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Clay-soils permeability and hazardous waste storage

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With increasing frequency, low molecular weight organic solvents are being recognized as widespread contaminants of ground water. Although there have been a number of studies conducted to evaluate the potential for migration of industrial wastes, none of these has focused on the rate of movement of organic solvents through soils. Specifically, there have been no measurements of the permeability of clays and soils to organic liquids; nor is there an adequate general theory of liquid transport through clays to allow predictions to be confidently made.

The hydrophobic nature of a solvent is more important than density or viscosity in predicting its permeation through soils.

The coefficient of permeability is probably the single most important laboratory-determined parameter for predicting the movement of hazardous solvents through clay liners. However, this is one parameter that can be measured only over long periods of time (typically on the order of a month), using equipment that is neither commercially available nor readily constructed. One of the objectives of this study has been to relate the coefficient of permeability to more easily measured parameters of clay-soils and solvents in order to estimate more readily permeability under a variety of circumstances.

EXPERIMENTAL METHODS

The clay-soils used in this study—Ranger Shale, Kosse Kaoline, and Fire Clay—were purchased from a clay supplier. They were analyzed for particle size distribution; percent montmorillonite, kaolinite, illite, quartz, and feldspar; optimum moisture content; Atterberg limits; cation exchange capacity (CEC); and total organic carbon content. The physical and chemical properties of these materials were discussed by Green *et al.*¹ All solvents were American Chemical Society (ACS) reagent grade or equivalent.

The coefficients of permeability were determined on remolded clay using thick-walled glass columns (Figure 1). These permeameters were designed and built es-

pecially for the study. The columns were Pyrex glass; all joints in the columns were lined with Teflon to make them suitable for use with organic solvents. The procedure followed for determining the coefficient of permeability was adapted from the American Society for Testing and Materials (ASTM),² and is given below.

A 1 000- to 2 000-g sample of well ground (to pass through a No. 4 sieve), air-dried clay-soil was weighed and transferred to a mixing pan. An amount of deionized water corresponding to the optimum moisture content was added. After it had been mixed, the sample was placed in a glass jar, fitted with Parafilm, and stored overnight. For samples that mixed readily with water and had low dry strength, it was sufficient to add water and mix the specimen immediately prior to testing. 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. The surface was leveled by pressing lightly with a wooden plunger. The sample was then compacted with a 2.5 kg (5.5 lb) standard hammer to conform to the standard compaction test procedures, that is, 5.9×10^5 J/m³ (12 375 ft lb/cu ft) of compacted volume. About 10 to 20% additional energy was applied depending on the amount of excess volume of compacted clay. Actual moisture content of the clay sample was determined separately, by oven drying a duplicate sample at 110°C for 24 hours. The excess clay in the mold was scraped and carefully leveled.

After this preparation, the molded clay-soil was placed in the permeability column and the test solvent was added. The level of liquid in the 8-mm graduated standpipe was adjusted using a pipet bulb. The open end of the standpipe was firmly covered with two layers of Parafilm and a hypodermic needle was inserted through the Parafilm to allow equilibration to atmospheric pressure. Using this technique, evaporation of solvent was reduced to an insignificant amount. If any clay-fluid system had had a coefficient of permeability less than 10^{-10} cm/sec, the open end of the standpipe could have been attached to a pressurized nitrogen tank and a constant pressure, in the range of 69 to 345 KN/m² (10 to 50 psi), could have been maintained. The coefficient of permeability K in cm/sec was computed

