Interaction of Clay Soils with Water and Organic Solvents: Implications for the Disposal of Hazardous Wastes

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■ Studies of the behavior of three compacted, moist clay soils when immersed in water and in organic solvents have been conducted. The correlation between the logarithm of the octanol–water partition coefficient (log K_{OW}) and the percent swelling of the clay soil suggests that swelling in these systems depends upon the transfer of immersion fluid into the clay soil pore waters. X-ray diffraction data obtained on air-dried clay soils treated with various liquids indicate that interlayer expansion does not occur in these systems. Slight shrinkage of clay soils in apolar, hydrophobic solvents such as carbon tetrachloride and xylene indicates that these liquids act to cause soil dehydration and possible cracking. It is concluded from this behavior that hydrophobic liquids could damage the integrity of clay liners used for hazardous waste disposal pits. On the basis of these results, it is recommended that laboratory shrink–swell testing be conducted on samples of clay liners and representative waste mixtures and soils of the type to be encountered at a storage site.

Introduction

Studies on the interaction of organic molecules with clays have been reviewed by Theng (1). A number of polar organics (alcohols, ketones, amines) have been observed to form interlayer complexes with clays and to cause expansion of the clay lattice. Nonpolar, saturated organics such as n-hexane and n-dodecane have also been reported to form interlamellar complexes with air-dried, Ca-saturated, Wyoming montmorillonite (2). Bradley (3) has shown that benzene, too, forms a complex with montmorillonite, an observation later confirmed by MacEwan (4).

The extent and ease with which intercalation occurs with nonpolar organics may depend upon the state of hydration of the clay itself. The Ca montmorilllonite used by Barshad (5), for example, was heated to 250 °C prior to immersion in several nonpolar organic liquids. None of these liquids caused interlayer expansion to occur. On the other hand, air-dried clay samples such as those used by Bradley (3) and MacEwan (4) were observed to form interlayer complexes. This was believed to be due to the presence of a sufficient number of water molecules to cause slight separation of the silicate layers. Theng (1) has pointed out that for some nonpolar molecules intercalation of partially dehydrated clays may be limited by the inability of these molecules to replace interlayer water or to bind with exchangeable cations through aquo bridges.

While considerable work has been done on interlayer swelling of clays in the presence of organic compounds, no data have been reported on the bulk swelling properties of natural clay soils exposed to organic liquids, particularly under soil moisture conditions that might approximate those found at hazardous waste disposal sites. Given the current interest in the prospects of on-land disposal of organic chemicals in clay-lined pits, it seemed appropriate to examine the behavior of moist clay soils immersed in organic liquids and water. This paper reports on the bulk

swelling or shrinking of three clay soils as measured by a sensitive consolidometer.

Experimental Section

The three natural clay soils used in this study, Ranger Shale, Kosse Kaoline, and Fire Clay, were obtained from a commercial supplier. These were analyzed for particle size distribution, percent montmorillonite, kaolinite, and illite, optimum moisture content, Atterberg limits, cation-exchange capacity (CEC), and total organic carbon content. The methods used were standard procedures for the characterization of clay soils and have been discussed elsewhere (6).

Swell properties of the clay soils in contact with bulk organic liquids [glycerol, acetone, trichloroethylene (TCE), carbon tetrachloride (CCl_4), benzene, and xylene] or water were measured by using remolded clay soil samples having optimum moisture content and a 6.4-cm diameter consolidometer manufactured by Karol-Warner, Inc. (Highland Park, NJ). Optimum moisture content was used to approximate the conditions that are normally specified for developing clay liners for hazardous waste disposal pits. All solvents were ACS reagent grade or equivalent. The degree of swelling or shrinkage of the clay soil samples was measured every day, or every several days, for a period of at least 2 weeks or until equilibrium had been established. The dial indicator on the consolidometer was capable of measuring displacements to 2.5×10^{-4} cm. All measurements were made with the clay soil, consolidometer, and liquid situated in a covered desiccator to prevent evaporation. The desiccator was housed in a constant-temperature room at 22 ± 1 °C. The detailed method for preparing the clay soil was adopted from the American Society for Testing and Materials (ASTM) procedures (7) and is given below.

