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Organic Solvent Alteration of Hydraulic Properties of Sedimentary Rocks of Low Permeability—A Review

D. S. Sklarew

May 1985

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PNL-5501

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Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
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226-250	A011
251-275	A012
276-300	A013

PNL-5501
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ORGANIC SOLVENT ALTERATION OF HYDRAULIC PROPERTIES OF SEDIMENTARY ROCKS OF LOW PERMEABILITY - A REVIEW

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Richland, Washington 99352

SUMMARY

At the request of the U.S. Department of Energy, Office of Energy Research, Pacific Northwest Laboratory conducted a review of the current literature on hydrophysical interactions of organic solutes with sedimentary rocks of low permeability. The motivation behind this study was the premise that low permeability rocks may act as secondary (aquifer) barriers for the containment of hazardous organic wastes, thus preventing these wastes from contaminating the groundwater. However, this premise may be incorrect if organic wastes can affect the hydraulic conductivity of these rocks. The results of this literature search as well as conversations with other researchers in this and related areas indicate that very little work has been done concerning interactions of organics with consolidated subsurface materials. Available information on three related topics was summarized in this report: the effect of organic compounds on the hydrophysical properties of clays, case studies concerning the interactions of organic compounds with clays and sedimentary rocks, and the effect of shales on inorganic transport. These studies give an indication of some research areas that need to be explored with regard to the effect of organic compounds on the hydrophysical properties of sedimentary rocks; these research needs are briefly summarized. The questions raised need to be addressed before it is possible to make accurate predictions of organic transport in the subsurface environment.

CONTENTS

INTRODUCTION

One proposed method for disposal of organic wastes has been below-surface injection into sites which are underlain by low permeability rocks. These rocks, such as mudstones and shales, have characteristics that are thought to make them suitable as in-situ barriers for the containment of the organic wastes, preventing these wastes from contaminating groundwater. If organic wastes can affect the hydrophysical properties (e.g., permeability and porosity) of subsurface materials, the use of these materials as barriers becomes suspect. Only when such changes in hydrophysical properties are taken into account, may accurate predictions of organic transport in the subsurface be made. To determine the extent of these changes, Pacific Northwest Laboratory reviewed the current literature related to the physical interactions of organic solutes with sedimentary rocks of low permeability and, based on this information, assessed research needs in this area.

This report is an outgrowth of a U.S. Department of Energy (DOE) research plan for the Subsurface Transport Program on "Geochemical, Hydrological and Biological Cycling of Energy Residuals" (Wobber 1982). This plan describes a 10-year fundamental research program planned by the DOE, Office of Health and Environmental Research (OHER), within the Office of Energy Research (OER), to develop the capability to predict the transport of organic contaminants in subsurface and groundwater environments. The goals of this plan are to develop an improved understanding of microbiological, chemical, and hydrologic processes which influence the transport of organic compounds and mixtures in subsurface porous media and to incorporate this knowledge into predictive hydrologic and transport models which reliably describe the movement, persistence, and biological availability of organic compounds and mixtures. The need for such a broad program is based on the production of a wide variety of organic compounds by energy extraction/utilization technologies and their generation as wastes by industrial, energy, and national defense programs. Planned or accidental disposal of these materials in the ground (e.g., by spillage, injection, landfill disposal) may lead to the migration of organic compounds (liquids, solutions, suspensions) through the soil/sedimentary rock environment into groundwaters, resulting in potentially irreversible contamination. Protection of these limited and valuable groundwater resources requires a better understanding of the movement and fate of organic contaminants within the subsurface environment. Such information is needed for scientifically based decisions on alternate energy technologies, establishment of waste management procedures, and development of methods for isolating and mitigating contaminant plumes.

This report deals with one aspect of this multifaceted problem, namely, the hydrophysical interactions of organic compounds with consolidated subsurface materials. As stated above, the major emphasis of this report is a review of the literature concerning the effects of organics on hydrophysical properties of sedimentary rocks. Based on this literature review, research needs in this area will be assessed and enumerated.

