hazardous wastes (Alther *et al.*, 1990; Boyd *et al.*, 1991), for water and wastewater treatment (Srinivasan and Fogler, 1989, 1990; Alther *et al.*, 1990), and for an immediate response to terrestrial chemical spills to limit the extent of contamination (Boyd *et al.,* 1991). Each application requires a blockage or a bulk transport of fluid through a treated soil matrix. Therefore, hydraulic conductivity plays an essential role in the study of the feasibility of organomodified technology in all applications. In fact, it is probably *the* most important parameter for assessing their hydraulic feasibility (Evans, 1991).

The dependence of hydraulic conductivity K, [L/T], on the media's permeability k, [L^2], and the fluid's specific weight γ and viscosity μ is well known (Freeze and Cherry 1979);

$$K = k\,{}^{\gamma}\!/_{\mu}$$

Based on this equation, the changes in hydraulic conductivity of a soil matrix can be attributed to changes in the permeant properties (of specific weight and viscosity) and changes in the soil matrix geometry (i.e. permeability).

While no generally accepted expression for permeability exists, two approaches have been taken in the literature to relate permeability of a soil matrix to 1) the physical properties of soil grains or 2) the pore space properties. The first approach bases its derivation primarily on the effect of soil grains on resisting the flow through a porous media. Thus, in this approach, factors such as grain sizes and their distribution, shape of the grains, and grains packing factor are considered the major parameters influencing the flow. The typical form of the expression for permeability in this approach can be formulated as;

$$k = Cd^2$$

where C is an empirical coefficient and d is a length characteristic of the soil grains (Leonard, 1962; Freeze and Cherry, 1979; Holtz and Kovacs, 1981). This approach has been mainly used for granular soils and is not valid when a significant amount of clay exists in the soil matrix (Leonard, 1962).

The second approach considers the model of "bundle of capillary tubes" for the soil matrix. In this approach, fundamental equations for flow through tubes with different cross sectional areas are used and the porous media is simulated to a pack of tubes with different diameters. Therefore, total porosity of the soil, some measure of the micro-scale pore radius, and wetted perimeter of pores are the primary variables which are taken into account in this approach. Hagen-Poiseuille and Kozeny-Carman equations, which relate permeability to porosity and a characteristic radius of the pores in the soil matrix are examples of this approach (Leonard, 1962; Corey, 1986). The mathematical relationships derived in this approach can be simplified as;

$$k = nr_e^2$$

in which n is the total porosity and r_e is an effective pore radius for the soil matrix (Allred and Brown, 1994). This approach was adopted in our study because of the presence of clays in the soil as well as the focus of study being the changes in hydraulic conductivity due to organomodification which primarily affects the clay structure.

In general, organomodification has the potential to alter hydraulic conductivity of a soil matrix by changing the size and orientation of clay particles, geometry of the pore space in the matrix, and also through its effect on the fluid-clay interaction. In the following subsection of this chapter, these microscale processes will be discussed when the soil is permeated with water and/or an organic permeant. The effect of clay content, and treatment of the soil to different levels in this regard will be presented in the second and third subsections, respectively. In each subsection, relevant studies that looked at the changes in hydraulic properties of soils due to organomodification will also be presented.

FROM MICRO-SCALE PROCESSES TO MACRO-SCALE HYDRAULIC PROPERTIES

Theng (1974) reported that the replacement of natural cations on clays by organic cations influences the structure of clays. He found that organomodification induces a face-to-face aggregation in clay particles, a process called flocculation. More recently, Xu and Boyd (1994) studied the effect of initial cation type on flocculation process when hexadecyltrimethyl ammonium (HDTMA) is used to replace the cation. They showed that initially dispersed Na-saturated clays flocculated when all Sodium cations were replaced by HDTMA. They rationalized this behavior by measuring the electrophoretic mobility of clays and showing that the replacement neutralized the net negative electrostatic charge on the clay particles.

Pure organic liquids are also known to produce flocculation in clays, however, by a totally different mechanism (Brown, 1988; Broderick and Daniel, 1990). Bowders (1985) mentions that the pertinent mechanisms are not well understood however, the process can be summarized in shrinkage of diffuse double layer due to low dielectric constant of organic liquids (compared to water) and aggregation or flocculation of clays. Bowders and Daniel (1987) mention that, in addition to flocculation of clays, mixing soils with pure organic compounds also destroys the cohesive, plastic nature of the soil for the same reasons.

In a somewhat macroscopic perspective, clay flocculation can be viewed as affecting particle size distribution, which in turn, affects consolidation behavior of the soil (Holtz and Kovacs, 1981). Fernandez and Quigley (1991) packed clay soils in a dry state and saturated them with water and two organic liquids (ethanol and dioxane). They applied effective stresses to all samples, and measured their consolidation. Their data indicate that the dry packed clay soil has less consolidation when saturated with an organic liquid compared to water. They rationalized that flocculation of dry clays in organic liquids (due to the collapse of diffuse double layer by pure organic liquids) strengthens the soil peds and makes the soil less compressible. The effect of clay flocculation, due to organomodification of the soil, on consolidation behavior of the soil matrix has not been reported in the literature.

Clay flocculation also affects pore sizes and their distribution which influences conductivity of the soil matrix (Bowders, 1985). In fact, clay flocculation is among the interactions that increase the hydraulic conductivity of clay soils significantly (Shackelford, 1994). Fernandez and Quigley (1991) reported increases of more than 10 to 1000-fold in conductivity of dry packed clay soils permeated with ethanol or dioxane compared to water. This increase in conductivity was sustained throughout an effective stress sequence of 0 to 160 kPa due to stronger flocculated soil peds which greatly resisted macropore closure under effective stresses (Fernandez and Quigley, 1991). Significant increase in conductivity of soils containing organobentonite, in replacements for untreated bentonite, has been reported by Smith and Jaffe (1994). The comparison between clay flocculation induced by the two totally different mechanisms (i.e. organic permeant and organomodification) and its effect on consolidation and hydraulic conductivity of the matrix is not explored in the literature.

Organomodified clays, which are flocculated in aqueous solutions, will disperse if placed in pure organic liquids (Jordan, 1949). The mechanism of dispersion is established by drawing the organic liquids (and not water) in between organoclay platelets. Wolfe *et al.* (1985) used X-ray diffraction studies of organomodified montmorillonite to determine that *d*-spacing of organobentonite increases when hexane is used as the wetting fluid relative to water.

Clay dispersion due to a different mechanism (high water content at the time of packing a clay soil) and its effect on hydraulic conductivity of a wet packed clay soil is discussed in geotechnical literature (Boynton and Daniel, 1985). According to Lambe's (1958) "particles orientation theory", the arrangement of individual particles, which is influenced by molding water content, controls hydraulic conductivity (Benson and Daniel, 1990). Lambe suggested that the soil particles are oriented in a random pattern (with larger voids and higher conductivities) when soil is compacted dry of optimum water content, and in a dispersed pattern (with smaller voids and lower conductivities) when compacted wet of optimum water content. Although the mechanism of dispersion of clays is different in this example (compared to dispersion of organoclays in organic liquids), however, it is insightful as to the potentials of clay dispersion influence on hydraulic conductivity of clay soils.

Another fundamental change in the clay surface property due to organomodification is that by replacing natural inorganic cations of clays with organic ones, their natural hydrophilic character changes to organophilic (Evans *et al.* 1989). Hydrophilic nature of the clays is due to hydration tendency of naturally occurring metal exchange cations on them. However, once these inorganic exchange cations are replaced by organic ones, the clay surface property changes from hydrophilic to hydrophobic (or organophilic) due to the affinity of organoclays for organic liquids (Jaynes and Boyd, 1990).

One implication of surface property change in organoclays is that they do not draw water in between their platelets. This causes a major change in hydraulic behavior of clays, especially swelling ones such as montmorillonite, in water. Results of free swell volume tests with many different organically modified swelling clays showed that they swelled less in water compared to organic liquids (Evans and Pancoski, 1989; Alther *et al.*, 1988; Evans *et al.*, 1990; Evans and Alther, 1991). Therefore, it is implied that clays (specially swelling ones) with low hydraulic conductivities will have higher conductivities when organically modified.

Smith and Jaffe (1994) studied the incorporation of organobentonites into landfill liners to retard the transport of organic contaminants through conventional liners. They mixed 88% (of total mixture mass) Ottawa sand, none (or 4%) organobentonite, 12% (or 8%) untreated bentonite, and water uniformly and compacted it to simulate sand and bentonite liners. Their results indicate that, due to partial replacement of organobentonite for untreated bentonite, hydraulic conductivity increased by 10-fold. Similarly, Smith *et al.* (1992) noted that the complete substitution of organobentonite for untreated bentonite, in the same composition of soil as above, results in a hydraulic conductivity increase of four orders of magnitude. Inability of organobentonite to intercalate any significant amount of water was identified by these authors as the likely cause of the large differences observed in their conductivities.

In conventional study of the flow through porous media, it is a fundamental assumption that at boundaries where the fluid is in contact with solid, the fluid velocity relative to the boundary is zero (Corey, 1986). This is referred to as "no-slip" boundary condition at solid surfaces. In the case of gas flow in porous media, at ordinary low pressures, no-slip condition is not satisfied. This phenomenon has been called "gas slippage" (Corey, 1986). As mentioned earlier, organomodification of clays changes their surface property from hydrophilic to hydrophobic. In the context of water flow through porous media, it could appear that a hydrophobic surface has a different potential to resist flow compared to a hydrophilic surface. In extreme, it may change the boundary condition at the clay water interface from "no-slip" to somewhat "yes-slip"! Furthermore, in a water saturated soil matrix, a hydrophobic surface might be capable of accommodating easier rearrangement of other particles under an external load, compared to a natural hydrophilic clay surface. To my knowledge, possibility of such differences has not been explored or investigated in previous researches in this area, nor was it studied in the present work. However, the lumped effect of all such microscale changes due to organomodification on consolidation and conductivity of soils was investigated and is reported in the present work.

CLAY CONTENT AND THE SOIL STRUCTURE

The structure of natural soils can be described as being composed of clay particle associations (microfabric) within a macrostructure of granular portion of the soil (Mitchell, 1976). In terms of porosity, the total pore volume of a soil matrix can be divided into micropores (within the microfabric) and macropores (in between larger aggregates) (Yang and Barbour, 1992). While the role of clay content and its structure (flocculated or dispersed) is critical to hydraulic properties of a soil matrix, there are only a few articles addressing organomodified clay content and its influence on the soil structure and its conductivity. However, in geotechnical literature, this subject has been studied extensively using natural clays combined with sand and gravel at different contents, for different engineering applications. Study of the influence of clay content on hydraulic properties of the soils used in those applications can provide an insight as to the sensible range of clay content and its potential effects on organomodified soil structure.

On the upper limit, researchers were concerned about how much of gravel or sand may be added to a clay deposit while keeping its very low hydraulic conductivity. Holtz and Kovacs (1981) indicated that when the sand content is below 50%, the sand grains are essentially floating in a clay matrix and have little effect on its engineering behavior. Shakoor and Cook (1990) performed hydraulic conductivity tests on silty clay mixed with different amounts of 13- to 19-mm diameter gravel particles and reported a large increase in conductivity for gravel contents greater than 50%. Shelly and Daniel (1993) conducted similar experiments on two different clay soils mixed with 10- to 19-mm diameter gravel and found the critical gravel content of 60% at which conductivity sharply increased. Both researchers indicate that at gravel contents of above 50 or 60%, amount of clays are not enough to totally fill the voids created by gravel particles. Therefore, it can be concluded that hydraulic behavior of the soil matrix is more sensitive to clay content if the clay content is kept below 50%.

On the lower limit, amount of bentonite used in clay sand liners, to achieve a low hydraulic conductivity of 10^{-7} cm/s, typically varies between 6 and 15% (Alther, 1987). Daniel (1987) has noted however, that the benefits derived from increasing the percent bentonite in a sand bentonite mixture diminish as the percent bentonite increases above 10-12%. Increasing the percent bentonite above this percent he concludes, causes little additional reduction in hydraulic conductivity. This is consistent with Kenney *et al.* (1992) who reported that in a sand bentonite mixture, depending on the amount of bentonite (varied from 4 to 22% in their experiments), clays resided in the pore space created by sand grains or in between them which made the clays part of the load bearing mechanism of the soil matrix. They concluded that by the contents of 12%, bentonite was completely filling the pore space created by the sand portion, and hence resulting in a low conductivity of the mixture. It is concluded, in a very general sense, that a minimum of 4 to 6% of any type of clay is needed before a detectable change in hydraulic conductivity of the soil matrix can be expected. In the experiments conducted in Chapters 2 and 3 of this dissertation clay contents was varied from 6 to 24%.

TREATMENT LEVEL AND THE SOIL STRUCTURE

Few studies on the effect of organomodification level on the clay structure show that clay particles can be flocculated or dispersed depending on the modification level (Xu and Boyd, 1994, 1995). Xu and Boyd (1995) description of the pertaining microscopic processes may be summarized as follows; starting with a Na saturated dispersed clay soil, HDTMA added in amounts far less than the cation exchange capacity (CEC), replaces the Na cations on clays via ion exchange process. Their quantity is not enough to totally neutralize the original net negative charge on the clays and therefore, not significant flocculation occurs. As HDTMA substitution approaches the CEC, the clay surfaces will become electrostatically neutral and the clays flocculate. The replacement of Na by HDTMA is still mainly cation exchange process. HDTMA's will continue to adsorb to the exterior clay surfaces beyond the CEC, however, via hydrophobic bonding which is the attraction of hydrophobic tails of adsorbed HDTMA's. This will create a net positive electrostatic charge on clays and cause their re-dispersion.

The effect of clay dispersion (though by other mechanisms) on soil structure and its influence on hydraulic behavior of the soil matrix was discussed earlier. Another adverse effect of hydrophobically bonded HDTMA is that it desorb in water easier than the cation exchanged one due to its weak bonding (Xu and Boyd, 1994). The effect of this desorption on the clay structure is not explored in the literature. However, based on Xu and Boyd's (1995) rationale on the cause of the dispersion (i.e. net positive charge on the clays due to hydrophobically bonded excess HDTMA), one can conclude that after desorption of excess HDTMA, clay particles will retain their flocculated structure which they had before hydrophobic adsorption of the excess HDTMA took place.

Redistribution of treatment profile in an *in-situ* modified soil column, possibly due to the desorption of excess HDTMA, its transport down gradient, and its re-adsorption to un-neutralized clay surfaces, is reported by Burris and Antworth (1992). They showed that the initial treatment level varied from ~0.5% organic carbon (OC) to zero in the first 10 cm of their 25-cm long columns. This profile spread down gradient (with a maximum of ~0.3% OC which dropped to zero in the first 20 cm of the column) due to 400 pore volume flushing of the column with HDTMA-free water. While their data does not distinguish whether the redistribution occurred due to desorption and later re-adsorption of hydrophobically bonded HDTMA or due to partial migration (and later entrapment) of the dispersed clay particles, it gives rise to concerns on potential adverse effects of treatment to levels far above CEC on conductivity of the soil, in an *in-situ* injection of organic surfactants. No specific study of the effects of treatment level on hydraulic conductivity of organomodified soils has been reported in the literature.

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Chapter 1

HYDRAULIC CONDUCTIVITY OF AN ORGANOMODIFIED SOIL TO WATER AND SOLTROL

ABSTRACT

Hydraulic feasibility of organomodified sorptive zones was studied by investigating the effects of batch organomodification (treatment) on hydraulic conductivity of a sandy loam under different effective stresses. Porosity and conductivity to water and Soltrol 170 (an LNAPL) were measured as a function of effective stress; and their correlation with clay flocculation or dispersion and its influence on pore size were sought. Treatment was accomplished in a well-mixed batch system by adding hexadecyltrimethyl ammonium (HDTMA) solution to the soil in an amount equivalent to its cation exchange capacity (CEC). A fixed ring consolidometer, in which treated and untreated soils were packed dry and loaded, was employed for conductivity measurements. Under no load, treated soils were 9 and 20-fold less conductive than untreated ones to water and Soltrol, respectively. This occurred because treatment collapsed the initially dispersed structure of untreated clays which had "fluffed up" the untreated soil matrix. Compared to untreated soil, treated soil saturated with water exhibited smaller loss of conductivity due to increased load, such that it became 5-fold more conductive than untreated soil at the highest effective stress (8 tsf). Observed

differences in conductivity were explained in terms of changes in fluid properties and soil matrix geometry. Changes in clay structure (flocculated or dispersed) due to the treatment and permeant were evaluated by measuring soil suspension turbidity. The role of clay structure in controlling the initial effective pore radius in soils and hence their conductivities, as well as, in controlling changes in effective pore radius during consolidation is discussed. It was found that *ex-situ* treatment of soils with HDTMA for the purpose of creating sorptive zones is hydraulically feasible under the experimental conditions used in this study.

INTRODUCTION

Organomodified subsoils and aquifer materials have recently been advocated as permeable sorptive zones for contaminant plume management (Boyd *et al.*, 1988, 1991; Lee *et al.*, 1989; Xu *et al.*, 1996). In this application, dissolved organic contaminants would be intercepted and immobilized when they flow through the zone. From a practical stand point, knowledge of the degree to which organomodification alters hydraulic conductivity is essential in assessing the hydraulic feasibility of these zones. Numerous investigations have revealed much about the micro-scale changes in clay physical structure brought on by organomodification and hence the potential it possesses to alter a natural soil's conductivity to both aqueous solutions and pure organic permeants (Xu and Boyd, 1994, 1995*a*, *b*, *c*). To date however, there has been very little investigation to determine the degree of change in conductivity brought about by organomodification of natural soils so that the hydraulic properties of sorptive zones remain unknown.

The limited sorptive capacity of some soils can be greatly improved by organomodification. Natural deposits of low organic matter content soils, subsoils, and aquifer materials have little sorptive capacity for removing nonionic organic compounds (NOCs) from water. Organomodification of soils is achieved by replacing their native inorganic cations with large organic cations through ion exchange reactions (Lee *et al.*, 1989; Jaynes and Boyd, 1991). The organic cations that have been studied most extensively are quaternary ammonium compounds (QACs) of the general form $[(CH_3)_3NR]^+$ where R is an alkyl or an aromatic hydrocarbon (Boyd *et al.*, 1991). When R is a relatively large alkyl hydrocarbon, as is the case for hexadecyltrimethyl ammonium (HDTMA) where $R=(CH_2)_{15}CH_3$, then the modified clays are rendered organophilic due to the alkyl hydrocarbon tails anchored to the clay surface (Jaynes and Boyd, 1991). The agglomeration of alkyl tails of sorbed QACs forms a highly effective sorptive phase for removing NOC's from water (Sheng *et al.*, 1996*a*, 1996*b*).

Permeable sorptive zones could be created ex-situ by excavating soil, treating it with cationic surfactants such as HDTMA, then returning the organomodified soil. The hydraulic conductivity of organomodified soil is important because it provides basic information required to determine the size of the sorptive zone needed to prevent contaminated fluid from flowing around the zone. From a design standpoint it is desirable to match the conductivity of the zone, as closely as possible, to that of the surrounding media. This could minimize either rapid funneling through the zone or fluid bypass. For sorptive zones placed downstream of an LNAPL spill, the organomodified soil could be exposed to both LNAPL and aqueous permeants. Therefore, knowledge of the conductivity to both permeants is of importance. Because the aqueous solubilities of common organic contaminants are usually low, the conductivity of soils to an aqueous solution is not expected to be effected by the presence of a dissolved organic compound (Abdul *et al.*, 1989; Evans *et al.*, 1989). Pure organic liquids, on the other hand, are known to affect the physical structure of both natural and organomodified clays and may therefore alter the conductivities of soil containing these materials (Theng, 1974; Weiss, 1963; Brown, 1988; Broderick and Daniel, 1990).

The microscopic differences between organomodified clays and untreated clays provide an indication of the possible affect of organomodification on hydraulic conductivity. For example, QAC molecules, added in an amount close to the soil's cation exchange capacity (CEC), will replace the naturally occurring cations on clays causing dispersed clays to flocculate in aqueous solutions (Xu and Boyd, 1994, 1995*a*, *b*). Pure organic liquids are also known to affect the flocculation and dispersion of clays. They flocculate natural clays (e.g. Na-bentonite) by shrinking their diffuse double layers (Bowders, 1985). Alternatively, organic liquids may be intercalated by organomodified clays (e.g. HDTMA-smectite) causing interlayer expansion and ultimately dispersion (Jordan, 1949; Theng, 1974; Weiss, 1963; Wolfe, 1974). Although clay flocculation typically increases the hydraulic conductivity of packed clay soils (Bowders, 1985; Shackelford, 1994), there are many other factors that may influence hydraulic conductivity of a batch treated organomodified soil, so that determination of the degree of change in hydraulic conductivity produced by organomodification of soils that conduct either water or organic liquids requires direct measurement of hydraulic conductivity.

Very few measurements of the hydraulic conductivity of organomodified soils to aqueous permeants have been reported, and there are apparently no measurements with regard to liquid organic permeants. Burris and Antworth (1992) employed columns and a sand box aquifer model to study the organomodification, using HDTMA, of an aquifer material with the objective of enhancing retardation of organic contaminants. They reported having observed no detectable increase in column back pressure, suggesting qualitatively that hydraulic conductivity of their soil may not have been significantly reduced by organomodification. More recently, Smith and Jaffe (1994) studied the use of organomodified bentonites to retard the aqueous transport of NOCs through conventional sand/Na-bentonite liners. Their results indicate that, due to partial or complete substitution of organobentonite for untreated Na-bentonite, hydraulic conductivity to water increased by 10 - 400 fold (Smith *et al.,* 1992). They attributed the increase in conductivity to the change in bentonite from a swelling to an essentially non-swelling clay due to organomodification. These authors apparently employed swelling clays (Na-bentonite) to achieve very low hydraulic conductivities required for liner application, and organoclays to retard NOC mobility. Their study focused on evaluating the suitability of using organomodified clays in liner applications. Investigating sorptive zone application, in the form of a permeable treatment wall, necessitates measurements of conductivity of different types of media at different effective stresses.

The objectives of this study were to evaluate the hydraulic feasibility of *ex-situ* treated sorptive zones by (i) determining the change in conductivity of an aquifer type soil due to batch organomodification using water and an LNAPL as permeants, (ii) monitoring this change under different effective stresses and (iii) seeking its relation to microscale processes of clay dispersion and flocculation. To evaluate changes in conductivity that might be encountered under field conditions, untreated soils were used essentially as they were obtained, and compared to treated soils that were subject to mechanical mixing and chemical modification.

MATERIALS AND METHODS

Two soils were employed in the hydraulic conductivity experiments. They differed only in that the treated soil was organomodified where as the untreated soil was not. The untreated soil was a B-horizon Oshtemo soil that was obtained at a depth of about 2 ft at the Kellogg Biological Station, Hickory corners, MI. The soil was air dried and passed through a US standard #20 (0.84 mm) sieve. Exchangeable cations of Ca^{2+}, Mg^{2+}, K^+, and Na^+ were present at relative amounts of 72%, 22%, 4%, and 2% respectively. The major clay minerals included the limited swelling clay (vermiculite) and the non-swelling clays (illite, kaolinite, and hydroxy-aluminum interlayered vermiculite) as determined by X-ray diffraction. Mechanical analysis showed 78% sand, 19% clay, 3% silt, and 0.4% organic matter content in the soil. Sieve analysis and hydrometer tests (ASTM C136 and D422) were performed on the soil using seven sieves (US standard sieve numbers 20, 30, 40, 60, 70, 100, and 200) and a gram-per-liter type hydrometer. The overall grain size distribution had a uniformity coefficient (D_{60}/D_{10}) of 13 and a curvature coefficient ($D_{30}^2/D_{10}*D_{60}$) of 4 so that the soil was considered well graded (Holtz and Kovacs, 1981). The soil also met a conservative sand filter criteria ($D_{15} \leq 0.5$ mm) for fine-grained clays (Sherard *et al.,* 1984) and hence, minimal loss of fines was expected. Specific gravity of solids was measured and found to be 2.67 (ASTM D854).

The treated soil was prepared by mixing HDTMA with the above soil in a batch process. HDTMA treatment level corresponded to the first plateau of the HDTMA adsorption isotherm which was 46.1 mmole/kg. This was taken as a practical estimate of the CEC. Treatment was accomplished by adding an aqueous solution of HDTMA-Cl to a 20:1 suspension of HPLC-grade water and soil which was stirred at 120 rpm for 1 minute followed by 20 rpm for 30 minutes. Treated soil was settled out of suspension and washed once with HPLC-grade water. Subsequently, it was airdried, gently ground with a mortar and pestle, sieved through a US standard #20 sieve, and kept in an open pan.

An aqueous solution of 1 mM NaCl, HPLC-grade water and Soltrol 170 (Phillips Petroleum Co.) were used as permeants. Soltrol 170, a mixture of C10-C15 isoalkanes, is a light non-aqueous phase liquid. The kinematic viscosity and specific weight of water and Soltrol were measured before and after contact with treated and untreated soils (ASTM D445-88 and D446-89a). For these measurements water and Soltrol were equilibrated with treated or untreated soil in a 5:1 ratio for 24 hrs. A Cannon-Fenske Routine viscometer was used to measure viscosity. All measurements were conducted in a constant temperature bath at room temperature.

Two sets of turbidity measurements were made. The first set was made to establish how the HDTMA treatment level affected soil suspension turbidity and thereby provide a clear link to the understanding of microscopic clay behavior already developed by Xu and Boyd. The procedure employed was consistent with that used by Xu and Boyd (1995*a*) and in compliance with ASTM D1889. Soil samples were mixed with an appropriate volume of an HDTMA aqueous solution in a 1:10 ratio in 25-ml Corex tubes at HDTMA concentrations that ranged from 0.01 to 3.0 times the CEC. The tubes were then shaken for 4 days in a rotating shaker and allowed to stand for 0.5 hr immediately prior to measurement. Turbidity was determined by a Hach Model 2100A turbidimeter on the soil suspension sampled from 1 cm below the liquid surface in each tube. The second set of turbidity measurements was made to determine whether the flocculated structure of treated clays, suggested by the first set of measurements, was altered because soil samples were air dried prior to packing in the consolidometer and to establish the dispersed state of treated clays in the presence of Soltrol. In these experiments, each soil (treated air dried soil, and untreated air dried soil) was mixed with either water or Soltrol, and the turbidity of each supernatant was measured. The soil to liquid ratio and mixing procedure employed above were followed here.