A 500–600-g aliquot of well-ground (to pass through a no. 8 sieve), air-dried sample was weighed and transferred to a mixing pan. The amount of deionized water required to achieve the optimum moisture content of the clay soil was added to the sample. After thorough mixing, the sample was placed in a glass jar tightly fitted with Parafilm and stored overnight or until ready for testing. For samples that mixed readily with water and had low dry strength, it was satisfactory to add water and mix the sample immediately prior to testing. A specially designed mold (7.6 cm long, 6.0 cm i.d.) and collar (7.6 cm long) were used to make the remolded sample. With the mold and collar clamped to the base of the compaction apparatus, about half of the mixed clay soil was placed in the mold, and the surface was leveled with a wood plunger. The sample was then compacted with 2.5-kg standard hammer to conform to the standard compaction test procedures [12 375 ft lb/ft^3 (5.9×10^5 J/m^3) of compacted volume]. About 10–20% additional pressure was applied depending on the amount of excess volume of the compacted clay. After removing the collar and shaping the sample with a straight edge, the sample was ejected with a specially designed plunger.

A 1.9 cm long sample was then cut and shaped properly by using a sharp knife and a straight edge. A 1.9 cm long

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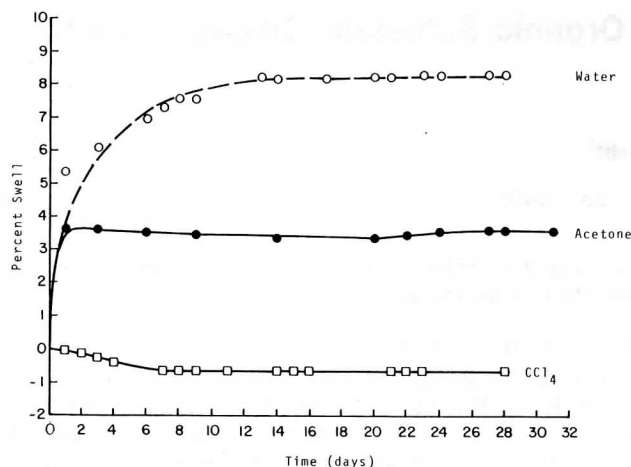0013-936X/83/0917-0278$01.50/0 © 1983 American Chemical Society

Figure 1. Comparison of swell properties of Fire Clay in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents.

Figure 2. Comparison of swell properties of Kosse Kaoline in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents.

Figure 3. Comparison of swell properties of Ranger Shale in CCl_4, acetone, and water: effects of low, intermediate, and high dielectric solvents (A and B are duplicate runs).

collar was used to create a precise finish on the sample. The molded sample was then transferred to a specially designed consolidometer (3.8 cm long, 6.4 cm i.d.) over a 0.6 cm thick porous stone. Another piece of porous stone of the same size was placed at the top of the sample. A load block was then placed at the top. The dial gauge indicator, capable of measuring displacements within a range of 0.002–13 mm, was mounted in proper position. The dial gauge indicator was adjusted to read initially at 0.025–0.05 cm to read any possible shrinkage of the sample. If more shrinkage was expected, the gauge was initially adjusted accordingly. The consolidometer was transferred to a desiccator (without the desiccant). Reagent grade solvent was then introduced up to a level 1.5 cm above the consolidometer. Measurements of the swell or shrinkage of the sample were made as a function of time, for up to 1 month.

Results

Table I summarizes the characteristics of the three clay soils. The clay fraction ranged from 40% to 53%. The Ranger Shale sample contained a significant fraction of expandable montmorillonite, whereas the Kosse Kaoline sample and Fire Clay sample had higher kaolinite contents. The Fire Clay sample had the greatest dry density 1.81 g/cm³. Optimum moisture contents ranged from 16% for Fire Clay to 31% for Kosse Kaoline. Only the Ranger Shale had a high ionexchange capacity due largely to the presence of Ca. All clay soils were very low in organic carbon.

Determination of the Atterberg limits for these solids showed that plastic and liquid limits and plasticity indices were in the order Kosse Kaoline > Ranger Shale > Fire Clay. The potential significance of the plasticity index in this study follows from the observations of Seed et al. (8) that the higher the value of this index, the greater the total potential expansion of the clay when exposed to water. The indices reported in Table I suggest that Ranger Shale and Kosse Kaoline should expand more than Fire Clay when exposed to water, a trend observed here.

