

Gasoline-ethanol(Gasohol)혼합액의 점토층 내 이동에 대한 연구

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Enhanced Migration of Gasohol Fuels in Clay Soils and Sediments

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ABSTRACT

Clay soils typically have low hydraulic conductivities in the presence of high polarity pore fluid, such as water. Low polarity fluids, such as hydrocarbon fuels and halogenated organic solvents, typically cannot migrate into clay pores because they cannot displace the pore water. Oxygenated additives in gasoline, such as alcohols and methyl-*tert*-butyl ether, are increasingly used to control air pollution emissions. These relatively polar and highly water-soluble compounds may facilitate displacement of pore water and enhance migration of fuels and solvents through clay-rich soil strata.

In the reported research, the migration of gasoline-alcohol fuel mixtures (gasohol) through consolidated clay was examined. Prepared kaolinite clay samples were consolidated from slurry, and various combinations of gasoline, alcohol, and water were applied to the clays under 152 Pa gauge pressure. Movement of the fluids into the clay samples was monitored by measuring displaced pore fluid and by magnetic resonance imaging of the samples. The structures of selected samples were examined using environmental scanning electron microscopy.

Results of the research suggest that alcohol added to hydrocarbon fuels can enhance migration through some clays significantly. Gasoline did not migrate appreciably into water saturated clay, even after 14 days under pressure. The gasohol mixture migrated readily into the clay in only 20 minutes. Increased hydraulic conductivity of the clay in the presence of gasohol is hypothesized to be due to the collapse of the clays pore structure when ethanol is present, creating larger pores. Increasing pore

diameter decreases the capillary pressure needed for the gasohol to replace water and allows gasohol to migrate through the clay.

Key word : Geochemistry, Hazardous waste, Infiltration, Soil Mechanics, Soil Contamination

요 약 문

점토는 물과 같이 극성이 큰 유체가 존재할 때 매우 낮은 투수계수를 갖게된다. 따라서 극성이 매우 낮은 탄화수소계연료나 할로겐화 유기용제등은 간극수(pore water)를 밀어내지 못하기 때문에 점토공극내로 이동할 수 없다. 최근들어 대기오염 저감대책의 하나로 알콜이나 MTBE(methyl-tert-butyl ether)등과 같은 가솔린 산소첨가제의 사용량이 늘어나고 있는 추세에 있다. 이들 산소첨가제는 극성을 띠고 있으며 물에 대한 용해도가 매우 높기 때문에 간극수를 교체하여 가솔린이나 유기용제등의 점토층내 이동을 촉진시킬 가능성을 갖고 있다.

본 연구에서는 가솔린-알콜-혼합연료(gasohol)의 암밀점토층 내에서의 이동을 실험적으로 살펴보았다. 카울린슬러리를 압밀시켜 제조한 점토층에 가솔린, 알콜, 그리고 물의 혼합액을 152 Pa하에서 접촉시켰다. 점토층내로의 유체이동은 교체된 간극유체유량을 측정함으로써, 그리고 현상학적인 관찰은 핵자기 공명상(magnetic resonance image; MRI)을 측정해봄으로 추적하였다. 또한 점토시료의 구조는 environmental scanning electron microscopy (ESEM)를 이용하여 분석하였다.

연구결과를 볼 때 가솔린만 존재시 접촉 14일 이후에도 물로 포화된 점토층내로 가솔린이 이동하지 못한 반면 gasohol혼합체는 접촉후 단 20분 이내에 점토층을 완전 통과하여 탄화수소계연료에 첨가된 알콜이 점토층내로의 이동을 한층 강화하는 것으로 나타났다. Gasohol과 접촉시 이러한 점토의 투수계수 증가는 알콜로 인해 점토의 공극구조가 붕괴되어 더 큰 공극을 형성시켰기 때문인 것으로 판단되었다. 또한 공극직경(pore diameter)이 증가함으로써 gasohol이 간극수를 교체하는데 필요한 모세압력이 감소되어 gasohol이 쉽게 점토층을 이동하게 되는 것이다.