A fixed ring consolidometer, which allows falling head conductivity measurements, and a load frame equipped with a precision displacement transducer (0.0001 inch) were employed to load the samples. Treated and untreated samples were packed by pouring air dried soil into the consolidometer ring with filter paper (Whatman #1) on the top and bottom of the sample. Samples were then tamped slightly to flatten the upper surface and compacted with a drop hammer to a nominal initial thickness of 2.5 cm and vacuum saturated in a desiccator with deaired, HPLC-grade water or Soltrol. Saturated samples were subjected to an effective stress (loading) sequence from 0 to 8 tsf using the conventional consolidation procedure (ASTM D2435-90). Each load was maintained for a duration greater than Taylor's time for 90% consolidation before porosity, conductivity, and temperature measurements were made.

Hydraulic conductivity of samples at different effective stresses was measured by the falling head method (ASTM D5084-90) at room temperature. Head losses in the tubes, connectors, porous stones, and filter papers were quantified by assembling the consolidometer without soil and measuring its conductivity (K_{blank}) at different effective stresses with water and Soltrol. Hydraulic conductivity of the soil sample was calculated accounting for the predetermined K_{blank}. Two or three conductivity measurements were made at each load and adjusted to reflect a fluid temperature of 20 °C. At each load, the sample thickness was measured and porosity was calculated from the measured thickness of the consolidated sample.

THEORY

The dependence of hydraulic conductivity K on the media's intrinsic permeability k and the fluid's specific weight γ and viscosity μ is well known:

$$K = k\frac{\gamma}{\mu}$$

Employing the analogy of Poiseuille flow through a bundle of capillary tubes (DeWiest, 1965; Corey, 1986; Allred and Brown, 1994) permits explicit expression of the contribution of porosity, n, to hydraulic conductivity:

$$K = nr^2\frac{\gamma}{\mu}$$

Here the porosity accounts for the volume of pore space available to conduct fluid while r, the effective pore radius, is a macroscopic parameter that provides a lumped indication of the relative size of the pores and the shape factor.

RESULTS AND DISCUSSION

Because of their influence on hydraulic conductivity, the hydraulic properties of the permeants and the clay structure of the soils are discussed before presenting the conductivity results.

Hydraulic properties of the permeants

Values of specific weight γ and viscosity μ were measured (Table 1) for the water and Soltrol that were employed as permeants. Prior to measurement, these permeants had been equilibrated with either treated or untreated soil. The changes in viscosity and specific weight of the permeants brought about by the addition of HDTMA to the soil were less than 1% in the case of water and less than 2.5% in the case of Soltrol (Table 1). Consequently, the differences in the conductivity to either permeant between the treated and untreated soils, which will be discussed later, were not the result of changes in the hydraulic properties of the permeants. On the other hand, the values of γ/μ for water and Soltrol were significantly different so that the conductivities of treated and untreated soils were expected to depend upon which permeant was employed.

Clay structure

Measurements of the soil-water suspension turbidity from soil samples that were equilibrated with different amounts of HDTMA in a batch process are shown in Figure 1. The turbidities plotted were normalized by the turbidity of a sample that contained no HDTMA. The amount of HDTMA added is shown as multiples of the CEC (46.1 mmole/kg). Untreated sample (0 CEC), and to varying degrees samples treated to levels above 1.2 CEC, were turbid. At treatment levels between 0.03 CEC and 1.2 CEC, soil-water suspensions had relative turbidities that were nearly zero.

On this basis the two soils selected for use in studying hydraulic conductivity, the untreated (0 CEC) and the treated (1 CEC) soils, appeared to possess different clay structures. The work of Xu and Boyd (1994, 1995*a*) supports this determination, having

Table 1: Hydraulic properties - specific weight γ and viscosity μ - of the two permeants equilibrated with treated and untreated soils at 18 °C

		Untreated soil	Treated soil
Water	**Specific weight (N / m^3)**	9767	9767
	Viscosity (Pa . s)	1.03×10^{-3}	1.03×10^{-3}
Soltrol	**Specific weight (N / m^3)**	7587	7592
	Viscosity (Pa . s)	3.31×10^{-3}	3.23×10^{-3}

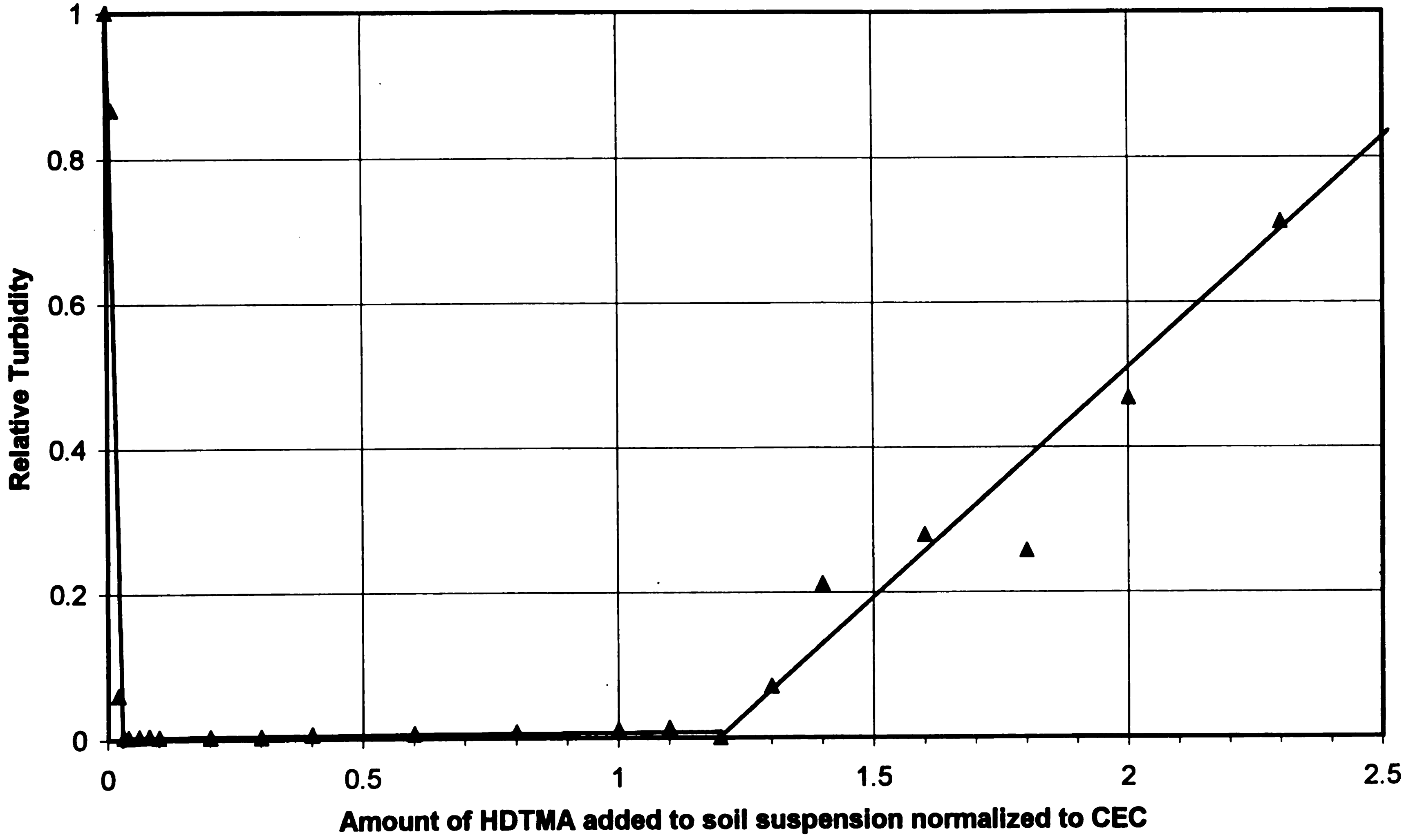

Figure 1: Turbidity of soil suspension as affected by HDTMA treatment level

established that the dispersed clay structure of the untreated soil is associated with high turbidity and the flocculated clay structure of treated soil is associated with low turbidity. Clay flocculation is among the interactions known to significantly increase the hydraulic conductivity of clay soils (Shackelford, 1994). Because the treated soil was air dried following treatment and then resaturated for conductivity experiments, we believed that it was important to determine that the flocculated structure of clays was retained despite air drying and resaturation.

A second set of turbidity measurements (Table 2) was made to evaluate the affect of air drying the treated soils prior to resaturating them and to provide an indication of the differences in the clay structure of the two soils when permeated by Soltrol. Turbidities of the soil suspension in both water and Soltrol were measured. As in the previously discussed set of turbidity measurements, the treated soil sample (1 CEC) was much less turbid in water than was the untreated sample; it had only 4% of the turbidity of the untreated sample. This indicated that the treated clays retained their flocculated structure although they were air dried prior to being packed in the consolidometer and then were saturated with water. Therefore, in the conductivity experiments that are discussed later where water was employed as the permeant the treated samples had a relatively flocculated clay structure and the untreated ones had a more dispersed clay structure. On the other hand, it was the untreated soil sample that was less turbid in Soltrol than was the treated sample; it had only 13% of the turbidity of the treated sample. Indicating that untreated clays were more flocculated compared to treated ones when Soltrol was the permeant.

Table 2: Relative turbidity of the supernatant for untreated and treated soil samples in the two permeants scaled to the turbidity of untreated soil (i.e. 945 NTU)

	Untreated soil	Treated soil
Water	1	0.04
Soltrol	0.003	0.03

Hydraulic conductivity

Under no load

Hydraulic conductivity to water of the untreated soil at zero load averaged 9-fold higher than that of the treated soil (Table 3). As indicated earlier this difference in conductivity was not influenced by differences in the hydraulic properties of the waters that had contacted the treated and untreated soils. All of the difference can be attributed to differences in the intrinsic permeabilities (Table 3) of the untreated and treated soils. Equation 2 shows that the additional pore volume provided by the 12% higher average porosity of the water saturated untreated soil (Table 3), compared to the treated soil, accounted for only 12% of the 9-fold higher conductivity of the untreated soil, and that the higher conductivity of the untreated soil was mainly attributed to that soil's larger effective pore radius (Table 3). The higher conductivity, higher intrinsic permeability, and larger effective pore size occurred in the untreated soil which had a dispersed clay structure; this will be discussed further below.

For the Soltrol saturated soils, the hydraulic conductivity of the untreated soil was on average 19-fold higher than the conductivity of the treated soil at zero load (Table 3). The higher conductivity of untreated soil was again entirely attributed to differences in intrinsic permeabilities (Table 3). The larger effective pore radius of the untreated soil was the primary reason for its higher hydraulic conductivity. Larger effective pore radius accounted for 87% of the 19-fold higher conductivity while porosity accounted for only 13% of this difference. The higher conductivity, higher intrinsic permeability, and larger effective pore size all occurred in the untreated soil which was similar to what was

Table 3: Average values of hydraulic properties of untreated and treated soils in addition to their clay structure at zero load. The values in parenthesis show one standard error of the reported average.

	Untreated soil			Treated soil		
	Dry packed[†]	**Water saturated[‡]**	**Soltrol saturated[‡]**	**Dry packed[†]**	**Water saturated[‡]**	**Soltrol saturated[‡]**
Hydraulic conductivity (*cm/s*)		1.2E-02± (3E-04)	1.7E-02± (3E-03)		1.3E-03± (2E-06)	8.8E-04± (9E-05)
Intrinsic permeability (cm^2)		1.3E-7± (3E-09)	7.4E-07± (1E-07)		1.4E-08± (2E-11)	3.7E-08± (4E-09)
Effective pore radius (*cm*)		4.9E-04± (8E-05)	1.2E-03± (4E-04)		1.8E-04± (2E-05)	2.9E-04± (9E-05)
Porosity (%)	49.3± (0.1)	50.3± (0.3)	49.2± (0.2)	42.8± (0.3)	43.1± (0.8)	42.2± (0.2)
Clay structure	Dispersed	Dispersed	Flocculated	Flocculated	Flocculated	Dispersed

[†] reported average values are from six replicate experiments

[‡] reported average values are from three replicate experiments

observed in the water saturated soils previously discussed. Unlike the water saturated soils where the higher conductivity was associated with the dispersed clay structure, the Soltrol saturated soil that exhibited the higher conductivity, the untreated soil, had a flocculated clay structure.

For each permeant, the untreated soil exhibited a higher conductivity than the treated soil prior to loading (Table 3). This was due to the initially dispersed structure of untreated clays which produced a larger effective pore radius in the untreated soil compared to the treated soil. Our porosity data for the dry packed soils (Table 3) showed that the untreated clays "fluffed up" the untreated soil matrix relative to the treated soil matrix when soil was first packed in the consolidometer. This "fluffed up" condition was maintained when the untreated soil was saturated, irrespective of which permeant was employed. The untreated soil's higher porosities (about 17%) were apparently due to the more dispersed structure of the dry untreated clays which produced a greater ability for the untreated clays to resist compaction during packing. For both permeants, the larger effective pore radii (Table 3) were associated with the "fluffed up" untreated soil matrices. As discussed earlier, this was the main contributor to the higher conductivity of untreated soils relative to treated ones. In the dry packed treated soil the clay sheets were stacked in flocs and this soil felt noticeably "greasier" both of which may have contributed to its greater susceptibility to compaction during packing and the occurrence of smaller effective pore radius (Table 3).

For the untreated soil, the difference between its hydraulic conductivity to Soltrol and to water depended in part on changes in the clay structure that were chemically induced by the Soltrol. This was apparent because the intrinsic permeability of the untreated soil that was Soltrol saturated was 5.7-fold larger than the intrinsic permeability of the untreated water-saturated soil. This chemically induced effect was not so apparent in the hydraulic conductivities because it was partially offset by the difference in the hydraulic properties (γ/μ) of the two permeants. The greater intrinsic permeability of the Soltrol saturated soil occurred because saturation with Soltrol caused the dispersed clay structure of the dry packed soil to flocculate. This produced the larger effective pore radius of the Soltrol saturated soil which was responsible for its larger intrinsic permeability (Brown, 1988; Broderick and Daniel, 1990).

Water saturated soils under load

As a confining load was placed on the water saturated soils and then serially increased, the untreated soil remained more conductive than the treated soil at low effective stresses (Figure 2). At the lowest load (0.25 tsf) the untreated soil was 3.6-fold more conductive than the treated soil; and the untreated soil exhibited a higher rate of conductivity loss with increased load than did the treated soil. This resulted in a situation where continued loading first eliminated the difference between untreated and treated soil conductivities and then reversed the situation, so that at loads greater than 1.3 tsf, conductivity of the treated soil was greater than that of the untreated soil. At the highest load (8 tsf) the treated soil was 5-fold more conductive than the untreated soil. Throughout the loading sequence, most of the difference in conductivity between the untreated and treated soils was due to the difference in their effective pore radii (Figure 3). At the lowest loads (0.25 tsf) the untreated soil had a larger effective pore radius than

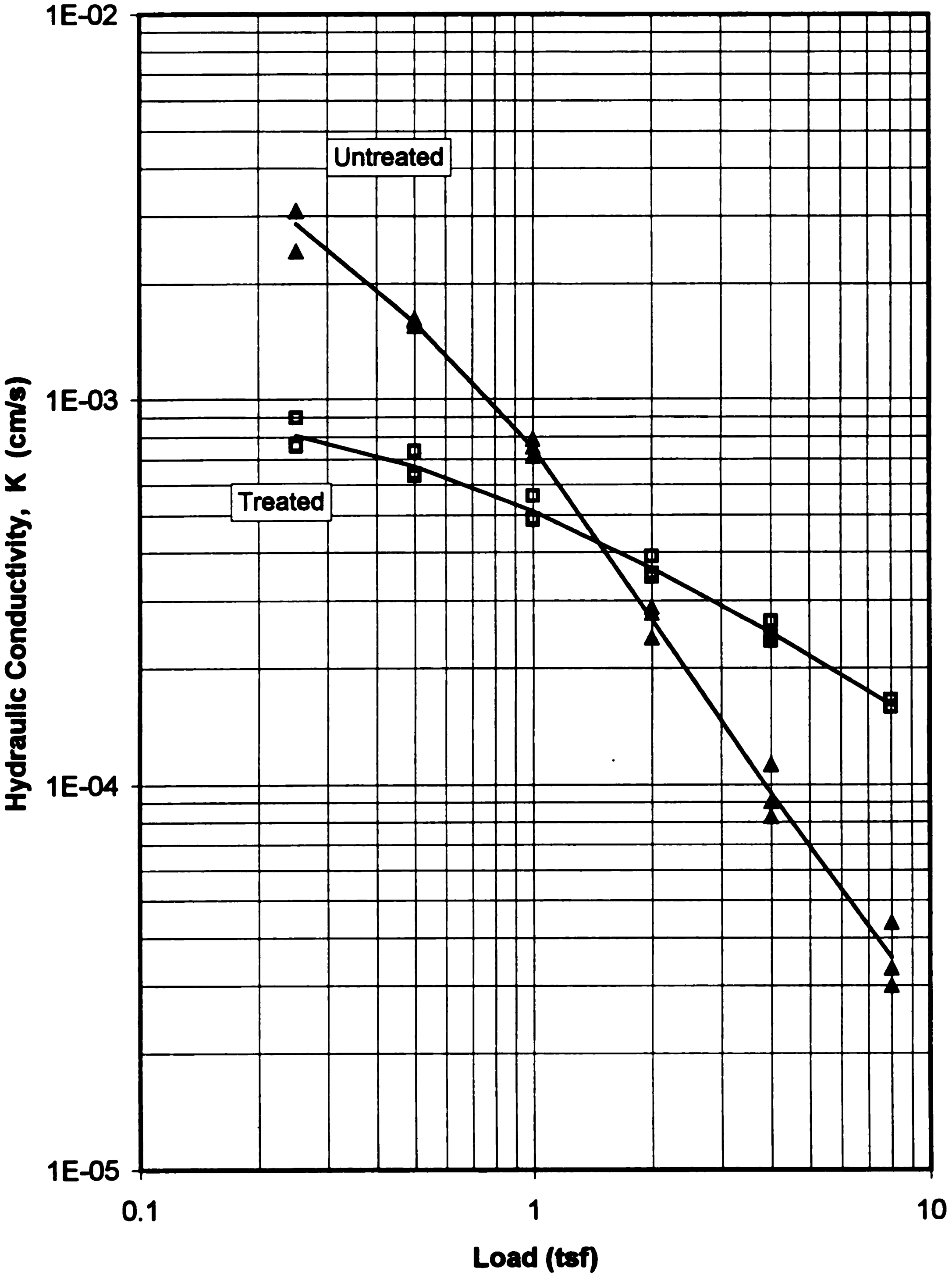

Figure 2: Hydraulic conductivity of treated and untreated soils permeated with water

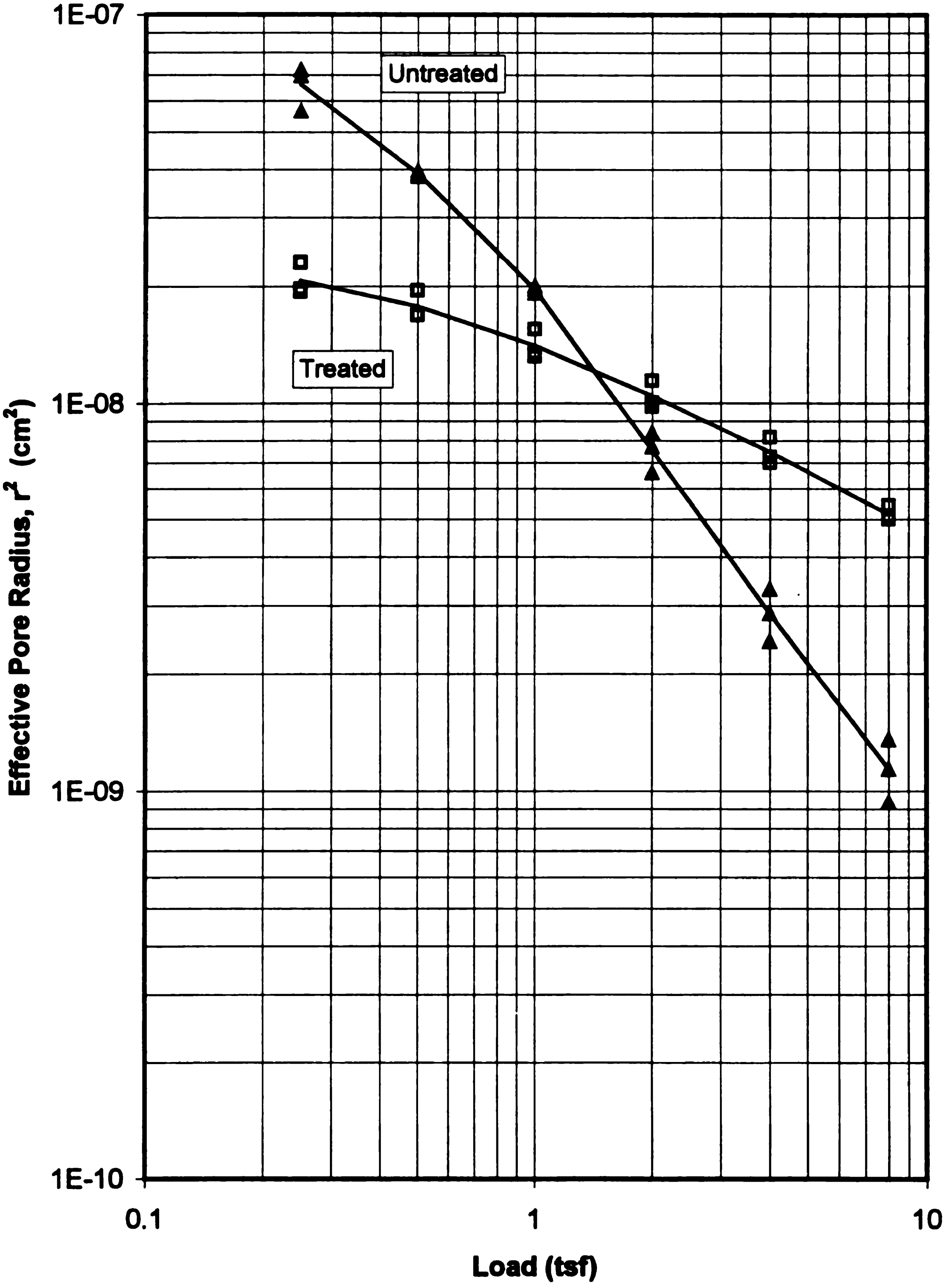

Figure 3: Effective pore radius of treated and untreated soil permeated with water

the treated soil had, where as the effective pore radius was larger in the treated soil at high loads. Untreated soil porosities which were greater than or equal to treated soil porosities (Figure 4) at all loads only made a minor contribution (<14%) to the higher conductivities of the untreated soil at loads below 1.3 tsf.

Differences between hydraulic conductivity of the treated and untreated soils during loading can be interpreted in terms of initial matrix structures and their different responses to load. The greater hydraulic conductivity of the untreated soil at the lowest load (0.25 tsf) was the result of its "fluffed up" matrix and the large effective pore radius associated with this state; both of which were produced by the soil's dispersed clay structure. Porosity was more sensitive to additional loading in this matrix than in the treated soil matrix (Figure 4) at loads that were less than 2 tsf; while at loads of 2 tsf or more, the porosities of the two soils were essentially identical. This is consistent with the observation of Mitchell (1993) who indicates that at low loads a soil with a dispersed clay structure is more compressible than the same soil with a flocculated clay structure. The significance of the dispersed clay structure to changes in conductivity with increased loading was even more apparent in the effective pore radius data. These data (Figure 3) showed that there was a higher rate of loss of effective pore radius with increased loading in the untreated soil and that this occurred throughout the entire range of loads; even throughout the range of loads where the porosities of the two soils were indistinguishable. Identical porosities of treated and untreated soils at loads greater than 2 tsf showed that consolidation proceeded independent of whether the soil's clay was dispersed or flocculated at high loads; i.e. clays accommodated rearrangement of granular particles in

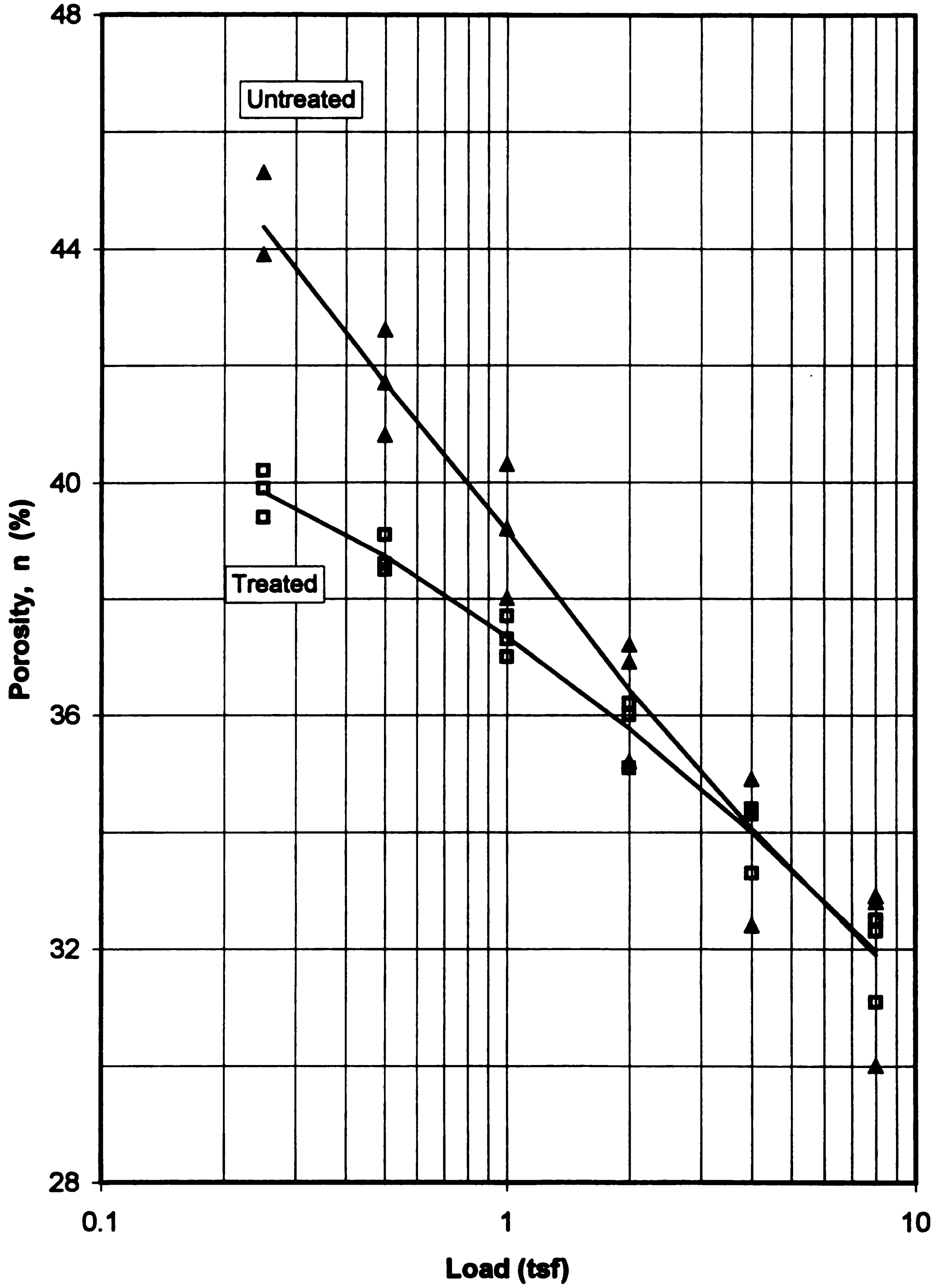

Figure 4: Porosity of treated and untreated soils permeated with water

the same manner regardless of their structure. If one imagines the clay in the space between larger grains at this point, the dispersed untreated clays expectedly sub-divided this space to a much greater degree than did the flocculated treated clays. Consequently, untreated soil exhibited smaller effective pore radius and lower conductivity than the treated soil at high loads (Figures 3 and 2).