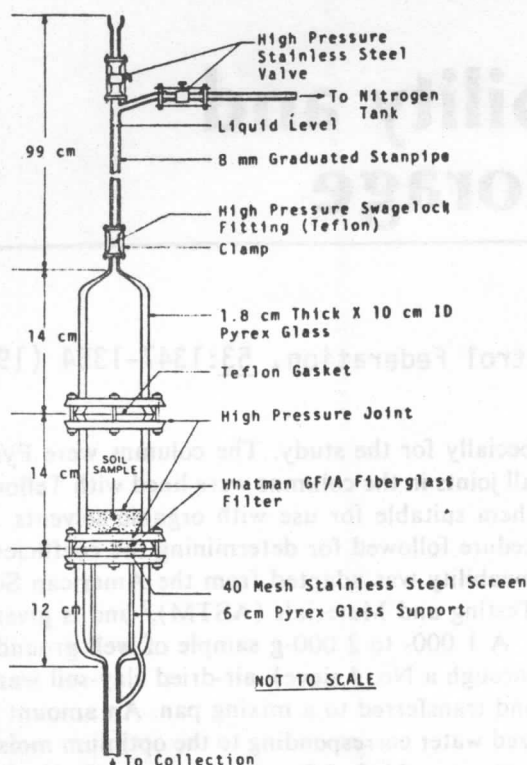


Figure 1—Pressure permeability column (after Green *et al.*¹).

as

$$K = QL/AH \quad (1)$$

where

- Q = the flow of the percolate in ml per second,
 L = the height of the sample in the column in cm,
 A = the cross-sectional area of the sample in square cm, and
 H = the average head of the fluid medium on the sample in cm.

All runs were made in a constant temperature room maintained at $22 \pm 1^\circ\text{C}$.

TABLE 1—Equilibrium permeabilities of clay-soils to organic solvents and water.^a

	($\times 10^{-9}$ cm/sec)		
	Ranger Shale	Kosse Kaoline	Fire Clay
Benzene	2 (Break)	— ^b	— ^b
Xylene	4	50	1 (Break)
Carbon tetrachloride	25	— ^b	— ^b
Trichloroethylene	2	— ^b	2.5
Acetone	2.5	65	7
Methanol	15	— ^b	— ^b
Glycerol	0.9	— ^b	— ^b
Water	38	220	13.5

^a After Green *et al.*¹

^b Not measured.

RESULTS

Fifteen permeability coefficients were determined. These values, presented in Table 1, represent equilibrium permeabilities and were estimated from curves of K (cm/sec) versus time. Figures 2 and 3 provide examples of typical permeability functions and show the typical, marked decrease in K during the early stages of the experiment, followed by a gradual leveling after a period of 2 weeks.

Whereas the profiles shown in Figures 2 and 3 were those most commonly observed, several systems, notably those involving xylene, exhibited a breakthrough phenomenon in which the equilibrium period was followed by a period of rapidly increasing permeability. This is shown graphically in Figure 4. In some trials with low dielectric liquids, the permeability became so large that it could not be measured. In the worst case, the liquid passed completely through the column overnight.

Based on the classification scheme of Terzaghi and Peck,³ all permeability values in Table 1 are low and indicate that these clay-soils are virtually "impervious" to the respective solvents. In general, Kose Kaoline, a relatively low-density, high Kaolinite clay-soil, showed the highest permeability, with Ranger Shale and Fire Clay being considerably more impervious. All clay-soils were more permeable to water than to organic solvents. Curves and data for all permeability work have been presented by Green *et al.*¹

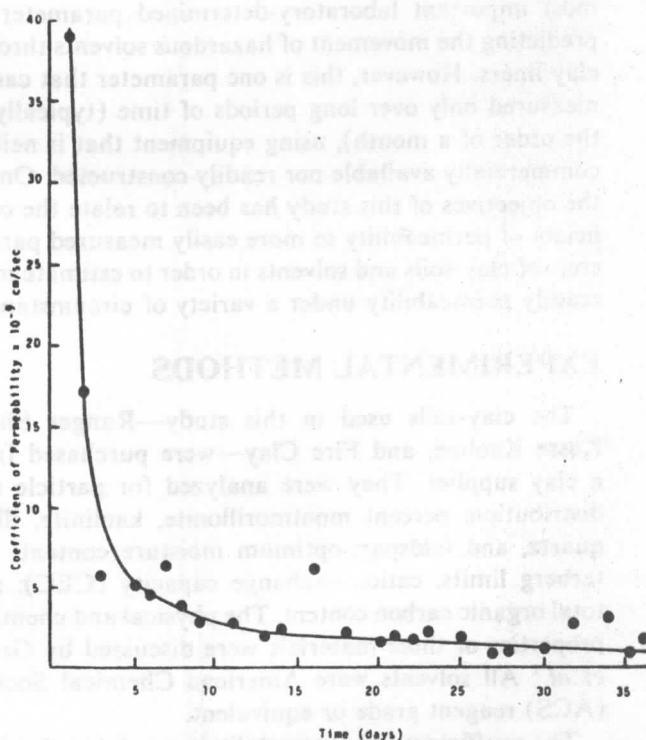


Figure 2—Coefficient of permeability of Ranger Shale to trichloroethylene (after Green *et al.*¹).