Table II presents equilibrium values for swelling of the three clay soils in water and in organic solvents, along with selected solvent physical properties. In general, the greater the solvent dielectric constant the greater the swelling, for a given clay soil. Figures 1–3 show typical swelling profiles for each clay soil in a solvent of high (water), intermediate (acetone), and low (CCl_4) dielectric constant. Low dielectric, low polarity, hydrophobic solvents such as CCl_4 and TCE generally caused little change in clay soil volume;
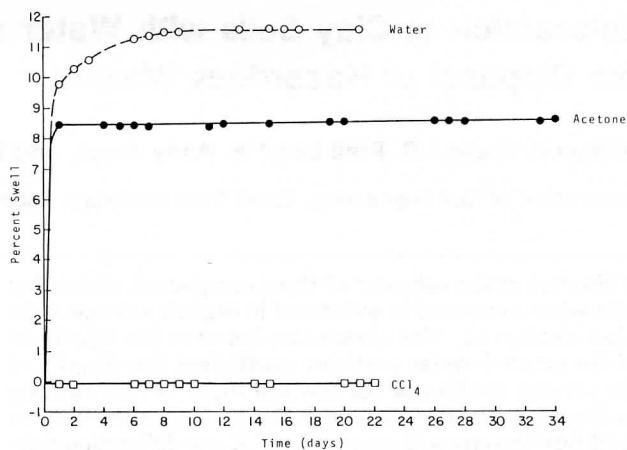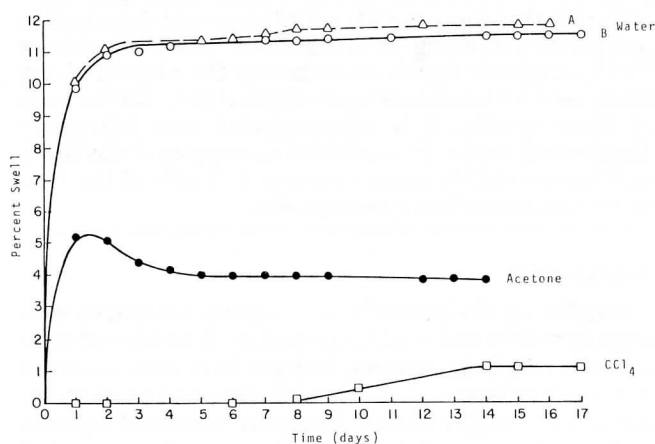
all values for these liquids were between ±1% swell. The hydrophilic solvent acetone caused all three clay soils to expand rapidly to equilibrium volumes 4–9% greater than the original volumes. Of all the solvents tested, water caused the greatest swelling (5–12%) to occur in all of the clay soils.

Discussion

All of the clay soils evaluated contained water at optimum moisture content to more accurately represent liners expected to be used for hazardous waste disposal pits. X-ray diffraction experiments on clay swelling reported in the literature have been made on air-dried or completely dehydrated clays, so it is difficult to say with certainty whether or not intercalation would have occurred under the conditions prevailing in this study, where water content was as high as 31% by weight. However, since intercalation under high moisture regimes involves competition between water and organic molecules for favorable sites in the interlayer region, it seems unlikely that the weakly polar compounds considered here would have been able to displace the strongly bound water. Thus, while interlayer swelling of air-dried clays by nonpolar compounds has been observed (2–4), the authors suspect that clay soils at optimum moisture content do not intercalate, especially with weakly polar molecules. Therefore, slight swelling observed in certain systems, benzene/Fire Clay, benzene/Ranger Shale, xylene/Kosse Kaoline, xylene/Ranger Shale, CCl_4/Ranger Shale, and two of the three clay soils

