

Alcohol's effect on the hydraulic conductivity of consolidated clay

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Abstract Centrifuge tests were carried out to determine the effect of different alcohols and one glycol on a thin consolidated disc of clay. The evolution of changes in the clay hydraulic conductivity with time was investigated and other structural changes due to chemical attack were monitored. The findings presented here demonstrate that the hydraulic conductivity of the clay appear to be generally related to the polarity of the chemicals and the dielectric constant, with the exception of butanol. In the case of butanol at low flow rate and low stress level, the action of the chemical caused the clay to crack, with a consequent large increase in flow. This effect on the clay hydraulic conductivity could be used for improving pollution remediation especially when alcohols are associated with gasoline.

Keywords Alcohols · Consolidated clay · Permeability · Gasoline remediation

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Introduction

A major environmental issue nowadays is the safe disposal of chemical waste. In simple clay-lined landfills there might be a potential risk of damage to the liner by chemical attack. The recent European Landfill Directive (2002) has a requirement to separate waste destined for landfill to be separated into hazardous and non-hazardous waste, and one of the consequences of this will help to prevent waste water soluble solvents from attacking single consolidated clay landfill liners in waste disposal facilities. Landfills for hazardous waste will be of double liner construction with a leachate collection system in-between. It is thus of interest to investigate the interaction of these chemicals with a clay layer.

These preliminary tests on clay form part of a wider study on contaminant transport at high pressure through a clay barrier detected using photometric fibre-optic sensors developed at Cambridge University by Lynch and Treadaway (Lynch et al. 2001), which were part of the European Union-funded NECER project (Network of European Centrifuges for Environmental Geotechnics Research). Four remote sensing technologies (photometric sensors, miniature Geiger tubes, resistivity arrays and an optical imaging technique) were applied to the study of contaminant transport phenomena in saturated and unsaturated soils and modelled in the geotechnical centrifuge.

In the tests to be described here, the very high g levels which are attainable in a small centrifuge have been used to accelerate transport through a simulated clay barrier.

It is an important to know if the integrity of clay liners may be affected by possible landfill chemical leachates.

For instance Quigley and Fernandez (1989) found that liquid hydrocarbons like ethanol or dioxane could damage them, in conducting hydraulic conductivity tests in a permeameter with compacted clay.

At more than 70% concentration the contaminants increased the hydraulic conductivity dramatically suggesting the influence of the dielectric constant of the chemical on the contraction of the double layer of the clay. The smaller the dielectric constant the larger the change in hydraulic conductivity.

Vipulanandan and Leug (1995) also used a permeameter with methanol as permeant in order to increase the hydraulic conductivity of the clay. They found an increase of 1,000-fold order. Like Quigley (1998), the authors suggest that the reduction of thickness of the double layer around the clay particles lead to a flocculation phenomenon causing shrinkage cracks and therefore an increase in hydraulic conductivity.

Budhu (1991) used acetone and methanol and a consolidometer. The hydraulic conductivity was measured at different stress level of the consolidated mixture clay/water/acetone or methanol and shown an increase with decreasing dielectric constant. They also found that this trend occurred when the concentration of the pollutant was more than 70% and Montmorillonite and Illite were more exposed to an increase in hydraulic conductivity than Kaolinite. Cowland and Leung (1991) used a different approach as they build their own Bentonite landfill liner to measure the hydraulic conductivity with water and leachate permeants. They found there were no significant differences between them for a concentration lower than 70%, limit from which the other authors found the clay starting to be affected by the chemicals.

More recently Al-Tabbaa and Walsh (1994) furthered these conclusions in studying the effect on clay of water soluble poly(ethyleneglycol) for different concentrations classing them into dilute, moderate and concentrated. They used Rowe cells and applied a 250 kPa vertical stress. They found at dilute concentration the dielectric constant is not high enough to affect the clay double layer and as the viscosity is increased the hydraulic conductivity is slightly reduced. At dilute concentration the effect occurs and the particles flocculate increasing the pore size and hydraulic gradients. At high concentration they return to a dispersed arrangement enhancing even more the phenomenon.

These studies showed that the hydraulic conductivity changes depend on different parameters like concentration and dielectric constant and the relationship is not obvious, therefore efforts have to be made to

simplify the effects in trying at the same time to use realistic vertical stress simulated in the centrifuge.