DISCUSSION

Relatively low permeabilities of organic liquids. Permeability data collected show that each organic solvent, when in contact with a given clay, had an equilibrium permeability smaller than that of water on the same clay, usually by an order of magnitude. That this is surprising can be seen from the following considerations. According to Davis and DeWiest,⁴ the coefficient of permeability, K , can be determined by

$$K = cd^2(\gamma/\eta) \quad (2)$$

where

- c = dimensionless constant or shape factor that includes grain size, packing and porosity,
- d = average pore size of the porous medium,
- γ = density of the solvent, and
- η = viscosity.

If the first two terms (c and d) are taken to be characteristic of the clay or soil, the coefficient of permeability will depend upon the ratio γ/η . Table 2 presents γ/η values for solvents evaluated in this study. Based on Equation 2, most of the organic solvents should have moved between 1.4 and 2.5 times more rapidly through the clay-soil column than water. The results of this work, however, contradict this prediction.

Taking another approach, it seems reasonable that the swelling of soil grains might tend to have a retarding effect on the transmission of fluids by decreasing the pore sizes. Data have been examined, therefore, for a

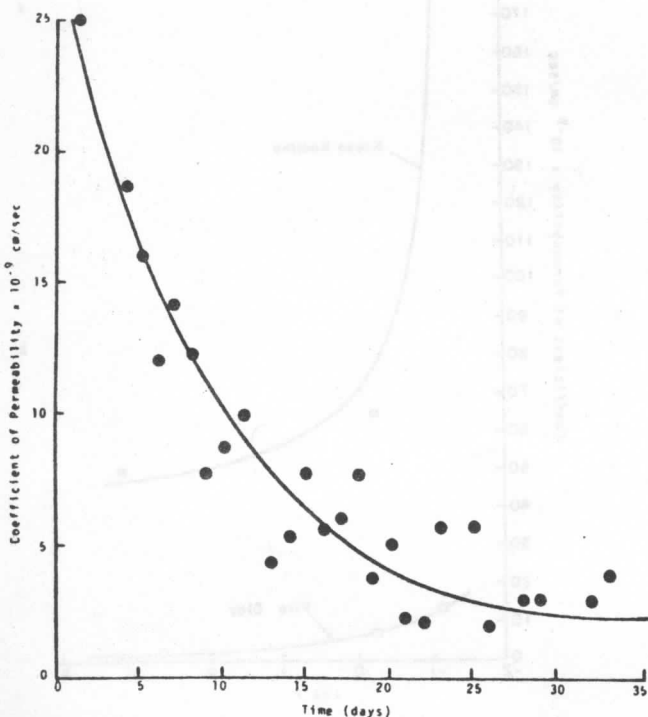


Figure 3—Coefficient of permeability of Ranger Shale to acetone (after Green *et al.*¹).

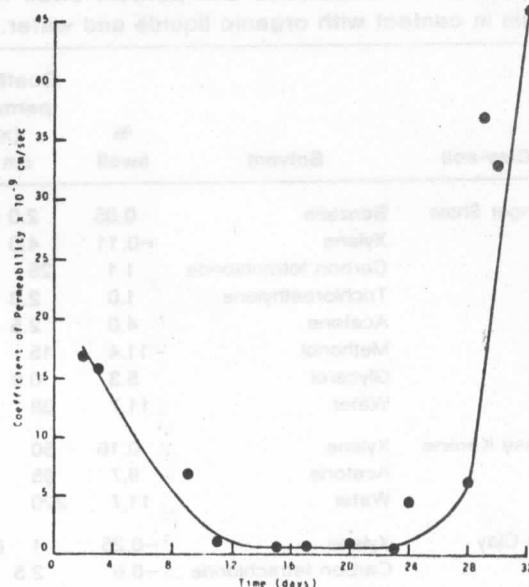


Figure 4—Coefficient of permeability of Fire Clay to xylene (after Green *et al.*¹).

possible correlation between the degree of swelling and the permeability. Table 3 lists the values for swell properties (discussed by Green *et al.*¹) and coefficients of permeability for all solvent systems tested. It can be seen that the markedly smaller permeabilities of the organic solvents cannot be attributed to attenuation of flow through swelling. In fact, the solvent that caused each of the clays to undergo the greatest swelling, namely water, had the largest coefficient of permeability—a result that seemingly conflicts with expectations based on earlier work with aqueous solutions.