LITERATURE REVIEW

The literature review was accomplished in three stages: (1) computerized searches of key words in several data bases (Chemical Abstracts, Biological Abstracts, NTIS, Georeferences, Water Resources Abstracts, DOE Energy Data Base); (2) review of relevant papers from the reference lists of the papers found in (1); and (3) phone calls to the authors of these papers, to additional scientists recommended by these authors, and to contacts at two petroleum companies and the National Institute of Petroleum and Energy Research (NIPER).

All three source types confirmed that very little information is available about the hydrophysical interaction of organic wastes with sedimentary rocks of low permeability. However, some information, albeit meager, is available on related subjects. Thus, this review has been divided into three areas in which information has been found. These areas were chosen to answer the following questions:

- What do we know about the effect of organic compounds on hydrophysical properties of clays?
- Is research under way concerning the interactions of organic compounds with clays and sedimentary rocks?
- What do we know about the related area of the effect of shales on inorganic transport? What other shale properties may play a role in organic interactions?

EFFECT OF ORGANIC COMPOUNDS ON HYDROPHYSICAL PROPERTIES OF CLAYS

The use of clay liners in landfills has recently led to a number of studies on the effect of organic wastes on these so-called "impermeable barriers" (i.e., impermeable to water). These studies have built on results known since at least the 1930s (e.g., Albrecht and Corey 1939, in Barshad 1952) that some clays under certain conditions expand or shrink in the presence of organic compounds. Theng (1974) has reviewed studies on the interaction of organic molecules with clays, including the formation of interlayer complexes and the mechanisms of expansion and contraction of clays. The latter is beyond the scope of this report.

Barshad (1952) evaluated the factors affecting interlayer expansion in montmorillonite and vermiculite. A major factor is the degree of dehydration prior to contact with the organic compound; complete dehydration resulted in lack of or reduced expansion for a number of organic solvents (hexane, benzene, butanol, glycerol, acetone). Other factors affecting expansion include the cationic form of the clay (greater expansion with smaller cation and larger valence charge on cation), the total charge on the crystal lattice (expansion increases with smaller total charge), the dielectric constant of the organic liquid (in one homologous series, as the dielectric constant increased, the expansion decreased, then increased, then decreased again), and the dipole moment of the organic liquid (expansion increased with increasing dipole moment). Brindley et al. (1969) studied the degree of expansion of Ca-montmorillonite with several organic solvents. For example, water swells montmorillonite to 19Å. Addition of as little as 1 mol% acetone results in further swelling. Addition of 20 to 60 mol% acetone results in expansion to 26.5Å. Addition of 80 to 90 mol% acetone causes shrinkage to 22Å, while pure acetone causes further shrinkage to 17.3Å. Similar results were observed with propanol, ethanol, 1,5-pentanediol, and ethylene glycol. Dioxane, by contrast, caused immediate collapse at all concentrations. Another measurement useful in determining the interactions between clays and organics is flocculation. The effectiveness of several organic compounds (including phenol, nitrophenols, quinones, phenylenediamine, gallic acids) on flocculation was shown in one study to follow the order: calcareous clays > noncalcareous, calcium - saturated clays > noncalcareous, sodium - saturated clays (Chang and Anderson 1968).

Other studies have dealt with the hydraulic conductivity[(a)] of clay to water and electrolytes. For example, Lutz and Kemper (1959) determined the permeability of four clays, each saturated with Na and Ca, to water and to electrolyte solutions. They found the following order of permeability: halloysite > Utah bentonite (granular) > Bladen clay > Wyoming bentonite. The Na clays were generally much less permeable to both water and electrolytes than were the Ca clays. In the presence of electrolyte, the Na clays showed relatively greater increases in permeability than did the Ca clays, though most of the clays were generally more permeable to electrolyte than to water. These effects are discussed in terms of the Gouy double-layer theory which is also invoked to explain the results of organic swelling experiments. Such a discussion is outside the scope of this report.