By considering the intrinsic hydraulic conductivity it is possible to separate the fluid effects from the solid effects on the flow. The intrinsic hydraulic conductivity, K_i , is that portion of the hydraulic conductivity (hydraulic conductivity), which is a function of the size of the pores through which the fluid moves (Fetter 1981).

$K = K_i(\rho g/\mu)$, where ρ = density of fluid, μ = fluid viscosity, g = acceleration constant due to gravity.

On the other hand, the association of alcohols with potential pollutants like Gasoline can also affect the hydraulic conductivity of Clay and may allow the use of remediation techniques such as classic or enhanced soil vapour extraction that are usually hampered by the low porosity and the low hydraulic conductivity of the polluted soil. For instance, Stallard et al. (1997) examined the migration of gasoline-alcohol (gasohol) fuel mixtures through consolidated clay. They explained the increase in hydraulic conductivity of the clay in the presence of gasohol by the collapse of the clay's pores thereby 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.

It is important to assess the extent of the phenomenon to identify what kind of alcohols may increase the Clay hydraulic conductivity and observe if any cracking mechanisms related to the duration of the experiments could occur.

Materials and methods

Material

The clay used was Speswhite Kaolinite because it is commercially available and because it has a low cation exchange capacity (CEC), five times lower than Smectite. Table 1 gives the properties of kaolinite.

In addition, the chemical composition of the Kaolinite is indicated in Table 2.

Experimental procedure

The apparatus used for this test was a 185 mm radius commercial centrifuge model (Mercury), fitted with four swinging stainless steel buckets. The centrifuge tube holders were removed from two opposite buckets and replaced with the double-skinned containers, shown in Fig. 1. The clay was mixed for 3 h to create a clay slurry that could be consolidated in the centrifuge

Table 1 Clay properties

Clay	Kaolinite
Dominant clay content	Kaolinite
Specific gravity of solids	2.64
Optimum water content (g/g)	32%
Maximum dry density (kN/m ³)	13.03
Liquid limit (g/g)	54%
Plasticity index (g/g)	23%
Linear Dry Shrinkage	5.8%
Particle size distribution	Silt and clay (<0.075 mm) 100% sand (0.075–4.75 mm) 0%
Cation exchange capacity (CEC) (meq/100 g)	5
Surface Area (m ² /g)	10–9
Oil Absorption (Gardner–Coleman)	60.0
pH Value (10% solids)	6.0

Table 2 Chemical composition of Kaolinite

Kaolinite composition	Wt (%)
Silicon dioxide SiO ₂	56.91
Iron oxide FeO	0.93
Aluminum oxide Al ₂ O ₃	39.68
Titanium dioxide TiO ₂	0.54
Calcium oxide CaO	0.16
Magnesium oxide MgO	0.16
Sodium oxide Na ₂ O	0.60
Potassium oxide K ₂ O	0.60

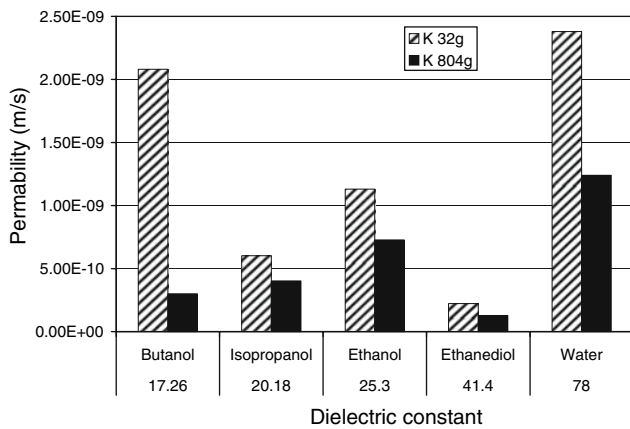


Fig. 1 Double shell sample container

model container. Water was added progressively to the Speswhite clay powder in the mixer to reach 100% moisture content so the clay would not sediment but will just consolidate. A 5 kg load was left overnight on top the clay sample to apply a preliminary stress. The load was then applied incrementally over 1 week by a pneumatic ram, up to 100 kPa.