Soltrol saturated soils under load

With application of the first load (0.25 tsf), the Soltrol conductivity of the untreated soil was 20-fold higher than that of the treated soil and its higher conductivity was sustained throughout the loading sequence (Figure 5). Each soil's conductivity was relatively insensitive to increased loading at loads below 2 tsf, and high loads were required to produce even small decreases in either of these two soil's conductivities. These results contrast greatly with what was observed when the soil was water saturated (Figure 2).

Most of the difference in Soltrol conductivity between the treated soil and the untreated soil was due to the difference between their effective pore radii; compared to the treated soil, the untreated soil maintained a much larger effective pore radius throughout the loading sequence (Figure 6). Higher porosity (Figure 7) made only a minor contribution (<7%) to the higher conductivity of the untreated soil.

The untreated soil's sustained higher conductivity throughout the loading sequence can be explained by the difference in conductivity that existed prior to loading and the relative incompressibility of both matrices. Compared to the treated soil, the greater Soltrol conductivity (Figure 5) of the untreated soil at the lowest load (0.25 tsf)

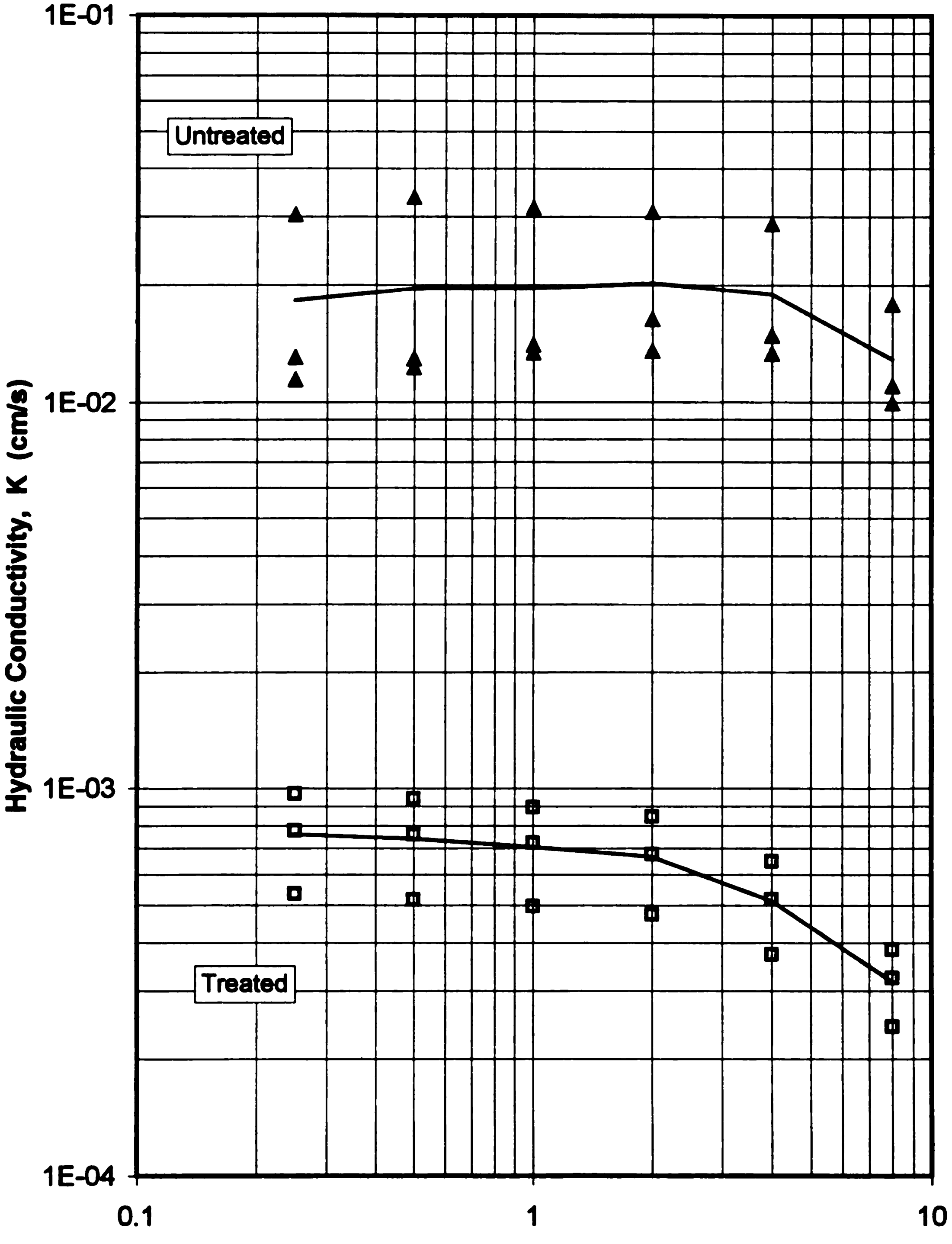

Figure 5: Hydraulic conductivity of treated and untreated soils permeated with Soltrol

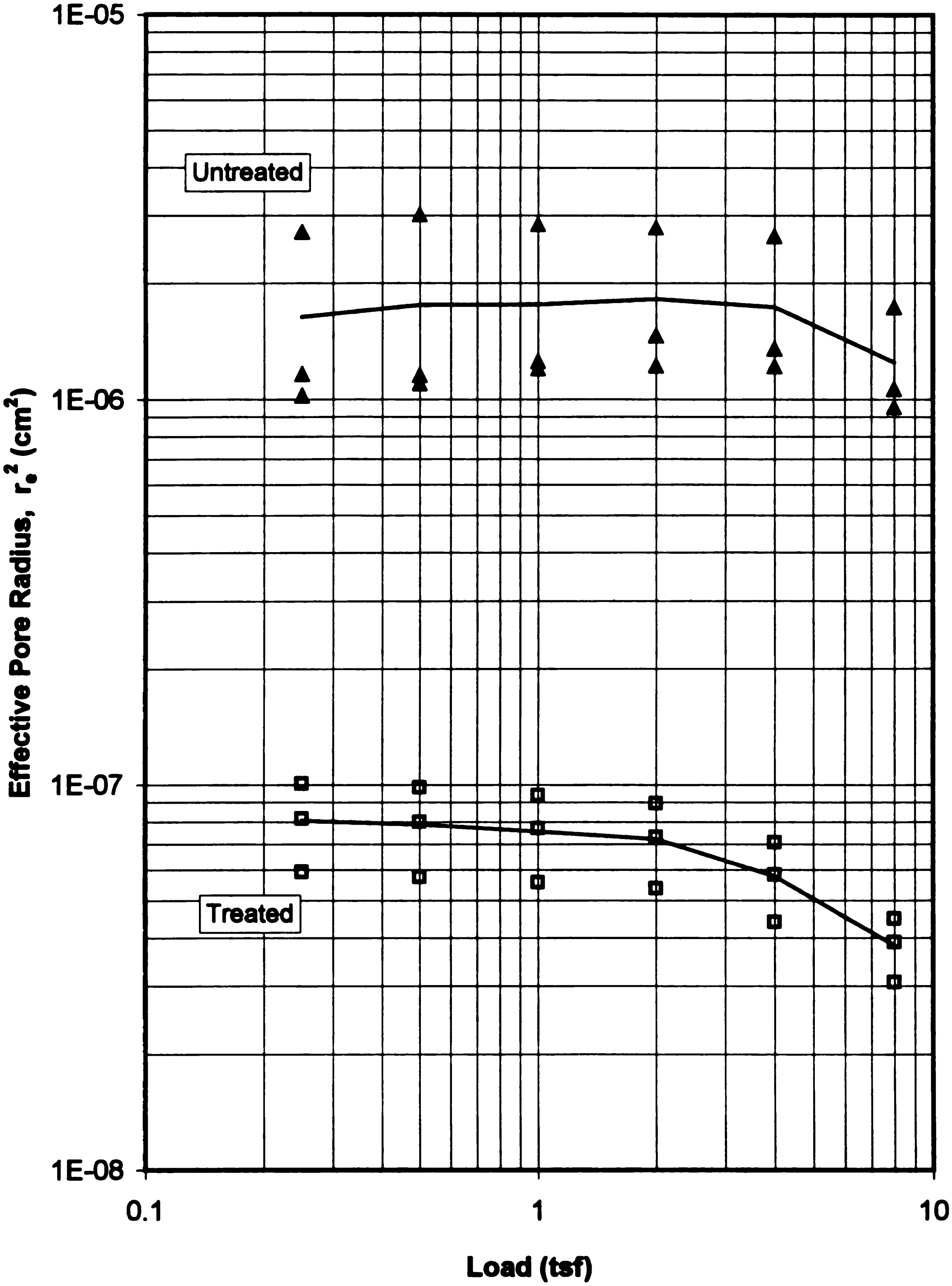

Figure 6: Effective pore radius of treated and untreated soils permeated with Soltrol

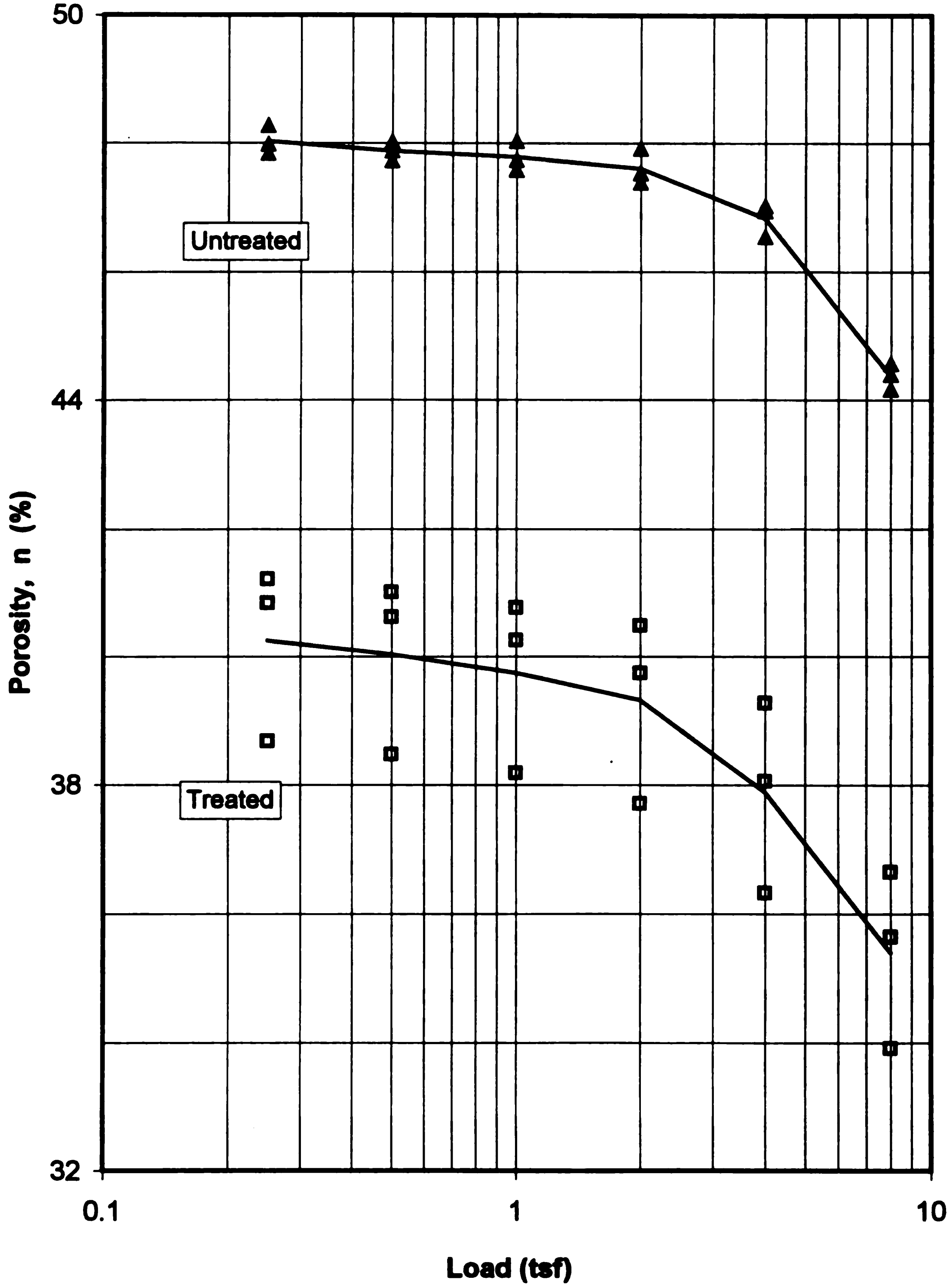

Figure 7: Porosity of treated and untreated soils permeated with Soltrol

was associated with the "fluffed up" character of this matrix that existed prior to loading (Table 3). Flocculated clays were responsible for the relative incompressibility of both matrices. The flocculation of dispersed clays that resulted from saturating the untreated matrix with Soltrol produced the untreated soil's incompressibility (Brown and Anderson, 1983; Foreman and Daniel, 1986; Bowders, 1991; Fernandez and Quigley, 1991). The Soltrol-saturated treated soil's relative incompressibility was achieved prior to saturation because the treated clays were flocculated when they were packed (Table 3).

IMPLICATIONS FOR FIELD APPLICATION

In *ex-situ* application of sorptive zone technology, soils down-gradient from the contaminated region could be excavated, organically treated in a batch reactor, and replaced. Feasibility of using such zones requires that the contaminated fluid pass through the zone rather than around it. This, in turn, relies on the hydraulic conductivity of the treated soil relative to the surrounding untreated soil.

It was shown that batch organomodification of a natural soil using the cationic surfactant HDTMA served to flocculate its clays. A comparison of packed treated and untreated soils showed that in the absence of an external load, the treated soil was denser with lower conductivity to water. The effect of increased effective stress (loading) on treated and untreated soils was found to be different. Upon loading, treated soils lost less hydraulic conductivity than untreated soils such that treated soils had higher relative conductivity at high loads. Treated soils were less compressible than untreated soils such that at high loads the difference in their porosities was eliminated. Saturation of packed treated and untreated soils with Soltrol and subsequent loading showed that both soils were relatively load insensitive. Substantially higher conductivity and porosity of untreated soil throughout the loading, compared to those of the treated one, was attributed to flocculation of untreated clays (and dispersion of the treated ones) in Soltrol.

The data suggested that *ex-situ* organomodified sorptive zone technology is hydraulically feasible as evidenced by the relatively small difference in conductivity of treated and untreated soils. Differences in hydraulic conductivity of treated and untreated soils to water remained less than one order of magnitude throughout the loading sequence. The somewhat small loss of conductivity due to treatment at shallow depths, as suggested by the data, could be accommodated by expanding the lateral dimensions of the sorptive zone to account for contaminant plume spreading that will result. However, the relatively greater resistance of treated soil to further loss of conductivity to water will offset this effect at higher depths where it becomes more conductive. Higher conductivity would effectively draw in flow lines from surrounding soils, and therefore increase the region of influence or capture area of the sorptive zone. Exposure of the organomodified sorptive zone to an LNAPL may cause a reduction in conductivity. As mentioned earlier, such a loss of conductivity could be accommodated by expanding the lateral dimensions of the sorption zone somewhat to account for pure contaminant plume spreading that will result. However, caution should be exercised in drawing conclusions based exclusively on these data as to field behavior of the soil. Conductivity changes may not occur to the same extent in the field for reasons such as subsoils having water as the wetting phase or being consolidated prior to encountering an LNAPL.

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Chapter 2

HYDRAULIC CHARACTERISTICS OF ORGANOMODIFIED SOILS FOR USE IN SORPTIVE ZONE APPLICATIONS

ABSTRACT

Modification of clay soils to increase their sorption capacity has been demonstrated in the laboratory and suggested as a potential means for preventing migration of contaminated groundwater. The hydraulic feasibility of organomodified soils for use in sorptive zone applications was studied by measuring hydraulic conductivity and porosity of treated and untreated samples of a sandy loam with different clay contents as a function of effective stress. Samples with 6, 12, 18, and 24% fine material were prepared by washing the soil on a standard US #200 sieve and recombining different amounts of the fines with the sand portion. Samples were then batch treated with hexadecyltrimethyl ammonium (HDTMA) to 80% of their cation exchange capacities. Upon initial packing all treated samples were denser than untreated ones but their conductivities did not exhibit a consistent trend. However, under the first load (24 kPa) all treated samples showed higher conductivities and similar or higher porosities than untreated ones. Higher loads decreased the difference in porosity between treated and untreated samples while increasing the difference between their conductivities. At loadings of 383 kPa and higher, all treated and untreated samples had similar porosities. At the highest load (766 kPa),

treated samples were 5 to 124 times more conductive than untreated ones depending on their clay contents. Observed differences in conductivities were explained in terms of the role of treated and untreated clays in controlling initial effective pore size and its change during consolidation. Creation of organomodified sorptive zones by batch soil processing is shown to be hydraulically feasible as evidenced by a marked increase in the conductivities of all treated samples compared to untreated ones. In addition, an increase in the sorptive capacity of the zone could potentially be achieved, without experiencing a loss in conductivity, by increasing the clay content during modification.

INTRODUCTION

The limited sorptive capacity of clays for organic contaminants can be greatly improved by replacing the naturally occurring inorganic cations with large organic cations through ion-exchange (Mortland *et al.*, 1986; Boyd *et al.*, 1988*b*, *c*, 1991; Jaynes and Boyd 1990, 1991, Sheng *et al.*, 1996*a*, *b*). The enhanced sorptive capability of the resultant organoclays suggests their utility in clay barrier technology (Smith *et al.*, 1992), for example as components of clay liners in hazardous waste disposal reservoirs and petroleum tank farms. Organic cations can also be used to convert soil clays to organoclays thereby enhancing the sorptive capabilities of soils, subsoils, and aquifer materials (Boyd *et al.*, 1988*a*, 1991; Lee *et al.*, 1989; Wagner *et al.*, 1994). Organomodified soil has been suggested for application in sorptive zones which could intercept and immobilize organic contaminant plumes (Boyd *et al.*, 1988*a*, 1991; Burris and Antworth, 1992; Xu *et al.*, 1996). A sorptive zone, coupled with subsequent biodegradation of contaminants within the zone, could provide a comprehensive aquifer remediation technology (Burris and Antworth, 1990; Nye *et al.*, 1994; Crocher *et al.*, 1995). *Ex-situ* modification is one method of placing such a zone for shallow contaminated aquifers. This could be accomplished by excavating soil down gradient from the contaminated region, organically treating the soil in a batch reactor, and placing it back in the excavation. This method would allow addition of clay or sand, if needed, to meet the desired sorption or conductivity requirements. It would also allow control of the modification agent and treatment level across the sorptive zone so that it best suits the type and level of contamination. In the simplest case, a constant treatment level throughout the modified zone can be created; something which is more difficult to achieve in an *in-situ* modification method.

Critical to the success of such sorptive zones is that organomodification not significantly reduce the hydraulic conductivity of the soil. Replacement of native exchangeable cations (e.g. Na^+) on clays with large quaternary ammonium cations such as hexadecyltrimethylammonium (HDTMA) results in flocculation of clay particles. However, over-saturation of the cation exchange capacity by organic surfactant molecules has been shown to cause clay particles to disperse due to the build up of positive charge on their surfaces (Xu and Boyd, 1994, 1995*a*, *b*, *c*). Clay flocculation and dispersion can be viewed as affecting particle size distribution, which in turn, affects the consolidation behavior of the soil (Holtz and Kovacs, 1981). More importantly, this affects pore size and pore size distribution which influences conductivity of the soil matrix (Bowders, 1985). In fact, clay flocculation and dispersion are the factors that alter the hydraulic conductivity of clay soils most significantly (Shackelford, 1994).

By changing the clay surface from hydrophilic to organophilic, organomodification also affects the ability of clays to intercalate water (Jaynes and Boyd, 1990, 1991*a*, *b*). In natural clays water hydrates the interlayer cations, causing a separation of clay platelets which is commonly referred to as swelling. In contrast, organophilic clays may swell in the presence of organic liquids but not water (Jordan, 1949). Thus the hydraulic behavior of natural swelling clays (e.g. Na-bentonites) and organically modified ones are fundamentally different. In the former case, swelling and clay dispersion can be caused by water, and in the latter by organic liquids.

The sorptive capacity of organoclay sorbent zones is likely to be directly proportional to, and limited by their organomodified clay content (Boyd *et al.*, 1988a; Lee *et al.*, 1989; Hatfield *et al.*, 1992). Therefore, adding more clay to the natural soil composition could be used to increase its sorptive capacity. However, the associated changes in hydraulic properties of the zone should be clearly defined in order to establish its hydraulic feasibility. Recently, Wallace *et al.* (1995) investigated the hydraulic feasibility of sorptive zone applications based on organomodification technology by employing an actual aquifer type soil (subsoil). They reported an initial decrease of 9-fold in hydraulic conductivity for treated soil compared to the untreated one. However, treated soils became progressively more conductive than the untreated ones with increased effective stress. The authors attributed this behavior mainly to the flocculation of treated clays and its effect on the effective pore radius of the soil matrix. It was concluded that the lateral dimensions of the sorptive zone could be increased to accommodate the lower conductivity of the treated soil at shallow depths.

Considering the early stage of organomodification technology in sorptive zone applications, it is apparent that there is a paucity of information about hydraulic behavior of modified aquifer soils. More research is needed on soils with different compositions, clay contents, and treatment levels to begin establishing practical criteria on the use of this technology. The objective of this work was to evaluate the hydraulic feasibility of *ex-situ* modified sorptive zones by investigating the effects of initial compaction, and subsequent loading on hydraulic conductivity of treated and untreated aquifer type soils with different fines contents. Conductivity changes are interpreted in the context of microscale processes such as flocculation of clays which affect the pore sizes of the soil matrix.

MATERIALS AND METHODS

An Oshtemo Bt-horizon soil (a coarse-loamy, mixed, mesic Typic Hapludalfs) from Hickory Corners, MI, was sampled at a depth of 3 to 4 ft. The soil was air dried, sieved through a US #20 standard sieve, and thoroughly mixed by hand. Sieve analysis and hydrometer tests showed particle sizes to be 87% sand, 10.5% clay, and 2.5% silt. The major exchangeable cations were 83% Ca^{2+}, 9% Mg^{2+}, 5% K^{+}, and 3% Na^{+}, as determined by Michigan State University Soil Testing Laboratory. The predominant clay minerals were vermiculite, illite, kaolinite, and hydroxy-aluminum interlayered vermiculite, as determined by X-ray diffraction analysis.

In order to compose soil samples with different fines contents from the same natural components, the Oshtemo soil was thoroughly washed with water on a US #200 standard sieve and the passed fine fraction collected and air dried. Dried fines were manually pulverized with a mortar and pestle and sieved through a US #100 standard sieve. They were then recombined with the clean, air dried sand-sized portion of the Oshtemo soil so that 6%, 12%, 18%, and 24% respectively of their masses were fine material. Recombination was accomplished by thoroughly mixing dry fines and sand and then adding 4 to 10% water by weight with additional mixing. Samples were then air dried, gently ground with a mortar and pestle, and sieved through a US #20 standard sieve. These comprised the untreated samples.

Organomodification of the reconstituted soils was accomplished by adding HDTMA-Cl (25% w/w in water) in an amount equivalent to 0.8 times the cation exchange capacity (CEC), to a 20:1 (w/w) suspension of 1 mM NaCl and soil, followed by stirring at 120 rpm for 1 minute, then at 20 rpm for 30 minutes. Treated soil was settled out of suspension and the clear solution was decanted. Subsequently, the treated soil was air dried, gently ground with a mortar and pestle, sieved through a US #20 standard sieve, and kept in an open pan (hereafter referred to as treated samples). For the purposes of this work, the CEC was determined by the first plateau of the HDTMA adsorption isotherm (Xu and Boyd, 1995*a*). This reference treatment level was found to be 27 mmole kg^{-1}, for the soil with 12% fines.

Turbidity of soil suspensions equilibrated with different amounts of HDTMA was measured utilizing 25-ml Corex tubes containing 1:10 mixtures of soil and 1 mM NaCl, to which appropriate volumes of HDTMA solution, corresponding to 0.01 to 3.0 times the CEC (0.01 to 3 CEC), were added and immediately mixed. The tubes were then shaken for 4 days on a rotating shaker and allowed to stand for 0.5 hr. Samples of the suspension (1 ml) were collected from 1 cm below the surface, diluted with water to turbidities within the range of 10-100 nephlometric turbidity units (NTU), for turbidity determination by nephelometry. The procedure employed was consistent with that used by Xu and Boyd (1995*a*) and in compliance with ASTM D1889.