These earlier results helped to arouse suspicions that checking clay liners for permeability to water may have little bearing on their structural integrity in the presence of organic or mixed organic-inorganic wastes. Four or five groups have recently published in this or closely related areas, sometimes with conflicting results. While much of the earlier work was concerned with interlayer swelling of clays, much of this later work deals with the bulk swelling properties of clay or clay soils exposed to organic liquids.

Green et al. (1981) determined the hydraulic conductivity for three clay soils (hydrated to optimum moisture content) using water and seven organic solvents (benzene, xylene, carbon tetrachloride, trichloroethylene, acetone, methanol, and glycerol). All the clay-soils were more permeable to water than to organic solvents. This was surprising, based on two considerations: (1) $K \propto \frac{\rho}{\eta}$ where K = hydraulic conductivity or (coefficient of)

(a) Hydraulic conductivity (K) is related to intrinsic permeability (k) by the equation $K = \frac{\rho g k}{\eta}$,

where ρ is density of the fluid, η is viscosity of the fluid, and g is the acceleration due to gravity. Intrinsic permeability (length^2) is a property of the soil/rock whereas hydraulic conductivity (length/time) is a combination of soil/rock and fluid properties. Because of common usage, "hydraulic conductivity" and "permeability" are used interchangeably but are distinguished from "intrinsic permeability" in the following discussion.

permeability, ρ = solvent density, and η = viscosity, and $\frac{\rho}{\eta}$ is greater for most of the organic solvents studied than for water; (2) water causes the greatest swelling of the clays which might have been expected to attenuate the flow. To resolve the problem, Green et al. (1981) attributed the low permeabilities to retardation of flow caused by preferential adsorption of the organic solvent by the clay-soil, and thus they postulated that the permeability is inversely related to the octanol-water partition coefficient (K_{ow}) and directly related to the dielectric constant [comment by Sivapullaiah and Sridharan (1984)]. Permeability also is related to the packed bulk clay density. Three exceptions to this theory were explained on the following bases. The low permeability of acetone, relative to more hydrophobic solvents, was attributed to microbial decomposition, production of CO_2, and subsequent pore clogging. The low permeability of glycerol relative to water was attributed to its high viscosity. Perhaps the most interesting anomaly was the relatively large permeability of carbon tetrachloride (CCl_4). This was due to the tendency of CCl_4 to shrink the soil and create shrinkage channels which increased the flow of solvent. The same phenomenon can also explain the eventual breakthrough of the less polar solvents used in the experiments (i.e., benzene and xylene). Green et al. (1983) explain the expansion/shrinkage phenomenon by suggesting that polar organics can become solubilized in the soil pore water and thus cause bulk clay expansion whereas nonpolar organics cannot interact in this way and, indeed, may cause migration of water out of the clay-soil and into the bulk organic liquid (due to water's slight solubility) with subsequent shrinkage. Breakthrough of solvents caused by shrinkage has important implications for the efficacy of storage of organic solvents in clay-lined landfills.

In another series of experiments, Anderson and Brown (1981) and Brown and Anderson (1983) tested the hydraulic conductivity (permeability) of four clay-soils (noncalcareous smectite, calcareous smectite, kaolinite, illite—all with low water permeabilities) to four classes of organic solvents—basic (aniline), acidic (acetic acid), neutral nonpolar (heptane, xylene), and neutral polar (acetone, methanol, ethylene glycol). All the soils showed large increases in permeability with all four classes of organic compounds relative to water. The kaolinitic and calcareous smectitic clay-soils showed somewhat greater resistance to permeability increase than did the illitic or noncalcareous smectitic clay-soils. (This seems to be inconsistent with Chang and Anderson's (1968) conclusion that calcareous clays flocculate more readily than non-calcareous clays in the presence of a number of organic compounds, and, therefore, permeability should increase more, all other factors such as water content and ionic strength being equal. However, the results are consistent with the fact that kaolinite swells or contracts less than illitic or smectitic clays.) Permeability increases were continuous with basic and neutral polar fluids but tended to reach a maximum with neutral nonpolar fluids. Acids caused dissolution and leaching of soil particles which resulted in temporarily decreased permeability, but further dissolution resulted in increased permeability.