A 5 mm thick, 40 mm diameter disc cut from a block of 100 kPa consolidated clay, Speswhite Kaolinite, was inserted inside the 51 mm diameter 150 mm high double pot sealed container.

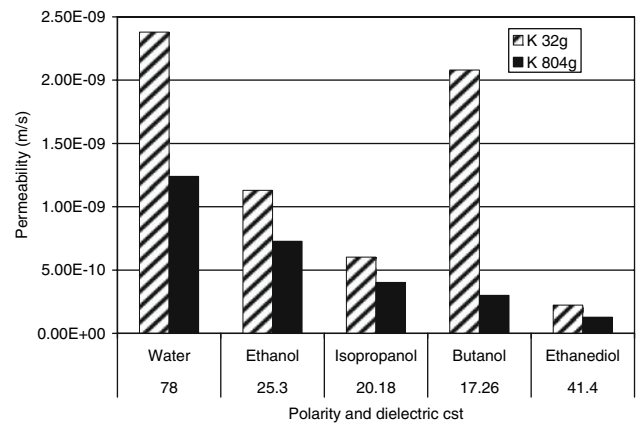


Fig. 2 Centrifuge set up

A small amount of slurry clay was used to fill in the gap between the disc and the wall. The sample was tested on the Mercury centrifuge shown in Fig. 2 for 1 min at 32 g to check the sealing. The centrifuge was stopped, the chemical poured on the top of the clay to a depth of 20 mm and the centrifuge restarted to 32 or 804 g as required. The seepage resulting followed the constant head experimental rules. The outer pot was weighed as the run time increased to determine the amount of liquid passing through the clay. From this, the measurement variation over time of the clay hydraulic conductivity was evaluated. A similar disc of clay taken from the same consolidated sample was used for initial moisture content determination.

Results

The aim of the present investigation was two-fold, to determine the mass of liquid passing through the clay versus time and to evaluate changes in the hydraulic conductivity of the clay for each chemical over time.

Stallard et al. (1997) examined the migration of gasoline-alcohol fuel mixtures through consolidated clay.

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

They assumed increased hydraulic conductivity of the clay in the presence of gasohol may be due to the collapse of the clay's pores thereby 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.

Alcohol plays a determinant role in changing the hydraulic conductivity of clay. That is why we decided to choose water-soluble solvents, with increasing molecular weight and decreasing polarity.

Six different fluids were used: water, ethanol, isopropanol, 2-butanol, ethanediol and in addition, the non-ionic surfactant Brij30 (Tetraethylene glycol monodecyl ether). The latter was chosen because of its higher viscosity in comparison to the others.

Figures 3 and 4 shows the cumulative weight of the chemical passing through the clay. The weight passing in a given time is related to the hydraulic conductivity of the clay to that fluid.

The tests at 804 g clearly showed that the clay has a high hydraulic conductivity for highly polar fluids (water and ethanol) relative to the other fluids with longer carbon chains.

The ability to crack the clay was specifically evident with butanol, which cracked the clay as soon as it was poured on the top of the sample after the slurry pre-consolidation in the test at 32 g. This cracking resulted automatically in a weight increase. The same rank order of relative hydraulic conductivity is observed for the other chemicals for the experiments at 32 g in comparison to the 804 g test.

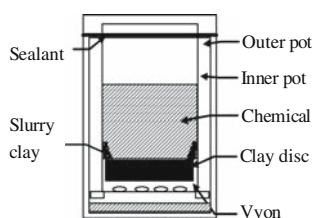


Fig. 3 Fluid weight passing through clay at 804 g

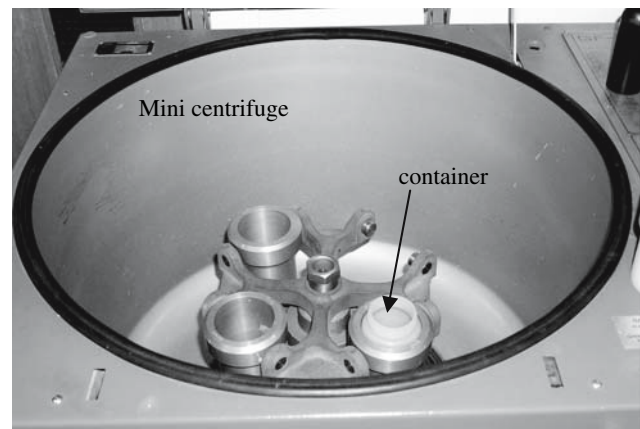


Fig. 4 Fluid weight passing through at 32 g

The same results expressed as intrinsic hydraulic conductivity in Fig. 5 shows that the amount of alcohol passing through the clay is approximately of the same order for all the alcohols investigated at 32 and 804 g except for the butanol at 32 g.

