



Project Summary

Review and Evaluation of the Influence of Chemicals on the Conductivity of Soil Clays

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Soil lined facilities have been used extensively for the containment and disposal of waste liquids. Often slowly permeable natural clay-rich deposits were relied upon to retard the movement of liquids. More recently, remolded layers of clay soils with hydraulic conductivities of 10^{-7} cm s⁻¹ have been constructed with the intention of retaining liquids. The hydraulic properties of both natural deposits and remolded clays have been characteristically evaluated by using water or dilute solutions of CaSO₄ as the permeating fluid. Many landfills and surface impoundments have been designed, built, and used across the country with the approval of state and federal regulating agencies, based on the conductivity standard of 10^{-7} cm s⁻¹ or less, as determined with water. Such facilities have received a wide range of waste liquids with properties that differ greatly from those of water.

Water is well known for its ability to hydrate clay soils by causing them to swell, resulting in low conductivities. Many organic liquids are known to cause the interlayer spacing of smectitic clays to decrease from those that occur when the same clay is wetted with water. Thus, organic liquids could possibly cause clay-rich soils to shrink and crack, which could result in increasing the conductivity of soils expected to retain organic liquids.

A series of experiments were undertaken to determine if organic liquids would increase the conductivity of clay-rich soils, to determine if changes were dependent on the clay mineralogy, and to determine the mechanism by which any changes in conductivity

could be explained. A theoretical evaluation of the influence of dielectric properties of liquids on the thickness of the double layer between adjacent clay minerals suggests that the spacing should decrease when liquids with dielectric constants lower than those of water wet the surfaces. Most common organic liquids have dielectric constants considerably lower than water, suggesting that they should cause clay-rich soil to shrink. An x-ray observation of smectitic clay minerals wetted with organic liquids confirmed that the D-spacings were less than those observed with water. Flocculation studies using dispersed clays indicated that smectitic, micaceous, and kaolinitic clays flocculated rapidly when they were added to organic liquids, which were only sparingly water soluble, and also flocculated when placed in a solution of water soluble liquids that contained greater than 50% organic liquid. Observation of bulk samples indicated that water wetted specimens containing each of the three above-mentioned clays swelled more than when similar samples were wetted with organic liquids.

Laboratory studies of conductivities using a range of organic liquids including both polar and nonpolar solvents, waste sorbents, and commercial petroleum products in fixed wall permeameters indicated that the conductivities to organic liquids were two to three orders of magnitude greater than those to water. Observation of the soils permeated with dye-labeled organic liquids revealed the formation of structural units near the surface. The organic liquids had also moved through cracks

that penetrated the soil, which originally had a massive structure. Field test cells were set up using three clays and two organic waste liquids. The conductivity measurements in the field confirmed the laboratory findings. The nonpolar solvent waste containing xylene, which was used to permeate the 1.5 M square and 15 cm thick field test section of compacted clay, broke through many of the replications within two weeks. The acetone waste took as long as two years to break through the test sections; however, in the end, sections of each type of clay were also permeated by the acetone waste.

It thus appears that organic liquids, which are only sparingly soluble in water, or water soluble organic liquids in concentrations greater than 50% will desiccate clays, causing them to shrink and crack. The liquids are then able to flow through the soil much more rapidly than when the soils are wetted with water.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Many landfills and surface impoundments depend on compacted soil liners as either the primary or secondary means for retarding the movement of chemicals to the ground water. Even though compacted soil liners are to have a conductivity of $1 \times 10^{-7} \text{ cm s}^{-1}$ or less, reports continue to appear documenting the leakage of liquid organics from clay lined facilities. One possible cause for this is that liners installed in the field have seepage paths such as cracks or flaws. A second possibility for the rapid movement of organics through compacted soil is that the chemicals interact with the soil matrix in such a way as to increase the conductivity.

A previous laboratory study revealed that compacted clay soils exposed to concentrated organic liquids underwent large conductivity increases. Uncertainties associated with the equipment used, pressure gradients used, and representativeness of the data necessitated further study. This project was, therefore, conducted to provide additional data on the effect of hydraulic gradient on

conductivity measured in the laboratory, to study the effect of dilute organic solutions on the conductivity of compacted soils, to provide field cell verification of laboratory measurements of conductivity, and to develop a mechanistic explanation for the observed data.