In addition to work with pure organic solvents, Brown and Thomas (1984) tested the effect of complex petroleum products on the hydraulic conductivity of clays. As with other nonpolar organics, kerosene, diesel fuel, gasoline, and motor oil all resulted in large increases in conductivity relative to water (1 to 5 orders of magnitude). Again, the smectitic clays were affected considerably more than the kaolinitic clay. Another research study (Khaleel et al. 1981) found a large variation in the degree of increase of hydraulic conductivity of soils as a result of different waste applications. Using compacted kaolinite, which in previous studies had been shown to be less subject to both swelling and intrinsic permeability changes, Acar et al. (1984) observed the effect of four organic solvents on hydraulic conductivity. They found that acetone caused an increase in permeability, phenol caused a slight decrease, and benzene and nitrobenzene caused substantial decreases (3 orders of magnitude). These observations were explained by differences in the surface forces of interaction between the different organic solvents and the clay. These different interactions were also observed in free swell tests of the kaolinite with the four organic solvents.

The results from the clay-organic experiments (summarized in Table 1) by Acar et al. (1984) differ from those by Green et al. (1981, 1983) which, in turn, differ from those by Anderson and Brown (1981), Brown and Anderson (1983), and Brown and Thomas (1984). For example, Green et al. (1981) and Brown and Anderson (1983) cite differences in hydraulic conductivities towards neutral polar fluids. Possible causes

TABLE 1. Effects of Organic Solvents on Swelling/Hydraulic Conductivity of Clays

A. Swelling of Clays (Relative to Effect of Water)

1. Shrinkage
   - hexane, benzene, acetone, butanol, glycerol (Barshad 1952)
   - > 80% acetone, propanol, ethanol, 1,5-pentanediol, ethylene glycol (Brindley et al. 1969)
   - dioxane (Brindley et al. 1969)
2. Expansion
   - < 60% acetone, propanol, ethanol, 1,5-pentanediol, ethylene glycol (Brindley et al. 1969)

B. Hydraulic Conductivity (Relative to Water)

1. Increased
   - heptane, xylene, acetone, methanol, ethylene glycol, aniline, acetic acid (Anderson and Brown 1981)
   - kerosene, diesel fuel, gasoline, motor oil (Brown and Thomas 1984)
   - acetone (Acar et al. 1984)
2. Decreased
   - benzene, xylene, carbon tetrachloride, trichloroethylene, acetone, methanol, glycerol (Green et al. 1981)
   - benzene, phenol, nitrobenzene (Acar et al. 1984)
   - 0.1% organics (slight decrease) (Acar et al. 1984)
3. No Effect
   - <1% organics (Ely et al. 1983)

for these conflicting results include differences in experimental protocol (e.g., pressure regime) or differences in clays. One difference in experimental protocol was discussed by Acar et al. (1984). The experiments by Acar et al. (1984) reported above were performed using a flexible wall permeameter. When they switched to a rigid wall permeameter (which was used by the Green et al. and Anderson and Brown teams), they found a 2-order of magnitude increase in hydraulic conductivity caused by sample shrinkage and side leakage. While this represents a major problem with the experimental design, it does point up the possibility of shrinkage in clay liners which could result in their failure. More studies are needed to resolve some of the incongruities and to understand the mechanisms for these changes. Amoozegar-Fard et al. (1982) are currently expanding a study to determine the mechanisms by which organic solvents affect the intrinsic permeability of soils. They have noted that acetone increases the intrinsic permeability of at least two soils; the increase remains when water is again introduced into the system. In contrast, tetrachloroethylene causes decreased intrinsic permeability of these soils which remains low when water is reintroduced. Another recent study by Fernandez and Quigley with benzene, cyclohexane, and xylene indicated that changes in hydraulic conductivity did not occur with water-wet samples; only when the rocks were first permeated with water- (and aromatic-) soluble alcohols did the aromatic hydrocarbons produce an extensive increase in conductivity (accepted for publication in Canada Geotechnical Journal).