To account for the permeability results, it is necessary to consider how an organic molecule (or water) might move through a sorbing, porous medium containing interstitial water. Such a medium has been described by van Genuchten and Wierenga⁶ (Figure 5) as consisting of the following five regions:

1. Air space,
2. Inter-aggregate water,
3. Intra-aggregate water,

TABLE 2—Density-viscosity ratios for organic solvents and water.^a

Solvent	γ (g/cc)	η	Ratio γ/η
Water	1.0	1.0	1.0
Glycerol	1.26	1.412	8.9×10^{-4}
Methanol	0.796	0.551	1.44
Acetone	0.79	0.32	2.46
Trichloroethylene	0.79	0.34	2.32
Carbon tetrachloride	1.59	0.100	1.59
Benzene	0.879	0.649	1.35
m-xylene	0.60	0.50	1.20

^a After Riddick and Bunger⁵

TABLE 3—Permeabilities and percent swell for clay-soils in contact with organic liquids and water.*

Clay-soil	Solvent	% swell	Coefficient of permeability ($\times 10^{-9}$ cm/sec)
Ranger Shale	Benzene	0.05	2.0 (Break)
	Xylene	-0.11	4.0
	Carbon tetrachloride	1.1	25
	Trichloroethylene	1.0	2.0
	Acetone	4.0	2.5
	Methanol	11.4	15
	Glycerol	5.3	0.9
	Water	11.7	38
Kosse Kaoline	Xylene	0.16	50
	Acetone	8.7	65
	Water	11.7	220
Fire Clay	Xylene	-0.25	1 (Break)
	Carbon tetrachloride	-0.6	2.5
	Acetone	3.6	7.0
	Water	8.2	13.5

* After Green *et al.*¹

4. A dynamic soil region, in contact with the inter-aggregate water, where sorption can occur readily, and

5. A stagnant soil region where sorption can occur only after organic molecules have diffused through the surrounding intra-aggregate water.

If this view is adopted, molecules of the permeant can be considered to move by diffusion and convection through the interaggregate water, where, at each stage along the way, they are partitioned between the aqueous phase and the dynamic soil region according to the Freundlich equation. Molecules weakly sorbed by soil particles tend to move quickly through the aqueous channels. Hydrophobic substances, such as benzene,

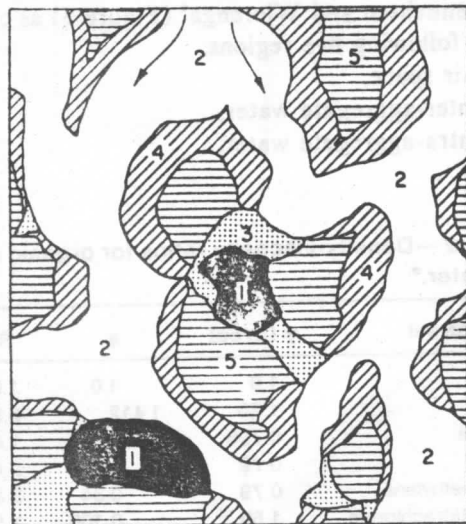
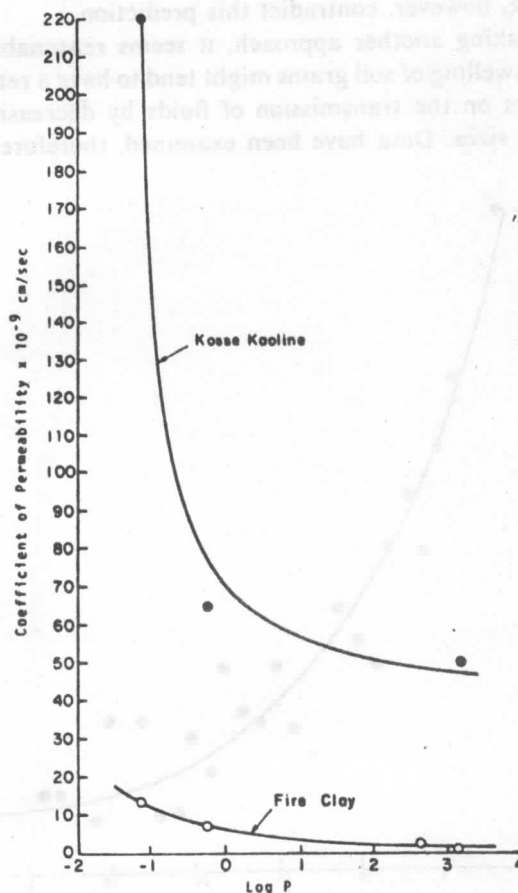
Figure 5—Representation of water-containing clay (after van Genuchten and Wierenga⁶). See text for discussion of areas.

