

An investigation into the use of smectitic clay soil for the containment and treatment of petrochemical waste

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Abstract

The manufacture, transport, use and disposal of organic chemicals may result in the release of significant quantities of organic substances into soil, from which they are subject to possible transport into underlying groundwater. Many of these organic chemicals are potentially toxic (Wilson *et al.*, 1981). Information is required concerning the chemical and physical behaviour of organic chemicals in the soil environment in order to implement measures that will protect groundwater but also permit reasonable usage of soil for waste containment.

This study deals with the interactions of a smectitic clay soil of the Rensburg form and two petrochemical wastes, which were sampled from storage dams, adjacent to a petrochemical plant at Secunda, South Africa. There is growing interest at the plant in utilizing soil for cost-effective waste containment and treatment. The objectives of this study were twofold: firstly, to determine the permeability of the Rensburg soil with respect to the two waste liquids (BP10 - aqueous and phenolic, and BP2 - non-aqueous); and, secondly, to investigate the sorptive capacity of the clay fraction of the soil for two common groundwater contaminants, benzene and phenol, in the context of the potential for using treated clays for decontaminating BP10 and other organic wastes.

The Rensburg soil was compared with a commercial bentonite for containing and treating petrochemical waste. Both met the minimum requirements in terms of Atterberg limits for achieving a hydraulic conductivity of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, and on this basis, both would make effective hydraulic barrier materials for containing waste. Atterberg limits cannot, however, be used to predict how the material will interact with a specific waste. Column leaching experiments were therefore conducted, but, due to a swelling-induced difficulty in pre-wetting the bentonite, only the Rensburg soil could be successfully investigated in columns.

Baseline hydraulic conductivity determinations using aqueous solutions (0.005M CaSO_4 , distilled water and 0.02M Na_2CO_3) were made on the Rensburg soil before testing with BP10 and BP2. It was interesting to note that hydraulic conductivity values for the columns leached with CaSO_4 and distilled water were of the same order of magnitude despite the greater dispersion of the clay in the distilled water-leached columns. A sharp drop in

hydraulic conductivity followed replacement of the CaSO_4 with Na_2CO_3 leaching solution, which was attributed to enhanced swelling.

The BP10 waste is predominantly aqueous, with electrical conductivity (EC) and pH values of $26.4 \text{ dS}\cdot\text{m}^{-1}$ and 9.63, respectively. Based on preliminary leaching experiments, the waste appeared to be best contained by the Rensburg soil when the latter was pre-wetted with distilled water. The dry and the CaSO_4 pre-wetted columns were almost as effective. The values obtained for hydraulic conductivity, however, exceeded the acceptable threshold for containment of hazardous waste ($10^{-7} \text{ cm}\cdot\text{s}^{-1}$) irrespective of the pretreatment. These results were obtained for a leaching period of 1-2 weeks and a longer time period might be needed for verification. Monitoring for leakage of liners containing BP10 could be achieved through pH and/or EC measurements of surrounding ground and surface water which would be quicker and cheaper than monitoring for specific organic pollutants. The hydraulic conductivity of BP2 with respect to the dry Rensburg soil is $< 1 \times 10^{-7} \text{ cm}\cdot\text{s}^{-1}$, suggesting that the degree of containment is satisfactory.

The additional swelling induced by Na_2CO_3 treatment appears to be the factor associated with the formation of visible cracks within the soil column during subsequent leaching with saline BP10. Because of the wetting problem already mentioned, the phenomenon was not tested on the bentonite but the possibility that it would respond in a similar manner when leached with BP10 should be investigated.

The removal of the non-aqueous phase and the change in colour of the leachate fractions suggest the removal of certain organic constituents from BP10. A chemical analysis of the leachate fractions revealed some attenuation of phenol and cresol by the Rensburg soil. As the sorptive capacity of soils for organic acids is known to be generally low, this sorption may be due to other constituents in BP10 providing a medium for adsorption on soil surfaces. However, this possible cooperative effect requires further investigation. In addition, biodegradation of phenol and cresol by soil microbes may be a contributing factor to the apparent removal of these constituents from BP10. The degradation would have to be fairly rapid due to the rate at which BP10 is passing through the column. This possible biodegradation could be tested by setting up two soil columns, sterilizing one of the column, and then leaching both with BP10.

The environmental impact associated with waste disposal can be reduced through treatment of waste as an alternative to, or prior to, disposal to remove the more hazardous constituents of the waste. A review of recent literature revealed growing interest in the use of treated clays for the removal of specific organic pollutants from water. The replacement of the basic cations on the clay by the hexadecyltrimethylammonium (HDTMA) cation does not appear to enhance the sorptive capacity of the Rensburg soil clay for phenol. The use of quaternary ammonium cation (QAC) treated clays, therefore, does not appear to represent an effective method for the removal of phenolics from BP10. According to the literature, clays treated with QAC may have greater potential in the removal of less soluble organic compounds, such as benzene, from aqueous solutions. Unfortunately, the experiments on benzene sorption were unsuccessful due to difficulties encountered with the method. Based on this work, various recommendations with respect to the method can be made. Firstly, the use of UV spectrophotometry as the method of analysis is not recommended, due to potential interference from dispersed clay particles which cannot be removed from the liquid phase by either centrifugation or filtration through a $0.2\mu\text{m}$ filter. Secondly, when working with compounds which are not expected to sorb significantly, the clay:water ratio should be large enough for sorption to be measurable with an acceptable degree of accuracy. Thirdly, the volatility and low solubility of benzene cast doubt on the results obtained from sorption experiments which employ centrifugation prior to analysis. Working conditions need first to be sought which will give full recovery of benzene in the absence of an adsorbing solid phase.

TABLE OF CONTENTS

Acknowledgements	i
Abstract	ii
Table of contents	v
List of abbreviations	viii
Introduction	ix
1. The interaction of smectitic clay soils with liquid wastes- a review of relevant literature	1-1
1.1 Introduction	1-1
1.2 The nature and properties of smectites	1-2
1.2.1 Structure and classification	1-2
1.2.2 Physical properties	1-4
1.2.2.1 <i>Electric double layer</i>	1-4
1.2.2.2 <i>Colloidal behaviour</i>	1-4
1.2.2.3 <i>Swelling behaviour</i>	1-7
1.2.3 Chemical properties	1-8
1.2.3.1 <i>Cation exchange and selectivity</i>	1-8
1.2.4 Molecular sorption	1-9
1.3 Hydraulic conductivity of smectitic clay soils with respect to liquid wastes	1-9
1.3.1 Darcy's Law	1-9
1.3.2 Methods of determining the hydraulic conductivity of a clay soil	1-10
1.3.3 Factors affecting the hydraulic conductivity of a clay soil	1-12
1.3.3.1 <i>Mineralogical properties of the clay</i>	1-12
1.3.3.2 <i>Chemical interactions between permeant and clay</i>	1-13
1.3.3.2.1 Type and concentration of electrolyte solution	1-13
1.3.3.2.2 pH of the liquid waste	1-14
1.3.3.2.3 Liquid organic wastes	1-15
1.3.3.3 <i>Physical factors</i>	1-18
1.4 Sorptive capacity of smectitic clay soils with respect to liquid organic wastes	1-18
1.4.1 Adsorption behaviour of organic molecules on natural clays	1-18
1.4.1.1 <i>Organic cations</i>	1-19
1.4.1.2 <i>Polar molecules</i>	1-20
1.4.1.3 <i>Nonpolar organic molecules</i>	1-21
1.4.2 Adsorption of organic molecules on soil organic matter	1-21
1.4.3 Adsorption behaviour of organic molecules on treated clays	1-22
1.5 General discussion	1-25
2. Characterization of the Rensburg clay soil and commercial bentonite	2-1
2.1 Introduction	2-1
2.2 Materials and methods	2-1
2.2.1 Materials studied	2-1
2.2.2 Methods used	2-2
2.3 Results from characterization procedures	2-3
2.3.1 General analyses	2-3