The preceding work was accomplished with pure organic solvents. While this scenario may occur initially when large volumes of solvents are dumped or spilled (and may be especially important when the migration route to the subsurface is short, decreasing the possibility of dilution), a more common scenario, especially for energy-related wastes, is that of organic solutes in low concentrations in water. Even fewer studies have been reported in this area. Ely et al. (1983) observed that concentrations of less than 1% organics have no significant impact on soil hydraulic conductivity. Acar et al. (1984) found that 0.1% solutions of organic compounds resulted in slight decreases of hydraulic conductivity of compacted kaolinite.

CASE STUDIES OF INTERACTIONS OF ORGANIC COMPOUNDS WITH CLAYS AND SEDIMENTARY ROCKS

This section can be divided into four topics of case studies: (1) accidental spills, (2) landfill sites, (3) deep waste injection, and (4) interactions of naturally occurring organics. All have provided various types of information that can be applied to the problem addressed in this report.

The study of Roberts et al. (1982) and Schwartz et al. (1982) is used here as an example of an accidental spill of large quantities (6800 to 21,000 l) of an organic fluid (PCBs). Their study area is underlain by Regina clay, Condie silt, till, glacial sands, and gravels. The Regina clay and Condie silt both have an abundant fracture system. The authors found that the contaminants spread more laterally than vertically, suggesting that the permeability of the fractured Regina clay was considerably less than the fill. They hypothesized that the Inerteen (70% PCBs, 30% chlorobenzenes) moved as a separate liquid phase along the largest fractures. As an oily phase, it would not wet the rock, but would form droplets which would be trapped as the fractures become smaller. Capillary forces would have to be overcome to force entry of this oily phase into pore openings saturated with water. The force needed becomes greater as porosity and permeability decrease. A high head in the system would be needed to overcome this force, making it unlikely that the Inerteen would continue to migrate downward as a distinct phase. However, the Inerteen does have a finite, though low, solubility in water which would allow it to migrate slowly downward through the low-permeability zone as a dissolved phase in water.

The study of Griffin et al. (1984) is used as an example of the interactions of organic compounds in a landfill area. Organic compounds were migrating 100 to 1000 times faster than predicted from the landfill studied. These authors invoked the studies of Anderson and Brown (1981), Green et al. (1981), and Brindley et al. (1969) in which clay-organic interactions caused swelling and shrinkage of clays to help explain the migration of organic contaminants in this landfill. They also found that field measurements of hydraulic conductivity yielded higher results than laboratory measurements and suggested that this may be due to small fractures or thin sand seams in field samples that are obliterated during recompaction of samples for laboratory studies. Such inhomogeneities frequently are dominant factors in field studies—an important point that needs to be considered in designing laboratory studies.

Deep-well injection has been an alternative method for disposal of industrial wastes for some time (Hower et al. 1971). Typical geologic formations into which the waste is injected are sands and sandstones, usually with a relatively impermeable barrier above and below. Because adsorption of the wastes on the sandstones at depth will play an important role in the migration of the wastes, adsorption properties of 10 organic compounds were determined on a sandstone under simulated subsurface conditions (Donaldson et al. 1975). Any single organic component in aqueous wastes treated for underground disposal is usually less than 1%; therefore, this was the maximum concentration used in these studies. The adsorption process was controlled by bulk and internal pore diffusion rather than by adsorption onto the site. The Freundlich adsorption constants were low; the adsorption mechanism was Van der Waal's bonding or physical adsorption. Rates of adsorption were slow. These properties suggest that adsorption on the sandstones is not very efficient and some barrier is important in preventing the spread of underground wastes.