Table I. Characteristics of Ranger Shale, Kosse Kaoline, and Fire Clay[a]

clay soil	% clay fraction	% of clay fraction as			optimum moisture content, % by wt	corresponding dry density, g/cm³	Atterberg limits			CEC,[b] mequiv/100 g	% organic carbon
		montmorillonite	illite	kaolinite			plastic limit moisture, %	liquid limit moisture, %	plasticity index moisture, %		
Ranger Shale	40 ± 0	50.5 ± 0.5	37 ± 0.0	12.5 ± 0.5	17.5	1.73	36	46	10	54.4 ± 0.4	0.28 ± 0.0
Fire Clay	44 ± 1	13.5 ± 0.5	13 ± 0.0	73.5 ± 0.5	16	1.81	31	32	1	11.2 ± 0	0.03 ± 0.00
Kosse Kaoline	53 ± 4	14.5 ± 2.5	7.5 ± 0.5	78 ± 2.0	31	1.36	38	50	12	13.4 ± 0.1	0.12 ± 0.01

[a] Error limits are deviation from the mean for duplicate determination, after Green et al. (6). [b] The dominant cation in all cases was Ca: Fire Clay contained 9.7 mequiv/100 g; Kosse Kaoline, 4.6 mequiv/100 g; Ranger Shale, ~59 mequiv/100 g of Ca.

in trichloroethylene, would seem to be attributable to another mechanism.

The presence of water in the clay soils suggests that swelling occurred as the result of organic liquid (or water) penetration into the soil pore water region and that the shrinkage in the four systems listed in Table II occurred as the result of migration of pore water out of the soil and into the surrounding bulk liquid. It can thus be expected that molecules of liquids that hydrogen bond with water or that interact with water through dipole–dipole forces will have a tendency to become solubilized in the soil pore water and will therefore cause bulk clay expansion. Apolar, hydrophobic liquids, on the other hand, should have little tendency to move into and be solubilized within the pore water region. These liquids will cause only slight swelling at most and may cause the clay soil to shrink. Shrinkage itself seems to be the result of migration of water out of the clay soil and into the bulk liquid.

That this explanation for shrinkage is reasonable can be seen from the following considerations. Water has a finite though quite low solubility in apolar organic solvents. For example, Masterton and Seiler (10) report that water dissolved in CCl_4 up to a mole fraction of 1×10^{-3} or about 0.18 g of water/L of CCl_4. In the authors' experiments the consolidometer was surrounded by approximately 2 L of solvent. This volume could have dissolved about 0.4 g of soil pore water and would have resulted in several tenths of a percent shrinkage in the clay soil plug. The slow migration of water from the moist clay soil into the relatively large volume of organic liquid surrounding it is suspected to be responsible for shrinkage under these laboratory conditions.

A suitable parameter for correlating shrink–swell behavior of clay soils with the hydrophobic or hydrophilic character of the solute is the octanol–water partition coefficient. The octanol–water partition coefficient, K_{OW}, has been used to measure the degree to which solute molecules are apt to partition themselves between n-octanol and water (11). It is also possible to use K_{OW}, or log K_{OW}, as an index of molecular transfer from the solvent itself into water, that is, as an index of aqueous solubility (12). Percent swell is plotted vs. log K_{OW} for the three clay soils, in Figure 4. The observation that clay soils swelled in solvents with large negative log K_{OW} values (hydrophilic) and may shrink in solvents having large log K_{OW} values (hydrophobic) is consistent with the view that shrink–swell behavior is related to solvent solubility in the soil pore water.

The behavior of carbon tetrachloride and xylene in this study requires additional comment. Of the solvents studied, these were the primary ones that caused a net shrinkage to occur in some clay soils. Carbon tetrachloride caused Kosse Kaoline and Fire Clay to shrink, while xylene caused shrinkage of Ranger Shale during part of the experiment and a net shrinkage of Fire Clay. In all experiments involving these solvents, there was shrinkage at some time during the run. In column permeability tests reported recently by Green et al. (6, 13), xylene and particularly carbon tetrachloride tended to "break through" the clay soil plug in the permeameter chamber, that is, these liquids underwent rapid advective transport through the clay soil columns. This phenomenon is related to the fact that xylene and carbon tetrachloride caused moist clay soils to shrink, and this shrinkage resulted in the formation of channels in the bulk of the clay soil. This laboratory behavior points to the possibility that under field conditions, solvents and other compounds that cause shrinking and cracking of clay liners might be transmitted along with