2.3.2	Atterberg limits	2-3
2.3.3	Particle size analysis	2-5
2.3.4	Specific surface area	2-6
2.3.5	Cation exchange capacity determination	2-6
2.3.6	Elemental analysis	2-7
2.4	Clay mineralogical characteristics	2-8
2.5	Conclusions	2-12
3.	Hydraulic conductivity of smectitic clay soil with respect to liquid organic waste	3-1
3.1	Introduction	3-1
3.2	Materials and methods	3-1
3.2.1	Organic waste studied	3-1
3.2.2	Column leaching apparatus	3-2
3.3	Results and discussion	3-3
3.3.1	Comparison of the Rensburg soil clay and commercial bentonite	3-4
3.3.2	Reproducibility	3-5
3.3.3	Baseline measurements with simple aqueous solutions	3-5
3.3.3.1	<i>CaSO₄</i>	3-5
3.3.3.2	<i>Distilled water</i>	3-6
3.3.3.3	<i>Na₂CO₃</i>	3-7
3.3.4	Measurements with waste organic liquids	3-9
3.3.4.1	<i>BP10 aqueous organic waste</i>	3-9
3.3.4.2	<i>BP2 oil organic waste</i>	3-14
3.3.4.3	<i>Salinity effects on Na₂CO₃ pre-treated columns</i>	3-14
3.3.5	BP10 leachate composition	3-15
3.3.5.1	<i>pH</i>	3-16
3.3.5.2	<i>Electrical conductivity</i>	3-16
3.4	DWAF requirements for waste disposal	3-16
3.5	Conclusions	3-19
4.	An investigation into the sorption of organic compounds by Rensburg soil and chemically treated clays	4-1
4.1	Introduction	4-1
4.2	Materials and methods	4-2
4.2.1	Clay preparation	4-2
4.2.2	Sorption experiments	4-2
4.3	Results and discussion	4-3
4.3.1	Phenol sorption	4-3
4.3.2	Benzene sorption	4-5
4.3.3	The use of chemically treated clays for the decontamination of BP10	4-6
4.4	BP10 leachate composition	4-6
4.5	Conclusions	4-11
5.	General discussion and conclusions	5-1
6.	References	6-1

List of appendices

Appendix A - Soil characterization procedures	A-1
Appendix B - Raw data from hydraulic conductivity trials	A-5
Appendix C - Details of organic analysis and raw data from sorption trials	A-10

List of figures

Figure 1.4: The crystal structure of smectites	1-3
Figure 1.2: Distribution of cations and anions close to clay surface	1-5
Figure 1.3: Representation of hydraulic conductivity	1-9
Figure 1.4: Tailored clay with adsorbed benzene	1-25
Figure 2.1: X-ray diffractogram (CoK α radiation) for Mg-saturated bentonite ..	2-10
Figure 2.2: X-ray diffractogram (CoK α radiation) for Mg-saturated Rensburg soil clay	2-10
Figure 2.3: X-ray diffractogram (CoK α radiation) for K-saturated bentonite ..	2-11
Figure 2.4: X-ray diffractogram (CoK α radiation) for K-saturated Rensburg ..	2-11
Figure 3.1: Schematic representation of column leaching apparatus ...	3-2
Figure 3.2: Hydraulic conductivity of five identically packed columns of Rensburg soil leached 0.005M CaSO $_4$	3-8
Figure 3.3: Hydraulic conductivity of two columns of Rensburg soil leached with distilled water	3-8
Figure 3.4: Hydraulic conductivity of five columns of Rensburg soil leached with 0.02M Na $_2$ CO $_3$ after leaching with 0.005M CaSO $_4$	3-8
Figure 3.5: Four Rensburg soil columns with BP10 as the leaching solution. ...	3-10
Figure 3.6 (a and b): Hydraulic conductivity measurements for columns leached with BP10	3-12
Figure 3.7: pH breakthrough of BP10 leachate through Rensburg soil	3-17
Figure 3.8: EC breakthrough of BP10 through Rensburg soil	3-17
Figure 4.1: BP10 leachate fractions collected from the Dry-a (top row) and the CaSO $_4$ pre-treated columns.	4-8

List of tables

Table 2.1: Results from soil characterization procedures	2-4
Table 2.2: Atterberg limits to achieve hydraulic conductivities (K) of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$ (from Benson <i>et al.</i> , 1994).	2-5
Table 3.1 Hydraulic conductivity measurements for columns leached with BP10	3-13
Table 4.1: Concentrations (mg/L) of organic constituents in BP10 liquid waste and in successive fractions of BP10 leached through the Rensburg soil	4-9
Table A.1: Results from phenol sorption experiments	A-10

List of abbreviations

BET	- Brunauer, Emmett and Teller
CEC	- cation exchange capacity ($\text{mmol}_c \cdot \text{kg}^{-1}$)
DWAF	- Department of Water Affairs and Forestry
GC	- gas chromatography
K	- hydraulic conductivity ($\text{cm} \cdot \text{s}^{-1}$)
HDTMA	- hexadecyltrimethylammonium
NOC	- nonionic organic compounds
OC	- organic carbon
PCP	- pentachlorophenol
QAC	- quaternary ammonium cation
TLC	- total load capacity
TMA	- tetramethylammonium
UPP	- Unutilized Petroleum Products
XRD	- X-ray diffractometry
XRF	- X-ray fluorescence spectrometry

Introduction

The manufacture, transport, use, and disposal of organic chemicals may result in the release of significant quantities of organic substances into soil, from which they are subject to possible transport into underlying groundwater. Many of these compounds are potentially toxic. Groundwater monitoring in the United States has revealed widespread pollution of groundwater by organic chemicals, for example, the pollution of a large body of groundwater by phenol in the vicinity of an accidental spill in Wisconsin (Wilson *et al.*, 1981). The protection of groundwater resources requires stringent control of the release of organic chemicals into the soil. Information is required concerning the physical and chemical behaviour of organic chemicals in the soil environment in order to implement control measures that will protect groundwater but also permit reasonable usage of soil for waste containment.

Soils with high clay contents are often used as natural and artificial barriers in landfills and toxic waste sites to limit the release of leachate into the environment. Chemical, biological and physical interactions between the soil barrier and the liquid permeant can result in changes in the hydraulic conductivity of the porous medium with respect to the fluid being contained. It has been well established that solutions of high electrolyte concentration will reduce the thickness of the clay electric double layer and consequently reduce the capacity of the clay particles to block soil micropores (Alther, 1987). With respect to organic permeants, studies have shown that pure organic liquids can increase the hydraulic conductivity of clay but the magnitude of the increase varies for different studies (Budhu *et al.*, 1991; Fernandez and Quigley, 1985). The nature of different organic chemicals in landfills is so variable that cooperative effects among different chemicals may render measurements on pure organic liquids of little use in predicting the permeability of mixtures (Budhu *et al.*, 1991). It is therefore important to determine the hydraulic conductivity of a specific clay soil with respect to a specific liquid waste by means of permeameter tests, prior to containment of the waste in lined sites.

This study deals with the interactions of a smectitic clay soil of the Rensburg form and two petrochemical wastes which were sampled from storage dams, adjacent to a petrochemical plant at Secunda, South Africa. There is growing interest at the plant in utilizing soil for cost-effective waste containment and treatment. The objectives of this

study were twofold: firstly, to determine the permeability of the Rensburg soil with respect to the two waste liquids (BP10 - aqueous and BP2 - non-aqueous) and secondly, to investigate the sorptive capacity of chemically treated Rensburg soil clay for two common groundwater contaminants, benzene and phenol, in the context of the potential for using treated clays for decontaminating BP10 and other organic wastes.