It has long been recognized that interactions of waste materials with reservoir fluids and rocks need to be considered to ensure the success of deep-well disposal of wastes (Hower et al. 1971). Formation plugging may be caused by reaction of chemicals to form a precipitate, emulsification of a water-oil mixture to form an emulsion block, swelling and migration of clays, presence of particulates and/or colloids in the waste solution, dissolution of part of the rock to produce fines, adsorption of chemicals on the rock surface causing a change in wettability or a reduction in pore dimensions, formation of gaseous reaction products such as CO_2 and CH_4. Of course, formation plugging is a disadvantage from the perspective of being able to inject the organic wastes into the formation. While this is not directly related to the acceptability of shales as barriers to waste migration, the mechanisms of formation plugging and the possibility of pressure buildups caused by plugging are certainly relevant. Some of the mechanisms and specific organic waste-rock interactions are mentioned here. Polar organic compounds can be adsorbed by silicates, especially clays, with the effect of changing the wettability of some rocks from water-wet to oil-wet. The resulting hydraulic conductivity reduction is especially severe with positively charged organic compounds that are very difficult to remove by water-washing (Hower et al. 1971). Waste organic acids such as aspartic, citric, salicylic, tartaric, and tannic were found to dissolve 5 to 75 times the amount of clay minerals than would be dissolved by water (Huang and Keller 1971, in Hower et al. 1971). The presence of carbonate minerals mixed in with the clay (as, for example, in a carbonaceous shale) will tend to cause neutralization of the acids (Caruccio and Geidel 1980) and may initially inhibit dissolution of clay minerals under such circumstances.

In a detailed study of the effects of subsurface waste injection near Wilmington, North Carolina, Leenheer et al. (1976) and Leenheer and Malcolm (1973) further discuss the effects of waste organic acids (formic, acetic, and phthalic) on the components of the receiving formation. The organic acids react rapidly with limestone in a neutralization reaction, less rapidly with iron and manganese oxides, and slowly with aluminosilicate minerals, forming CO_2 (dissolved), and releasing alumina, silica, Fe, Mn, and Ca. Microbial oxidation of waste to CO_2 and H_2O lowers Eh by O_2 depletion and lowers pH by solution of CO_2. This, in turn, results in conversion of Fe^{+3} to the more soluble

Fe^{+2}; Fe is also solubilized by complexation with aromatic dicarboxylic acids in the waste. $CaSO_4$ is reduced to H_2S by microorganisms using acetic acid as an energy source. Silica dissolution is high at low pH and at pH greater than 10. The coatings on the primary minerals can be dissolved by organic acids. At low pH values present in some parts of the waste, organic acids become less soluble, less mobile, and more readily adsorbed. Dissolution of aquifer materials by organics may cause leakage problems at injection and observation wells resulting in possible upward leakage of waste into zones with different and less desirable properties than the zone intended to receive the waste. These organic reactions could, if extensive enough, gradually have an effect on the microfractures and the permeability of the injection formation zone.

Similar types of reactions and interactions can occur with natural organic materials found associated with rocks. Studies of these interactions can also be useful in predicting effects of organic wastes on the physical properties of sedimentary rocks. For example, dissolved and particulate organic matter in the unsaturated zone is oxidized by bacteria, forming CO_2 which can become quite concentrated at depth (relative to atmospheric conditions). Such high concentrations of CO_2 lead to a dissolution of carbonate and aluminosilicates creating void spaces (secondary porosity) (Wood and Petraitis 1984; Wood and Osterkamp 1984). Organic acids are another product of maturation reactions. Organic acid solutions (such as acetic acid and oxalic acid) at concentrations similar to those found in some oil field formation waters (up to 5000 ppm, at 80 to 200°C) can increase the solubility of aluminum by $\frac{1}{2}$ to 1 order of magnitude. These organic acid solutions can also destroy carbonate cement and debris. Aluminosilicate and carbonate dissolution again results in secondary porosity, in sandstone in this example (Surdam et al. 1982).