Methods

The conductivity of three soils of differing mineralogies (mica, kaolinite, and bentonite) when permeated with water, acetone, and xylene at hydraulic gradients of 31, 91, 181, and 272 was measured using fixed wall permeameters. Soils were tested at moisture contents equivalent to the moisture content at the time of compaction (hereafter referred to as nonsaturated) and after the passage of one pore volume of water (hereafter referred to as saturated) to evaluate the effect of moisture content on conductivity. The conductivity of each soil to dilute concentrations of organics was measured in the laboratory through the use of 0, 60, 80, and 100% ethanol and 0, 60, 80, and 100% acetone solutions as the permeants. Conductivities were also measured using waste organic chemicals and a group of petroleum products.

To document whether or not the laboratory measurements provided an accurate estimate of how the soils behave under field conditions, special field cells were constructed. Each cell was 1.5 m x 1.5 m x 1.8 m tall and equipped with a removable platform. A 100-mil HDPE liner was installed in each cell, followed by a leachate collection system. Above this, a 15-cm thick layer of compacted soil was installed in two lifts. Four perforated barrels were placed on top of the liner, and the cell was backfilled with soil and capped with soil and plastic to exclude rainfall. Approximately 1400 L of dyed-tagged xylene or acetone were pumped into the four perforated barrels through a standpipe. Leachate was collected twice weekly, quantified, and subsampled for analysis. Leachate volumes and times were used to calculate the conductivity and the number of pore volumes that passed through the soil. After the conductivity was measured at $2 \times 10^{-7} \text{ cm s}^{-1}$ or greater, each cell was disassembled, and the clay liner was visually observed and sampled for analysis.

To elucidate the effects of organic chemicals on the flocculation and dispersion state of the clay fraction of the soils,

each of the soils was subjected to particle size analysis using 0, 50, 60, 70, 80, and 100% by volume acetone and 0, 20, 50, 60, 70, 80, 90, and 100% by volume ethanol. The apparent % clay in each solution was compared to that measured in water. The bulk shrinkage or swelling of compacted samples of each soil exposed to water, acetone, and xylene was measured using a volume change apparatus. Changes in D-spacing of the bentonite were measured using standard x-ray analysis of bentonite equilibrated with solutions containing 0, 2, 5, 50, 60, 80, and 100% by volume acetone and 0, 20, 40, 60, 80, and 100% by volume ethanol. Additional measurements of the mobility of clay particles in various solutions and exposed to an electric field were made. Measurements were converted to electrophoretic mobility and zeta potential.

Results and Conclusions

Laboratory testing using three soil and numerous chemicals verified the data that concentrated organics increase the conductivity of compacted soil. No consistent significant effect of hydraulic gradient or initial moisture content on the final conductivity could be found. Concentrated organic solvent wastes, as well as petroleum products including kerosene, diesel fuel, gasoline, and motor oil all resulted in dramatic increases in conductivity of all three soils tested (Table 1). Increases ranged from one to five orders of magnitude and generally were least for the bentonite soil. Concentrated organic solvents, acetone and xylene, resulted in similar conductivity increases. A representative figure depicting the influence of concentrated organic solvents on the conductivity of compacted soil as a function of the pore volumes of effluent is given in Figure 1. Presaturated soil conditions resulted in the passage of typically 0.1 to 0.7 pore volumes of water at initial conductivities followed by a very rapid increase in conductivity. When the soils were not saturated before exposure to solvents the conductivity rose immediately to values often two to four orders of magnitude greater than the initial conductivity to water. Solvent concentrations in leachate from the non-saturated soils ranged from 95 to 100% from the very first appearance of leachate. For the presaturated soils, only 0.2 to 0.7 pore volumes passed through the soil before solvent concentrations of 95 to 100%

Table 1. Mean Conductivity of Each Soil to Each Fluid Tested

Fluid	CC1	CC2	CC3
Water	$3.61 \times 10^{-8}b^*$	$2.58 \times 10^{-8}b$	$1.57 \times 10^{-8}b$
Acetone	$5.05 \times 10^{-5}b$	$1.41 \times 10^{-6}b$	$2.51 \times 10^{-7}b$
Xylene	$1.76 \times 10^{-4}a$	$7.28 \times 10^{-4}a$	$1.00 \times 10^{-4}a$
Gasoline	$1.96 \times 10^{-4}a$	$9.07 \times 10^{-5}a$	$6.19 \times 10^{-5}b$
Kerosene	$1.49 \times 10^{-4}a$	$9.10 \times 10^{-5}a$	$5.68 \times 10^{-5}b$
Diesel Fuel	$5.17 \times 10^{-5}b$	$4.53 \times 10^{-5}ab$	$6.29 \times 10^{-7}b$
Motor Oil	$6.13 \times 10^{-6}b$	$2.13 \times 10^{-6}b$	$9.48 \times 10^{-7}b$

*Values in a given column followed by the same letter do not differ significantly ($P = 0.05$).

were reached, thus indicating that only the water from the large macropores was displaced.