A fixed ring consolidometer was used to perform falling-head conductivity measurements while a vertical stress was applied to the sample. A load frame equipped with a precision displacement transducer (0.0001 inch; 0.00025 cm) was used to apply different effective stresses and measure the thickness of the sample at each stress. Head loss in the consolidometer channels, connections, porous stones, and filter papers was assessed by assembling the device without any soil in it and measuring its conductivity (K_{blank}) at different effective stresses. Treated and untreated soil samples were packed by pouring 130 g air dried soil into the consolidometer ring; Whatman #54 filter paper was placed on both ends of the soil column. Samples were then tamped slightly to flatten the upper surface and compacted gently with a drop hammer. The entire consolidometer was placed into a desiccator and vacuum saturated over night with an aqueous solution of 1 mM NaCl.

Saturated samples were placed in the load frame and subjected to an effective stress (loading) sequence from 0 to 766 kPa using the conventional consolidation procedure (ASTM D2435-90). At each load hydraulic conductivity (K) was measured by the falling head method (ASTM D5084-90) and the thickness of the sample was measured. An aqueous solution of 1 mM NaCl in deionized, deaired water was used as the permeant. Porosity was calculated from the measured thickness of the consolidated sample and hydraulic conductivity of the soil sample was calculated from the predetermined K_{blank} and three to five conductivity measurements at that load, adjusted to 20 °C (Daniel, 1989).

RESULTS AND DISCUSSION

Treatment and clay structure

The amount of HDTMA added to soils with different clay contents determined the turbidity of their suspensions (Figure 8). In untreated (0 CEC) and over saturated (>2 CEC) samples, clay particles were dispersed as indicated by turbid suspensions. Clays were flocculated at treatment levels near 1 CEC. The general U shape curve relating turbidity to HDTMA added is consistent with findings of Xu and Boyd (1994, 1995a) who discussed the microscopic mechanisms underlying this behavior. A treatment level of 0.8 CEC was selected for conductivity measurements as representative of the region where the clays are fully flocculated and the majority of cation exchange sites are occupied by HDTMA. These measurements were then contrasted to those from untreated soils, where the exchange sites occupied predominately by Na^+ and the clays were dispersed. The turbidity results were consistent with qualitative observations made during conductivity experiments that effluent from the consolidometer reservoir was clear with treated samples and cloudy with untreated ones.

Porosity

Prior to saturation, dry-packed untreated samples were 5 to 13% more porous than treated ones, depending on their clay content (Table 4). Average porosities of both treated and untreated samples increased with their clay content with the magnitude of the

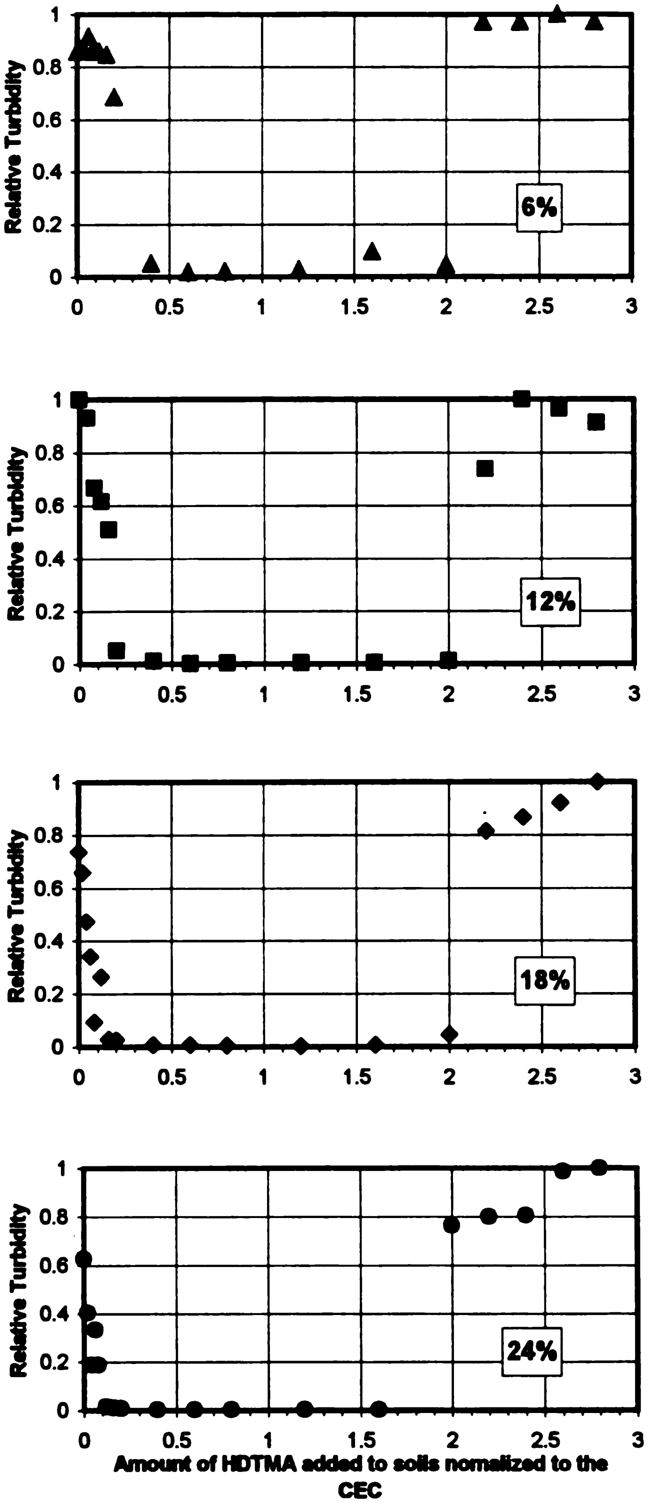

Figure 8: Turbidity of soils with different fine contents

Table 4: Average porosity, $\bar{n}$ ($\pm S_{\bar{n}}$) of soils at zero load, the first load, and porosity decrease due to application of the first load

Fines	$\bar{n}$ in untreated soils (%)				$\bar{n}$ in treated soils (%)			
Content (%)	Dry packed[†]	Saturated[‡]	First load[§]	Δ[¶]	Dry packed[†]	Saturated[‡]	First load[§]	Δ[¶]
6	44.2± (0.2)	44.3± (0.2)	42.1± (0.3)	2.2	41.3± (0.2)	41.6± (0.2)	40.9± (0.3)	0.7
12	44.8± (0.2)	45.2± (0.1)	38.9± (0.1)	6.3	42.3± (0.1)	42.5± (0.2)	41.0± (0.1)	1.5
18	47.0± (0.2)	47.4± (0.2)	40.5± (0.2)	6.9	44.8± (0.2)	45.5± (0.2)	44.4± (0.1)	1.2
24	50.3± (0.3)	51.0± (0.3)	41.5± (0.2)	9.4	44.7± (0.1)	45.9± (0.1)	44.3± (0.1)	1.6

[†] Prior to saturation at zero load

[‡] Saturated samples at zero load

[§] Saturated samples at load of 24 kPa

[¶] $n_{\text{at zero load}} - n_{\text{at the first load}}$

increase being greater in the untreated samples. As the fine content increased from 6% to 24%, porosity of untreated samples increased by 6.1%, while this increase was only 3.4% in treated ones. The variation in porosity with clay content, especially in untreated samples, highlights the role of the clay and its structure in the initial assemblage of the soil matrices. Saturation with water increased the porosity of treated and untreated samples less than 3%. Untreated samples remained more porous than treated ones after saturation.

With application of the first load a decrease in porosity was observed that was much higher in untreated samples compared to the treated ones (Table 4). This decrease for the untreated soils was approximately proportional to the clay content. This resulted in the untreated samples having porosities approximately equal to or less than the treated ones at the first load (24 kPa).

Clay particles may reside in the pore space created by sand grains, or in between sand grains, in which case they are part of the load bearing mechanism of the matrix (Kenney *et al.*, 1992). It appears that in the untreated samples, dispersed clays resided between the sand grains, especially at high clay contents. Furthermore, the clay platelets may be poorly ordered relative to one another (e.g. in an edge-to-face arrangement). This resulted in a relatively unstable but more porous matrix at zero load. Application of the first load collapsed this unstable structure, resulting in a relatively large consolidation of the soil matrix. This trend was more profound in samples with higher clay contents. Treated samples were initially not as porous as untreated samples, apparently due to the highly ordered, parallel structure of the flocculated clays. As a result, the first load only slightly decreased the porosity; far less than the magnitude of the drop in their untreated counterparts.

Subsequent load applications, following the first, produced additional consolidation with no observable abrupt changes (Figure 9). In the 6% fine soil (Figure 9*a*), untreated samples were more porous on average, but relatively high variations between samples were observed in both the treated and untreated case. Soils with higher clay contents exhibited less variation and treated samples were generally more porous than untreated samples except at the highest loads where they were similar (Figure 9*b-d*). At low loads, untreated samples were less porous, and somewhat less compressible than the treated ones. Apparently, the dispersed clays in the untreated soil facilitated rearrangement of particles under a relatively low load causing the matrix to collapse and lose more porosity than was the case with the treated soil matrix. Higher loads were then sustained more effectively by the untreated soil matrix which had limited space for further consolidation. Treated soils had more stable structures at zero load. The magnitudes of their porosity loss due to the first load were comparable to their compressibility throughout the loading sequence. This means that their flocculated clay structure resulted in a relatively dense and stable initial pack which consolidated gradually as the loading increased. Therefore, flocculated clays may have actually been an essential part of the load bearing mechanism of the treated soil samples, thereby producing higher porosities compared to untreated samples at low loads.

Differences in the porosities of treated and untreated samples decreased with load such that nearly identical porosities were observed for the two materials at high loads.

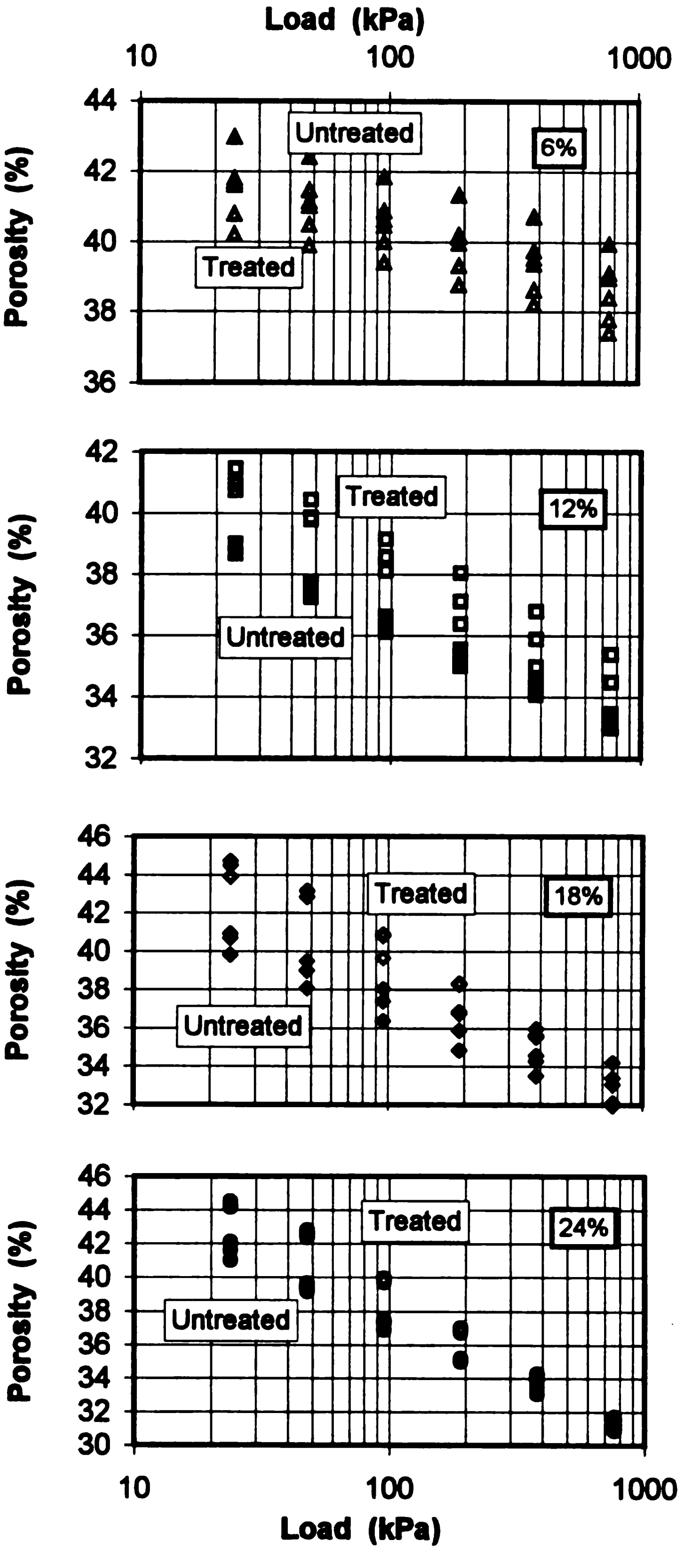

Figure 9: Porosity of soils with 6%, 12%, 18%, and 24% added fines at different loads

This similarity suggests that consolidation was ultimately controlled by the larger soil particles which were identical in the two materials. At such high loads, clays evidently accommodated rearrangement of granular particles, and hence consolidation, in the same manner regardless of their structure.

Fines content influenced the porosity of untreated and treated samples (Figure 10). Untreated samples with 6% fine material were the most porous throughout the loading sequence (Figure 10-*a*). They showed very low compressibility which is similar to the response of a sand matrix. Apparently, sand particles were the main load-bearing fraction in these samples. All samples with higher clay content were more compressible and in all cases the compressibility increased with increasing clay content. This suggests that higher clay content facilitated rearrangement of the soil particles. This behavior is also consistent with the fact that in general, clay soils are more compressible than sands (Freeze and Cherry, 1979).

Porosity of treated samples with different clay contents reveals that at low loads, average porosities of treated samples with 6 and 12% fines were similar (Figure 10-*b*). Porosities of samples with 18 and 24% fines were similar as well, but larger than those of the first group. This observation suggests that the load bearing mechanism was different in the two groups.

Conductivity

Conductivities of treated and untreated samples at zero load did not show a consistent trend (Table 5). However, application of the first load (24 kPa) resulted in a substantial decrease in the conductivity of each of the untreated soils, and a minor

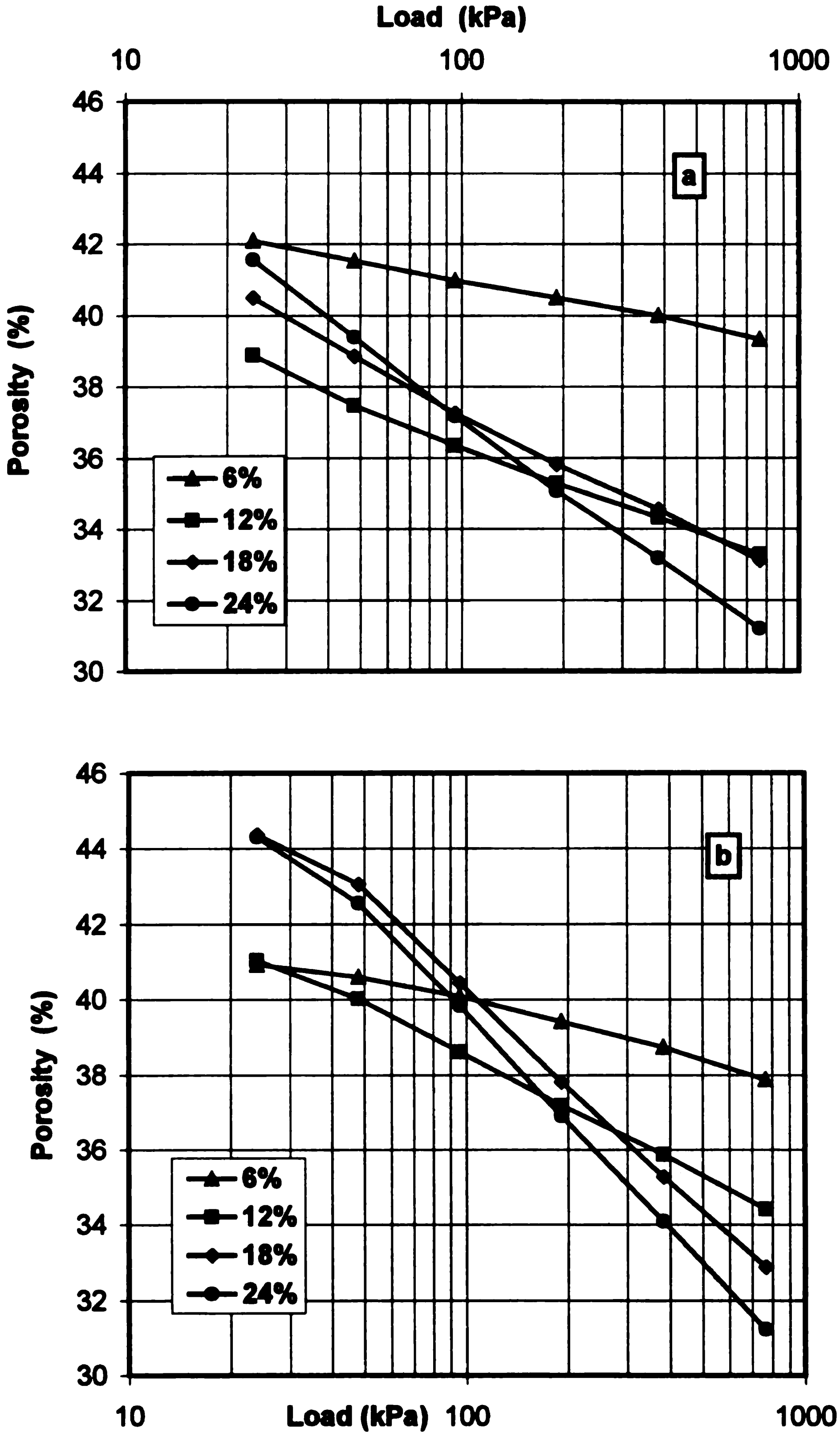

Figure 10: Average porosity of a) untreated and b) treated soils with 6, 12, 18, 24% added fines

Table 5: Average hydraulic conductivity, K (±S_K) of soils at zero load, the first load, and its drop due to application of the first load

	K in untreated soils (*cm* s^{-1})			*K* in treated soil (*cm* s^{-1})		
Fines Content (%)	Saturated[†]	First load[‡]	Δ[§]	Saturated[†]	First load[‡]	Δ[§]
6	0.034± (0.001)	0.010± (0.0007)	3.3	0.096± (0.012)	0.079± (0.006)	1.2
12	0.022± (0.002)	0.003± (0.0003)	7.4	0.012± (0.001)	0.009± (0.001)	1.3
18	0.023± (0.002)	0.012± (0.00004)	19.5	0.068± (0.008)	0.052± (0.005)	1.3
24	0.016± (0.003)	0.004± (0.00001)	36.9	0.015± (0.001)	0.011± (0.001)	1.4

[†] Saturated samples at zero load

[‡] Saturated samples at load of 24 kPa

[§] $K_{\text{at zero load}} / K_{\text{at the first load}}$

decrease for each of the treated soils such that all untreated soils were less conductive than treated ones at that load. The drop in conductivities, with the initial load, depended on the clay content in both treated and untreated samples. These results are consistent with the observed decreases in porosity, so it is constructive to evaluate the extent to which these two parameters are linked and what other characteristics of the soil matrix might affect conductivity.

Hydraulic conductivity is a function of the soil matrix property, intrinsic permeability (*k*), and the fluid properties of viscosity (μ) and density (ρ);

$$K = k\frac{\rho g}{\mu}$$

To eliminate the possibility that the soil treatment altered fluid properties as the water percolated through treated and untreated soils, viscosity and density of permeant water from both materials was measured. Since less than a 1% difference was found in these properties, it was concluded that conductivity differences resulted exclusively from changes in the soil permeabilities. The analogy of Poiseuille flow through a bundle of capillary tubes can be used to describe permeability as a function of porosity (*n*) and an effective pore radius (r_e) (Allred and Brown, 1994);

$$k = nr_e^2$$

Using this relationship, the differences in porosities accounted for less than 17% of the differences in conductivities of treated vs untreated soils at low loadings. We therefore conclude that change in effective pore radius was the primary cause of the conductivity difference observed in these soils.

The untreated soil formed a more porous matrix upon packing which was very sensitive to external load in terms of its effective pore radius. Application of the first load collapsed the matrix and apparently forced the clay particles from between the sand grains into the interior regions of pores. This had the effect of partitioning the pores into smaller sections (i.e. smaller pores) and lowered conductivity. Higher clay contents initially produced a more porous matrix, and they resulted in higher drop in conductivity with application of the first load. Application of the first load also dropped conductivities of the treated samples, but to less of an extent. Flocculated clays in treated samples, forming bigger aggregates, evidently were less easily forced into the interstitial spaces and were less able to partition the pore space into small sections, manifesting smaller drops in conductivity.

Changes in conductivities of treated and untreated soils with increasing load are shown in Figure 11. Solid lines on the graphs represent two standard deviations on either side of the data, established by the maximum of either the variance in the averages, or the error propagated from estimated measurement uncertainties. It can be observed that all treated samples had higher conductivities than untreated ones throughout the loading sequence. These differences were sustained over the range of loads employed with similar systematic decreases in conductivity with increased load for both types of soils. Treated samples were 3 to 129 times more conductive depending on load and clay content.

At these higher loads, differences in porosities accounted for less that 11% of observed differences in conductivities between treated and untreated soils, again suggesting that treatment primarily alters the sizes of conductive pores, and that this is

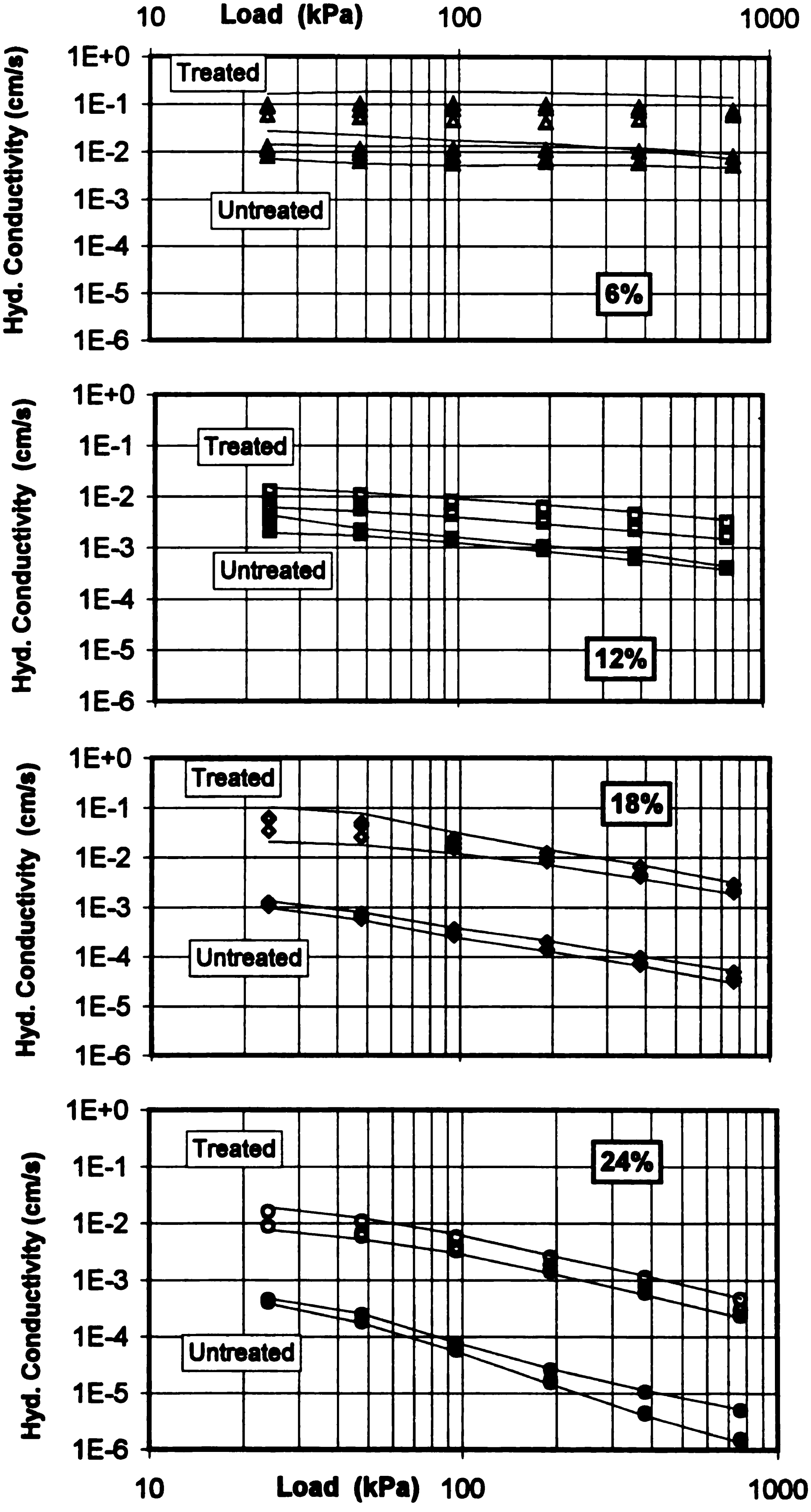

Figure 11: Hydraulic conductivity of soils with different fines contents

applicable to the full range of the loading sequence. It is interesting to note that at high loads, where treated and untreated samples had identical porosities (Figure 9), conductivities were substantially different. Because the clays were occupying the same total volume in both treated and untreated samples, differences must result from large significant differences in pore geometry. The larger pores sustained by the flocculated treated clays produced conductivities up to 129 times higher.