주제어 : 토양화학, 유해폐기물, 침투, 토질역학, 토양오염

1. INTRODUCTION

Clay-rich strata in the subsurface form natural and man-made barriers to the migration of liquids and dissolved solutes. Natural barriers, such as clay lenses, are important in retarding the downward migration of spilled and leaked materials. Man-made clay structures, including liners and slurry walls, are among the most widespread containment facilities in use today. The hydraulic integrity of these natural and man-made barriers is, in part, dependent on the microstructure of the clay fabric. Changes in the chemical composition of pore fluids can alter the microstructure and permeability of clay-rich strata

Table 1. Urban Areas Required to use Oxygenated Fuels During the Winter of 1992-93¹⁾.

State	Urban Area	State	Urban Area
Alaska	Anchorage Fairbanks	Nevada	Las Vegas
Arizona	Phoenix Tucson	New York	New York-Northern New Jersey Syracuse
California	Chico Fresno Los Angeles-Anaheim- Modesto Riverside Sacramento San Diego San Francisco-Oakland- San Jose	North Carolina	Greensboro-Winston Salem Cleveland-Akron-Lorain
Colorado	Stockton Colorado Springs Denver-Boulder	Ohio	Grant's Pass
Maryland	Baltimore	Oregon- Washington	Klamath Falls Medford Portland-Vancouver Seattle-Tacoma Spokane
Montana	Minneapolis-St. Paul Missoula	Pennsylvania- New Jersey	Philadelphia-Trenton- Wilmington
	Nevada	Texas	El Paso
		Utah	Provo
		District of Columbia	Washington, D.C.

through its influence on particle-particle interactions¹⁻⁶.

Recent increases in the use of oxygenates in reformulated gasoline has prompted interest in the influence of oxygenated compounds on the transport of gasoline through clay-rich strata. The Environmental Protection Agency (EPA), under provisions of the 1990 Clean Air Act amendments, requires areas that do not meet federal carbon monoxide standards to use oxygenated fuels during the winter of 1992-93 (Table 1). Oxygenates, such as methyl-*tert*-butyl ether (MTBE), other ethers, or ethanol, are added to gasoline to reduce automobile carbon monoxide emissions⁷. MTBE is the most commonly used oxygenate, with U.S. production of MTBE at more than 24 billion pounds in 1993⁸. On June 30, 1994, the EPA issued a mandate requiring at least 30 percent of reformulated gasoline to use oxygenates from renewable sources, typically ethanol, after January, 1996.

Recent research has focused on the influence of pore fluid chemistry on the structure and hydraulic conductivity of clay-rich strata^{3-6, 9-12}. Polar pore fluids with high dielectric constants, such as water, generally correspond with low permeability in clay-rich strata. Water and other polar pore fluids affect the chemical and physical interactions between clay particles such that the porous media forms a high porosity structures with pores of small diameter. Nonpolar organic solvents, which typically have low dielectric constants, can produce significantly different pore structures and generally higher hydraulic conductivities, though in some cases more complex behavior is observed⁶. Observed effects of organic solvents on clay hydraulic conductivity depend upon

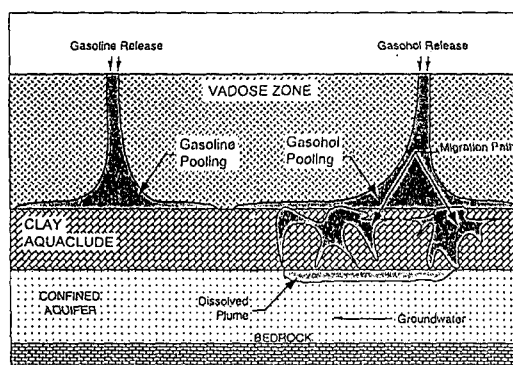


Fig. 1. Comparison of hypothesized groundwater contamination by gasoline and gasohol spills

several parameters, including the experimental procedure (e.g., permeameter used), type of clay, and the type and concentration of organic solvent.

The presence of oxygenates in nonaqueous-phase liquids (NAPL), such as gasoline, can influence NAPL transport through soils in potentially three ways. First, addition of oxygenates change the physicochemical properties of NAPLs, such as viscosity. Second, oxygenates can act as cosolvents and affect the solubility of specific compounds in the aqueous and NAPL phases¹³⁻¹⁵. Third, oxygenates can affect the properties of the geologic porous medium¹⁰. The idealized transport of gasoline and gasohol through clay-rich strata is compared in Figure 1.