Table II. Percent Swell of Test Clays in Contact with Liquids Compared to Dielectric Constants and Dipole Moments of Liquid

immersion liquid	dielectric constant[a]	dipole moment,[a] D	log K_{OW}[b]	Ranger Shale	Kosse Kaoline	Fire Clay
				% swell[c]		
water	79.38	1.82	−1.15	12.0	12.0	8.0
glycerol	42.5	d	−2.56	5.3	d	d
acetone	20.70	2.69	−0.24	4.0	8.0	3.5
trichloroethylene	3.42	0.80	2.37	1.0	0.6	−0.1
carbon tetrachloride	2.24	0.0	2.64	1.1	−0.03	−0.6
benzene	2.28	0.0	2.13	0.5	d	1.3
xylene	2.32	0.3	3.15	0.11	0.16	−0.2

[a] After Riddick and Bunger (9).   [b] After Hansch and Elkins (11).   [c] After Green et al. (6).   [d] Not tested.
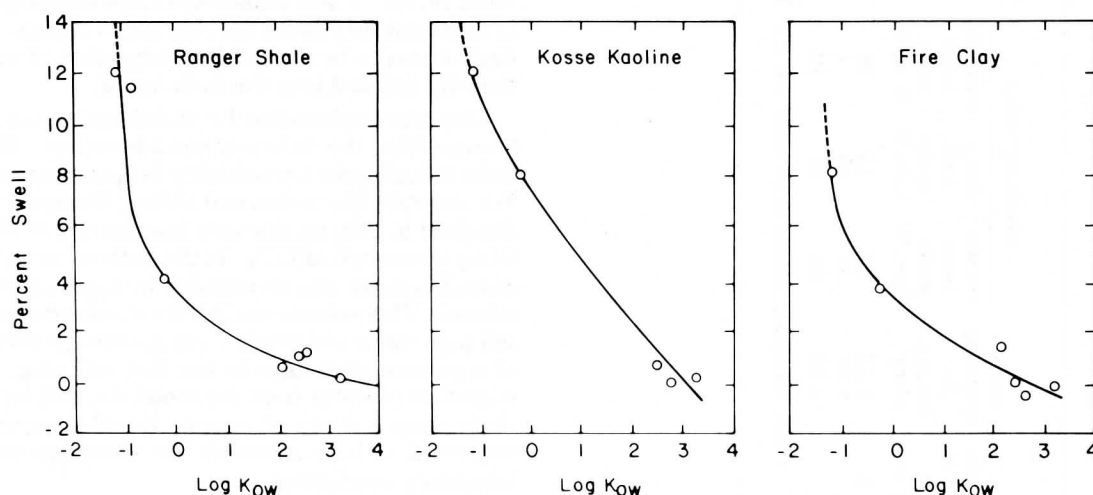
Figure 4. Swelling of three clay soils as a function of solvent octanol–water partition coefficient.

other liquids in the pit to the surrounding groundwater. The results of this study have shown that such behavior might be expected for hydrophobic solvents, as measured by the octanol–water partition coefficient.

Implication of Results for Hazardous Waste Management

One of the primary methods for hazardous waste disposal as part of the U.S. EPA's Resource Conservation and Recovery Act (RCRA) program is the use of clay-lined disposal pits. Typically, clays are packed in these pits at optimum moisture density. Then, over a period of time, waste materials are added. Eventually, when full, the pits are covered. This type of disposal is sometimes referred to as the "clay boat" method, in which the clay liner is supposed to keep the hazardous materials from reaching groundwater. A review of the literature (6) shows that many state and federal regulatory agencies concerned with hazardous waste disposal attempt to achieve a permeability of the clay liners of about 10^{-7} cm/s. This measurement is typically made in packed clay columns with distilled or tap water as the test solvent. There have been few investigations (none at the time this study was initiated) on the impact of hazardous organic and inorganic compound wastes on the integrity of clay liners used for these pits. This study has shown that some of the organics that have been and will continue to be disposed of at hazardous waste disposal sites may interact with the packed clay liners to adversely affect the ability of the liner to properly retain hazardous chemicals. One implication of this work is that regulatory agencies should require that clays to be used at a given site be subjected to detailed permeability and shrink–swell testing with typical mixtures of hazardous materials and leachates that could be developed therefrom, in order to determine whether these might significantly alter the ability of the packed clay liner to retain wastes.

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