TABLE 4—Permeabilities and octanol/water partition coefficients for solvents on three clay-soils.*

Clay-soil	Solvent	Equilibrium coefficient of permeability ($\times 10^{-9}$ cm/sec)	Log octanol/water partition coefficient
Ranger Shale	Benzene	2.0	2.13
	Xylene	4.0	3.15
	Carbon tetrachloride	25	2.64
	Trichloroethylene	2.0	2.37
	Acetone	2.5	-0.24
	Methanol	15	-0.32
	Glycerol	0.9	-2.56
	Water	38	-1.15
Kosse Kaoline	Xylene	50	3.15
	Acetone	65	-0.24
	Water	220	-1.15
Fire Clay	Xylene	1.0	3.15
	Carbon tetrachloride	2.5	2.64
	Acetone	7.0	-0.24
	Water	13.5	-1.15

* After Green *et al.*¹

xylene, carbon tetrachloride (CCl_4), and trichloroethylene, that are highly partitioned at any instant onto the soil or clay-soil phase, would be expected to have permeabilities lower than those of water and acetone. This

Figure 6—Relationship between coefficient of permeability and octanol/water partition coefficient (after Green *et al.*¹).

model suggests that there may be a relationship between the coefficient of permeability, that measures the rate of movement of the permeant along the column, and the octanol/water partition coefficient, that measures the tendency of permeant molecules to escape from the aqueous phase. Along these lines, Briggs⁷ has shown that the rate of movement of un-ionized pesticides through soils correlates well with their octanol/water partition coefficients. It is reasonable to expect a similar relationship in this case.

It can be seen in Table 4 that, in general, the permeability to a liquid decreases as the log of its octanol/water partition coefficient, P , increases. Because P is a measure of escaping tendency of the organic material from water,⁸ those substances least compatible with water should move most slowly through the column. This generalization seemed to hold for solvents on Kosse Kaoline and Fire Clay, as can be seen when the coefficients of permeability are plotted against the logs of the octanol/water partition coefficients for solvents on these clays (Figure 6). In both cases, the more positive the value of $\log P$, the smaller the value of K ; or, in other words, the more hydrophilic the organic, the more rapidly it moves through the clay. However, this relationship did not apply as consistently in the case of Ranger Shale. The three solvents which exhibited anomalous behavior may have done so for the following reasons:

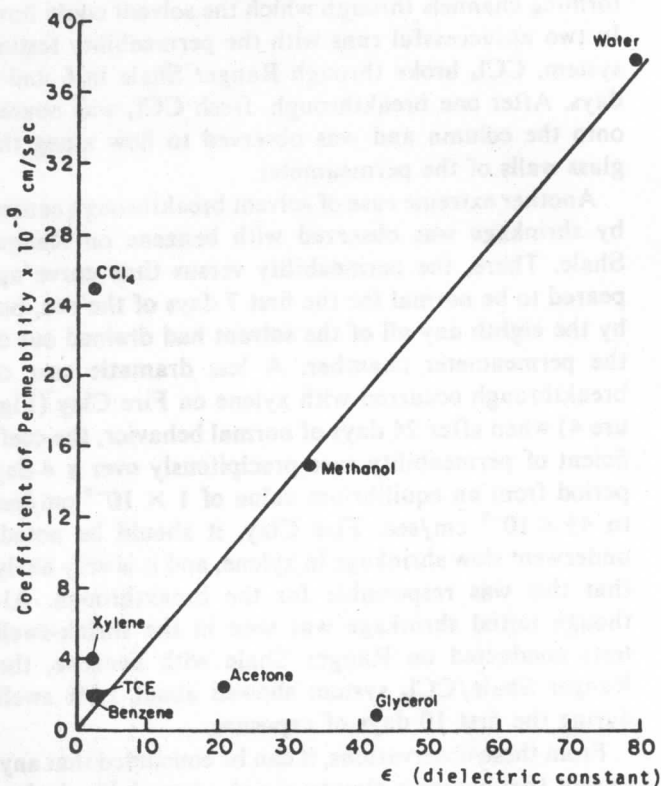


Figure 7—Relationship between coefficient of permeability and dielectric constant for solvents in Ranger Shale (after Green *et al.*¹).

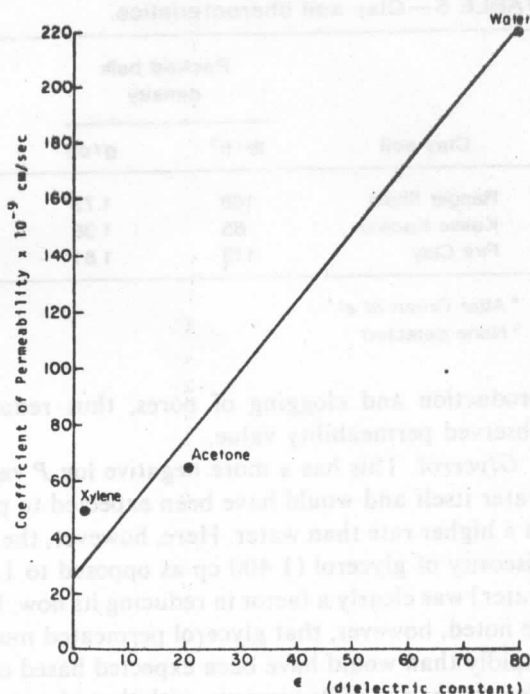


Figure 8—Relationship between coefficient of permeability and dielectric constant for solvents in Kosse Kaoline (after Green *et al.*¹).

Carbon tetrachloride. Despite a high value for $\log P$, carbon tetrachloride had a coefficient of permeability much larger than that of the other hydrophobic solvents studied (that is, benzene, xylene, and trichloroethylene). This can be attributed to its ability to cause clay shrinkage as discussed below.

Acetone. This is a hydrophilic substance having a negative value for $\log P$; it would have been expected to move through the clay-soil much more rapidly than benzene and xylene. That it did not suggests the possibility that microbial decomposition of acetone on the biologically active clay, Ranger Shale, resulted in CO_2

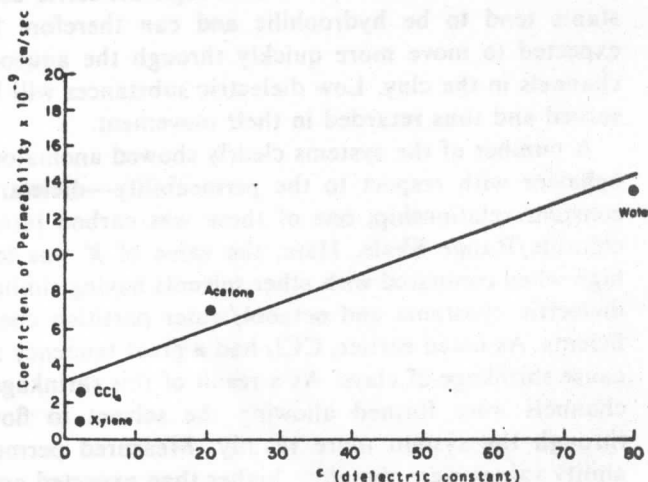


Figure 9—Relationship between coefficient of permeability and dielectric constant for solvents in Fire Clay (after Green *et al.*¹).

TABLE 5—Clay-soil characteristics.