The hydraulic conductivity of the Rensburg soil with respect to the two samples of petrochemical waste was determined through permeameter tests. The mobility of certain organic constituents in the aqueous organic waste was also investigated through analysis of the leachate fractions. Constituents which are highly mobile are more likely to contaminate groundwater than those compounds which are attenuated by the liner.

The environmental impact associated with waste disposal can be reduced through treatment of waste as an alternative to, or prior to, disposal to remove the more environmentally hazardous constituents of the waste. A review of recent literature revealed growing interest in the use of treated clays for the removal of specific organic pollutants from water (Boyd *et al.*, 1988a; Mortland *et al.*, 1986; Lee *et al.*, 1990). This is accomplished through exchange of the base cations of clay with an organic quaternary ammonium cation. The exchange renders the clay organophilic. As a result, the organo-clay complex acts as a sorbent for specific organic compounds, removing them from an aqueous solution. In this study, the sorptive capacity of the Rensburg soil for two common organic pollutants, benzene and phenol, was investigated in an attempt to establish the suitability of the Rensburg soil for the treatment of organic waste, specifically BP10.

1. The interaction of smectitic clay soils with liquid wastes- a review of relevant literature

1.1 Introduction

Due to the low hydraulic conductivity of carefully constructed clay liners with respect to certain wastes, clay has been used extensively in the construction of landfill liners. When optimum clay conditions are met, hydraulic conductivities of less than 1×10^{-7} cm/s can be obtained. Interactions with the landfill leachate may alter the hydraulic conductivity of the clay liner, making the liner more permeable and creating a potential source of contamination of ground water. There has been much recent concern with regards to the interaction of organic wastes with clays which has resulted in various studies being conducted (Budhu *et al.*, 1991; Fernandez and Quigley, 1985). Most studies found an increase in permeabilities when the clay is leached with pure organic chemicals but the magnitude of the increase varies to a large extent.

In general, the adsorptive capacity of natural clays with respect to organic wastes is minimal with soil organic matter having a higher sorptive capacity for liquid organic wastes (Lee *et al.*, 1993). If the exchangeable metal cations on clay are replaced with quaternary ammonium cations, the sorptive capacity of clays for certain organic molecules can be greatly enhanced (Boyd *et al.*, 1988a; Mortland *et al.*, 1986; Lee *et al.*, 1990). The rendering of clays more organophilic has potential applications in the treatment of water and liquid wastes.

1.2 The nature and properties of smectites

1.2.1 Structure and classification

The minerals of the clay fraction of soils are known as secondary minerals as they are the product of chemical weathering. These minerals which consist of aluminosilicates and hydrated oxides strongly influence the chemical and physical behaviour of the soil. The aluminosilicates consist of i) silicon-oxygen tetrahedron, and ii) aluminium, magnesium or iron atoms bonded to oxygen or hydroxyl groups in an octahedron (Wild, 1993). Three of the four oxygen atoms of the silicon-oxygen tetrahedron are shared by neighbouring tetrahedra creating what is called a tetrahedral or silica sheet. Similarly, with the Al, Mg or Fe octahedron, the sharing of oxygen atoms results in an octahedral sheet. The symmetry of the tetrahedral and octahedral sheets allow the sharing of the fourth oxygen atom from the silicon tetrahedron with the octahedral sheet. With the 1:1 layer minerals such as kaolinite, the sharing of atoms occurs between one silica and one alumina sheet. The 2:1 layer minerals which include illite, vermiculite and smectite consist of one octahedral sheet sharing oxygens with two silica sheets. The 2:2 layer minerals to which chlorite belongs consist of two tetrahedral, one octahedral plus an octahedral interlayer of magnesium or aluminium hydroxide (Borchardt, 1989). These layers, stacked one above the other results in platy crystals with large planar surfaces but little edge surface (Wild, 1993).

The chemical composition of the clay minerals is not fixed as cationic substitution can occur in both the octahedral and tetrahedral sheets. This occurs primarily in the 2:1 and 2:2 clay minerals. In the tetrahedral sheet, Si^{4+} is sometimes substituted for by Al^{3+} and in the octahedral sheets, trivalent cations such as Al^{3+} and Fe^{3+} can be replaced by divalent Mg and Fe. The substitution results in a net permanent negative charge of the clay mineral structure as the substituting ions have a lower valence. Only 2:1 clay minerals have a predominantly permanent charge which is responsible for the cation exchange capacity of clay (to be discussed in greater detail in section 2.4.1). As the substituting ions are of similar size to the ions they replace the substitution is described as isomorphous. Within the 2:1 clay minerals the extent of isomorphous substitution is illite > vermiculite > smectite. This results in a higher charge density and consequently more tightly held layers for illite than for smectite (Wild, 1993).

Smectites are classified on the basis of cationic substitution. Dioctahedral smectites include montmorillonite - a magnesium rich smectite, beidellite - an aluminium rich smectite, and nontronite - an iron rich smectite (Figure 1.1). Montmorillonites develop their negative charge due to isomorphous substitution on the octahedral sheet, beidellite on the tetrahedral sheet, and nontronite on both. Soil smectites generally derive about half of their negative charge from the octahedral sheet and half from the tetrahedral sheet. They are often collectively called montmorillonites as they all contain at least a small amount of Fe and varying amounts of tetrahedral Al. The dioctahedral smectites form as a result of weathering whereas trioctahedral smectites which are rarely found in soils are inherited from the parent material. These include a Li rich hectorite, a Mg rich saponite, and a Zn rich sauconite (Borchardt, 1989).

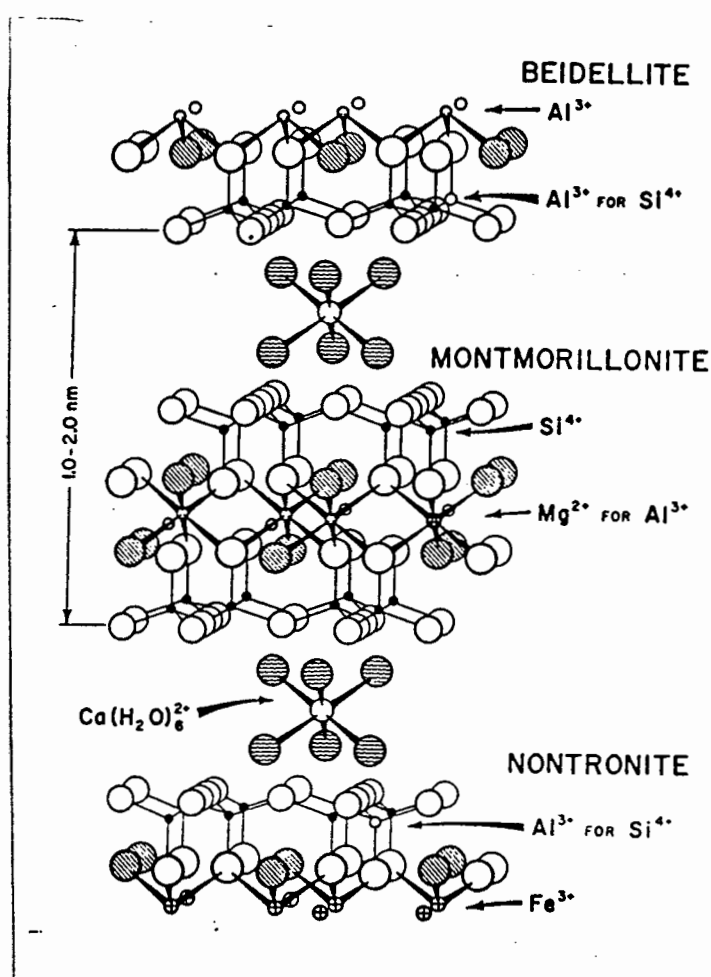


Fig. 1.1: The crystal structure of smectites (Borchardt, 1989).