There have been few investigations of the effects of mixtures of polar and nonpolar organic chemicals on the hydraulic conductivity of soils. Brown and co-authors¹⁶ reported 10^1 to 10^4 times increases in hydraulic conductivity for a compacted micaceous soil in a rigid wall permeameter using mixtures of xylene and acetone compared to single solvent system.

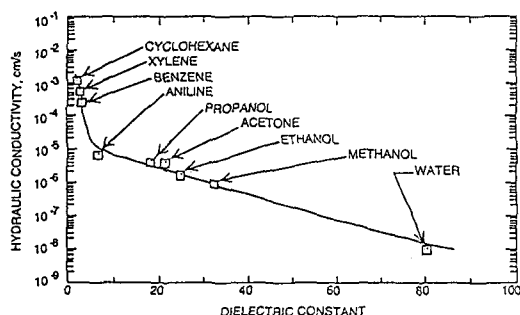


Fig. 2. Relationship of hydraulic conductivity to dielectric constant of pore fluid for clay soils¹⁰.

Fernandez and Quigley¹⁰ applied a number of organic liquids to mechanically compacted naturally occurring silty clays and measured hydraulic conductivity. The tests were run on plugs compacted from samples initially saturated with the applied permeants, and samples with the permeant applied to water-saturated plugs. Application of the permeants to the plugs prepared with permeant pore fluid resulted in the hydraulic conductivity values shown in Figure 2.

Fernandez and Quigley¹⁰ observed essentially no change in hydraulic conductivity for benzene, xylene, and cyclohexane applied to water-saturated plugs. In further sets of experiments, Fernandez and Quigley¹⁰ first displaced pore water with ethanol, and then applied the non-polar organics. The hydraulic conductivity observed with ethanol acting as cosolvent increased as much as 4 orders of magnitude over observed values when ethanol was not applied. These initial experiments indicate the potential influence of cosolvents on NAPL transport.

The influence of ethanol content on gasoline/gasohol migration through kaolinitic soils was investigated using rigid-wall permeameters. The

research included measurement of selected clay and organic liquid properties, and characterization of the migration of the organics into soil columns. Changes in gasoline/gasohol transport through the clay soil were related to changes in the permeability of the porous media. Based on porous media permeability changes as a function of applied permeant composition and direct observations of the pore structure of the clay by nuclear magnetic resonance techniques and environmental scanning electron microscopy, the particle-scale mechanisms controlling permeability changes as a function of pore fluid composition were inferred.

2. EXPERIMENTAL METHOD

A series of fixed-wall permeameter experiments were conducted to quantify the hydraulic conductivity of kaolinitic clay plugs as a function of ethanol concentrations in gasohol. The first set of experiments consisted of the measurement of the intrinsic permeability measurements of the clay with water, gasoline, and gasohol as initial pore fluids and applied fluids. In the second set of experiments, water, gasoline, and gasohol were applied to clay that was initially saturated with water and the relative rates of migration of the applied fluid into water-saturated kaolinite was determined. Pressure (152 Pa) was maintained to the applied fluids over the course of the experiment. In addition to measurement of hydraulic conductivity/permeability, the clay plugs were directly examined by magnetic resonance imaging (MRI) and environmental scanning electron microscopy (ESEM) techniques in an attempt to determine macroscale and microscale structural changes in the clay.

Table 2. Physical and Chemical Properties of Water and Organic Solvents used in experiments^a.