The transport of petroleum is another area that is applicable to the problem of organic waste transport. The conductivity (permeability) of oils is dependent in a complex fashion on the saturation of pores. As saturation increases, conductivity increases in a nonlinear fashion. Mull (1978) discusses the case of a hypothetical two-layer system in which the upper layer is more permeable than the lower one. As fluid reaches the boundary of the layer, it accumulates above the boundary, thus increasing the saturation. As fluid penetrates into the less permeable layer, saturation in this layer becomes greater and increases the permeability relative to the upper layer. Thus the difference between the effective conductivities decreases. Permeability is also dependent on the wettability of the porous material. Oil is a wetting fluid when in contact with air but is non-wetting when in contact with water (Alföldi 1978). Wettability also affects saturation. If a layer of low permeability between two layers of higher permeabilities has a high water content, its permeability to oil is reduced. The oil spreads in a horizontal direction until the pressure head becomes strong enough to allow the oil to penetrate the low permeability layer (Dracos 1978). A separate oil phase will also infiltrate groundwater if the pressure head is sufficient but will tend to spread horizontally in the capillary fringe (Fried and Zilliox 1978). Wettability controls the location of water and oil in the pores and thus influences the capillary forces that affect the movement of oil and water (Donaldson and Crocker 1980). Wettability of an oil is strongly influenced by the presence of polar components which concentrate at water-oil or solid-oil interfaces. These components tend to enhance displacement of water from the small pores by oil, which affects capillary pressure relationships and movement of oil. These components are also relatively more soluble in groundwater; oil dissolved in the groundwater will travel with the groundwater and spread contamination further. Observations such as those presented here in a natural system can be useful in determining factors that may influence the hydrophysical interactions of organic waste components with consolidated subsurface materials.

EFFECT OF SHALES ON INORGANIC TRANSPORT; OTHER SHALE PROPERTIES

While essentially no work has been reported on the hydrophysical interactions of organic compounds with shales, a number of studies have been reported on inorganic-shale interactions and much work has been done on the physical properties of shales. Hanshaw (1962) has discussed the properties of shales (and clays) that cause them to act as macroscopic semipermeable membranes [i.e., a material which selectively restricts the passage of matter (i.e., in this case prevents the passage of charged species but allows relatively unrestricted flow of neutral species)]. The compacted clays can act as ion excluders for solution concentrations as high as 0.1N because of their negatively charged surfaces. Doubly charged cations or anions are retarded relative to singly charged cations or anions, respectively. However, as the salt concentration increases, the degree of ion exclusion decreases rapidly because of membrane leakage. One can hypothesize that charged organic compounds will exhibit the same kind of ion exclusion effect, whereas uncharged organics will be unaffected. Shales can deflocculate quickly in the presence of a salt concentration gradient. Pressure directly affects the porosity, density, and number of negative sites per unit volume of clays; therefore pressure also directly affects the degree of ion exclusion. Osmotic transfer of water across shales because of a salt gradient can result in swelling or contraction of thick sequences of shale with important hydrologic consequences. However, water flow through cracks and fissures in the shale may dilute this filtration effect (Long and Larson 1983). Thus, as Schubert (1980) points out, determination of the relative importance of fracture versus primary hydraulic conductivities is necessary to assess potential interactions in groundwater flow systems.

Another set of properties that is important in groundwater flow, matrix diffusion versus fracture flow, is discussed by Grisak and Pickens (1980) and Grisak et al. (1980). When solute diffusion coefficients are relatively large, as in surficial clays and tills, matrix diffusion has a strong effect on solute transport through fractures. However, diffusion coefficients in compacted clays or consolidated sediments with limited pore spaces are less well documented. The net effect of diffusion from fractures into the matrix material is solute dispersion and subsequent decrease in the flow of solute along the fracture. If no more solute enters the fracture, the concentration gradient between the fracture and adjoining matrix is reversed and solute will move from the matrix into the fracture. If the fracture size decreases (for example, due to swelling of the minerals), the amount of solute transported in the fracture decreases and matrix diffusion becomes more important. The greater the reactivity of the solute with the matrix (e.g., the greater the adsorption tendency and capacity), the greater the effect of diffusion in the matrix material. If the matrix porosity is large, more solute is lost from the fracture. The clayey till used by Grisak et al. (1980) had matrix properties that promoted matrix diffusion even though the hydraulic conductivity was low.