1.2.2 Physical properties

1.2.2.1 Electric double layer

Clay surfaces possess a net negative charge which is compensated for by positive cations which accumulate near the clay surface. These exchangeable cations are distributed in a diffuse layer from the clay surface as a result of two opposing forces: i) the attractive force of the negative clay surface and ii) diffusion of the cations towards the bulk of the solution where the concentration is lower (Van Olphen, 1977). The result of these opposing forces is the distribution of cations such as Na^+ , Mg^{2+} and Ca^{2+} and to some extent K^+ and NH_4^+ in a diffuse electrical double layer whereby the ions in the diffuse layer and the ions in the outer solution are in dynamic equilibrium. In addition, there is a deficiency of negatively charged ions such as Cl^- and NO_3^- near the clay surface (Figure 1.2) (Wild, 1993). The distribution of both cations and anions with respect to the clay surface can be calculated as a function of the distance from the surface using the Poisson-Boltzman equation (McBride, 1989). However, in doing this, certain assumptions must be made such as assuming the charges are point charges and the layer-silicate surface is planar and structurally featureless with an evenly distributed negative charge (McBride, 1989). The Gouy-Chapman model is a theoretical treatment of the counter ion distribution. The equation, which mathematically describes the counter-ion atmosphere which is often referred to as the diffuse or Gouy layer is as follows:

$$t = \sqrt{\frac{\Sigma KT}{8\pi ne^2 v^2}}$$

where t = double layer thickness, Σ = the dielectric constant, K = Boltzman's constant, T = temperature, n = electrolyte concentration, e = electric charge, v = valence of cations in pore fluid (Alther, 1987).

Using the Gouy-Chapman model, Alther (1987) lists the factors which affect the thickness of the double layer as 1) electrolyte concentration; 2) ionic valence; 3) dielectric constant; 4) temperature; 5) size of the hydrated ion; 6) pH; and 7) anion adsorption.

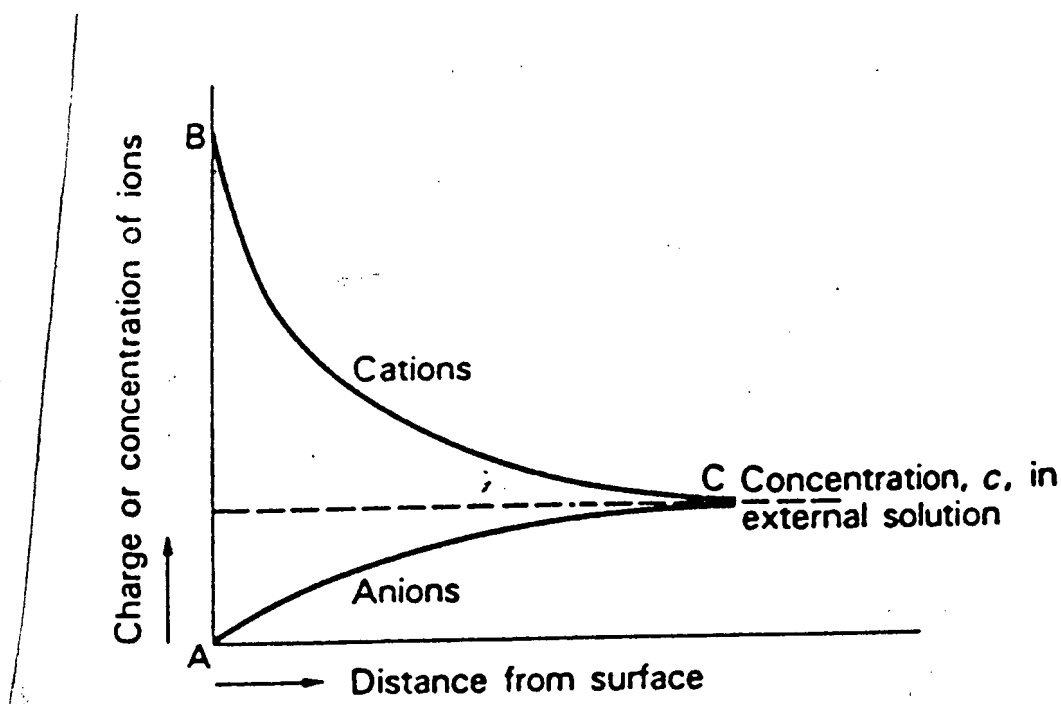


Figure 1.2: Distribution of cations and anions close to the clay surface (Wild, 1993).

As predicted by the Gouy-Chapman model, the diffuse layer becomes compressed in solutions of high electrolyte concentration primarily because diffusion away from the surface is less (Wild, 1993). With respect to ion valence, ions of higher charge are more strongly held and consequently the diffuse layer is more compact. As sodium ions have only a single valence and they are hydrated, they are less strongly held than ions such as calcium. When the double layer thickness is reduced, inter-particle association of negatively charged colloids is enhanced which can result in flocculation of the soil solution. Molecules of low dielectric constants will also decrease the double layer. On the other hand, temperature increases the double layer thickness which in turn increases the dispersibility of the soil solution (Alther, 1987).

1.2.2.2 Colloidal behaviour

Colloids are solid particles with diameters ranging between 0.01 and 10 μ m with low water solubility (Sposito, 1989). Soil clays are classified as colloids due to their high

surface charge and very small particle size (10 to 2000 nm) (McBride, 1989). A colloidal suspension in which the clay particles are dispersed is said to be stable. The Brownian motion of the clay particles cause them to collide frequently in a similar fashion to the diffusive motion of molecules in solution (Sposito, 1989).

Unstable colloidal suspensions undergo gravitational settling and coagulate. Particles no longer repel each other as they do in stable solutions but stick together when they collide. Flocculation is said to have occurred when an initially turbid solution separates out into a clear supernatant and bottom sediment (van Olphen, 1977).

The basic forces which determine soil colloidal behaviour are i) gravitational forces, ii) van der Waals forces, and iii) electrostatic forces. Gravitational forces due to the property of mass, not electric charge, bring about the coagulation of a suspension via particle settling (McBride, 1989).

The van der Waals force is an attractive force between particles whose magnitude depends on the size and shape of the particle (van Olphen, 1977). When two particles are brought close together, each induces a dipole moment. This dipole moment produces an attractive interaction whose energy is inversely proportional to the distance of separation (Sposito, 1989). Hence, as particles approach each other more closely, the van der Waals force can be strong enough to cause particles to flocculate.

In stable solutions, particles remain dispersed as the particle attractive forces are balanced by repulsive forces. As clay particles carry a net negative charge, a repulsive force arises and the tendency of particles to collide and stick together is minimized. If however an electrolyte is introduced into a solution, the repulsive force becomes less effective due to a reduction in the electric double layer thickness. Once the repulsive force is no longer able to counteract the van der Waals attractive force the clay particles flocculate.

1.2.2.3 Swelling behaviour

Smectites have a unique capacity amongst clays to shrink and swell with changes in moisture content. A doubling of the dry volume of the clay is possible through the adsorption of water molecules in the interlayers of the clay (van Olphen, 1977). Generally, up to four layers of water can be adsorbed. As the smectite layers are weakly held in comparison to illite, water molecules can enter the interlayer spaces and cause the mineral to swell. Na-montmorillonite is capable of adsorbing significantly greater proportions of water than other montmorillonites. Possible reasons for this are discussed in this section.