Field tests confirmed the laboratory data. For the kaolinitic and micaceous soils exposed to xylene, only two to three days elapsed until leachate appeared. When acetone was the permeant, 21 to 28 days elapsed before leachate began. The bentonite soil exposed to xylene and acetone required 70 and 704 days, respectively, before the appearance of leachate. Agreement between laboratory and field data is summarized in Table 2.

Conductivity to pure acetone in the laboratory averaged about 1.5 orders of magnitude greater than the conductivity to water. Laboratory measurements with waste acetone from the field experiment showed only slight increases in conductivity. The conductivities measured in the field, however, were a full order of magnitude greater than the laboratory value. Laboratory measurements with pure xylene indicated conductivities three to four orders of magnitude greater than that to water. Conductivities of waste xylene permeated in the laboratory

averaged 2.5 orders of magnitude greater than laboratory values with water. Field conductivities to waste xylene averaged two orders of magnitude greater than water. It thus appears that laboratory testing using fixed wall permeameters and elevated hydraulic gradients can provide a reasonable field estimate response of compacted clay liners to organic liquids. Visual observations of the dissected clays indicate that the organic liquid moved through only a small fraction of the pores.

A study of the mechanism causing the observed changes in conductivity was undertaken. It was found that as the concentration of organics in water increased there was a concentration at which the suspended clay flocculated. The point at which the apparent clay content was reached when the solution dielectric constants ranged from 31 to 49 for the three soils tested (Table 3). A decrease in the basal spacing of the bentonite soil to values below that observed with water was found to occur when the dielectric constant of the solution reached 28 and 47 for ethanol and acetone solutions, respectively. Electrophoretic mobility and