Solvent	Specific Gravity	Dynamic Viscosity ($\times 10^{-3}$ N · s/m ²)	Interfacial tension with water (N/m)	Dielectric Constant
Water	1.00	1.002	-	80.1
Ethanol	0.79	1.203	-	24.3 ^b
Gasoline	0.73 ^c	0.480 ^c	0.051 ^d	1.95 ^e

^a Unless otherwise noted, all values from ref.19, and expressed at 20°C

^b at 25°C

^c from ref.28

^d value for *n*-octane and water

^e value for *n*-octane

2.1 Material

The clay used for these studies was a well characterized, high purity kaolinite. Its porosity was 70%. The kaolinite clay was saturated in a 0.005 M CaSO₄ solution for 48 hours prior to preparation of slurries of the clay and the initial pore fluid. The kaolinite was subjected to tests with five pore fluid combinations. The combinations included 0.005 M solution of CaSO₄ in deionized H₂O, 10%(v/v) ethanol in H₂O, 100% ethanol, 10%(v/v) ethanol in commercial unleaded gasoline, and 0%(v/v) ethanol in commercial unleaded gasoline. Physical and chemical properties reported in the literature for the experimental fluids are summarized in Table 2.

Gasoline is a multicomponent mixture, whose composition varies with supplier and season¹⁷. The gasoline used in these experiments was purchased locally, and its physical and chemical properties may vary from those shown in Table 2. Values for interfacial tension and for dielectric constant are for *n*-octane and water, and *n*-octane respectively. Values for gasoline are unavailable, but are expected to be similar to those for *n*-octane. Gasoline is essentially

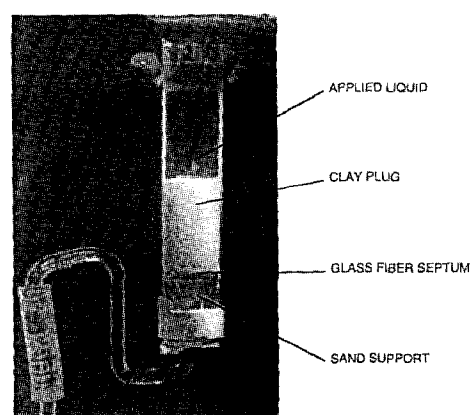


Fig. 3. Photograph of column apparatus.

immiscible in water while ethanol is completely miscible in water.

2.2 Permeameter Tests

The studies were conducted in a column apparatus, shown in Figure 3. The apparatus consisted of a 1cm(i.d.) glass tube with Teflon™ coated stoppers at each end. A sand support layer was placed on top of the bottom stopper, with a fiberglass septum on top of the sand. Air pressure was maintained at the top of the apparatus through the top stopper.

The clay plug was consolidated on the septum under 152 Pa gauge pressure from a slurry of the clay in the initial pore fluid. The pressure was maintained for 24 hours before each experiments was begun, with the slurry

fluid replenished as required to maintain saturation in the clay plug and in the sand layer. Following the consolidation period, excess slurry was removed from the apparatus, and the applied fluid was introduced. All tests were conducted with 152 Pa gauge pressure applied to the top of the test fluid. Displaced fluid was collected from the bottom of the apparatus.

Intrinsic permeabilities of the consolidated clays initially saturated with the five liquids were measured in a rigid wall permeameter test. Displacement rates of applied fluid into the initially water-saturated kaolinite plugs were measured as the rate of drainage of pore fluid from the bottom of the apparatus. The rates correspond to specific yield in a Darcy expression.

2.3 Magnetic Resonance Imaging and Electron Microscopy

Vertical section magnetic resonance images (MRI) of the water-saturated kaolinite plugs that had gasoline and gasohol applied to them were prepared by the Engineering Imaging Laboratory at Texas A&M University in a General Electric 2.0T/0.33 m CSI imager with gradient coils. The MRI images quantified ^1H present in liquid water and gasoline throughout the samples. Magnetic resonance imaging (MRI), like other nuclear magnetic resonance (NMR) spectroscopic techniques, measures the absorption and re-emission of energy in the radio-frequency range by NMR active nuclei, such as ^1H . The frequency of absorption is characteristic of the isotope (^1H), while the intensity is proportional to the abundance of the isotope. The MRI images had a horizontal resolution of 25×10^{-6} m in a 1×10^{-4} m thick imaging plane. MRI is unable to image ^1H in

Table 3. Results of Hydraulic Conductivity and Pore Fluid Displacement Rate Tests