The swelling behaviour of smectites is considered to be due to interactions between the large surface area of the clay, its exchangeable cations and water (Borchardt, 1989; McBride, 1989). Borchardt (1989) states that there is currently no consensus on the most appropriate model of clay expansion. Sposito et al. (1983) [cited in Borchardt (1989)] suggests that the swelling behaviour of smectites is primarily osmotic in nature and that the adsorbed water on Na-montmorillonite is solvation water of the exchangeable cations. Low and Margheim (1979) [cited in Borchardt (1989)] state that the swelling of smectites may have a small osmotic component but the swelling pressure is due primarily to a reduction in the potential energy of the interlayer water as a result of direct interaction of H₂O molecules with the silicate surface.

McBride (1989) states that the initial expansion of smectites is a result of the hydration of interlayer cations and that the hydration of the clay surface as suggested by Low and Margheim (1979) plays a secondary role in smectite swelling since the hydrogen bonding of H₂O to the surface oxygen of the clay mineral is weak. As a result of the hydration of the interlayer cation, the H₂O molecule acts as a "dielectric link" to the surface, transferring charge from the cation to the mineral surface. Due to this hydration of the interlayer cations, up to four layers of water can be adsorbed. McBride (1989) emphasizes that this model does not explain the further swelling capacity of Na-montmorillonites. He attributes this swelling capacity to the weak attractive forces between layers as a result of the large hydration radius of the Na⁺ ion. In the absence of any significant "dielectric links" between the clay surfaces, expansion is facilitated as water molecules migrate into the interlayers of the clay in response to an osmotic

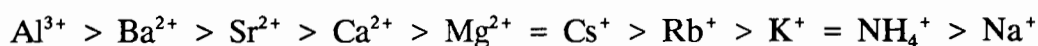
potential difference between the interlayer solution and the more dilute bulk solution. McBride (1989) adds that the additional osmotic swelling does not apply to clays with mostly divalent cations and polyvalent cations on their exchange sites. This is primarily due to the larger attractive electrostatic force which tends to hold layers together.

1.2.3 Chemical properties

1.2.3.1 Cation exchange and selectivity

As discussed earlier, smectites possess a permanent negative charge due to the structure and chemical composition of the mineral. This negative charge is balanced by adsorbed cations. Those cations held at the outer clay surface are called exchangeable cations. As smectites have a lower negative charge density, the silicate sheets are not held together as strongly as with illite which has a higher charge density. Consequently, some of the cations in the smectite interlayer spaces can diffuse into the outer solution and so they are also exchangeable cations (Wild, 1993). The total amount of these exchangeable cations is expressed as the cation exchange capacity (CEC) of the clay. The approximate CEC for illite is $0.3 \text{ mol}_c \cdot \text{kg}^{-1}$ (moles of charge per kilogram) and for smectites it is $1.0 \text{ mol}_c \cdot \text{kg}^{-1}$ (Wild, 1993). The CEC contributes to the fertility of a soil as cations such as K^+ and NH_4^+ are held against leaching effects.

If two cations are added to a smectite soil solution in equal amounts, one cation may be adsorbed to a greater extent than the other. Many factors may be involved in preferential adsorption but in general the affinity of most cations for an adsorbing surface is greater i) for cations of higher valence and ii) for cations of small radius meaning non-hydrated cations as opposed hydrated cations. The usual affinity series is (Wild, 1993):



It should be noted that smectites also possess a small pH dependent charge due to the broken oxygen bonds on the edges of the clay structure. At a pH below neutrality, the broken bonds attract H^+ which neutralizes the charge. As the pH of the solution increases however, the measured CEC of the clay increases as the H^+ concentration is

lowered and other cations take the place of H^+ in neutralizing the charge (Borchardt, 1989).

1.2.4 Molecular sorption

The net negative surface charge and the positive charge associated with the exchangeable cations can induce a dipole moment in neutral molecules which results in dipole-ion interactions between clays and neutral molecules. The large internal surface area of smectites provides much of the adsorption surfaces of soils. This is augmented by the small particle size which leads to a large external surface area. The adsorption of polar molecules such as ethylene glycol is often used to measure the internal surface area of expanding clays (Borchardt, 1989). The interaction between clays and neutral organic species will be discussed in greater detail in Section 3.

1.3 Hydraulic conductivity of smectitic clay soils with respect to liquid wastes

1.3.1 Darcy's Law

Hydraulic conductivity is defined as being the ratio of the flux or discharge rate of a fluid to the hydraulic gradient or the slope of the flux versus gradient curve (Figure 1.3) (Hillel, 1982). The hydraulic conductivity of a fluid through a soil can be determined experimentally using Darcy's Law.

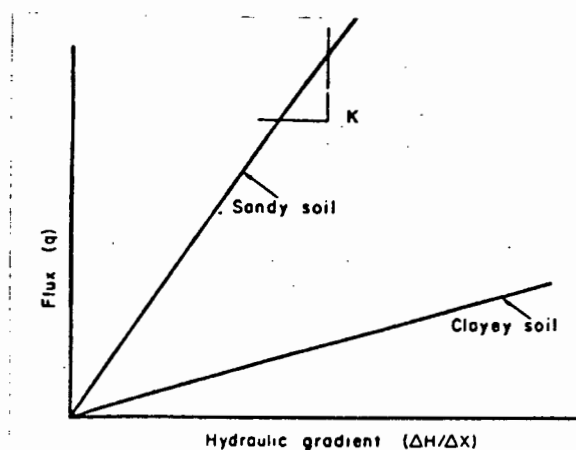


Figure 1.3: Representation of hydraulic conductivity (Hillel, 1982).

Due to the irregular nature of soil pores it would be very complicated to describe the fluid velocity as the sum of the separate flow rates through individual soil pores. Using Darcy's Law one can calculate the flow velocity as an overall average, treating the soil as a uniform medium. Assuming that the soil volume is sufficient to allow averaging of pore velocities, one can establish the relationship between the rate of flow, the dimensions of the soil body and the hydraulic conditions (Hillel, 1982).

The basis for Darcy's Law is that the discharge rate Q which is the volume V flowing through a column per unit time t is directly proportional to the cross sectional area A and the hydraulic head drop H , and inversely proportional to the length L of the column:

$$Q = \frac{V}{t} \propto \frac{A\Delta H}{L}$$

where H is the difference between the two heads at the inflow and outflow boundary (Hillel, 1982).

If the flux, denoted by q is the specific discharge rate Q/A and the head drop per unit distance in the direction of the flow (H/L) is the hydraulic gradient, then one can establish the following relationship:

$$q = \frac{Q}{A} = \frac{V}{At} \propto \frac{\Delta H}{L}$$

and the proportionality factor K which denotes hydraulic conductivity establishes Darcy's Law:

$$q = \frac{K\Delta H}{L}$$

One should note that hydraulic conductivity K is a property of both soil and fluid and may not remain constant with time. Properties of the soil which affect the value of K are pore size and how porous the medium is whilst the properties of the fluid which affect K include density and viscosity (Hillel, 1982). Chemical, physical and biological processes may change the hydraulic conductivity of a soil. Some of these processes will be discussed in greater detail later in this section.

Hillel (1982) distinguishes between hydraulic conductivity and permeability of soils. He states that whilst hydraulic conductivity is a property of both soil and fluid, permeability, in the strict sense, is a property of the soil only provided that the fluid does not interact with the soil medium.