Loss of conductivity with consolidation for untreated soils was directly related to the amount of fine material (Figure 12-*a*). This is entirely consistent with the common observation that higher clay contents correspond to lower conductivity and higher compressibility. Higher amounts of clays partition the pore space to smaller sections and facilitate easier rearrangement of particles. In contrast, the treated soils showed more complex behavior as clay content increased (Figure 12-*b*). The 6% fines sample exhibited high conductivity and low compressibility. With 12% fines, the conductivity at low loads dropped substantially and slightly higher compressibility was observed. At 18%, the initial conductivity was greater than the 12% material, nearly equaling the 6%, but a high compressibility was observed. Finally, the 24% material had both low initial conductivity, similar to the 12% material, and substantial consolidation due to the loading sequence.

Previous studies have established that in Na-bentonite sand mixtures, as the clay content increases, it first fills the pore space created by sand grains and then resides between the grains (Kenney *et al.*, 1992). At a certain "cut off" clay content, when clays completely fill the pore space created by sand grains, a very low conductivity is achieved.

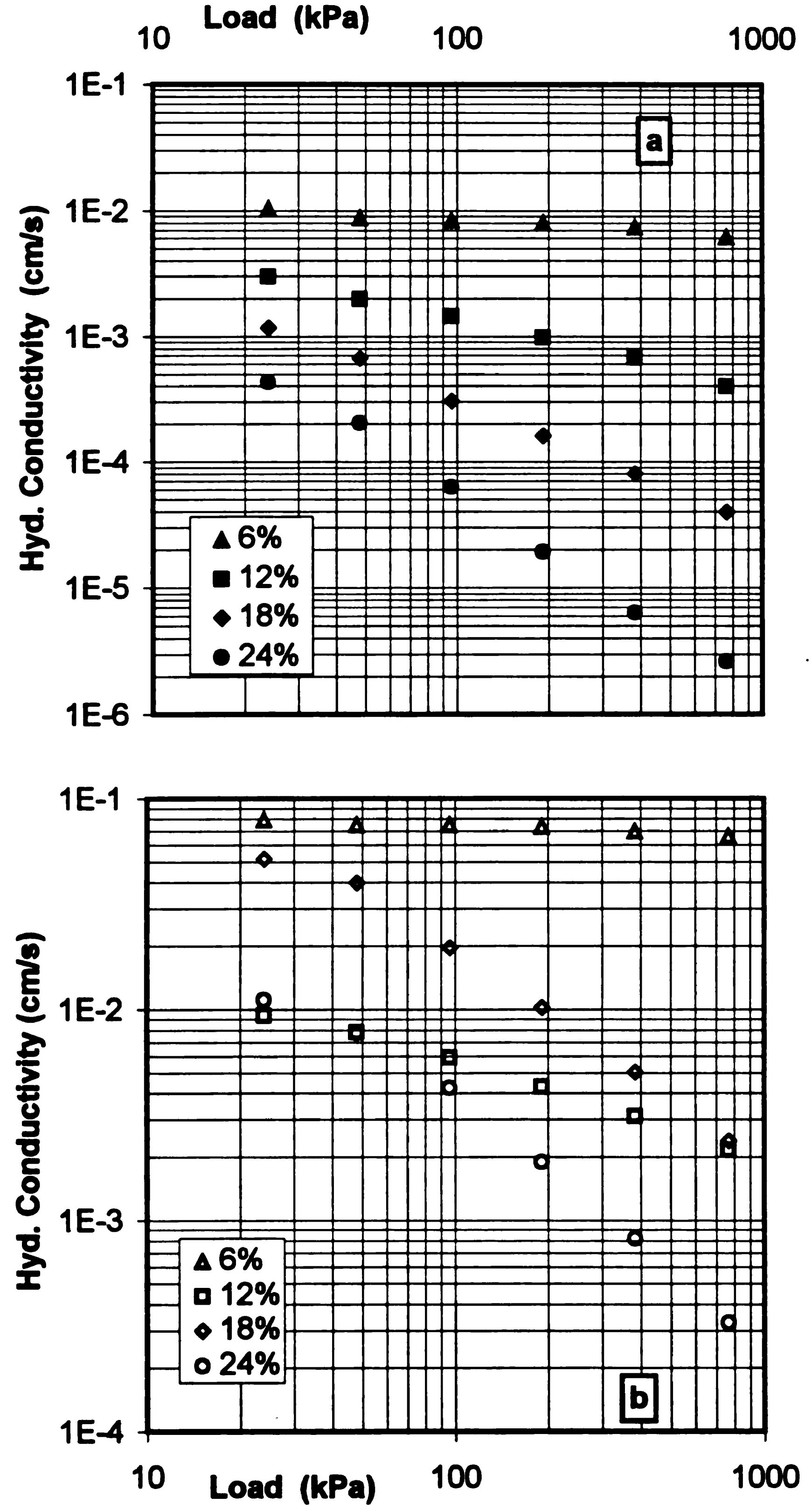

Figure 12: Hydraulic conductivity of a) untreated, and b) treated soils with different fines contents

The minimal additional reduction in hydraulic conductivity caused by increasing the clay content beyond that point has been used to infer the cut off clay content (Daniel, 1987; Kenney *et al.*, 1992).

These concepts can be used to help explain the porosity and conductivity data for the treated samples (Figure 10-*b* and 12-*b*). In the 6% fine samples there was not enough clay to fill the void space created by the sand grains of the matrix. High conductivities were observed because the flocculated nature of the clays left relatively large conductive pores and only minimal consolidation occurred because the load was supported primarily by the sand matrix. At the 12% fines level, the fines filled this pore space and probably some additional portion resided between the sand grains. In this arrangement, with the fines mostly residing in the pore space created by sand grains, porosities similar to those of 6% fine samples were obtained (Figure 10-*b*) but conductivities were much lower (Figure 12-*b*). The increase in compressibility presumably resulted from the clays between the sand grains which accommodated easier rearrangement of sand particles with increased loading. The additional clay in the 18% fine samples was apparently placed between some sand grains, creating new large pores, and hence increasing both initial porosity (Figure 10-*b*) and conductivity. However, with the clays in between sand grains, the sample was more sensitive to increased loading in terms of loss of porosity and conductivity. Finally, at a level of 24% fine material, the new large pores created in 18% fine samples, were filled with the additional fines whereby the porosity remained similar to the 18% samples, but the conductivity was lowered substantially. Similar high sensitivity of 18 and 24% fine samples to increased loading in terms of their porosity and conductivity indicates that in both samples clays were dominating the response of the matrix to load.

All hydraulic conductivities of samples with different clay contents increased as a result of treatment with HDTMA (Figure 13-*a*). Ratios of conductivity in treated and untreated soils ($K_{treated}/K_{untreated}$) reveal that treatment produced a much greater increase in conductivity for the 18 and 24% fine samples than for the 6 and 12% fine samples. This provides another evidence that pore geometry, which controlled the conductivity, was different between the two groups. In samples with 6 and 12% fines, the clays were mostly residing in pore spaces created by the sand grains, and treatment increased their conductivity by flocculating the dispersed clays and "opening up" these pore spaces. In samples with 18 and 24% fines, clays were not only filling these pore spaces, but also residing in between sand grains. Here, treatment opened up larger pores in both spaces, which in turn, increased conductivity substantially.

IMPLICATIONS FOR FIELD APPLICATION

In *ex-situ* applications of sorptive zone technology, soils down-gradient from the contaminated region could be excavated, organomodified in a batch reactor, and replaced. Feasibility of using such zones requires that the contaminated fluid pass through the zone rather than around it. This, in turn, relies on the hydraulic conductivity of the treated soil relative to the surrounding untreated soil. Furthermore, in *ex-situ* modification technology, addition of clay to the natural soil in order to increase the net sorption capacity can be considered as long as the zone remains hydraulically feasible.

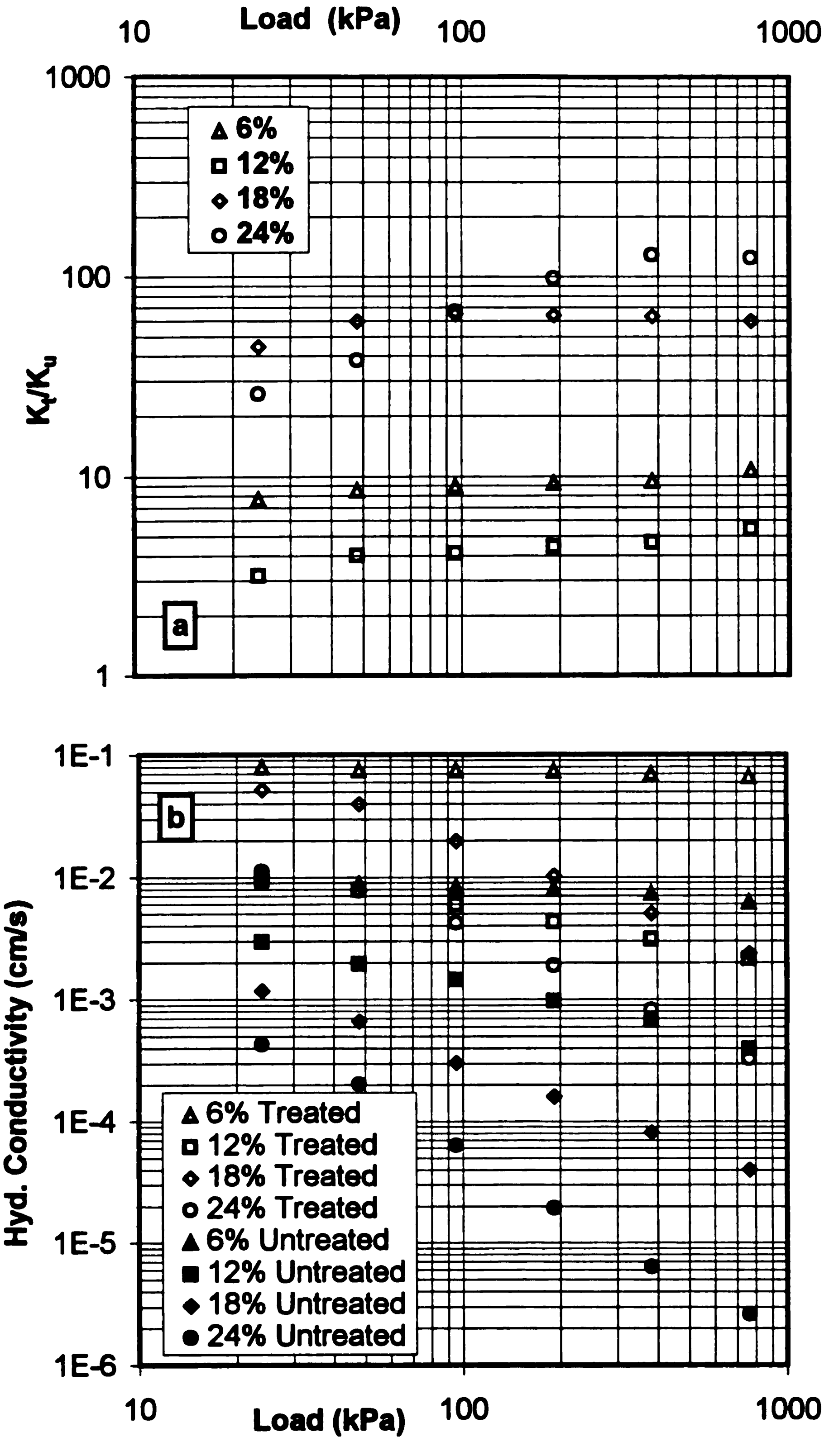

Figure 13: Comparison of average hydraulic conductivities (K); a) ratio of treated and untreated soils, and b) all samples

The data demonstrated that *ex-situ* organomodified sorptive zone technology was hydraulically feasible as evidenced by a marked increase in conductivity of all treated samples compared to untreated ones. This increase varied from 3 to 129-fold depending on the clay content and the load (Figure 13-*a*). In the design of sorptive zones developed by batch treatment, such increases of conductivity could effectively draw in flow lines from surrounding soil, and therefore increase the region of influence or capture area of the sorptive zone. It is important to note that the baseline used for comparison was soil permeated with 1 mM NaCl which would promote clay dispersion. Thus, the increase in conductivity associated with HDTMA treatment may represent maximal values. In addition, the data represent the increase in conductivity of recombined samples which may have different matrices compared to natural soils. Therefore, for field applications, a similar lab study of the particular soil under consideration is necessary prior to feasibility determination of the technology. Nonetheless, the results suggest that there are no fundamental hydraulic barriers to *ex-situ* soil modification using cationic surfactants.

Superposition of average conductivities of treated and untreated samples with different clay contents shows that in general, treated samples with higher clay contents had comparable conductivities to untreated samples with lower clay content (Figure 13-*b*). This suggests that it may be possible to increase the sorptive capacity of a zone by increasing its clay content prior to modification, without lowering its conductivity. In fact, the data suggests that at shallow depths it would be possible to quadruple the sorptive capacity by quadrupling the clay content of a 6% soil without lowering its conductivity. At higher depths doubling the clay content of a 12% clay soil would not lower its conductivity while this would double its sorptive capacity.

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Chapter 3

HYDRAULIC FEASIBILITY OF *IN-SITU* MODIFIED SORPTIVE ZONES; HYDRAULIC CONDUCTIVITY OF SOILS ORGANOMODIFIED TO DIFFERENT LEVELS IN A BATCH SYSTEM

ABSTRACT

Hydraulic feasibility of *in-situ* organomodification of soils for sorptive zone applications was studied by measuring hydraulic conductivity of a sandy loam with different clay contents, batch treated to 0.1 (low-treated) and 2.2 (high-treated) times its cation exchange capacity (CEC), and subjected to different effective stresses. The results were viewed in combination with our previous study on the same soil treated to 0 (untreated) and 0.8 (mid-treated) times the CEC in order to provide a full spectrum of treatment level consideration. Samples with 6, 12, 18, and 24% fines were prepared by washing the soil on a Standard US #200 sieve and recombining different amounts of the fines with the sand portion. Samples were treated with hexadecyltrimethyl ammonium (HDTMA) in a batch system and subsequently air dried and sieved through a US #20. Upon initial dry packing, all high-treated samples were denser than low-treated ones. Saturation with water induced less than 3% change in their porosities while their

conductivities didn't exhibit a consistent trend. However, under the first load (0.25 tsf) all high-treated samples showed higher conductivities with similar or higher porosities than low-treated ones. Higher loads decreased the difference in porosity of high- and low-treated samples while increased the difference between their conductivities. Turbidity of suspensions from high- and low-treated soils was used to infer the clay structure in our soils. Observed differences in conductivities were explained in terms of the role of clay structure in controlling initial effective pore radius and its change during consolidation. Treatment of soil to levels above its CEC, which can occur in creation of *in-situ* organomodified sorptive zones is hydraulically manageable as evidenced by higher hydraulic conductivity of high-treated samples compared to low-treated ones.

INTRODUCTION

It has been shown that large organic cations can be used to replace the metal cations associated with the clay matrix of a soil in order to increase the limited sorptive capacity for organic contaminants (Boyd *et al.*, 1988*a*). Previous studies have suggested that this increased sorptive capacity of organomodified soils could be managed to create a sorptive zone which immobilizes the dissolved organic chemicals in contaminated ground waters (Burris and Antworth, 1992; Wallace *et al.*, 1995; Xu and Boyd, 1994, 1995). A sorptive zone, coupled with subsequent bioremediation of contaminants within the zone, could provide a comprehensive aquifer remediation scheme (Burris and Antworth, 1990). Hydraulic feasibility of *ex-situ* modified sorptive zones has been established by measurement of their higher conductivity compared to untreated surrounding (Rakhshandehroo *et al.*, submitted).

Underground injection of an aqueous solution of organic cations through a set of injection wells has been proposed to create an *in-situ* organomodified sorptive zone (Boyd *et al.*, 1988*a*). Hexadecyltrimethyl ammonium (HDTMA) was identified as one of the most effective cations for this purpose due to its excellent cation exchange properties, effectiveness in modifying a variety of clay mineral types, and high sorptive capacity for many organic contaminants (Lee *et al.* ,1989; Boyd *et al.*, 1988*b*,*c*; Jaynes and Boyd, 1990, 1991). Burris and Antworth (1992) simulated *in-situ* injection of HDTMA to their soil columns and box model aquifer material and reported that effective sorptive zones were created.

In-situ injection will likely result in a non-uniform distribution of the treatment (Xu and Boyd, 1995). It may occur vertically due to the different overburden loads on the soil at different depths which can result in different pore geometries, pore velocity of treatment solution, and accessibility of sites to surfactant molecules. It may occur radially from the point of injection due to surfactant consumption with distance from the injection point as well as changes in velocity. Field heterogeneity may also be responsible for producing a non-uniform treatment level in an *in-situ* modification process. In general, one may imagine that in regions far away from point of injection the treatment level correspond to less than CEC of the soil, and in regions close to the point of injection the treatment would exceed the CEC of the soil. Burris and Antworth (1992) injected HDTMA to their column and box model aquifer soils and found that such treatment profiles were in fact created in the *in-situ* injection of the surfactant under their experimental conditions.

Organomodification of clays to different levels has a major effect on their flocculated or dispersed structure (Theng, 1974). Xu and Boyd (1994, 1995) found that in originally dispersed soils, treatment with HDTMA to levels far below and far above the CEC resulted in clay dispersion, while treatment to levels slightly below the CEC produced flocculation in clays. The mechanisms of dispersion at low and high ends however are quite different. In high-treated soils, excess HDTMA is hydrophobically bonded on the clay surfaces, creating a net positive hydrostatic charge that causes dispersion. On the other hand, dispersion in low-treated clays is due to the net negative charge on their surfaces from unneutralized exchange sites (Xu and Boyd, 1995). In any case, clay dispersion and flocculation are demonstrates to significantly affect hydraulic conductivity of soils (Shackelford, 1994).

While Burris and Antworth (1992) reported no apparent overall change in hydraulic conductivity of their *in-situ* modified columns or box model aquifer, their apparatus was incapable of separately measuring conductivity of sections treated to different levels. Despite the fact that a typical column study with the soil packed and treated in-place has practical appeal, a simpler experiment serving as the first indicator of basic effects is more appropriate, considering the early stage of our understanding of this relatively new material (i.e. organomodified soils). Soils may be treated to different levels in a batch system and their conductivities measured under different stresses. Batch experiments require less technical development and appear to have the advantages of being simple, easily reproducible, and insightful. To our knowledge, no specific study of the effects of treatment level on hydraulic conductivity of soils has been previously reported.

The effects of batch treatment on hydraulic conductivity of soils with different clay contents was studied by authors in a previous paper. The focus of that work was the *ex-situ* application of sorptive zone technology, therefore a treatment level of 0.8 times the CEC was employed. It was shown that the treatment increases hydraulic conductivity of all soil samples under the applied range of effective stresses and concluded that the technology is hydraulically feasible (Rakhshandehroo *et al.*, submitted).

In the present study, which focuses on the *in-situ* application of the technology, authors wish to extend this understanding to soil samples treated to different levels. The objectives of the study were to evaluate the hydraulic feasibility of *in-situ* treated sorptive zones by (i) investigating the changes in conductivity of soils with different clay contents induced by batch treatment to levels far below and far above the CEC, (ii) monitoring this change under different effective stresses and seeking its correlation with the microscale processes such as clay dispersion (or flocculation) in determining the pore geometry of the soil matrix, and (iii) incorporating these results with those from the previous study to assess the feasibility of field application of the *in-situ* injection technique.

MATERIALS AND METHODS

A sandy loam B-horizon soil (Oshtemo series; a coarse-loamy, mixed, mesic Typic Hapludalfs from Hickory Corners, MI) from the depth of 3~4 ft was obtained for these experiments. The soil was air dried, sieved through a US standard #20 sieve, and carefully blended until a homogenized mixture was obtained. Particle size analysis indicated the sample was 87% sand, 10.5% clay, and 2.5% silt based on sieve analysis and hydrometer tests. Quantity and type of exchangeable cations were 83% Ca^{2+}, 9% Mg^{2+}, 5% K^{+}, and 3% Na^{+}, as determined by Michigan State University Soil Testing Laboratory. The predominant clay minerals were vermiculite, illite, kaolinite, and hydroxy-aluminum interlayered vermiculite, as determined by X-ray diffraction.

In order to construct soil samples with different clay contents from the same natural components, the Oshtemo soil was thoroughly washed on a US standard #200 sieve and the passed fine fraction was collected and air dried. Dried fines were manually pulverized with a mortar and pestle and sieved through a US standard sieve #100. They were then recombined with the clean, air-dried sand portion of the Oshtemo soil at levels of 6%, 12%, 18%, and 24% fine material. Recombination was accomplished by thoroughly mixing dry fines and sand and then adding water (4 to 10% wt/wt) with additional mixing. Samples were then air dried, gently ground with a mortar and pestle, and sieved through a US standard #20 sieve.

Organomodification of the reconstituted soils was accomplished by adding HDTMA chloride (25% wt/wt in water) in an amount equivalent to 0.1 and 2.2 times the CEC, to a 20:1 (wt/wt) suspension of 1 mM NaCl and soil, followed by stirring at 120 rpm for 1 minute, then at 20 rpm for 30 minutes. Treated soils were settled out of suspension and the clear suspension was decanted. Subsequently, the treated soils were washed from the jars into a large container and allowed to air dry. Treated air dried soils were then gently ground with a mortar and pestle, sieved through a US standard #20 sieve, and kept in open pans for conductivity experiments. Small amount of soils were treated to a mid point (0.8 CEC) in the same manner as explained above, for comparison in the turbidity experiments. Hereafter in this paper, low-, mid-, and high-treated soils refer to the soils treated to 0.1, 0.8, and 2.2 CEC, respectively. For the purposes of this work, the CEC was determined by the first plateau of the HDTMA adsorption isotherm (Xu and Boyd, 1995). This reference treatment level was found to be 27 mmole/kg for the soil sample with 12% fines.

According to our previous study and the work of Xu and Boyd (1995) we expected the low- and high-treated soils to have a dispersed clay structure and the mid-treated soil a flocculated one. A set of turbidity measurements was conducted to verify that whether after the samples were air dried and rewetted with water the clay structure was changed. For these measurements 2.4 gr air dried sample from untreated, low-, mid-, or high-treated soil was mixed with 25 ml aqueous solution of 1 mM NaCl in small Corex tubes. The tubes were then shaken for 4 days in a rotating shaker and allowed to stand for 0.5 hr. Turbidity of the supernatant was determined by nephelometry on the soil suspension sampled from one cm below the surface in each tube. The procedure employed was consistent with that used by Xu and Boyd (1995) and in compliance with ASTM D1889.

A fixed ring consolidometer, which allows falling head conductivity measurements, and a load frame equipped with a precision displacement transducer (0.0001 inch sensitivity) were employed for conductivity experiments. Treated and untreated samples were packed by pouring air dried soils into the consolidometer ring with filter paper (Whatman #54) on the top and bottom of the sample. Samples were then tamped slightly to flatten the upper surface, and compacted with a drop hammer to a nominal initial thickness of 2.5 cm, and vacuum saturated in a desiccator with an aqueous solution of 1 mM NaCl. Saturated samples were then subjected to an effective stress (loading) sequence from 0 to 8 tsf using a conventional consolidation procedure (ASTM D2435-90).

Hydraulic conductivity of the system at different effective stresses was measured by the falling head method (ASTM D5084-90). Head losses in the tubes, connectors, porous stones, and filter papers were quantified by assembling the consolidometer without any soil and measuring its conductivity (K_{blank}) at different effective stresses. Hydraulic conductivity of the soil sample was then calculated from the predetermined K_{blank} and two or three conductivity measurements at that load and adjusted to 20 °C. At each load, the sample thickness was measured and porosity was calculated from the measured thickness of the consolidated sample.

RESULTS AND DISCUSSION

Treatment level and clay structure

Treatment of soils with HDTMA to different levels determined the turbidity of their suspensions (Figure 14). Closed symbols on Figure 14, which follow a general L shape curve relating turbidity to HDTMA added, are the results from the present study. For ease of comparison, turbidity results from our previous study are superimposed on the figure and shown in open symbols. We reiterate here that the only difference in soil samples prepared for turbidity tests in two studies is that in the previous study untreated soil samples were equilibrated with HDTMA solutions (with different concentrations)

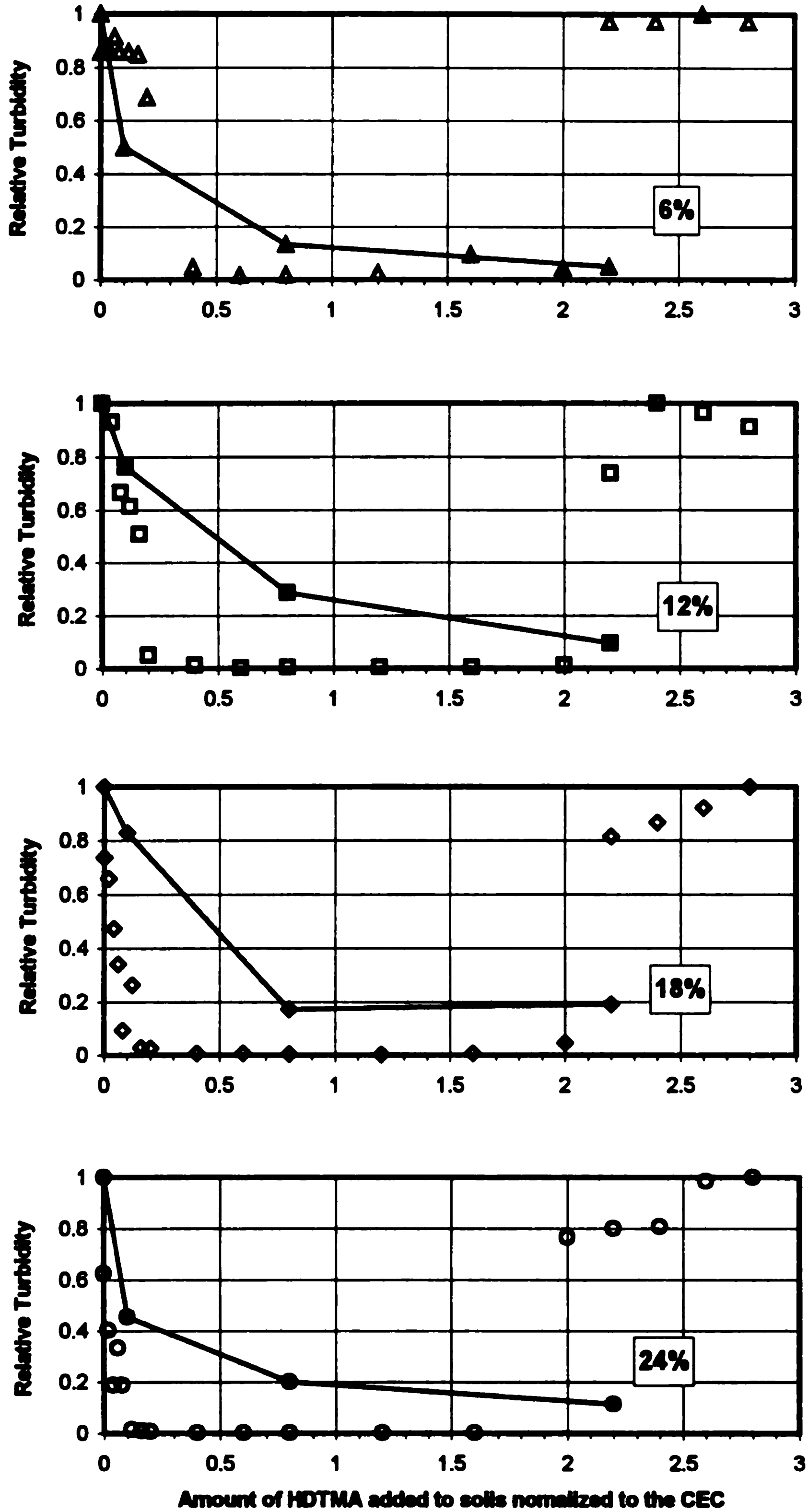

Figure 14: Turbidity of soils with different fine contents

and in that wet condition, turbidity of their suspension was measured. In the present study low-, mid-, and high-treated soil samples were first air dried and then rewetted with HDTMA-free water, and then turbidity of their suspension was measured.