Applied fluid	Intrinsic permeability (m^2)	Displacement rate into water saturated clay (m/s)
100 percent gasoline	1.2×10^{-12}	nil
10 percent ethanol in gasoline	6.0×10^{-13}	8.02×10^{-7}
100 percent ethanol	5.4×10^{-13}	3.80×10^{-6}
10 percent ethanol in water	9.6×10^{-14}	4.05×10^{-6}
100 percent water	3.4×10^{-14}	4.07×10^{-6}

water or gasoline present in pores smaller than this scale. The surfaces of the clay samples were directly examined with an ElectroScan E-3 environmental scanning electron microscope (ESEM) with tungsten electrode at the Electron Microscopy Center at Texas A&M University in order to ascertain changes in pore structure of the clay. Unlike other electron microscopy techniques, ESEM can examine wet samples, making the technique useful for the direct examination of relatively undisturbed geologic materials.

3. RESULTS AND DISCUSSION

Intrinsic permeabilities of the consolidated clays initially saturated with the five liquids and displacement rates of applied fluid into the kaolinite plugs initially saturated with water are presented in Table 3. As observed by Fernandez and Quigley¹³⁾, intrinsic permeability was indirectly correlated with the dielectric constant of the pore fluid saturating the clay. The migration of ethanol and gasohol into clay plugs initially saturated with water was dramatically faster than gasoline. The displacement rate of gasohol in the water-saturated clay plugs (8.02×10^{-7} m/s) was less than one order of magnitude lower than the rate observed for pure water (4.07×10^{-6} m/s).

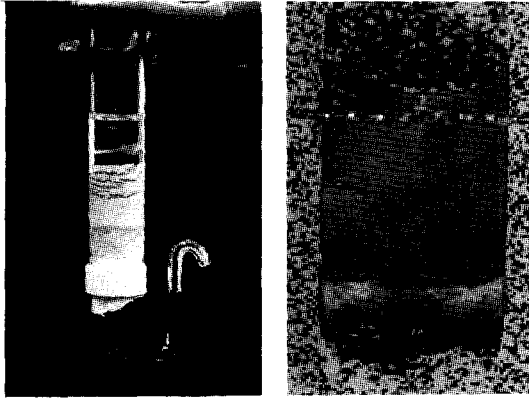


Fig. 4. Photograph and MRI image of water-saturated kaolinite and gasoline after 14 days at 152 N/m^2 applied pressure.

The MRI image obtained for the clay initially saturated with water and gasoline as the applied fluid is shown in Figure 4, along with a photograph of the corresponding experimental apparatus. The plane of the MRI image is normal to the plane of the photograph. There is virtually no difference in the magnetic intensity if the clay sample throughout its depth, indicating that there was little if any encroachment of gasoline into the water-saturated clay. The result is confirmed by the fact that no water was displaced from the bottom of the permeameter during the course of the experiment. There is also no evidence for the formation of syneresis cracks in the clay plug. The horizontal cracks in the clay visible at the top of the clay plug in the photograph correspond to the depression in the clay surface at the left of the MRI image. The depression resulted from uneven deposition of the clay during consolidation from the slurry, rather than interaction between the clay and the gasoline.

The MRI image and photograph of the clay initially saturated with water and gasohol as the

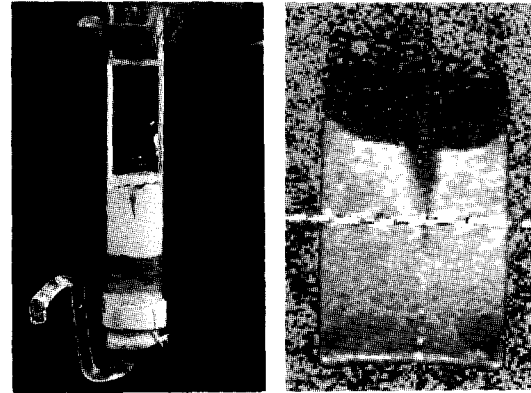


Fig. 5. Photograph and MRI image of water-saturated kaolinite and gasoline after 20 minutes at 152 N/m^2 applied pressure.

applied fluid is shown in Figure 5. The plane of the MRI image is approximately the same as the plane of the photograph. A vertical crack in the clay is visible in both images. The crack is a typical syneresis crack resulting from shrinkage of the plug in a fixed wall permeameter due to dehydration of the clay as the pore water is replaced by the gasohol.