1.3.2 Methods of determining the hydraulic conductivity of a clay soil

For laboratory determinations of hydraulic conductivity there are essentially two types of devices: rigid wall permeameters and flexible wall permeameters (Boynton and Daniel, 1985). The rigid wall permeameter is a simpler device to use but care must be taken to limit flow down the walls of the container which is not usually a problem with flexible wall permeameters. Flow through the column is driven by gravity and one can establish either a constant head or a falling head apparatus. A consolidation-cell permeameter applies an additional pressure to the column to essentially squeeze the fluids out of the pores (Boynton and Daniel, 1985).

Budhu *et al.* (1991) state that measured permeabilities for similar soils and fluids using each of the above mentioned devices often yield vastly different results but give no examples or references for this. Boynton and Daniel (1985) compared the rigid wall, the flexible wall and the consolidation-cell permeameter and found little variation in measured hydraulic conductivities from one permeameter to the next, but stress that great care must be taken in preparing the columns.

The applicability of these types of laboratory experiments has been questioned by numerous authors including Budhu *et al.* (1991), Anderson (1982), and Alther (1987). Budhu *et al.* (1991) state that the soil samples collected in the field and subsequently remolded in the laboratory bear little relation to the field situation. This may not be the case, however, if the clay liner has been constructed by laying down and compacting a layer of clay rich soil. Alther (1987) emphasizes that before a liner is installed, field and laboratory experiments should be conducted on the clay in order to determine the stability and permeability of the clay when in contact with liquid wastes.

1.3.3 Factors affecting the hydraulic conductivity of a clay soil

1.3.3.1 Mineralogical properties of the clay

To effectively contain liquid waste, a compacted clay liner should have a low hydraulic conductivity which in many cases is considered to be less than $1 \times 10^{-7} \text{ cm.s}^{-1}$ (Benson *et al.*, 1994). This guideline can be met if certain factors which affect hydraulic conductivity such as clay content and degree of compaction of the liner are optimized. The primary properties of clay which make it suitable for lining materials are 1) the small particle size, 2) the dispersibility of clay particles and 3) the swelling capacity of the smectitic clay fraction. The particle size distribution of compacted liners affects the hydraulic conductivity. Low hydraulic conductivity is achieved when a soil is well graded and the clay fraction governs the hydraulic behaviour of the soil. Tests of the hydraulic conductivity of sand-bentonite mixtures show that the hydraulic conductivity decreases significantly (10^{-4} to $10^{-8} \text{ cm.s}^{-1}$) as the percentage of bentonite increased from 0 to 8%. As the clay content of the soil increases, the clay-size particles fill the voids between the sand particles and effectively reduce the hydraulic behaviour of the soil (Benson *et al.*, 1994). Typical application rates of bentonites to soil are on the order of 6 to 15% by weight to render a hydraulic conductivity of less than $1.0 \times 10^{-7} \text{ cm.s}^{-1}$ (Alther, 1987).

The dispersibility of the clay fraction affects the permeability of clay liners as finely dispersed clay can reduce the permeability by blocking off soil macropores. Dispersed clay is transported through the soil until it eventually flocculates in pore openings, thereby reducing permeability. Frenkel *et al.* (1987) state that the plugging of pores by dispersed clay particles is the major source of reduced of montmorillonitic soils even under conditions of relatively high exchangeable sodium (30%) in the interlayer positions and high clay content (18%).

If the clay fraction is flocculated, the clay develops a porous structure which tends to increase the hydraulic conductivity of the clay liner. If however the flocculated clay is localized, it can essentially act as a trap for dispersed clay from overlying layers, through a sealing off pores and reducing the permeability of the clay (Nowicki and Fey, 1994).

Other authors (Alther, 1987; Clem, 1985; McBride, 1994) state that the swelling capacity of smectitic clays, in particular Na-montmorillonite, has a marked effect on hydraulic conductivity as swollen clay particles effectively block off macropores. The varying swelling capacity of montmorillonites based on their exchangeable cation composition affects their suitability as liner materials. Na saturated montmorillonites, due to their high swelling capacity, are most suitable for landfill liners. Mixed Na-Ca montmorillonites are less suitable but can be activated by Na_2CO_3 treatment which enhances the swelling capacity but apparently not to the same extent as natural Na-montmorillonites. Ca-saturated montmorillonites have a poor swelling capacity which generally does not improve with sodium carbonate treatment. They are generally unsuitable for use as liner materials (Clem, 1985). The montmorillonite with the highest swelling capacity have a balance of 60% Na, 20% Ca and 20% Mg as exchangeable cations (Alther, 1987).

1.3.3.2 Chemical interactions between permeant and clay

When clay liners are leached with liquid wastes, various interactions can occur between the clay and leachate that affect the permeability of the liner. Organic and inorganic contaminants such as salts, acids, bases and hydrocarbons can all affect the permeability of the clay liner. Some of these interactions are discussed in this section.

1.3.3.2.1 Type and concentration of electrolyte solution

As predicted by the Gouy-Chapman model, a solution with a high electrolyte concentration will cause a reduction in the double layer thickness which reduces the effective size of clay particles that block pore spaces thereby increasing permeability. In addition, leachate which contains predominantly divalent cations will also reduce the double layer thickness and reduce the swelling capacity of Na-montmorillonite if sodium ions are replaced by divalent cations. Rollins (1969) [cited in Alther (1987)] showed a positive correlation coefficient between permeability and high concentrations of Ca, Mg and total salts, and a negative correlation coefficient between sodium content and permeability.

Due to changes in permeability which can occur due to chemical interactions, Anderson (1982) criticizes the laboratory tests whereby clay liner permeabilities are established using pure water as the leachate. If the liner meets specifications, it may then be used to contain industrial waste which may subsequently increase the hydraulic conductivity of the clay liner. Anderson (1982) states that it is essential that clay liners be tested with not just pure water but also evaluated with:

- 1) standard leachate such as 0.01 N CaSO_4 for a comparison of liners;
- 2) any possible aqueous waste that may be produced by water percolating through the landfill;
- and 3) any liquid organic wastes that are being disposed of.

Tests carried out by Alther (1987) using leachate from typical sanitary landfill (TDS 36840 mg/L) showed no significant changes in permeability. Alther (1987) concludes that when clay liners are properly installed and prehydrated, they are capable of containing a variety of wastes and adds that a) suspended solids that block pores b) microbial growth in the pores and c) possible precipitation of salts within pores will also contribute to a reduced hydraulic conductivity of a clay liner with respect to municipal landfill leachate.

1.3.3.2.2 pH of the liquid waste

When strongly acidic or basic solutions are in contact with clay liners an increase in permeability can occur due to the dissolution of clay minerals resulting in increases in effective pore space (Anderson, 1982). Uppot and Stephenson (1989) ascribe the three-fold increase in permeability of Mg-montmorillonite leached with acetic acid to the dissolution of the calcium carbonate in the soil. Bowders and Daniel (1987) found very little change in hydraulic conductivities using various concentrations of acetic acid with the exception of pure acetic acid which resulted in an increase. They attribute the lack of change to the dissolution of some of the soil constituents at the influent end followed by precipitation of these constituents further down the column. After prolonged exposure to acidic solutions, however, the buffering capacity of the soil was diminished and increases in hydraulic conductivity occurred. From this one may conclude that prolonged

exposure to solutions of sufficiently low pH will result in increases in hydraulic conductivity.

Basic solutions are reported to cause similar problems (Anderson, 1982) but no references to experiments are given. Anderson (1982) does stress the necessity of neutralizing acidic or basic wastes before disposal in landfills to prevent changes in the permeability of liner materials.