Discussion

A factor to consider is the effect of the permeant on the electrical clay adsorbed double layer. For example water H_2O bonds to the alumina silicate through three methods, electrostatic bonding, surface tension and inter particle friction.

The electrostatic bonding mechanism can be defined as dipolar forces initiated by the preferential absorption of positive and negative ions within the hydrous solution. The key component is that this solution has an ionic component that has enough strength to retain the hydrous element.

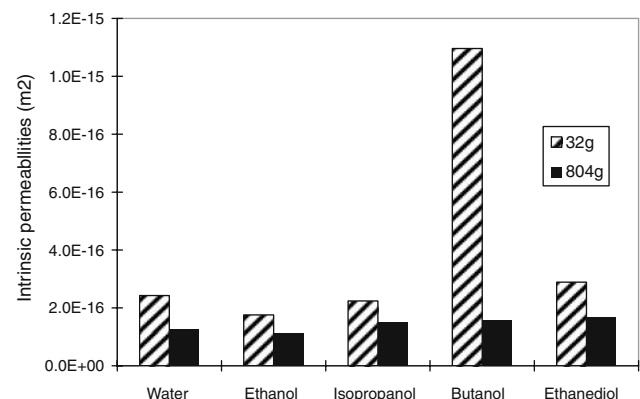


Fig. 5 Intrinsic permeabilities of water-miscible solvents through kaolinite at high and low stress

Alcohol can play a determinant role in changing the clay hydraulic conductivity by the effect it has on the collapse of clay diffuse double layer causing shrinkage. The diffuse double layer occurs at the interface between the clay surface and the soil solution. It is made up of the permanent negative charge of the clay and the cations in the soil solution that balance the negative charge. The cations are influenced by the electrical force attracting the positive ion to the negative surface, and the diffusive or thermal forces which tend to move the cations away from the surface. The balance of these two forces gives rise to a distribution of cations in water or alcohol adjacent to the clay surface. The stability of the clay fabric is affected by the ionic strength of the pore fluid. The clay used in our experiments, Kaolinite, has a very low base exchange, its hydrous quality is very low too with non-gel forming. Here Butanol is in contact with the negatively charge surfaces of the Kaolinite. One surface is made of $6OH^-$ ions and the other is made of $6O^-$.

In order to verify the various theories explaining the hydraulic conductivity changes in clay, the viscosity and the dielectric constant have been indicated for each solvent in Table 3.

The dielectric constant of the fluid influences both the surface potential and the diffuse layer thickness (Mitchell and Soga 2005). The double layer thickness varies with the square root of the dielectric constant, for example in ethyl alcohol the double layer is reduced by a factor of $(24.3/80)^{0.5}$ or 0.55 compared to that in water (Mitchell and Soga 2005).

For 1-butanol the ratio is $(17.8/80)^{0.5}$, which is 0.47, suggesting even more shrinkage of the double layer.

Budhu (1991) carried out some measurements on hydraulic conductivity using a consolidometer. He found that the dielectric constant had a direct correlation with the change in clay hydraulic conductivity. In our case the results show for the alcohols used that when the dielectric constant increases, the hydraulic conductivity follows the same trend, as in Fig. 6. However, it is not verified for Ethanediol, also known as diethylene glycol. Kinsky et al. (1971) found that the

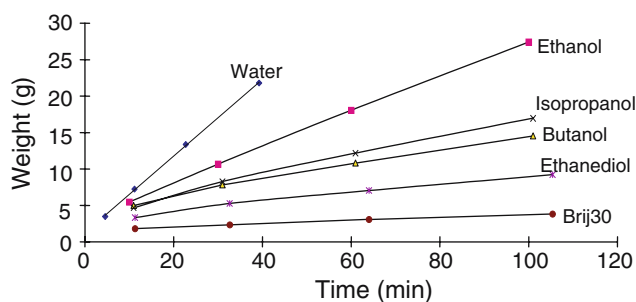


Fig. 6 Permeabilities of water-miscible solvents versus increasing dielectric constant

hydraulic conductivity changes were directly connected to the difference in dielectric constant, so an increase in hydraulic conductivity would be caused by an increase in dielectric constant.