As shown in Figure 14, in untreated and low-treated (0 and 0.1 CEC) samples, the suspension was turbid indicating a dispersed clay structure while in mid- and high-treatedsamples (0.8 and 2.2 CEC) the clear suspension indicated a flocculated clay structure. High-treated soil obviously had a very different turbidity than the same soil in the previous study. This result is also inconsistent with findings of Xu and Boyd (1994, 1995) who reported high turbidity for samples treated to levels far above the CEC.

It is known that sorbed HDTMA in excess of CEC forms a relatively weak hydrophobic bonding to the clay surfaces, giving rise to easy desorption if the HDTMA equilibrium concentration in the liquid is perturbed (Xu and Boyd, 1994). This phenomenon apparently manifested itself in redistribution of the treatment profile in the *in-situ* modified soil columns studied by Burris and Antworth (1992). They injected HDTMA to a soil column and showed that most of the HDTMA's were adsorbed close to the column inlet. However, this profile was redistributed to a more uniform one after they flushed the column with HDTMA-free water.

It is likely that in our treatment process during washing, air drying, and saturating the high-treated soils with HDTMA-free water, some (or all) of the hydrophobically bonded HDTMA molecules were desorbed, such that the clay particles retained a flocculated structure which normally corresponds to a treatment level slightly below CEC. Since the low- and high-treated samples prepared for conductivity tests were processed in the same manner as the samples for turbidity (i.e. air dried and then saturated with HDTMA-free water), it was believed that low-treated samples had a dispersed clay structure and conversely, high-treated ones had a flocculated clay structure in our conductivity tests. This is consistent with qualitative observations made during conductivity experiments that effluent from the consolidometer reservoir was clear in all high-treated conductivity experiments while cloudy in low-treated ones.

Porosity

Dry packed low-treated samples were 2 to 9% more porous than high-treated ones depending on the clay content (Table 6). Average porosities of both low- and high-treated samples increased with their clay content. However, this increase had a smaller overall magnitude in low-treated samples than in high-treated ones. As the fine content increased from 6% to 24%, porosity of low-treated samples increased by 3.7%, while this increase was 5.4% in high-treated ones. The dependence of porosity on fine content (especially in high-treated samples) highlights the role of clay content (and its structure) in the initial assemblage of the soil matrices.

Saturation with water changed the porosity of low- and high-treated samples less than 3% (Table 6). All low-treated samples remained more porous than high-treated ones after saturation. This minimal change, which was attributed to procedural handling of the samples, verifies that the type of clays in this soil were primarily non-swelling. In general, variation in porosities of triplicates were small compared to their means, indicating that the packing procedure was capable of establishing repeatable overall volumes in replicate samples.

Table 6: Average porosity, $\bar{n} \pm (S_{\bar{n}})$, of soils at zero load, the first load, and porosity decrease due to application of the first load

Fines	$\bar{n}$ in low-treated soils (%)				$\bar{n}$ in high-treated soils (%)			
Content (%)	Dry packed[†]	Saturated[‡]	First load[§]	Δ[¶]	Dry packed[†]	Saturated[‡]	First load[§]	Δ[¶]
6	44.5± (0.2)	44.7± (0.2)	42.2± (0.2)	2.5	40.9± (0.1)	41.4± (0.1)	40.7± (0.1)	0.7
12	44.9± (0.2)	45.2± (0.2)	40.1± (0.2)	5.1	42.3± (0.2)	42.8± (0.2)	41.8± (0.2)	1.0
18	46.2± (0.1)	46.9± (0.1)	40.1± (0.1)	6.8	45.4± (0.1)	45.7± (0.4)	44.6± (0.3)	1.1
24	47.0± (0.2)	48.4± (0.2)	40.5± (0.2)	7.9	45.5± (0.2)	46.8± (0.1)	45.8± (0.1)	1.0

[†] Prior to saturation at zero load

[‡] Saturated samples at zero load

[§] Saturated samples at load of 0.25 tsf

[¶] $n_{\text{at zero load}} - n_{\text{at the first load}}$

With application of the first load, porosity of the low-treated samples dropped much more than that of the high-treated ones (Table 6). This difference in drops increased with the clay content such that at the first load, low-treated samples with 6% fine samples were more porous than high-treated ones but at higher fine contents the situation was reversed. The difference in porosities of low- and high-treated samples at zero load and their different response to the first load suggest that there is a correlation between the structure of clays and load bearing mechanism of the soil matrices which is different in low- and high-treated samples.

The role of dispersed and flocculated clays in the consolidation behavior of low- and high-treated soil samples can be conceptualized in order to explain the trends in the data. In general, clay particles may reside in the pore space created by sand grains or partly there and partly in between sand grains of a soil matrix which makes them part of the load bearing mechanism of the matrix (Kenney *et al.*, 1992). It appears that in our low-treated samples, dispersed clays resided between the sand grains, especially in samples with high clay contents. Furthermore, the clay platelets may be poorly ordered relative to one another (i.e. in a "house of cards" arrangement). This resulted in a relatively unstable but more porous low-treated soil matrix at zero load. Application of the first load collapsed this unstable structure, resulting in a relatively large consolidation of the matrix. This trend was expectedly more profound in samples with higher clay contents. On the other hand, high-treated samples were not as porous initially, apparently due to the highly ordered (parallel) structure of their flocculated clays. As a result, the first load only slightly decreased their porosity; far less than the magnitude of the drop in low-treated samples.

Subsequent load applications (following the first), produced additional consolidation but no abrupt changes were observed (Figure 15). In the 6% fine case (Figure 15*a*), low-treated samples were, on average, more porous than high-treated ones but a relatively high variation was observed in all samples. The soils with higher clay contents exhibited less variation and a clear distinction between low- and high-treated samples was observed (Figure 15*b*~*d*). At low loads, low-treated samples were less porous, and somewhat more resistant to consolidation than the high-treated ones. Apparently in the low-treated matrix, the dispersed clays facilitated rearrangement of particles under a relatively low load causing the matrix to collapse and lose most of its porosity under the first load (0.25 tsf). Higher loads were then sustained by the packed soil matrix which had limited space to consolidate. High-treated soils, on the other hand, had a more stable structure at zero load. The magnitude of their porosity loss due to the first load was comparable to their consolidation rate throughout the loading sequence. This means that their flocculated clay structure resulted in a relatively dense and stable initial pack which consolidated gradually as the loading increased. Therefore, flocculated clays may have actually been an essential part of the load bearing mechanism of the high-treated soil samples, resulting in higher porosities compared to low-treated samples at low loads.

The differences between porosity of low- and high-treated samples decreased with load such that nearly identical porosities were observed for the two materials at high

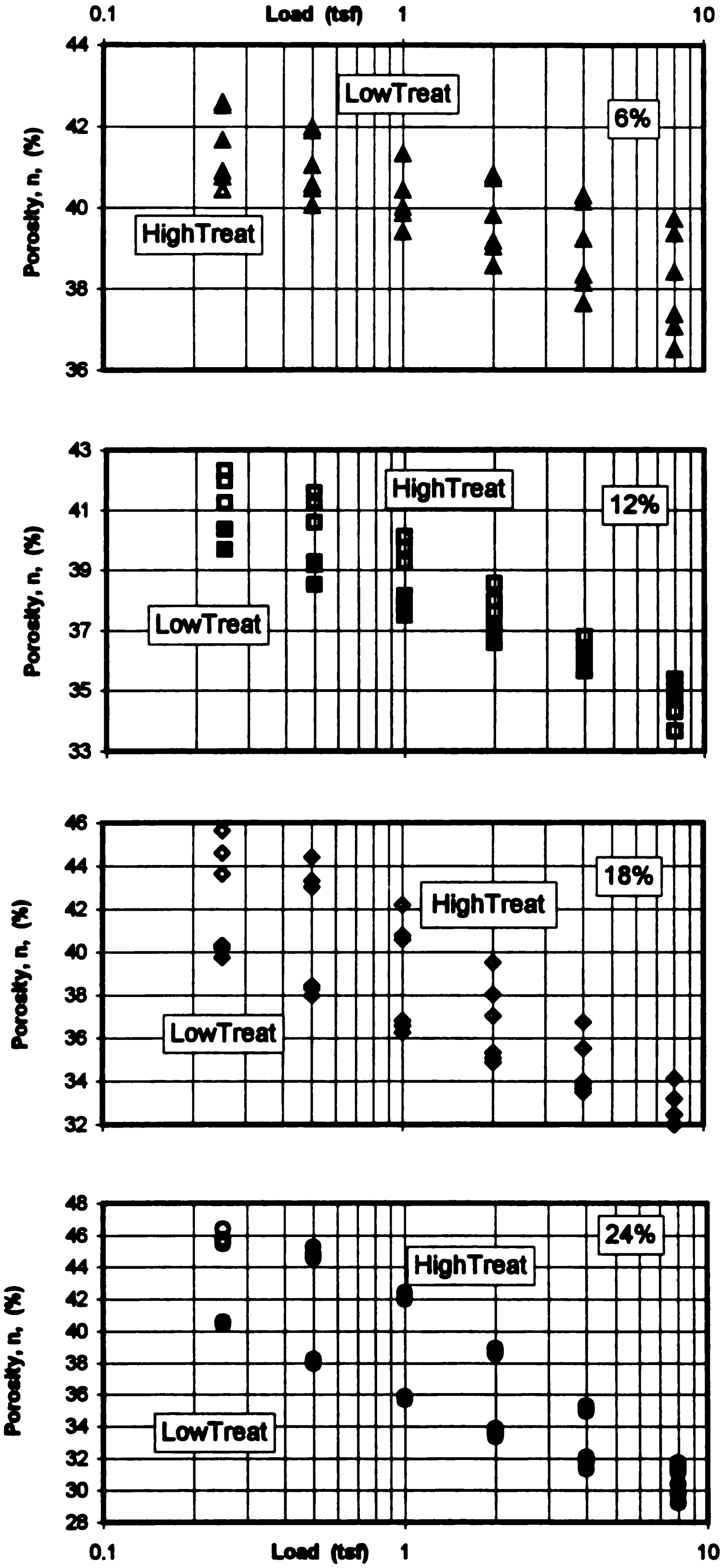

Figure 15: Porosity of soils with 6%, 12%, 18%, and 24% fines

loads. Identical porosities in low- and high-treated samples at high loads, suggest that consolidation proceeded essentially independent of the differences between the structure of the clays (i.e. dispersed or flocculated). In other words, consolidation was ultimately controlled exclusively by the larger soil particles which were identical between the two materials. At such high loads, clays evidently accommodated rearrangement of granular particles (and hence consolidation) in the same manner regardless of their structure.

The same data may be viewed in combination with untreated and mid-treated samples from previous study (Figure 16). Average values for porosity of low-treated samples from the present study (closed symbols) and that of untreated samples from the previous study (open symbols) as a function of clay content are shown on Figure 16-*a*. As it can be seen, samples with 6% fine material (untreated or low-treated) were the most porous throughout the loading sequence. Their consolidation rate was very low which, in general, is similar to the response of a sand matrix to the load. Apparently, sand particles were the main load bearing fraction of the soil in these samples. On average, samples with higher clay contents showed steeper consolidation rates which suggest that more clays facilitated easier rearrangement of particles. This behavior is consistent with the common observation that clay soils are more compressible than sands (Freeze and Cherry, 1979). In comparison of low-treated samples to untreated ones, samples with the same fine contents had nearly identical consolidation behaviors. This is a manifestation of the same dispersed clay structure in both soils.

A plot of the porosity of high-treated samples with different clay contents and its comparison to the mid-treated samples, from our previous study, reveals that porosity of

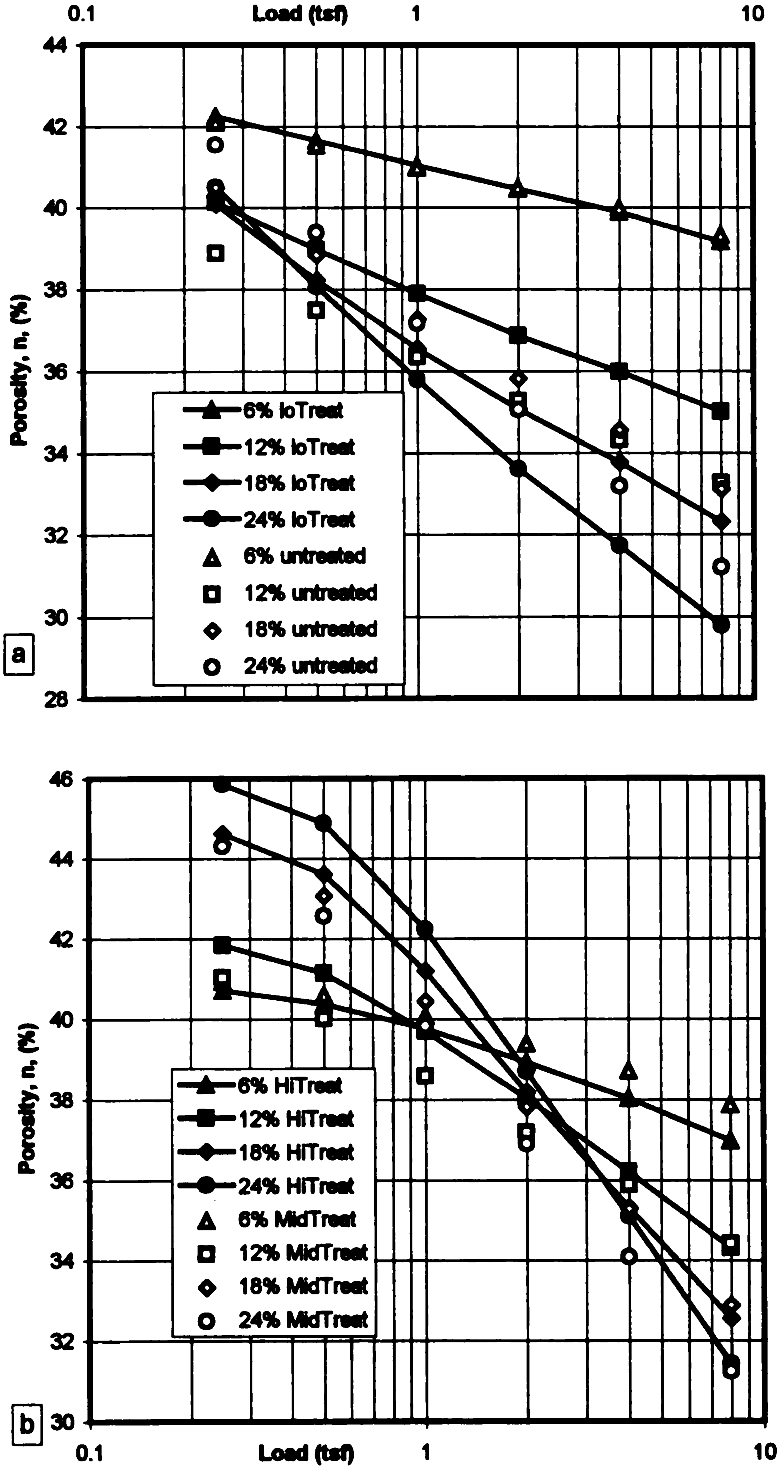

Figure 16: Porosity of a)low-treated and untreated, and b)mid and high-treated samples (untreated and mid-treat data from the previous study)

corresponding samples from the two groups had very similar consolidation behaviors (Figure 16-*b*). This demonstrates that they both had similar (i.e. flocculated) clay structures. Typically, samples with higher clay contents showed steeper consolidation rates under the load. This resulted in a reversed situation at high loads where greater clay contents corresponded to lower porosities. Evidently, higher clay contents accommodated easier rearrangement of particles and hence produced higher consolidation with each load. The general trend in porosities of untreated and low-treated soils with the load (Figure 16-*a*) was a diverging trend, while it was an intersecting trend in the case of mid- and high-treated soils (Figure 16-*b*). This fundamental difference in the response of these soils to the load portraits the significance of the role of clay structure (i.e. dispersed in untreated and low-treated soils and flocculated in mid- and high-treated soils) in consolidation behavior of soils. As will be discussed in the following section, clay structure also played an important role in conductivity of the these soils.

Conductivity

Hydraulic conductivity is a function of soil matrix property (permeability) and the fluid properties of viscosity and density (Freeze and Cherry, 1979). This implies that a difference in conductivity of two soils can be produced by a difference in water characteristics as it permeates through the soils or by difference in soil structures. The viscosity and density of the permeant (i.e. water) were measured to vary less than 1% as a result of contact with low- and high-treated soils. Therefore, the observed differences in conductivities were all attributed to the differences in permeability of the soils. Permeability of a packed soil matrix, on the other hand, can be further characterized by its total porosity and effective pore radius (Wallace *et al.*, 1995). Based on the porosity results, contribution of each component (i.e. porosity and effective pore radius) to the measured difference in conductivity of low- and high-treated soils is established.

Conductivities of low- and high-treated samples at no load did not show a consistent trend (Table 7). However, application of the first load (0.25 tsf) resulted in a substantial decrease in conductivity of the low-treated soil, and a minor decrease in the high-treated one. The drop in conductivity, with the initial load, depended on the clay content in both low- and high-treated samples. These results are consistent with the observed decreases in porosity, however, porosity decreases only made a minor contribution (< 19%) to the observed difference in conductivities. We therefore conclude that the change in effective pore radius was the primary cause of conductivity variation in these soils.

The low-treated soil formed a more porous matrix upon packing which was very sensitive to external load in terms of its effective pore radius. Application of the first load collapsed the matrix and apparently forced the clay particles from between the sand grains into the interior regions of pores. This had the effect of partitioning the pores into smaller sections (i.e. smaller pores) and lowered conductivity. Higher clay contents produced a more porous matrix initially, resulting in a higher drop in conductivity with application of the first load. This also dropped conductivities of the high-treated samples, however to less of an extent than in the low-treated ones. Flocculated clays in the high-treated samples apparently formed bigger aggregates, which were less easily forced into

Table 7: Average hydraulic conductivity, K ±(S_K) of soils at zero load, the first load, and its drop due to application of the first load

	K in low-treated soils (*cm/s*)			*K* in high-treated soils (*cm/s*)		
Fines Content (%)	Saturated[†]	First load[‡]	Δ[§]	Saturated[†]	First load[‡]	Δ[§]
6	0.130± (0.036)	0.028± (0.001)	4.6	0.082± (0.002)	0.069± (0.005)	1.2
12	0.061± (0.003)	0.005± (0.0003)	13.6	0.077± (0.016)	0.058± (0.006)	1.3
18	0.024± (0.001)	0.002± (0.00006)	12.6	0.033± (0.004)	0.025± (0.002)	1.3
24	0.026± (0.003)	0.001± (0.00016)	20.3	0.029± (0.003)	0.026± (0.003)	1.1

[†] Saturated samples at zero load

[‡] Saturated samples at load of 0.25 tsf

[§] $K_{\text{at zero load}} / K_{\text{at the first load}}$

the interstitial spaces (as discussed in the *Porosity* section) and were less able to partition the pore space into small sections.

Triplicate conductivities of low- and high-treated soils with different clay contents are shown in Figure 17. Conductivity of soils with 6% fine showed slight unrealistic trend of increase with the load and had a relatively high variation. This is likely due to limitations in precision of the apparatus at such high conductivities. Solid lines on the graphs represent two standard deviations established by the maximum of 1) observed variance among triplicates, or 2) error propagated from measurement uncertainties. As shown in Figure 17, all high-treated samples had higher conductivities than low-treated ones throughout the loading sequence. These differences were sustained over the applied range of loads with similar systematic decreases in both types of soils. High-treated samples were 4 to 71 times more conductive depending on the load and clay content.

As indicated previously, the relative contributions of porosity differences to the observed differences in conductivities were calculated and found to be less than 19%. This suggests that we can extend the interpretation that treatment to different levels primarily affected the sizes of the conductive pores to the full range of the loading sequence. It is interesting to note that at high loads, where low- and high-treated samples had identical porosities (Figure 15), conductivities were substantially different. Because the clays were occupying the same total volume in both low- and high-treated samples, differences must result from large significant differences in pore geometry. The larger pores sustained by the flocculated high-treated clays produced conductivities up to 71 times higher.

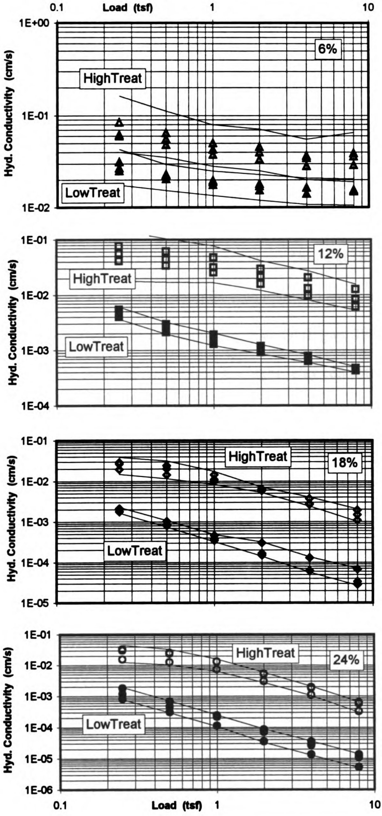

Figure 17:Hydraulic conductivity of soils with 6%, 12%, 18%, and 24% fines

As with porosity, it is insightful to view the conductivity data over the full range of treatment levels (Figure 18). On this figure, average values for conductivity of low- and high-treated samples from the present study (closed symbols) and that of untreated and treated samples from previous study (open symbols) as a function of clay content are shown. In general, hydraulic conductivity of treated and high-treated samples were higher than conductivity of untreated and low-treated ones. This is obvious from a comparison of the number of log cycles on conductivity axes on Figures 18-*a* and 18-*b*. It can be seen that the loss of conductivity with consolidation for both untreated and low-treated soils was similar and directly related to the amount of fine material (Figure 18-*a*). This is entirely consistent with the common observation that higher clay contents correspond to lower conductivities and higher load sensitivities. Average conductivities of high-treated samples with different clay contents show that the higher the clay content, the lower the conductivity (Figure 18-*b*). It can be seen in Figure 18-*b* that a similar trend was also observed in treated samples. Conductivities of samples with higher clay contents were generally more load sensitive such that the difference in conductivities was magnified at high loads.

IMPLICATIONS FOR FIELD APPLICATION

The introduction of cationic surfactants such as HDTMA into the subsurface could be utilized for creation of an *in-situ* sorptive zone. This could be achieved by injection of an aqueous solution of HDTMA through a set of injection wells into the soil down gradient from the contaminated aquifer. The *in-situ* sorptive zone would then serve to intercept and immobilize the dissolved organic chemicals as the contaminant water

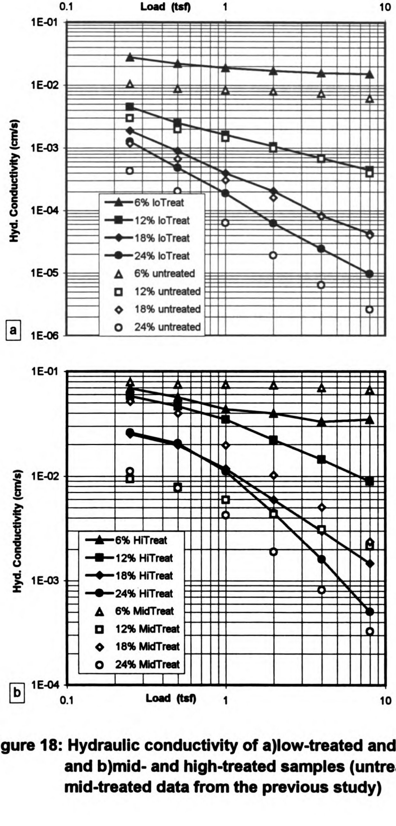

Figure 18: Hydraulic conductivity of a)low-treated and untrea and b)mid- and high-treated samples (untreated an mid-treated data from the previous study)

permeates through it. However, for the reasons discussed earlier, it is likely that the treatment level of the soil in the regions close to the injection wells will exceed the CEC of the soil. In contrast, in the regions far away from the injection well, it is reasonable to expect a low treatment level in the soil, possibly far below the CEC. Treatment of the soil to different levels has the potential to alter conductivity in expected ways and hence its characterization is essential in determination of hydraulic feasibility of *in-situ* created sorptive zones.

From the standpoint of field application, the combined results of this and the previous study show that the creation of a sorptive zone by *in-situ* injection of HDTMA is hydraulically feasible. Soil samples treated to different levels of 0.1, 0.8, and 2.2 times the CEC all had similar or higher conductivities when compared to the untreated soil under the experimental conditions used in this study. This higher conductivity was up to 71 times greater in high-treated and up to 129 times greater in mid-treated samples in our experiments. In an *in-situ* created sorptive zone, higher conductivities of treated soil relative to the untreated soil in its vicinity could effectively draw in flow lines from surrounding soils, and therefore increase the region of influence or capture area of the zone.