The MRI image (Figure 5) shows much higher intensity, corresponding to lighter shades in the figure, for the top two-thirds of the clay plug than in the water-saturated region at the plug bottom. The image and the extent of the syneresis crack suggest that the gasohol had migrated approximately 7 mm into the plug in only 20 minutes. This result is inconsistent with the displacement rate reported in Table 3. At the displacement rate reported in Table 3, adjusted for porosity, the front should have migrated approximately 1 mm in 20 minutes. The syneresis crack resulted from a reduction in clay porosity as the plug shrank. The increased intensity in the top portion of the clay indicates

that many of the pores were larger in the gasohol-saturated region than in the water-saturated region of the clay, even though the overall porosity of the clay decreased. One explanation, consistent with the higher hydraulic conductivity of the clay in the presence of the gasohol, is that although the porosity of the clay decreased, the diameter of many pores in the gasohol-saturated region increased as the clay flocculated due to the presence of the gasohol.

ESEM images of the clay samples initially

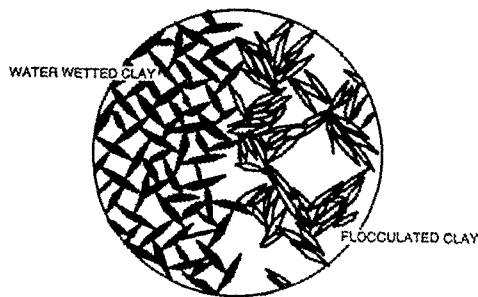


Fig. 6. Idealization of unflocculated and flocculated structures of kaolinite clays.

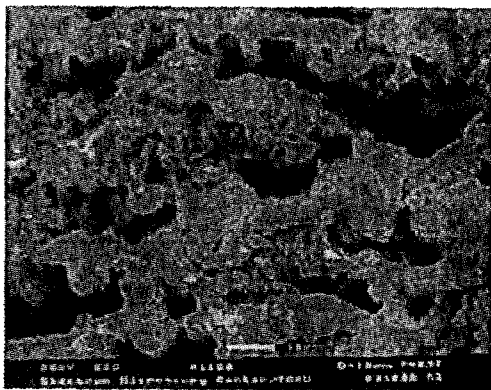


Fig. 7. Environmental scanning electron micrograph of clay surface wetted with water.

saturated with water and subjected to water and gasohol as the applied fluids are shown in Figure 6 and 7, respectively. There appeared to be more order and structure in the clay with water-saturated pores than the clay with gasohol-saturated pores. Given the poor quality and low resolution of the ESEM images, however, they should not be regarded as conclusive evidence of pore structure changes.

Nonaqueous phase liquids in the subsurface are acted upon by hydrostatic, capillary, and hydrodynamic pressures¹⁸. Downward transport is governed by hydrostatic pressure r pressure due to gravity while capillary pressure restricts movement of the nonwetting phase, which is almost always the NAPL, from larger to smaller pore spaces⁴⁻⁶. In this experiment, the gasoline and aqueous phases were affected only by hydrostatic and capillary pressures. Capillary pressure restricted the movement of the gasoline into the clay layer and counteracted the pressure applied on the gasoline in the small columns.

Capillary pressure is a function of the pore size of the porous media as well as the properties of the wetting and nonwetting fluids. Capillary

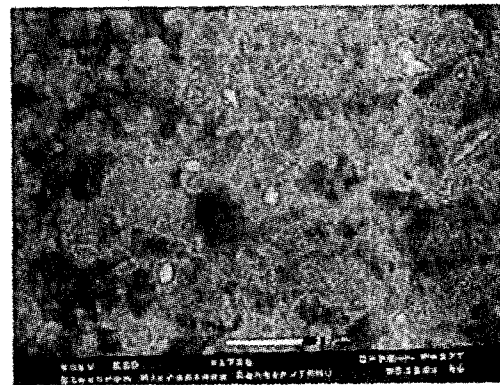


Fig. 8. Environmental scanning electron micrograph of clay surface wetted with gasohol.

pressure, when the immiscible fluid forms a subsection of a sphere, is given by

$$P_c = \frac{2 \sigma \cos \phi}{r} \dots\dots\dots (1)$$

where P_c is the capillary pressure (N/m² or Pa), σ is the interfacial tension between the NAPL and water (N/m), ϕ is the contact angle, and r is the pore radius (m). No observable movement of the gasoline into the saturated clay indicated that the applied pressure was smaller than the capillary pressure in the column, while observable movement of gasohol into the saturated caly showed that the presence of ethanol decreased the capillary pressure of the system.