Mesri and Olson (1971) noticed that the polarity difference between water and organic fluids, could affect the hydraulic conductivity. This is confirmed in our experiments, as the polarity decreases, the hydraulic conductivity decreases, with the exception of butanol which shows a particularly aggressive effect on clay causing it even to crack at 32 g, as shown in Fig. 7.

Gilligan and Clemence (1984) focused on the clay fabric changes due to the interaction with the chemicals creating some agglomerations of clay minerals due to a polarising effect, creating a granular matrix. Van

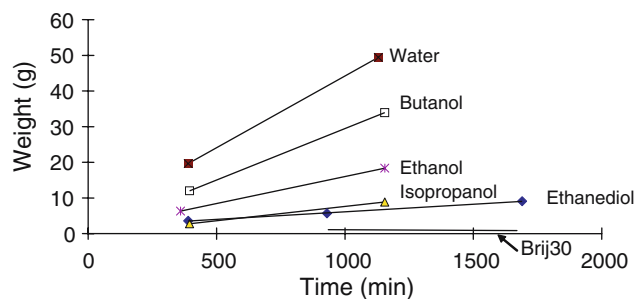


Fig. 7 Permeabilities of water-miscible solvents versus increasing polarity

Table 3 Physical properties of chemicals used

Permeant	Molecular weight (g)	Viscosity at 20°C (cP)	Dielectric constant	Density (g/cm ³)	Boiling point (°C)	Vapour pressure (kPa) at 25°C	Water solubility
Water (H ₂ O)	18.0152	1	78	0.99	100	3.17	–
Ethanol (C ₂ H ₆ O)	46.0688	1.2	25.3	0.789	78.3	7.86	≥10 g/100 ml at 23°C
Isopropanol (C ₃ H ₈ O)	60.0956	2.86	20.18	0.785	82.4	5.86	Miscible
1-Butanol (C ₄ H ₁₀ O)	74.1224	4.21	17.8	0.81	117.6	0.82	6.32 g/100 ml at 25°C
Ethanediol (C ₂ H ₆ O ₂)	62.0682	14.19	41.4	1.1155	195	0.0093	≥10 g/100 ml at 17.5°C

Olphen (1963) concluded a different view that the hydraulic conductivity effects were due to direct changes in the clay matrix, such as flocculation. Viswanadham and Mahesh (2002) have investigated non-uniform settlements, which is one of the failures associated with clay liners. They experienced severe cracking in the form of deep and wide cracks at the maximum curvature zone but the crack failure pattern is suppressed by shearing with an increase in overburden pressure. Based on model test results, the clay liner with an adequate overburden is found to be free from cracking failure even when subjected to sharp curvatures.

This was also the case observed in our experiments as the cracking due to butanol on the thin consolidated disc of clay seemed to “heal” with a higher self weight centrifugal acceleration at 804 *g* contrary to what happened at 32 *g*.

Conclusions

The way to consolidate the slurry clay, which fills the gap between the compacted clay disc and the sample container wall, is essential to prevent any cracks. It has to be done at no more than 32 *g* acceleration in order to achieve the best repartition and insulation.

At high accelerations cracks seem to be reduced by the increasing stress while at 32 *g* the lower effective stress seems to allow greater chemical attack, especially for butanol and so more chemical passes through. The viscosity of the chemical needs also to be taken into account at this level as ethanediol and Brij30, which have the highest viscosities (4.21 and 14.19) hardly pass through the clay. The more polar the fluid the more permeable is the clay.

This first series of experiments have given the opportunity to identify one alcohol to be tested on a larger scale and also to be associated for a gasoline sample to see if the collapse of the clay structure and a further increase of the clay hydraulic conductivity could be observed in comparison to the other alcohols studied.

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