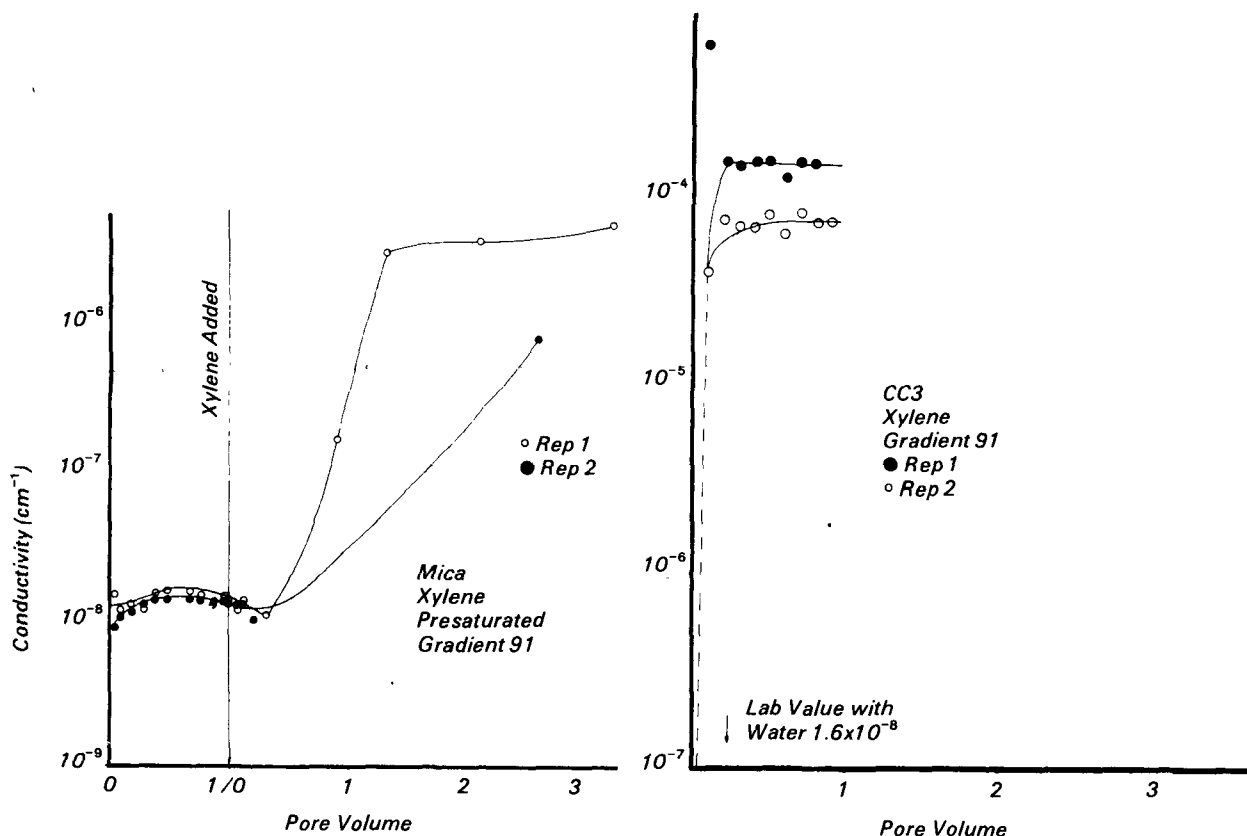


Figure 1. Conductivity of presaturated and nonsaturated mica soil to xylene measured with a fixed wall permeameter at a gradient of 91.

Table 2. Conductivities of Three Soils to Water, Pure Chemical, and Wastes in Both Laboratory and Field Cells

	Average Laboratory Conductivity to Water	Laboratory Conductivity to Pure Acetone at a Gradient of 181	Laboratory Conductivity to Waste Acetone at a Gradient of 181	Field Cell Conductivity to Waste Acetone at a Gradient of 7	Laboratory Conductivity to Pure Xylene at a Gradient of 181	Laboratory Conductivity to Waste Xylene at a Gradient of 181	Laboratory Conductivity to Waste Xylene at a Gradient of 7
Kaolinite	1.1×10^{-8}	3.7×10^{-6}	4.6×10^{-9}	7.7×10^{-8}	1.0×10^{-4}	6.1×10^{-6}	1.1×10^{-6}
Mica	1.5×10^{-8}	4.5×10^{-8}	2.4×10^{-8}	1.0×10^{-7}	2.2×10^{-5}	6.4×10^{-6}	2.1×10^{-6}
Bentonite	3.5×10^{-9}	1.5×10^{-7}	--	3.4×10^{-8}	1.5×10^{-4}	8.5×10^{-7}	1.3×10^{-7}

zeta potential served as indicators of the bulk charge on the clay particles. Measurements indicated that changes in these parameters also occurred in the dielectric constant range of 26 to 41. Increased hydraulic conductivities were observed for solutions having dielectric constants below 35 to 50. These data coupled with that of the other portions of the project indicate that as organic chemicals permeate the soil, they cause it to shrink and crack and thereby increase the hydraulic conductivity.

The full report was submitted in fulfillment of Cooperative Agreements CR-808824 and CR-811663 by Texas A & M University under the sponsorship of the U.S. Environmental Protection Agency.

Table 3. Dielectric Constants at Which the Apparent Clay Concentrations Reached 0.5, the d-Spacing Dropped Below 1.8 NM, the Electrophoretic Mobility was Midway Between Zero and the Plateau, the Zeta Potential was Midway Between Zero and the Plateau, and the Hydraulic Conductivity Increased

	Apparent Clay Content	Basal d-Spacing	Electrophoretic Mobility	Zeta Potential	Conductivity	Average
Acetone	K	31	31	35	48	36
	M	37		26	35	31
	B	38	47	37	41	41
Ethanol	K	30	28	32	50	35
	M	33		31	-	31
	B	49	28	38	39	40

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The complete report, entitled "Review and Evaluation of the Influence of Chemicals on the Conductivity of Soil Clays," (Order No. PB 88-170 808/AS; Cost: \$25.95, subject to change) will be available only from:

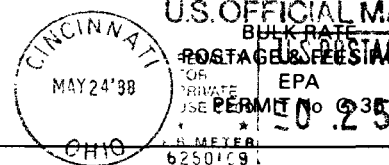
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