The observed decrease in capillary pressure of the gasohol-water system is potentially due to the effect of ethanol on the chemical properties of gasoline and water. The interfacial tension of ethanol-water is 0 N/m because ethanol is completely miscible in the aqueous phase¹⁸⁾. The interfacial tension between *n*-octane and water is 0.508 N/m¹⁹⁾. Assuming gasoline has a similar interfacial tension, the addition of ethanol to gasoline decreases the interfacial tension with water, thereby reducing the capillary pressure, and making the entry of gasohol into saturated pores easier than the entry of gasoline alone. A decrease of interfacial tension of gasoline due to the addition of ethanol from 0.05 Nm⁻¹ to 0.02 Nm⁻¹ decreases the capillary pressure less than one order of magnitude.

The presence of ethanol in gasoline also affects the contact angle, though this effect is more difficult to predict due to the heterogeneous nature of the surfaces present. Typical contact angles for NAPL-water on clays are between 15° and 50° with effects due to the

presence of cosolvents on the order of 10-20 percent¹⁸⁾. Given these changes in the interfacial tension and contact angles when ethanol is added to gasoline, the effect on capillary pressure can also be calculated using Eqn. 1. Capillary pressure varies approximately one order of magnitude over reasonable ranges of interfacial tension and contact angle, given an assumed pore size of 5 × 10⁻⁷m. This pore size approximates the average pore size of the clay plug in the columns.

Capillary pressure is also a function of the pore size. This research suggests that gasoline can affect the microstructure of the clay particles and the pore size distribution and that the presence of ethanol in the gasoline can significantly facilitate those effects. An increase in pore size can have a large effect on capillary pressure, according to Eqn. 1. A 0.5 mm crack, as observed in these experiments, in a clay plug can decrease capillary pressure by 3 orders of magnitude. The effect of changes in pore size on capillary pressure are much more significant than variations in contact angle or interfacial tension. The formation of large pores, indicated by the MRI due to dewatering of the pore fluid and a collapse of the clay structure, best explains the rapid transport of gasohol in the columns.

Clay particles orient themselves, in part, in response to the effect of three interparticle forces : the electrostatic force, the van der Waals dispersion force, and the solvation force²⁰⁾. The electrostatic force repels two similarly charged particles and is a result of net charge on the phyllosilicate minerals and the formation of a net volumetric charge density produced in the aqueous solution near the surface of the particles. The van der Waals dispersion force is

actually an attractive force that can bind two particles. The force results from the formation of instantaneous dipoles due to nonuniform charge distribution of the atoms within the phyllosilicate structures. Dipoles of two particles act to strongly attract these particles at small interparticle distances. The solvation force is a repulsive force that acts at extremely small interparticle distances, and results from the energy required to strip water molecules from the hydration spheres of exchangeable ions bound to the surfaces of the phyllosilicate minerals as two particles are brought closer and closer together. The electrostatic and van der Waals dispersion forces depend on the nature of the solvent through the macroscopic dielectric constant. The solvation force, on the other hand, depends on the molecular properties of the exchangeable ion and its hydration sphere.

The surface charge of phyllosilicate minerals is a result of isomorphic substitution in the mineral and of broken chemical bonds at the edges of the mineral crystals²⁰. The surface charge of phyllosilicate minerals is typically negative, though some minerals, such as kaolinite, can be positively charged at low pH. Surface charge and the net volumetric charge density can be modeled using Guoy-Chapman theory and the diffuse double layer (DDL) model²⁰. The distance that the DDL extends from the particle surface is directly dependent on the dielectric constant of the solvent in the pore spaces. Water has a very high dielectric constant (80.1 @ 20°C) which results in a large DDL and a large separation between similarly charged particles²⁰.