While the presented data indicate that an *in-situ* created sorptive zone will function favorably in groundwater flow situations, a general recommendation can be made as to the injection scheme. In order to prevent the development of hydrophobically bonded HDTMA (as would be expected at high treatment levels) a flushing period may prove to be desirable after the injection of HDTMA. Hydrophobically bonded HDTMA would likely be desorbed, washed down gradient, and re-adsorbed to the soils treated to levels lower than their CEC. This would result in a more uniform and stable HDTMA distribution and hence a more uniform and permanent sorptive capability. Furthermore, it is likely that clays will retain a flocculated structure, following the desorption of hydrophobically bonded HDTMA, which generally means a higher conductivity in the treated soil.

CONCLUSIONS

The combined results of this and the previous study show that the creation of a sorptive zone by *in-situ* injection of HDTMA is hydraulically feasible. Soil samples treated to different levels of 0.1, 0.8, and 2.2 times the CEC all had similar or higher conductivities when compared to the untreated soil under the experimental conditions used in these studies. This is interpreted as resulting from neutralization of surface charge on untreated soils, causing naturally dispersed clays to flocculate. Contrary to our expectations deriving from previous reports, high-treated clays were also highly conductive and the clays were apparently flocculated. It is believed that this resulted from desorption of the hydrophobically bonded HDTMA at levels above the CEC during washing with water.

High-treated samples displayed similar or higher porosities compared to low-treated ones. This was attributed to easier rearrangement of particles in the presence of dispersed low-treated clays. Higher conductivity of all high-treated samples (with different clay contents) compared to that of low-treated ones was attributed to their flocculated clays resulting in larger effective pore radii in those samples.

In an *in-situ* organomodification scheme, our data suggest that washing with HDTMA-free water may desorb the weakly bonded excess HDTMA close to an injection well and transport it to downstream regions. Expected differences in modification levels that might result as the solution moves out from an injection point or from soil heterogeneity, will be naturally dampend by this apparent tendency of the soil not to retain HDTMA at levels far above the CEC. The process of creating a uniform zone of modified soil may be as simple as following a period of injection by a flushing step.

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APPENDIX

APPENDIX

DETAILED MATERIALS AND METHODS

This appendix contains detailed explanation of the materials used and experimental procedures followed in the course of this study. It includes material and procedures used in all three chapters of this dissertation and should be used in conjunction with them. Methods and procedures common in all chapters are explained without reference to any specific chapter. Materials and methods specific to each chapter are stated as such in this appendix.

SOIL PROCESSING

Approximately 100 lbs of Oshtemo soil was obtained from a pit located at the Kellogg Biological Station (KBS) for experiments conducted in Chapter 1 of this dissertation. The soil was taken from a depth of 1.5~2.5 ft from the surface and hauled to Engineering Research Complex (ERC) in 2 plastic buckets. The collected soil was spread outside ERC building on plastic sheets and left on sunshine for 2 days untill air dried. During air drying process the soil was occasionally mixed on the plastic sheets to ensure a uniform drying and any plant root was taken out. Air dried Oshtemo soil was sieved through a US standard #20 in a Ro-tap shaker for 5 minutes and then thoroughly mixed to obtain a homogenized stock soil. In order to determine the quantity and type of exchangable cations and also organic matter content, approximately 0.5 lb of the stock soil was sent to MSU soil testing laboratory located at the Plant and Soil Sciences

Building. Similar amount of the stock soil was sent to Dr. Boyd's laboratory (Crop and Soil Sciences Dept., MSU) for determination of CEC by HDTMA.

Original Oshtemo soil for experiments conducted in chapters 2 and 3 was obtained from a different pit located at the KBS. Approximately 150 lb of the soil was taken from a depth of 2~3 ft. The collected soil was air dried, sieved and mixed in identical manners to the previously described procedures and the obtained soil was named orginal soil. Exchangeable cations and organic matter content of the original soil was determined by MSU soil testing laboratory. HDTMA batch iotherm and CEC determination of the original soil was performed by J. Gellner (thesis, 1996).

Soil samples used in chapters 2 and 3 were prepared by recombination of the original soil's components. The recombination process was as follows; original soil was thoroughly washed by tap water on long wall US standard sieve #200 until the suspension passing the sieve was clear. Meanwhile, the passing suspension was collected in big plastic buckets and trays and left for 15 to 20 hrs. Clear supernatant was subsequently decanted from the buckets and trays and fine materials were combined into one tray and left for air drying. By this procedure the original soil was divided into clean sand and fines fractions. Air dried fines were manually pulverized with a pestle and mortar, sieved through a US standard #100, and kept in closed plastic containers. The clean sand fraction was first spread on plastic sheets and left to air dry and then collected in a galvanized bucket. Soil samples with 6, 12, 18, and 24% fines were prepared by dry recombination of appropriate amounts of pulverized fines with clean sand. Each dry recombined soil sample was first thoroughly mixed. Each batch of soil sample preparation usually contained total of 400 gr soil. Therefore, 24, 48, 72, or 96 gr fines were mixed with 376, 352, 328, or 304 gr clean sand in order to make soil samples with 6, 12, 18, or 24% fines, respectively. Dry recombined soil samples were then mixed with deaired deionized water in order to create adhesion of the fines to the sand fraction. In this process 4, 6, 8, or 10% water content was employed for soil samples with 6, 12, 18, or 24% fines, respectively. Therefore in batches of soil sample preparation which contained 400 gr soil, total of 16, 24, 32, or 40 ml water was added to the soil samples with 6, 12, 18, or 24% fines, respectively. These waters were added in three equal amounts and each time soil samples were mixed until the added water was distributed evenly throughout the sample. The recombined soil samples were then spread on plastic sheets and left for 15 to 20 hrs to air dry. Subsequently, soil samples were gently crushed with a pestle and mortar, sieved through a US standard sieve #20, and kept in clean containers. These samples constituted the untreated soil samples with different fine contents which were later packed in the consolidometer for conductivity tests in Chapters 2 and 3. Treated soil samples were prepared from these untreated soil samples by further processing.

Batch treatment of the soil samples for all three chapters was conducted in 2 liter glass jars. In Chapter 1, HPLC grade water and in Chapters 2 and 3 DI water equilibrated with 1 mM NaCl was used for this purpose. In treated soils prepared for Chapter 1, 60 gr of the untreated soil was placed in each of the 6 jars and one liter water was added to it. In separate 1 liter glass jars, one liter water was mixed with HDTMA solutions corresponding to 1 CEC of the soil. While the jars with soil samples in them were being mixed in a Phipps and Bird 7790-400 stirrer at 120 rpm, HDTMA solutions from 1 liter jars were added to them. In treated soils prepared for Chapters 2 and 3 a different soil to water ratio was employed. In these preparations, 131 gr of untreated soil was placed in the 2 liter jars. Then 1365 ml DI water (equilibrated with 1 mM NaCl) was added to the soils and the stirrer was turned on and set at 120 rpm. Subsequently, appropriate amounts of HDTMA solution from the manufacturer stock solution was added to jars. This amount of HDTMA corresponded to treatment level of 0.8 CEC for the soil employed in Chapter 2 and to 0.1 and 2.2 CEC for the soil employed in Chapter 3. In all treatment procedures the mixing process continued for one minute followed by a slow mixing of 20 rpm for 30 minutes. At this point the stirrer was stopped, paddles were taken out of the jars, and the jars were allowed to sit for 15 to 20 hrs. At the end of this settling period, the clear supernatant was decanted and the soil samples were all washed into a ceramic drying bowl. Air drying usually took 1 to 3 days but at times blow drier was used to shorten this time. In any case, the soil was frequently mixed, while drying, in order to prevent any segregation of the soil fractions based on their settling velocity. Treated air dried soil was sieved on a US standard sieve #4 and the retaining fraction was gently crushed with a pestle and mortar and sieved again. This process was repeated few times until the entire soil passed through the sieve. Treated air dried soils were kept in open plastic pans for future experiments.

TURBIDITY TESTS

Fundamental turbidity tests were performed on all untreated soil samples. In these experiments, a small sample of the soil, placed in 25 ml Corex tubes, was used to determine turbidity of its suspension when different amounts of HDTMA was added to the soil. 2.4 gr air dried untreated soil was weighed into each of 24 tubes and 25 ml solution of 1 mM NaCl water was added to each tube. Different amounts of HDTMA, from the manufacturer's stock solution, corresponding to 0, 0.01, 0.02, 0.03, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.6, 1.8, 2.0, 2.3, 2.6, and 3.0 times CEC of the soil sample were added to the tubes. The tubes were then sealed, agitated gently by hand, and placed in a rotating shaker for 4 days. At the end of the 4 day period, tubes were removed from the shaker and allowed to sit for 30 minutes. At the end of the settling period, 1 ml of supernate was taken from 1 cm below the surface. The sample was then diluted with 20 mls of 1 mM NaCl water. Turbidity of the diluted solution was then determined using a Hach 2400 turbidimeter. If turbidity of the diluted solution was greater than the designated range in the turbidimeter, a 1 ml sample of the diluted solution was taken and this sample was subsequently diluted with an additional 20 mls of the 1 mM NaCl water.

The turbidimeter used in these experiments had 5 different ranges of measurements (0-0.2, 0-1, 0-10, 0-100, and 0-1000 NTU's) and a standard solution with known turbidity for each range. Depending on the turbidity of the solutions which were being tested, one range was selected. Prior to the turbidity measurements, the turbidimeter was calibrated in the selected range using the standard solution (with known turbidity) provided by the manufacturer. In each set of turbidity measurements only one range was used and, as mentioned earlier, dilution of the soil suspension was employed in order to keep the turbidities within the selected range. The turbidities were then determined based on the dilution employed, and were recorded as the fundamental turbidity data for that soil.

The second set of turbidity tests was performed on treated air dried soil samples. Soil samples were obtained from the pans containing treated air dried soils explained earlier. In this process, 2.4 gr soil was weighed into each 25 ml Corex tube and then 25 ml solution of 1 mM NaCl water was added to each tube. The tubes were then sealed, agitated gently by hand, and placed in a rotating shaker for 4 days. At the end of the 4 day period, the processes of settling time, sampling, dilution, and turbidity measurements were followed in the same manner as explained earlier for the fundamental turbidity experiments. These turbidities were recorded as turbidity of treated air dried soils in water. An additional turbidity experiment was conducted only on the soil used in Chapter 1 with Soltrol as the fluid. In this additional experiment, 2.4 gr air dried treated or untreated soil was weighed into each of two 25 ml Corex tubes and then 25 ml Soltrol was added to each tube. Shaking the tubes, settling, sampling, and turbidity measurements were performed similar to the fundamental turbidity experiments. These turbidities were recorded as turbidity of treated and untreated soils in Soltrol. Therefore, total turbidity measurements in the second set of turbidity tests included treated air dried and untreated soils equilibrated with water or Soltrol (Chapter 1) and soils treated to 0.1, 0.8, and 2.2 CEC equilibrated only with water (Chapters 2 and 3).

CONSOLIDOMETER ASSEMBLAGE

The separate pieces of the consolidometer are shown in Figure 1A. Prior to any assembly, each piece of the consolidometer was cleaned and air dried. In addition, the

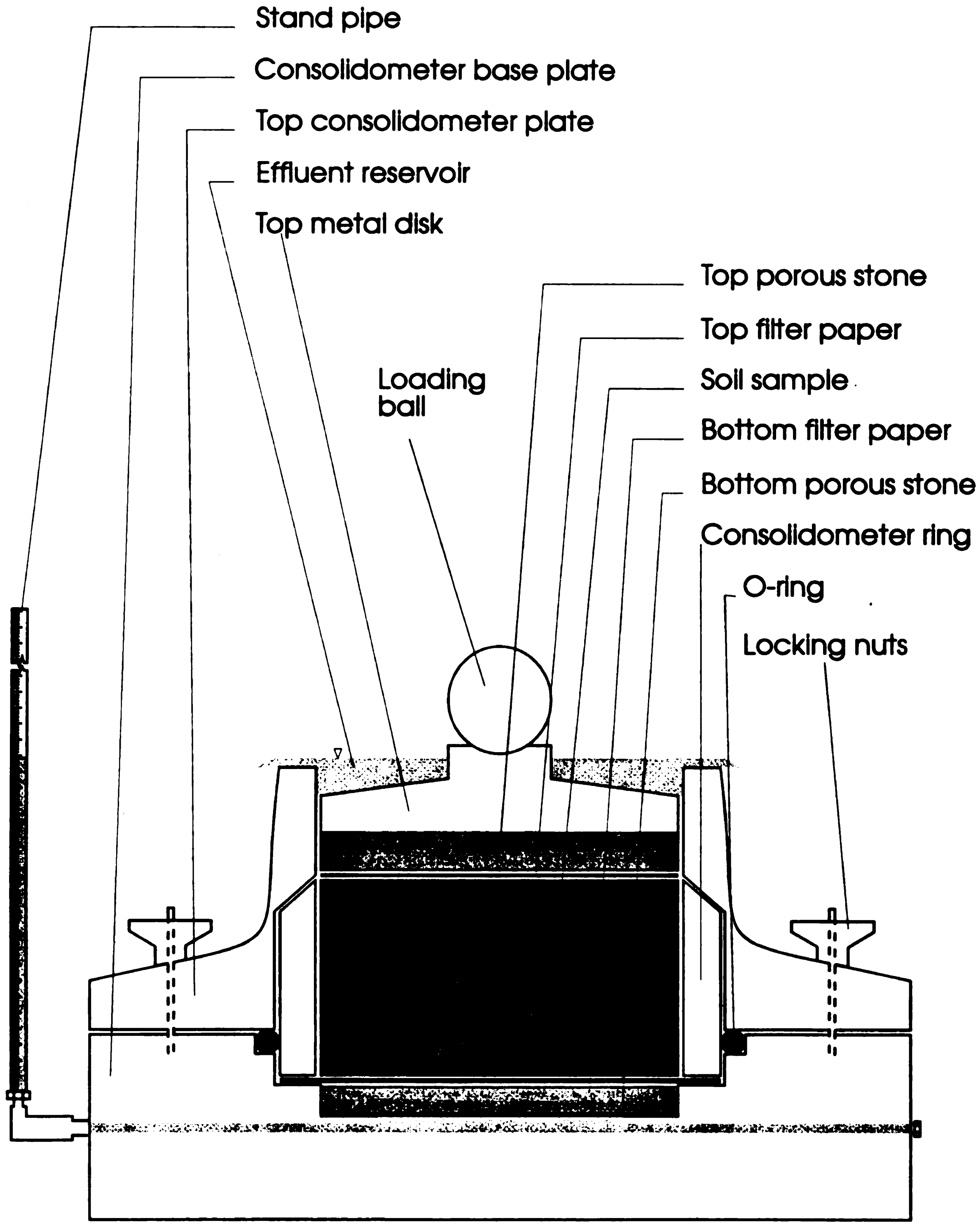

Figure 1A: Components of the consolidometer upper and lower porous stones were sonicated in 0.01 N HCl (PH<2) for 12 minutes, rinsed thoroughly, and dried. Two pieces of Whatman #54 filter paper (7 cm diameter) were used for each assembly. The top filter paper was prepared by taking the consolidometer ring and placing it in the center of the filter paper. The inside of the ring was then traced using a fine point pen. The consolidometer ring was then removed, and the filter paper was carefully cut along the outside edge of the traced circle. This tracing and cutting procedure produced a filter paper that would just fit inside the sample area of the consolidometer ring and the top consolidometer plate.

After cutting the top filter paper, the consolidometer base plate was placed on the ground. The lower porous stone was then placed in the base plate. Care was taken so that no particulates were present when the lower porous stone was placed in the base. To verify that no debris was lodged under the porous stone, it was spun with one hand. If no particulates were present, the porous stone spun freely, rotating several times with each spinning motion initiated by hand. If the rotation was restricted in any way, the stone was removed and the base was checked for any particulates present. The aforementioned steps were then repeated. After the porous stone was placed in the consolidometer base plate and was in a "free spinning" condition, the lower filter paper (the one that was not cut) was placed on top of the lower porous stone. The lower filter paper was slightly larger than the lower porous stone and effectively covered the entire diameter of the surface created by the upper surface of the lower porous stone and the consolidometer base plate.

The viton O-ring was then placed in the consolidometer base plate. The viton O-ring had a diameter that was large enough to allow a tight seal between the O-ring and the consolidometer ring. The consolidometer ring was then seated in the consolidometer base plate by placing it in the ceter of the O-ring and pushing gently downward. Proper seating was achieved when the consolidometer ring slipped inside the O-ring and rested against the filter paper resting on the metal surface of the base plate. Once the consolidometer ring was seated in the consolidometer base plate, few grams of vacuum grease was placed over the O-ring. The vacuum grease was applied by placing a small amount of vacuum grease on one finger and then by running the finger around the base of the consolidometer ring. This should have resulted in a continuous, beveled surface of vacuum grease which completely covered the surface of the O-ring.

After application of the vacuum grease, the top consolidometer plate was placed over the threaded dowels atached to the base plate. The bottom surface of the top plate should have rested securely against the O-ring. The two locking nuts were then placed on the threaded dowels and were tightened into place. Locking nuts were tightened simultaneously to ensure proper formation of the vacuum grease seal not only on the O-ring but also on the sealing surface of the consolidometer base plate.

The consolidometer was then ready for referencing and packing of a sample (soil packing section). Once a sample was packed, or if a blank conductivity experiment was to be performed, the top porous stone was screwed into the top metal disk. The top filter paper was then placed on top of the sample (or placed in the middle of the consolidometer if a blank system was to be tested) followed by placement of the top porous stone and metal disk.

VACUUM SATURATION

Vacuum saturation of soil columns or blanks were achieved using a vacuum dessicator and 4 liter vacuum flask, attached to a tap vacuum system. The entire vacuum saturation system is shown in Figure 2A. Prior to any saturation procedure, the vacuum flask was filled with 1 mM NaCl solution from a stock carboy. The 1 mM NaCl solution was prepared by filling the carboy with distilled, deionized water to the level marked on the outside of the carboy, corresponding to 17.3 liter of water. Then 1.013 gr of NaCl was added to the carboy and the solution was mixed manually. The vacuum dessicator was emptied and cleaned using tap DI water. This cleaning process was repeated at least once daily to remove any particulates and any possible build up of microbial growth. The vacuum dessicator was then filled with 1 mM NaCl solution to a level just below the ceramic plate (water level 1 in Figure 2A). If the dessicator was cleaned, excess water was poured out of the dessicator so that the remaining water filled the dessicator to water level 1.

The consolidometer containing the sample to be saturated (or blank consolidometer) was then placed in the vacuum dessicator on top of the ceramic plate. Two 500 ml bottles filled with water were also placed in the dessicator to reduce the volume of water needed to fill the dessicator to levels 2 and 3 (Figure 2A) during saturation. The rim of the dessicator was coated with a thin film of vacuum grease to ensure an air tight seal. The top of the dessicator was then placed on the rim and moved laterally back and forth to ensure that a seal had formed. The appropriate tubes and stopper were then placed in the top of the dessicator. The stopper and appropriate tubes

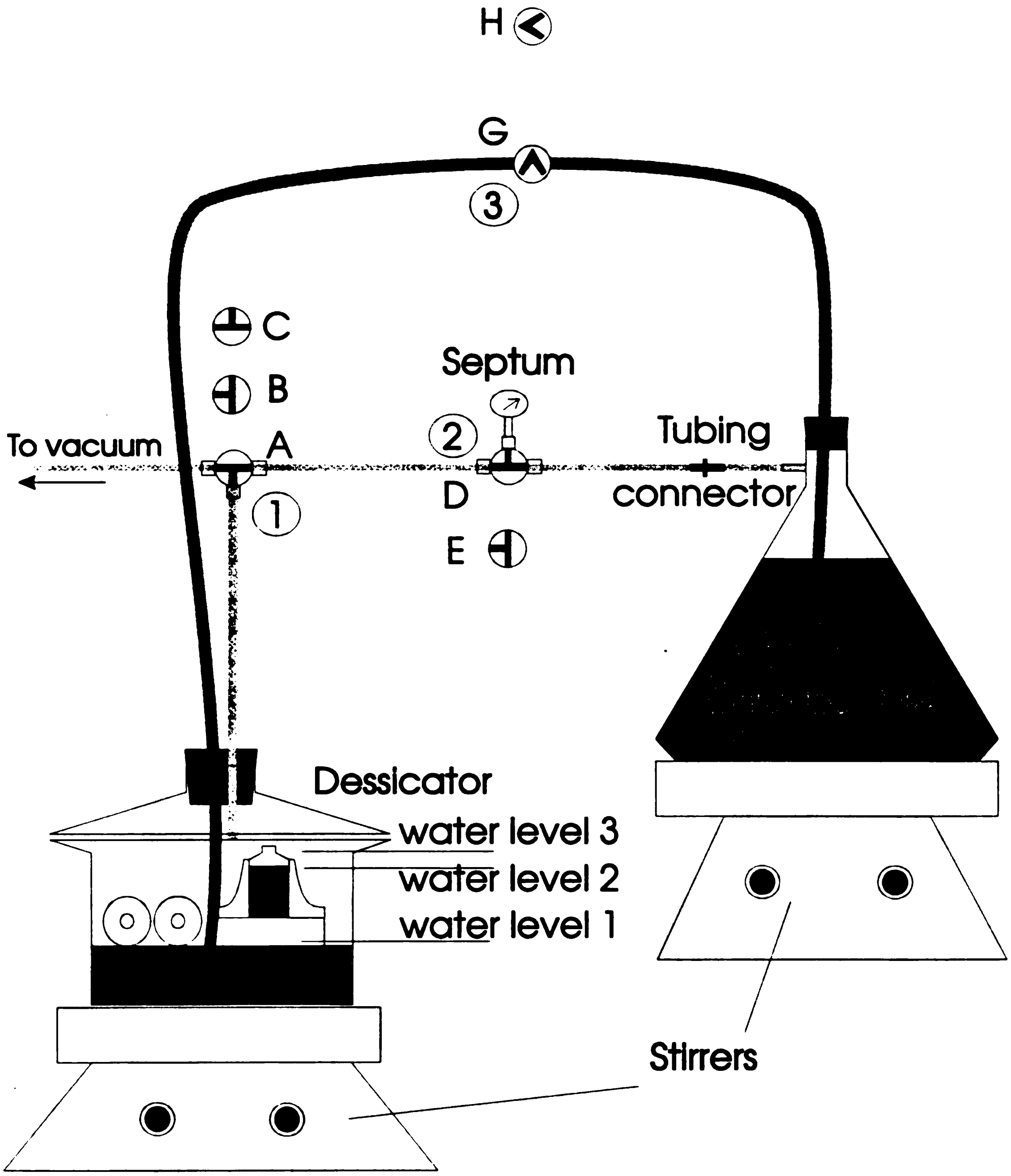

Figure 2A: Schematic of the Vacuum Saturating set up were also placed in the top of the vacuum flask, making sure that the stopper was securely in place. The tubing leading from valve 2 to the vacuum flask was then put together with a tubing connector as shown in Figure 2A.

The tube leading from the tap water vacuum system to valve 1 was then put into the vacuum connection at the base of the tap water vacuum system. Valve 1 was moved to position A, valve 2 was moved to position D, and valve 3 was moved to position G. Moving valve 3 into position G shut off any flow between the vacuum flask and the dessicator system. The building tap was then turned on, allowing a vacuum to be applied to both the vacuum flask and the dessicator. The stirrers under both the vacuum flask and the dissicator were then turned on. During the deairing process, the vacuum achieved by the system was checked with a pressure tensiometer at the septum attached to valve 2. The vacuum achieved should have exceeded 900 mbars. Failure to reach this vacuum generally indicated a leak in the system.

The vacuum was applied to both vessels for at least one hour if a sample was to be saturated or at least 30 minutes if a blank consolidometer was to be saturated. This time period was intended to deair the water contained in the system. At the end of the deairing period, valve 2 was turned to position E. This disconnected the vacuum from the vacuum flask. The vacuum in the vacuum flask was then released by disconnecting the tubing between valve 2 and the vacuum flask at the tubing connector. The stopper in the vacuum flask was then loosened, but not removed, and the stirrer under the vacuum flask was turned off. Valve 3 was then moved to position H and water was allowed to flow from the vacuum flask to the dessicator. Valve 3 was left in position H until the water level in the dessicator had risen to just below the lip of the consolidometer (water level 2). Valve 3 was then moved to position G, shutting off water flow from the vacuum flask to the dessicator.

The system configuration was left in the indicated configuration (valve 3 position G, valve 2 position E, valve 1 position A, tubing connector disconnected) until the saturation period was complete. Saturation period was 30 minutes if a blank consolidometer was being saturated, and overnight (at least 12 hours) if a soil sample was being saturated. Overnight vacuum saturation of the consolidometer allowed the soil sample to completely saturate under the vacuum. At the end of the saturation period, valve 3 was moved to position H and the water level in the desiccater allowed to rise to water level 3, above the rim of the consolidometer. Once the water level in the desiccater rose to level 3, valve 3 was moved back to position G.

After inundating the consolidometer with water (water to level 3), the tap water was turned off. This stopped the supply of vacuum to the system. Then the tubing which connects the tap water vacuum system to valve 1 was removed from the connection to the tap water vacuum system. This released the vacuum remaining on the dessicator. Valve 2 was then moved to position D, allowing further release of the applied vacuum. Once the vacuum had completely dissipated, the top of the dessicator was carefully removed from the dessicator and the standpipe was attached to the consolidometer while the consolidometer remained under water. Any residual air which was left in the fittings or the canal of the consolidometer was then removed by applying a small vacuum on the standpipe. Water was brought into the standpipe at least four times and until no air was observed escaping from the standpipe during application of the vacuum. The plug was screwed in the consolidometer base and secured. Teflon tape was applied to ensure the seal and the consolidometer was removed from the dessicator. The remaining water in the vacuum flask (if any) was used to supply the squeeze bottles used in the conductivity experiments.

BLANK CONDUCTIVITY MEASUREMENTS

Blank conductivity measurements, separate from the conductivity experiments, were performed to establish the conductivity of the system without soil, K_{blank}, and to establish a variance due to variation in the filter papers employed. Before assembling the consolidometer, prelabeled stones were sonicated in 0.1 N HCl (PH<2) solution for 12 minutes. Stones were then rinsed with tap water and dried manually.