The porosity of recently deposited sediments is highly variable both in terms of mean pore size and sorting and skewness of the pore size distribution. As compaction increases, the mean pore size of shales decreases to a limiting value of ~3.5 nm and small pores dominate over large. The pore-size distribution of most argillaceous sediments is well-sorted either within a time span of 50 million years and/or a depth of burial of 1200 m (Borst 1982). The clay mineralogy may also change during diagenesis (Blatt et al. 1972). In one case, montmorillonite was converted to a mixed-layer illite-montmorillonite and then to an illite without interlayer montmorillonite. Thus the process of diagenesis of argillaceous sediments and formation of shales results in changes in properties that will obviously affect the interactions of these materials with organic materials. It is impossible to extrapolate from the studies of organic interactions with clays described above to organic interactions with shales and mudstones. However, these earlier studies do give an indication of some research areas that need to be explored with regard to the effect of organic compounds on the hydrophysical properties of sedimentary rocks.

RESEARCH NEEDS

Much work has been or is being done on the chemical and physical interactions of organics with clay and hydrous oxide minerals and with soils in general. However, the results of this literature search as well as conversations with other researchers in these fields indicate that very little has been done concerning interactions of organics with consolidated materials. Consolidation or lithification generally involves some combination of cementation, compaction, desiccation, and/or crystallization. These processes will obviously affect the permeability, porosity, surface area, mineralogy of surfaces exposed to migrating wastes, and organic content of the sedimentary materials. Because hydrophysical properties of consolidated materials need to be considered in waste management (for example, in deep-waste injection and accidental spills), it is important to extend organic waste transport studies to include consolidated geological materials. Specifically, studies are needed that deal with the effect of selected organics on the hydraulic properties of sedimentary rocks of low permeability, such as mudstones and shales, and, concurrently, the attenuation of organics by these sedimentary rock types during transport.

First, it is important to determine whether organic solvents and other organic compounds physically alter the hydrologic properties (e.g., porosity, permeability) of sedimentary rocks under saturated and unsaturated conditions. If these alterations do occur, it then becomes important to define the mechanisms by which they occur.

Some principal questions have arisen as areas to be pursued:

1. Will organic compounds affect the hydraulic conductivity/intrinsic permeability/porosity of the shales/mudstones in a manner similar to their effect on shale/mudstone constituents (i.e., clays, silicates, carbonates)? What are the macro effects? If there are effects, by what mechanisms is the microstructure of the shale/mudstone altered by the passage of an organic fluid? What types of organic compounds affect rock permeability—is there a

correlation with structure, polarity, dipole moment, charge, concentration?

2. Will the organic compounds migrate mainly along microfractures and affect the microfracture by causing swelling/shrinkage/dissolution/geochemical changes in the minerals lining the microfractures? How will this affect the permeability of the rock? How does the importance of this process compare to permeability effects caused by non-fracture flow; i.e., is fracture flow or primary hydraulic conductivity more important under a given set of conditions?

3. When it is claimed that organic solvents cause increased permeability of clays, is this due mainly to shrinkage and side leakage in fixed permeameter experiments? Will the confining pressure found in rocks associated with deep-well injection negate this shrinkage and result in a decreased effect?

4. What is the effect of various concentrations of miscible fluids and immiscible fluid phases on these processes? How do these types of fluids affect the wettability and permeability of the rocks? How does saturation/unsaturation of the zone in which the waste is disposed affect these processes?

5. What sort of time scale is involved? What is the rate of change of hydraulic properties? Is the process reversible or irreversible?

6. Will field studies, laboratory studies, or a combination be the best approach to the problem? How does one accommodate the scale problem in the laboratory that can lead to a hydraulic conductivity that is 2 orders of magnitude less in the laboratory than in the field (Griffin et al. 1984)? How does one deal with the heterogeneity problem?

All these questions need to be addressed before it is possible to make accurate predictions of organic transport in the subsurface environment.

ACKNOWLEDGMENTS

This report was reviewed by F. Wobber at DOE and by J.S. Fruchter, G.W. Gee, C.T. Kincaid, R. Wildung, and J. Zachara at PNL. I am grateful for their helpful comments.

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