The pore structure of kaolinite clay is dependent on the balance of these forces between the kaolinite particles. In the presence

of water, kaolinite particles tend to adopt a relatively rigid edge to face structure characterized by high porosity (about 60 percent) and low hydraulic conductivity, and are dominated by pores of small diameter²¹. The plates are held at near right angles to one another, preventing closer approach and flocculation. An idealized kaolinite clay structure is illustrated on the left side of Figure 6. The introduction of gasohol into the column potentially affects that balance in two ways. First, ethanol diffuses from the gasohol into the water within the clay pores, suppressing the DDL of the kaolinite particles due to the lower dielectric constant of the ethanol-water mixture. Some particles would flocculate due to increasing van der Waals dispersion force. Flocculation, illustrated on the right side of Figure 6, results in shrinkage, syneresis cracking, and increases in hydraulic conductivity²², allowing easier entry of the gasohol into the large pore spaces, further dewatering those pores. At the same time, the water within the smaller pores would have become sequestered, effectively sealing those smaller pores to the movement of the gasohol.

The sequestering of water in the smaller pores helps to explain the apparently greater migration rate of the gasohol in the MRI images than is calculated based on the water displaced from the column. The MRI images suggest that the front is moving at approximately seven times the rate at which the pore water is being released as indicated in Table 3. Apparently, those pores that still contain water are not available for NAPL flow, and, therefore, the effective porosity of the clay is reduced. This residual water does not appear in the MRI images because those pores are

much smaller than the resolving power of the technique. Similar influences on the particle-particle interactions of kaolinite have been observed for kaolinite suspension in 8-9% water-organic solutions of dimethylsulfoxide, formamide, and N-methyl formamide²¹.

The proposed mechanism for the effect of gasohol on the particle-particle interactions within clay-rich strata suggests potential remediation efforts to minimize these effects. Both the phyllosilicate mineralogy^{23,24} and the nature of adsorbed species on the mineral surface²⁵⁻²⁷ influence the sorption of water to the mineral surfaces and the resistance of the hydrophilic organic polymers or bivalent or trivalent metal cations to clay particles should decrease the effect of organic solvents on particle-particle interactions and clay flocculation. These techniques may offer inexpensive methods for mediating the influence of oxygenates on the transport of NAPLs through clay-rich strata.

4. CONCLUSIONS

Clay initially saturated with gasoline exhibited a hydraulic conductivity approximately 40 times greater than clay initially saturated with water. Only about half of the increase can be ascribed to the lower viscosity of the gasoline. The low polarity gasoline appeared to flocculate the clay, consistent with results from other researcher reported in the literature. The gasoline did not displace pore water from the consolidated kaolinite plug initially saturated with water, even after two weeks of contact at relatively high pressure. Hydraulic conductivity measurements and magnetic resonance images revealed essentially no movement of gasoline

into the water-saturated clay. The environmental scanning electron micrographs revealed apparent effects only at the surface of the clay plug. Addition of ten % ethanol to the gasoline dramatically increased the migration of the gasoline into the water-wetted clay plug. In only 20 minutes, the gasohol had migrated 7 mm into the clay plug, approximately one order of magnitude slower than water migrated into the clay. The final hydraulic conductivity of the clay to the gasohol mixture was about 20 times that of the clay to water, and about the same order of magnitude as the clay to gasoline.

The MRI images and the conventional hydraulic conductivity tests tended to confirm one another. MRI in particular appears to have substantial promise as a technique for monitoring migration and structural changes in clays that result from organic liquid saturation of the porous media. The resolution obtainable with the environmental scanning electron microscope was not high enough to support substantial conclusions.

Further experimentation on the migration of gasohol in subsurface materials is needed given the potential increase of the use of gasohol in the United States. These experiments should focus on the migration of gasohol into different types of clay minerals as a function of gasohol composition. In addition, the influence of surfactants and inorganic pretreatments of the clays should also be examined to delineate potential remediation techniques.

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