1.3.3.2.3 Liquid organic wastes

The interaction of organic permeants with clay liners has been the subject of much recent investigation. Work in this area is essential as hazardous organic constituents are being contained by clay soil liners. Clay optimization based on inorganic aqueous wastes may not apply to organic wastes, and therefore an understanding of the interactions between clays and organic wastes is essential in maintaining a sufficiently low hydraulic conductivity.

Liquid organic wastes include those in which an organic fluid is the solvent and the solutes are organic chemicals dissolved in the organic solvent, for example motor oil. Aqueous organic wastes include those whereby water is the solvent and the solutes are primarily organic for example wood preserving wastes (Alther, 1987).

Both types of wastes are currently being contained in clay liners with apparently little consensus on how effectively they are being contained. At the present time, the literature on the hydraulic conductivity of clays permeated with organics appears very contradictory.

Anderson (1982) measured a 1000-fold increase in the permeability of smectite permeated with pure acetone and a 100-fold increase using methanol and xylene. Uppot and Stephenson (1989), also using smectite, found that aniline and xylene did not permeate through the clay at all, and measured only a threefold increase with pure acetic acid and a twofold increase with methanol. Uppot and Stephenson (1989) attribute the difference in results from Anderson (1982) to the fact that Anderson (1982) used a rigid

wall permeameter and did not allow the soil columns to become fully saturated with water prior to testing.

Bowders and Daniel (1987) and Budhu *et al.* (1991) tried a different approach as they believed that clay liners permeated with dilute organics may not be susceptible to large changes in hydraulic conductivities. They wanted to identify the concentration limit that separates solutions that will not alter the hydraulic conductivity from those that will cause large increases. Using methanol, they found no increase in hydraulic conductivity until the solution was approximately 75% methanol in volume and the increase was only approximately 25-fold. In addition, Bowders and Daniel (1987) found that heptane at its solubility limit caused no change in hydraulic conductivity but for pure heptane there was a 500-fold increase.

For clay samples that were not pre-wetted, Fernandez and Quigley (1985) found a huge range in K values from 10^{-8} cm.s⁻¹ for clays permeated with water to 10^{-4} cm.s⁻¹ for clays permeated with simple aromatics (benzene and xylene). If, however, the clay was pre-wetted with water, insoluble aromatics such as benzene and xylene yielded no increase in K values. They believe that the aromatic compounds are unable to penetrate the interlayer spaces of the clay and can only displace water from the macropores between the peds. For an immiscible liquid to displace water from pores, energy is required to overcome the interfacial tension. The energy required depends on the pore size: the smaller the pore size the larger the energy required. Thus, under the experimental conditions used, there may not have been a sufficient pressure gradient to replace the water from the pores. Had the gradients been increased, the hydraulic conductivity of the clay with respect to the organic fluid may have increased.

An interesting result from the experiments of Fernandez and Quigley (1985) was that sequential permeation of water-wet samples by alcohol then aromatics (benzene, xylene) and cyclohexane yielded a 10 000-fold increase in the original K tested with water. They attribute this to the mutual solubility of alcohol in both water and aromatic hydrocarbons resulting in a large contraction of the clay double layer and enlargement of both micro and macro pores of the clay. The author knows of no other case in the literature where sequential saturations of this nature were performed.

The data appears to suggest that organic permeants may not pose a serious threat to liner integrity unless the concentration is greater than approximately 70%. When the organic concentration is low, the permeant behaves much the same as pure water. Once the concentration is greater than approximately 70%, the trend seems to be a general increase in hydraulic conductivity, magnitudes varying from one experiment to the next (Bowders and Daniel (1987), Budhu *et al.* (1991), Fernandez and Quigley (1985)). Fernandez and Quigley (1985) note the change in the structure of the soil when organic fluids are permeated through the columns. They record agglomeration of the soil peds and extensive cracking after sequential permeation of water wet samples by alcohols and then aromatic compounds.

It is clear that more work is needed in understanding the cooperative effects of different organic chemicals as shown by Fernandez and Quigley (1985). As fluids present in many toxic landfills are complex mixtures of different organic chemicals, measurements on mixtures would be far more applicable than tests on pure organic liquids.

Various ideas have been proposed to explain the differing permeabilities of soils with organic fluids as permeants compared with water. Kinsky *et al.* (1971) [cited in Budhu *et al.* (1991)] suggest that the dielectric constant of the pore fluid is the major cause of the change in hydraulic conductivity. A decrease in the dielectric constant reduces the thickness of the double layer at the surfaces of the soil minerals which induces flocculation (van Olphen, 1977). Flocculation of the clay particles will provide more pore space for the fluid thereby increasing permeability. Budhu *et al.* (1991) support this idea. They tested differences in physical properties between water and organic liquids (dielectric constant, viscosity, dipole moment, specific gravity and surface tension) and found that only the dielectric constant provided a consistent correlation with permeability. Bowders and Daniel (1987) and Fernandez and Quigley (1985) both found no alteration in K for liquids with a dielectric constant greater than 40 and substantial increases in K for liquids with a dielectric constant less than 35.

Daniel (1993) proposes that dehydration of the clay interlayers enhances the hydraulic conductivity. Gillingham and Clemence (1984) [cited in Budhu *et al.*, 1991] suggest that the interaction of organic fluids with the soil minerals results in the formation of tactoids (spindle-shaped agglomerations of clay). This results in a more granular fabric with

enlarged pore spaces and consequently increased permeability. Mesri and Olsen (1971) [cited in Budhu *et al.*, 1991] suggest that as organic liquids tend to have smaller polarities than water, they are less strongly bonded to soil minerals and consequently the organic fluid flows through pores more easily.

1.3.3.3 Physical factors

Various physical properties of the clay need to be optimized in order to reduce the permeability of the clay liner. Benson *et al.* (1994) outline various factors which influence the behaviour of a clay liner and these include soil composition (clay percentage and composition, previously discussed in 1.3.3.1), degree of saturation and degree of compaction.

Benson *et al.* (1994) show a trend of decreasing hydraulic conductivity with increasing degrees of initial saturation. They attribute this to reductions in the size of inter-particle pores at the microscale, and at the macroscale, the elimination of inter-aggregate pores due to swelling.

With respect to compaction, Benson *et al.* (1994) found that as the degree of compaction increased, the hydraulic conductivity decreased. They attribute this to the breakdown of clay aggregates at the macroscale and a reduction in the size of inter-particle pores due to a reorientation of clay particles at the microscale.

1.4 Sorptive capacity of smectitic clay soils with respect to liquid organic wastes

1.4.1 Adsorption behaviour of organic molecules on natural clays

The mineral and organic surfaces of soils may adsorb organic molecules weakly or strongly depending on the strength of the interaction between the adsorbate (the organic molecules) and the adsorbent (the soil surface). Chemisorption occurs when the interaction is strong, forming a covalent or short-range electrostatic bond. Physical adsorption occurs when the interaction is not a strong (McBride, 1994). Adsorption may

retard the migration of pollutants through soils as a result of an increase in the chemical concentration of a species on soil particle surfaces with respect to the chemical concentration in interstitial waters.

Due to the large internal surface areas of smectites, they have a high capacity to adsorb certain types of pollutants including certain organic pollutants. Ion-exchange, ion-dipole, hydrogen bonding and van der Waals forces can all give rise to molecular adsorption of organic molecules (Cadena, 1989). The extent to which adsorption or desorption of organic molecules occurs is dependant on surface properties of the soil and chemical properties of the organic molecule. Polarity and charge of the organic molecule tend to be the most important properties of the organic adsorbate which strongly influences the extent to which it is adsorbed (McBride, 1994).