The consolidometer was then assembled without soil and placed in the vacuum dessicator. The entire system was deaired by vacuum as described before for approximately 30 minutes. The water in the dessicator was then brought up to a level just below the lip of the consolidometer reservoir (water level 2 in Figure 2A). The system was then allowed to saturate for 30 minutes under vacuum. Saturation was verified by observation of water inside the consolidometer reservoir.

After saturation, the blank consolidometer system was inundated with water (water level 3) and the vacuum was released. While the consolidometer was under water, the standpipe was attached to the consolidometer system, ensuring that no air entered the system while being attached. Any residual air left in the canal beneath the bottom porous stone was purged from the consolidometer by applying a small vacuum on the standpipe while the consolidometer remained below the water surface with both valves open. Vacuum was applied by a rubber tube attached to the tap water vacuum system. Water was drawn into the standpipe at least four times and until no air was observed in the standpipe during application of the vacuum.

Once all of the air was purged from the consolidometer system, the plug on the consolidometer base was screwed in and secured. Teflon tape was applied to ensure the seal. The consolidometer was then removed from the dessicator and the external parts dried manually. The loading ball was then placed in the top metal disk and the consolidometer was placed in the load frame. With the middle load shaft well above the loading ball and the low pressure regulator opened until a negative reading was observed on the pressure transducer readout, the regulator selector was moved to the low position and the load/unload valve moved to the load position. The load frame pressure was then tarred by slowly increasing the applied pressure using the low pressure regulator and observing the stage movement relative to a reference line marked on the stage shaft beneath the stage. The low pressure regulator was then adjusted until no movement was observed, relative to the reference line on the stage shaft. Once no movement was observed, the load/unload valve was moved to the off position and the pressure output tarred by pressing the down arrow button on the pressure transducer readout. The pressure reading on the pressure transducer readout then read 0 psi. The load/unload valve was then moved to the unload position and the stage allowed to lower to its lowermost position. For detailed instructions on the operation of the load frame and digital readouts the reader is referred to the manuals for both provided by the manufacturer.

The middle load shaft was then lowered by turning the shaft with two fingers. The consolidometer was manually adjusted to a central position while lowering the middle load shaft. The central position was verified by lifting the loading ball slightly with two fingers to the position in the receptacle of the middle load shaft and taking note of the gaps between the set position in the top metal disk. The consolidometer was then moved laterally on the stage until sufficiently centered. This centering process was performed several times as the middle load shaft was lowered. The middle load shaft was seated on the consolidometer by lowering the middle load shaft with two fingers until a small resistance was felt. Again, the centering of the consolidometer was checked by attempting to raise the loading ball from the top metal disk. Proper centering was indicated by no movement of the ball. This configuration represented a 0 tsf condition during the blank conductivity measurements. Once the middle load shaft was sufficiently seated on the consolidometer, the load/unload valve was moved to the off position. The reservoir was filled with 1 mM NaCl water from a squeeze bottle until the water just spilled from the top of the effluent reservoir.

If the old load frame was used for the blank conductivity measurements, a slight modification of the aforementioned procedure was used. After the consolidometer was placed on the stage, the load frame was tarred as before, the load/unload valve was moved to the unload position and the stage was allowed to move to its lowermost position. The load/unload valve was then moved to the off position. Then, a small metal ring was placed over the loading ball of the consolidometer. At this point, conductivities were determined as before and corresponded to the 0 tsf condition. After determination of the conductivity the load/unload valve was moved to the load position. The low pressure regulator was then turned slowly to slightly increase the pressure on the pressure transducer readout. The stage was then allowed to raise util the metal ring which was positioned on the load ball touched the load arm and became snug. The load/unload valve was then moved to the off position. The same procedure as described in the following paragraphs was then used for the rest of the experiment.

Conductivity was then measured at the 0 tsf condition by the following procedure. Temperature measurements were then taken from both the squeeze bottle and the effluent reservoir and were recorded. These values were averaged to obtain the temperature value used for correction of conductivity to 20°C. Once the temperature readings were taken, conductivity was measured 12 times by quickly filling the standpipe with the squeeze bottle and measuring the time of drop of water between two prerecorded reference heights. Each time value was recorded individually. After twelve replicates were performed, the water in the standpipe was allowed to drop to its lowermost position (i.e. equilibrium) and this value was recorded as the datum. The procedure for measuring the conductivity conformed to the conventional falling-head permeability test with constant tail water level (ASTM D5084-90).

The load on the consolidometer was then increased to the next increment (0.25 tsf) by adjusting the load pressure regulator to the predetermined values prescribed by the manufacturer while the load/unload valve was in the off position. Once the reading of the pressure readout indicated the needed pressure, the load/unload valve was moved to the load position. This applied the 0.25 tsf load to the consolidometer system. After the load was applied to the consolidometer, the aforementioned procedure for measurement of conductivity was repeated. After measurement of conductivity at that load, the load/unload valve was moved to the off position and the pressure increased with the low pressure regulator to the next pressure corresponding to the desired effective stress. Conductivity measurements were taken at each of the following additional load conditions (0.5, 1, 2, 4, and 8 tsf). After the measurement of conductivity at the 2 tsf condition, the load/unload valve was moved to the off position as before. The regulator indicator was then moved from the low to the high position. The high pressure regulator was then used to adjust the system pressure to its desired value. While adjusting the high pressure regulator to the desired system pressure, the low pressure regulator was loosened to relieve the pressure behind the low pressure regulator valve. When the low pressure regulator moved easily, the pressure was sufficiently reduced so as not to put undue stress on the internal regulator for the course of the experiments. After hydraulic conductivity was measured at each of the effective stresses, the load/unload valve was moved to the unload position and the stage allowed to lower to its lowermost position.

Conductivity was calculated from each of the twelve time readings at each load. These values were averaged to obtain an average conductivity for each load. A total of ten experiments were performed on each set of stones for characterization, the stones sonicated before each experiment as before. At each load, a value of hydraulic conductivity of the stones (K_{blank}) was established by taking the average of the values of conductivity determined from the ten experiments. An uncertainty value was also established by taking twice the standard deviation of the conductivity values determined from the ten experiments. The average and uncertainty were propagated through the calculations from the conductivity experiments to establish hydraulic conductivities of the soil columns. Average hydraulic conductivity of the stones (K_{blank}) and its uncertainty for three sets of stones, two types of filter papers, and permeated with water or Soltrol are presented in Table 1A.

After each conductivity experiment at least one experiment with new filter paper was performed to verify the blank conductivity value assigned to the stones. Stones were sonicated in acid solution, as before, prior to the experiment. Initially, one experiment was performed and the average conductivity values at each effective stress were determined as before. The values calculated were then compared to the characterization values from the ten initial experiments. If the average values from the experiment fell within the range of conductivity values determined by the initial characterization, the blank conductivity of the stones was deemed acceptable. The initial characterization values were then used for the next experiment. If the blank conductivity did not fall within the range, two additional experiments were performed with the same procedure as before. The conductivities from the three new experiments were then averaged to establish a new blank conductivity value for the stones. The higher uncertainty calculated from the three experiments and the ten initial experiments was carried as the uncertainty for the blank system.

Table 1A: Hydraulic conductivity of stones used in water and Soltrol experiments

Average K_{blank} and its variance for stone set #2, filter paper #54, permeated with water

Load	(tsf)	0	0.25	0.5	1	2	4	8
K_{blank}	(cm/s)	6.63E-3	6.35E-3	6.19E-3	5.92E-3	5.53E-3	4.93E-3	4.31E-3
$2\sigma/K_{blank}$	(%)	6.9	5.8	3.9	4.9	5.3	7.4	6.5

Average K_{blank} and its variance for stone set #3, filter paper #54, permeated with water

Load	(tsf)	0	0.25	0.5	1	2	4	8
K_{blank}	(cm/s)	6.85E-3	6.65E-3	6.48E-3	6.22E-3	5.78E-3	5.17E-3	4.41E-3
$2\sigma/K_{blank}$	(%)	11.1	10.5	10.5	10.6	10.3	10.6	11.1

Average K_{blank} and its variance for stone set #4, filter paper #1, permeated with water

Load	(tsf)	0	0.25	0.5	1	2	4	8
K_{blank}	(cm/s)	5.04E-3	4.52E-3	4.30E-3	3.87E-3	3.26E-3	2.57E-3	1.94E-3
$2\sigma/K_{blank}$	(%)	9.6	9.3	8.3	7.4	8.8	8.5	10.3

Average K_{blank} and its variance for stone set #4, filter paper #1, permeated with Soltrol

Load	(tsf)	0	0.25	0.5	1	2	4	8
K_{blank}	(cm/s)	1.33E-3	1.27E-3	1.24E-3	1.21E-3	1.17E-3	1.11E-3	1.01E-3
$2\sigma/K_{blank}$	(%)	3.8	4.0	4.2	4.8	4.2	5.7	8.1

SOIL PACKING

Prior to assembling the consolidometer system, the stones (prelabeled and characterized as described previously) were sonicated and dried as in the characterization experiments. The consolidometer system was then assembled, including everything except the top filter paper, top metal disk and porous stone, and loading ball. A reference puck (664 gr; 6.35 cm diameter; 2.54 cm thickness) was then inserted in the consolidometer and allowed to slide along the walls of the consolidometer ring until seated against the bottom filter paper. The top filter paper, cut to just fit in the to ring, was then place on top of the puck, followed by the top metal disk and porous stone assembly. The consolidometer was placed in the load frame with the load/unload valve in the unload position and the stage at its lowermost position. Prior to placing the conslidometer in the load frame, the load arm was checked to verify that it was level. The load arm was leveled using a small, two way level that could be placed on top of the load arm. Adjustments were made by loosening the jam nuts on the sides of the load arm and using the load arm position nuts to raise or lower the sides of the load arm until level. Once level, the jam nuts were tightened.

The LVDT shaft was lowered by loosening the mounting wing nut holding the shaft. The consolidometer was placed on the center of the loading stage while lowering the LVDT shaft. The LVDT shaft was then lowered until its stem touched the top leveled circular surface of the top metal disk and the LVDT transducer readout was approximately 0.0100-0.0200". The mounting wing nut was then tightened and the LVDT reading was recorded. The consolidometer was then turned two complete rotations and at each rotation four LVDT readings were recorded at perpendicular locations along the circumference of the top leveled circular surface of the top metal disk. The average value of these eight LVDT readings was recorded as the LVDT_{ref} reading. The LVDT stem was then gently pushed up by hand until the consolidometer could be removed from the load frame.

After removing the consolidometer, the top metal disk, top porous stone, and top filter paper were removed. The consolidometer was then inverted slightly, being careful to place a hand over the opening of the consolidometer to catch the puck, until the puck began to slide out of the consolidometer. After the puck was removed, the puck was attached to the compaction assembly if the puck was used for both referencing and packing. The compaction assembly consisted of the puck, screwed into a threaded metal dowel, and a compaction hammer which slid along the metal dowel.

Soil packing process started with weighing 130 gr air dried Oshtemo B soil in to a ~5½" aluminum pie plate. The soil was then poured in the consolidometer (the consolidometer without top filter paper, top metal disk, and top porous stone). The soil was poured into the consolidometer by slightly bending the pie plate so as to pour the soil over a smaller width and placing the bottom of the pie plate against the top rim of the top ring of the consolidometer. As the soil was poured into the consolidometer, the consolidometer was slowly turned to keep the surface of the soil in the consolidometer as level as possible. The consolidometer was turned approximately 2 to 4 complete rotations, depending on the speed with which the soil was poured. Once all of the soil was poured into the consolidometer, the pie plate was gently tapped over the consolidometer to ensure that all of the fines were removed.

The consolidometer was then tapped gently from four positions (once at each position) to further level the soil. The compaction assembly was then carefully placed in the consolidometer until the puck (screwed onto the end of the threaded, metal dowel) rested on top of the soil. Both hands were then used to turn the entire compaction assembly four times while the puck rested on the soil. One turn consisted of a comfortable rotation achieved without removing either hand from the dowel of the compaction assembly. After four turns, the hammer of the compaction assembly (1.47 kg) was dropped onto the puck 4 times from an upper position on the dowel (7.5 cm of drop), marked by masking take on the dowel. The compaction assembly was then carefully removed from the consolidometer so as not to disturb the compacted soil.

The top filter paper, porous stone and top metal disk were then placed on top of the soil in the consolidometer. Caution was used to ensure that disturbance of the upper surface of the soil did not occur during placement. The consolidometer assembly was then placed in the load frame, again with the load/unload valve in the unload position and the stage at the lowermost position. The LVDT stem was then pushed up and the consolidometer was slid under the LVDT shaft such that the LVDT stem seated on the top leveled circular surface of the top metal disk. The consolidometer was then turned two complete rotations, as before, and at each rotation four LVDT readings were recorded at perpendicular locations along the circumference of the top leveled circular surface of the top metal disk. The average value of these eight LVDT readings was recorded as the

$LVDT_{pack}$ reading. The LVDT stem was then gently pushed up by hand until the consolidometer could be removed freely from the load frame.

The consolidometer was removed from the load frame and was placed in the vacuum dessicator. The vacuum system was sealed and the water deaired under vacuum for at least one hour. After the water was deaired, the water was brought into the dessicator until the level was just below the lip of the consolidoeter (water level 2, Figure 2A). The sample was then allowed to saturate for at least twelve hours (overnight) under vacuum. Vacuum saturation was verified after the saturation period by observation of water in the consolidometer reservoir above or around the top metal disk. At the end of saturation, water was allowed to enter the vacuum dessicator until the water level was above the rim of the consolidometer (water level 3, Figure 2A). The vacuum was then released and the top of the dessicator removed. While the consolidometer was still under water, the standpipe was attached to ensure that no air entered the consolidometer system. Any residual air which was left in the fittings or the canal of the consolidometer was then removed by applying a small vacuum on the standpipe while the plug was not screwed in. Water was brought into the standpipe at least four times and until no air was observed escaping from the standpipe during application of the vacuum. The plug on the consolidometer base was then screwed in and secured. For more details on the vacuum saturation procedure see the Vacuum Saturation section in this appendix.

LOADING AND CONDUCTIVITY MEASUREMENTS

After the consolidometer was taken out of the dessicator with the standpipe and the plug attached to it, the external parts of the consolidometer were dried with paper towels. The consolidometer was then carefully placed in the load frame so as not to hit the standpipe or the LVDT shaft. The consolidometer was oriented so that the standpipe was just in front of the left load arm support. As before, the load/unload valve should have been in the unload position and the stage at its lowermost position. The LVDT stem was then pushed up and the consolidometer was slid under the LVDT shaft such that the LVDT stem seated as before on the top leveled circular surface of the top metal disk. The LVDT reading from the displacement readout was then recorded. The consolidometer was carefully turned such that two more LVDT readings were recorded at locations along the circumference of the top leveled circular surface of the top metal disk. The process of LVDT reading was duplicated such that total of six LVDT readings were made. The average value of these six LVDT readings was recorded as the $LVDT_{sat}$ reading. The LVDT shaft was then raised such that the stem no longer rested on the top metal disk and the consolidometer was taken out of the load frame. The load/unload valve was then moved to the off position and the regulator selector moved to the low position. The low pressure regulator was then adjusted until a negative pressure readout was observed.

The loading ball was then placed on the top metal disk and the consolidometer was placed in a flat plastic bowl which served to catch the water (or Soltrol) spill from the effluent reservoir of the consolidometer. The consolidometer (with the bowl) was then placed back in the load frame. The load frame was then tarred by moving the load/unload valve to the load position, slowly increasing the pressure with the low pressure regulator, and observing the stage movement relative to a reference line marked on the stage shaft beneath the stage. The low pressure regulator was then adjusted until no movement was observed, relative to the reference line on the stage shaft. Once no movement was observed, the load/unload valve was moved to the off position and the pressure output tarred by pressing the down arrow button on the pressure transducer readout. The pressure reading on the pressure transducer readout then read 0 psi.

The loading arm was then lowered by loosening the jam nuts on the sides of the arm and using the loading arm position nuts. The consolidometer was manually adjusted to a central position while lowering the loading arm. The central position was verified by lifting the loading ball slightly with two fingers to the position in the receptacle of the loading arm and taking note of the gaps between the set position in the upper metal disk. The consolidometer was then moved laterally on the stage until sufficiently centered. This centering process was performed several times as the loading arm was lowered. The loading arm was seated on the consolidometer by loosening the loading arm position nuts until a small resistance was felt. Again, the centering of the consolidometer was checked by attempting to raise the loading ball from the top metal disk. Proper centering was indicated by no movement of the ball. This configuration represented a 0 tsf condition. Prior to tightening the jam nuts, the load arm was checked to verify that it was level. The load arm was leveled using a small, two way level that could be placed on top of the load arm. Adjustments were made by loosening the jam nuts on the sides of the load arm and using the load arm position nuts to raise or lower the sides of the load arm until level. Once level and sufficiently seated on the consolidometer, the jam nuts were tightened. The LVDT shaft was then lowered until the stem rested on the locking nut of the consolidometer and the LVDT reading was 0.0100~0/0200". The mounting wing nut of the LVDT shaft was then tightened and the displacement readout was recorded as the LVDT of the sample at 0 tsf. The reservoir was filled with 1 mM NaCl water from a squeeze bottle until the water just spilled from the effluent reservoir.

Conductivity was determined at 0 tsf by falling head (ASTM D5084-90). Prior to measurement, temperatures of both the effluent reservoir and the permeant to be used in the test were determined with a conventional thermometer and recorded. Water (1 mM NaCl) or Soltrol, that had been deaired for at least two hours under a vacuum of approximately 900 mbars, was used as the permeant. Then, 4 falling head measurements were performed by filling the standpipe with the squeeze bottle and measuring the time for the standpipe fluid level to drop approximately 12 cm. Each time was recorded individually. After the four tests, the fluid level in the standpipe was allowed to drop to its equilibrium level. This level was recorded as the datum at this load.

After the datum was recorded for the 0 tsf load and with the load/unload valve on off position, the low pressure regulator was used to increase the pressure to the pressure reading corresponding to the 0.25 tsf effective stress condition. The load/unload valve was then turned to the load position and the sample allowed to consolidate under the load. The consolidation procedure was a modified form of the conventional consolidation test (ASTM D2435-90) and was justified by Grant (thesis 1995). The samples were allowed to consolidate under each load for approximately 1 hour, after which the LVDT reading was recorded and the conductivity and temperature were measured using the aforementioned procedures. The pressure was then increased to the next pressure corresponding to the next effective stress state, allowing the sample to consolidate under that load. The samples were consolidated incrementally to 0.25, 0.5, 1, 2, 4, and 8 tsf stress states using progressively larger loads as described in Blank Conductivity Measurements section. After the measurement of conductivity at the 2 tsf condition, the load/unload valve was moved to the off position as before. The regulator indicator was then moved from the low to the high position. The high pressure regulator was then used to adjust the system pressure to its desired value. After hydraulic conductivity, temperatures and LVDT were measured at 8 tsf effective stress, the experiment was concluded and the load/unload valve was moved to the unload position allowing the stage to lower to its lowermost position.

CONSOLIDOMETER DISASSEMBLY

Once the load/unload valve was moved to the unload position and the stage was moved to its lowermost position, the LVDT shaft was loosened and moved up to a position that allowed free movement of the consolidometer without the possibility of the consolidometer hitting the LVDT shaft. Both pressure regulators on the load frame were then loosened until a negative pressure was observed on the pressure readout when the regulator selector was in either the high or the low position. Then the consolidometer was removed from the load frame and taken to the sink for cleaning. The plug on the consolidometer base was unscrewed and allowed to freely drain. The standpipe was then removed , rinsed, and allowed to air dry.

The loading ball was then removed from the top metal disk, rinsed, and allowed to dry. The top metal disk and porous stone were then carefully removed and were separated. The top metal disk was rinsed and dried. The top porous stone was then rinsed thoroughly to remove any fines particle on its surface (if any). Upon removing and cleaning the top metal disk and porous stone, the locking nuts of the consolidometer were loosened and removed. The seal between the base plate and top plate of the consolidometer (created by the vacuum grease) was then broken by prying the top plate with a spatula. After the seal was broken, the top plate of the consolidometer was carefully removed. The consolidometer ring containing the soil column, the bottom filter paper, and the O-ring sometimes remained connected to the top plate, so that removing the top plate also removed these pieces. In this case, caution was used so as not to let the consolidometer ring fall on the floor accidentally.

The soil sample and filter papers (top and bottom) were visually checked for any unusual segregation of particles or discoloration and, upon not finding any, were subsequently discarded. The O-ring was then removed from around the consolidometer ring, cleaned, and dried. The remaining pieces of the consolidometer were then rinsed thoroughly with building DI water to remove residual soil particles and then were cleaned with paper towels to remove vacuum grease. The cleaned pieces were then placed in a storage area prior to the next experiment. The bottom porous stone was rinsed completely to remove any particulate and then was placed, along with the top porous stone, in a 500 ml beaker. The stones were then covered with 0.01 N HCl solution and were sonicated for 12 minutes. Subsequently, the stones were thoroughly rinsed with tap water, dried, and stored prior to further testing.

CALCULATIONS AND DATA REDUCTION

All hydraulic conductivities determined by falling head measurements (blank and total conductivities) were calculated using the following equation:

$$K = 2.303\frac{a.L.C_t}{A.t}.\log\frac{(h_1 - h_{dat})}{(h_2 - h_{dat})}$$

K : hydraulic conductivity, [L/T]

a : cross sectional area of the stand pipe, [L^2]

L : total length through which flow occured, [L]

C_t: correction factor to adjust the conductivity to 20° C, []

A : cross sectional area of the sample, [L^2]

t : time for the fluid drop from height h_1 to h_2, [T]

h_1: height of the initial hydraulic head, [L]

h_2: height of the final hydraulic head, [L]

h_{dat}: height of the datum at equilibrium, [L]

For the consolidometers used in this study, the cross sectional area of the stand pipe was measured to be 0.335 cm^2 and the cross sectional area of the consolidometer ring (which was the same as the cross sectional area of the soil sample) was 31.7 cm^2. The total length through which flow occured (L) including the soil sample, porous stones, and filter papers in soil conductivity tests, and only the porous stones and filter papers in blank conductivity measurements. The coefficient 2.303 appears in the above equation to account for the use of "*log*" rather than "*ln*" in the equation. In all cases the hydraulic conductivity calculated here represented either K_{total} if soil was in the consolidometer, or K_{blank} if soil was not used.

It was found experimentally that the conductivity of the stones and filter papers, K_{blank}, exerted some influence on the hydraulic conductivity of the system especially at low loads where conductivity of soils were relatively high. Therefore, it was necessary to separate the effects of the blank system to accurately determine the hydraulic conductivity of the soil column. Based on this, when conductivities of the porous stones and filter papers were being measured, the hydraulic conductivity was labeled as K_{blank}. When hydraulic conductivity was measured with the soil sample packed in the consolidometer, the calculated conductivity represented conductivity of the total system, including the soil, stones and filter papers, and therefore was labeled as K_{total}.

In order to separate the effects of porous stones and the filter papers from the measured total conductivities, the equation for a layered soil system was employed. Consequently, the hydraulic conductivity of the soil sample was calculated using the following equation, derived from a layered soil system (Freeze and Cherry, 1979):

$$K_{soil} = \frac{L_{soil} \cdot K_{total} \cdot K_{blank}}{[(L_{total} \cdot K_{blank}) - (K_{total} \cdot L_{blank})]}$$

where K_{soil} was the conductivity of the soil sample under various effective stresses, L_{soil} was the length of the soil sample at the time of conductivity measurement, K_{total} was the hydraulic conductivity of the entire system, K_{blank} was the hydraulic conductivity of the blank, and L_{total} was the length of the stones and filter papers.

Lengths of the system and the soil were based on LVDT readings taken at various times during the experiment. The length of the porous stones and filter papers (i.e. L_{blank}) was assumed to remain constant throughout the experiments. L_{blank} was determined to be 1.618 cm, based on measurements of the thicknesses of stones with caliper and the manufacturer standards for the filter papers. The length of the soil prior to any consolidation was based on the reference LVDT reading ($LVDT_{ref}$) taken with the machined brass puck in the consolidometer assembly and the LVDT readings taken after packing ($LVDT_{pack}$) or after sample saturation ($LVDT_{sat}$). The length of the soil sample and the length of the entire system (cm) were calculated from the following equations:

$$L_{soil}(pack, sat) = 2.54.[1 + (LVDT_{pack, sat} - LVDT_{ref})]$$

$$L_{total}(pack, sat) = L_{soil}(pack, sat) + 1.618$$

Based on the method used to determine the lengths of the system, the length of the soil sample (and entire system) at 0 tsf was equal to the corresponding length after saturation, determined from equations above. Therefore, the length of the soil or entire system at any desired point was determined from the LVDT reading at that point compared to the LVDT at 0 tsf (recall that the LVDT shaft was moved after recording $LVDT_{sat}$ and was therefore different from the LVDT at 0 tsf). The following equations were used to calculate the length of the soil and lengths of the entire system (cm) at any time during the experiments:

$$L_{soil}(0tsf) = L_{soil}(sat)$$

$$L_{soil}(load) = L_{soil}(0tsf) - [2.54.(LVDT_{load} - LVDT_{0tsf})]$$

$$L_{total}(load) = L_{soil}(load) + 1.618$$

Porosity of the soil sample was calculated under each load. It was calculated based on the length of the soil sample using the following equation:

$$n = \frac{V_v}{V_t} = \frac{(A.L_{soil}) - \frac{M_s}{G_s}}{(A.L_{soil})} = 1 - \frac{M_s}{G_s.A.L_{soil}}$$

where *n* was the porosity (obviously without units), V_v was the total volume of the pore space [L^3], V_t was the total volume of the soil sample [L^3], *A* was the area of the sample (31.7 cm^2), L_{soil} was the length of the soil sample in the direction of the flow [L], M_S was the mass of solids used in the experiment (130.0 gr), and G_S was the specific gravity of the soil solids (measured to be 2.65).

Uncertainty was propagated through all calculations based on statistical analysis. This propagation, while straightforward in its application, involved relatively complex equations. Therefore, the exact equations used for each variable is not mentioned here. The reader is referred to calculation sheets included in records kept during the experiments and to the spreadsheets used in the computations.

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