Clay-soil	Packed bulk density		% Organic carbon	% Montmorillonite	Void ratio	K ($\times 10^{-9}$ cm/sec) for H ₂ O
	lb/ft ³	g/cc				
Ranger Shale	108	1.73	0.28	4	0.4–0.53	38
Kosse Kaoline	85	1.36	0.12	N.D. ^b	0.37–0.74	220
Fire Clay	113	1.81	0.03	N.D. ^b	0.19	13.5

^a After Green *et al.*¹

^b None detected.

production and clogging of pores, thus reducing the observed permeability value.

Glycerol. This has a more negative log *P* value than water itself and would have been expected to permeate at a higher rate than water. Here, however, the extreme viscosity of glycerol (1 400 cp as opposed to 1.0 cp for water) was clearly a factor in reducing its flow. It should be noted, however, that glycerol permeated much more rapidly than would have been expected based on a simple comparison of its viscosity with that of water. Given this consideration alone, it should have moved at one 1 000th the rate of water. That it had a *K* value of one thirty-sixth that of water can be explained in terms of its high affinity for the aqueous phase. Work with glycerol points out the need to consider viscosity in any complete model of solvent flow through clays; this property is not, however, as important as the hydrophilic or hydrophobic character (as measured by *P* or by the dielectric constant) of the permeating liquid.

There also appears to be a good relationship between the permeability of a clay-soil to a solvent and the solvent's dielectric constant, so that the greater the dielectric constant, the greater the value of *K* (Figures 7 to 9). This is to be expected in light of the above model, because the dielectric constant serves as an approximate measure of a liquid's hydrophobic or hydrophilic character. Substances with high dielectric constants tend to be hydrophilic and can therefore be expected to move more quickly through the aqueous channels in the clay. Low dielectric substances will be sorbed and thus retarded in their movement.

A number of the systems clearly showed anomalous behavior with respect to the permeability—dielectric constant relationship; one of these was carbon tetrachloride/Range Shale. Here, the value of *K* was too high when compared with other solvents having similar dielectric constants and octanol/water partition coefficients. As noted earlier, CCl₄ had a great tendency to cause shrinkage of clays. As a result of this shrinkage, channels were formed allowing the solvent to flow through the system more readily. Measured permeability values were therefore higher than expected and this caused the point for CCl₄ to be far from the line of best fit in Figure 7. Glycerol, as discussed previously,

had an unusually low permeability probably because of its high viscosity. This is reflected in its position in Figure 7.

Although the benzene/Ranger Shale system showed solvent breakthrough because of clay shrinkage during several permeability tests, it appeared to fit the general relationship between permeability and dielectric constant shown in Figure 7. Xylene in Fire Clay also eventually showed solvent breakthrough. The point for this system in Figure 7 represents the equilibrium position seen in Figure 4.

Solvent breakthrough. An important aspect of the effect of organic solvents on clay permeability is the breakthrough phenomenon observed in a number of solvent/clay-soil systems. These cases were related to the fact that certain solvents caused the clay to shrink, forming channels through which the solvent could flow. In two unsuccessful runs with the permeability testing system, CCl₄ broke through Ranger Shale in 6 and 8 days. After one breakthrough, fresh CCl₄ was poured onto the column and was observed to flow along the glass walls of the permeameter.

Another extreme case of solvent breakthrough caused by shrinkage was observed with benzene on Ranger Shale. There, the permeability versus time curve appeared to be normal for the first 7 days of the run, but by the eighth day all of the solvent had drained out of the permeameter chamber. A less dramatic case of breakthrough occurred with xylene on Fire Clay (Figure 4) when after 24 days of normal behavior, the coefficient of permeability rose precipitously over a 4-day period from an equilibrium value of 1×10^{-9} cm/sec to 45×10^{-9} cm/sec. Fire Clay, it should be noted, underwent slow shrinkage in xylene, and it is very likely that this was responsible for the breakthrough. Although initial shrinkage was seen in the shrink-swell tests conducted on Ranger Shale with benzene, the Ranger Shale/CCl₄ system showed about 1.1% swell during the first 10 days of exposure.

From these observations, it can be concluded that any solvent that causes a clay to shrink appreciably during any stage of a shrink-swell experiment is a potential hazard when stored in a clay-lined disposal area. Even though such a solvent may move slowly through a wet

clay by diffusion and convection, there is, in principle, a danger that it will eventually cause shrinking and cracking and thereby allow fluid transmission in bulk. Because of its implication for the storage of commercial organic solvents in clay-lined pits, breakthrough should be a significant consideration in future waste disposal planning. Tests on actual clay-lined pits would be useful in this regard.

Properties of clays of potential importance in governing permeability. Table 5 summarizes several clay properties that might be influential in governing their permeability to solvents.

Montmorillonite content. Montmorillonite is an expandable layer clay; exposure to liquids could cause swelling of individual montmorillonite grains and clogging of soil pores and channels. Based on this consideration, Ranger Shale, with the highest montmorillonite content (4% by weight) would have been expected to have the lowest permeability. This was not observed.

Void ratio. The void ratio, or volume of voids divided by volume of solids ($e = V_v/V_s$), is generally acknowledged to be an important factor in determining permeability (see Amer and Awad⁹). For the limited number of clay-soils evaluated in this study, there was no relationship between void ratio and permeability.

Clay density. Packed bulk clay density, which is a function of mineral composition and packing, seemed to be the clay-soil property that most directly influenced permeability. In general, as clay density increased, the permeability of the clay to a given solvent decreased (Figure 10).

CONCLUSION

This study has shown that it is the hydrophobic or hydrophilic nature of the solvent (as measured by the octanol/water partition coefficient or roughly, by the dielectric constant) and not its density or viscosity that is important in predicting the solvent's rate of flow through clay-soils. In addition, it has been found that packed bulk clay density is apparently crucial in determining how permeable a clay will be to a given solvent.

Whereas these generalizations hold for all solvents during normal (that is, diffusion and convection controlled) flow, they are invalid for situations where breakthrough and bulk transport occur. Breakthrough was observed only for those solvents of low dielectric constant that tended to cause shrinking and cracking of clays in both consolidometer and column tests. The results of this study suggest the need to exercise caution in storing wastes such as benzene, xylene, or carbon tetrachloride. These materials might best be co-disposed with a higher dielectric and, preferably, miscible liquid.

Based on the systems examined, the following empirical relationship has been derived for estimating the coefficient of permeability, K (in cm/sec):

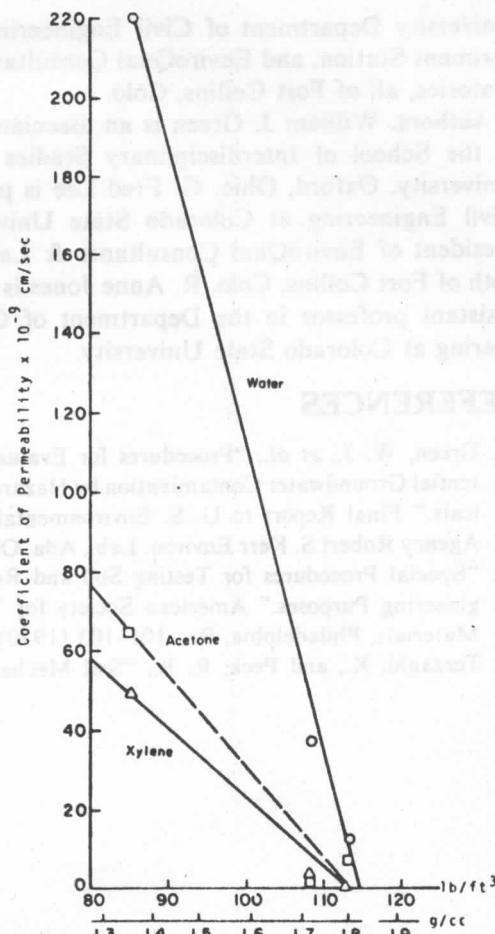


Figure 10—Coefficient of permeability as a function of packed bulk clay density (after Green *et al.*¹).

$$\log K = 1.17 (\log (\epsilon^{0.75}/d')) - 7.23 \quad (3)$$

where " ϵ " is the solvent dielectric constant and " d' " is the packed bulk clay density (g/cc). Whereas most of the data obtained in this study fit this relationship, with further work it is likely that a more widely applicable relationship can be developed.

An important conclusion of this study is that the effect of organic solvents on the coefficient of permeability may be estimated from readily obtainable information, namely, the dielectric constant of the solvent and packed bulk density of the clay.

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