Adsorption data can be represented by adsorption isotherms which are plots of the quantity of adsorbate retained by a solid as a function of the equilibrium concentration of the adsorbate in the solution phase (McBride, 1994). One should note that a good fit of sorption data to a particular adsorption isotherm does not prove the adsorption mechanism involved as adsorption isotherm equations can not be used to distinguish adsorption from secondary precipitation (Sposito, 1989).

1.4.1.1 Organic cations

Certain organic cations, for example quaternary ammonium cations are strongly adsorbed by cation exchange on smectites. The selectivity for these organic cations is strong. This is reflected in the H-type isotherm which can be drawn from the sorption data (McBride, 1994). H-type isotherms are indicative of very strong adsorbate-adsorbent interaction, often described as chemisorption. Zhang *et al.* (1993) report that the exchange reaction for the quaternary ammonium cation hexadecyltrimethylammonium (HDTMA) proceeds to 98.9% completion when the cation was added at 100% of the CEC of the Na-saturated clay. In addition, the adsorbed quaternary ammonium cations were not easily desorbed in the presence of 0.1 M NaCl and KCl solutions. Organic matter adsorbs these cations less strongly than do silicate layers, the organic matter displaying L-type adsorption isotherms. Organic cations sorb more effectively on clay minerals with lower

charge densities as more interlayer space is provided on smectites for example than with vermiculites (McBride, 1994).

Two properties of the organic cation determine the degree of selectivity. The higher the molecular weight, the higher the selectivity. Thus the order of preference on smectite is: $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+ > (\text{CH}_3\text{CH}_2)_4\text{N}^+ > (\text{CH}_3)_4\text{N}^+$. This selectivity is entropy driven as the larger the cation, the more water molecules are displaced. The second property relates to the hydration energy of the cation. Organocations which can become hydrated ($\text{CH}_3\text{CH}_2\text{NH}_3^+$ as opposed to $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+$) adsorb with lower selectivity (McBride, 1994).

1.4.1.2 Polar molecules

The neutral forms of basic and acidic polar molecules are adsorbed sparingly by relatively weak forces onto soil surfaces. The dipole character of polar organic molecules allows adsorption to occur through hydrogen bonding or ion-dipole interactions between the organic molecule and soil surfaces (van Olphen, 1977). For example amines and alcohols can adsorb on clay minerals by coordinating directly with the positively charged exchange cations on the surfaces or by hydrogen bonding to hydration water of the cations (McBride, 1994). As with organic cations, polar organic compounds such as alcohols and glycols can penetrate the interlayers and displace the interlayer water. This can be shown using XRD whereby changes in basal spacings reflect the size of the molecule and its orientation (van Olphen, 1977). However, these mechanisms are not likely to be effective under moist conditions in soils because the excess water can easily displace physically adsorbed organic molecules from the surfaces. Water has the competitive advantage of usually being present greatly in excess of the organic, and having a greater polarity than most organics (McBride, 1994).

Acidic polar molecules such as phenols are generally considered to be highly mobile and susceptible to leaching in soils. The anion forms of these acidic molecules adsorb little, if at all on soil organic matter and layer silicate clays because of electrostatic repulsion between the molecules and the negative charge of these soil particles. The neutral form is weakly retained by physical adsorption (on organic matter in particular). In general,

acidic organic compounds are adsorbed most effectively when the soil pH is low and organic matter content is high (McBride, 1994).

1.4.1.3 Nonpolar organic molecules

The bonds that form between nonionic nonpolar molecules tend to be even weaker than the bonds of polar nonionic organic molecules between soil surfaces as hydrogen bonding and ion-dipole interactions are insignificant. Adsorption of these molecules on wet layer silicate and oxide minerals is often very low, if detectable at all. However, adsorption of nonpolar or weakly polar organics does appear to occur on soil organic matter although there is some debate as to whether it is really partitioning of the molecule into the organophilic phase in the humic material as opposed to adsorption (McBride, 1994). This is discussed in greater detail in the following section.

As clay walls and liners are often used to isolate organic wastes, it is important to know how effectively the clay binds with the organic pollutants, preventing their passage offsite. Schwarzenbach *et al.* (1993) state that a clue to the nature of nonionic compound binding to mineral surfaces is that temperature studies have shown the overall process for many nonionic organic compounds to be exothermic. Since the dissolution of many nonpolar compounds in water is an endothermic process, some of the energy yield on mineral sorption comes from the removal of these nonpolar compounds from an aqueous environment.

1.4.2 Adsorption of organic molecules on soil organic matter

The sorption process of nonpolar organic matter can be described as a partitioning mechanism where nonpolar sorbates can physically penetrate the organic matter and find themselves "dissolved" in the nonaqueous medium. Two important variables that have been used to predict sorption of nonpolar organics by soils are:

- 1) the octanol/water partition constant, K_{ow} , a property of the sorbate and;
- 2) the fraction of soil that is organic carbon, f_{oc} , a property of the sorbent.

Karickhoff *et al.* (1979) [cited in Samiullah, 1990] showed that organic carbon content adsorption coefficients (K_{oc}) could be estimated from K_{ow} and f_{oc} as:

$$K_{oc} = \frac{K_{ow}}{f_{oc}}$$

Since K_{oc} can be determined independently of other soil properties, some prediction of the movement of an organic chemical through any soil is possible if the organic carbon content is known. Evidence indicates that if organic matter is present to the extent of 1% or more, it usually dominates sorption of nonpolar organics (Lee *et al.*, 1993). At low organic carbon contents (< 1%) the sorptive capacity of clays becomes important.

Wilson *et al.* (1981) studied the transport and fate of certain organic pollutants in sandy soils. They found that the transport of many compounds through soil is retarded with respect to water due to sorption to soil solids. Using the organic carbon content of the soil and the octanol/water solubility of the organic compound, they found that they could predict the retardation factors of the pollutants to within a factor of three.

As with polar molecules, the only "bonds" between the nonpolar sorbate and the natural organic matter are through relatively weak intermolecular attractions. Therefore, only small activation energies are required to separate these compounds from their points of solid attachment.

1.4.3 Adsorption behaviour of organic molecules on treated clays

The type of exchangeable cations on clays strongly influences their sorptive capacity for nonionic organic compounds (NOC) (Boyd *et al.*, 1988a and 1988b; Lee *et al.*, 1989a; Cadena, 1989). By exchanging the neutral metal cations with large organic cations, the clay can be made increasingly organophilic. This has potential applications in the use of clays as adsorbents in the treatment of water and liquid wastes. Adsorption by activated carbon is used to remove pollutants from drinking water but the process is non-selective (Cadena, 1989). Studies have shown (Boyd *et al.*, 1988a; Mortland *et al.*, 1986; Lee *et al.*,

1989a) that clays can be tailored to remove certain hazardous organic constituents commonly found in liquid wastes.

Mortland *et al.* (1986) used quaternary ammonium cations (QAC) as exchange ions on smectite clays and studied the uptake of phenols and chlorophenols. They found that QAC's with large alkyl groups, for example hexadecyltrimethylammonium (HDTMA) created the most organophilic surface and adsorbed the phenols from water in proportion to the hydrophobicity of the phenol. Phenols substituted with chlorines were more readily adsorbed than phenol. Phenol interacts strongly with water through hydrogen bonding and is therefore not sufficiently attracted to the hydrophobic surface created by the HDTMA cations. The addition of chlorine to the phenol structure reduces its energy of interaction with water allowing a more significant hydrophobic interaction with the HDTMA treated surface. Smectite saturated with smaller organic cations like tetramethyl ammonium (TMA) showed very weak sorptive capabilities for phenol and its chlorinated congeners.

Brixie and Boyd (1994) found that organo-clays with large alkyl groups were more effective in reducing the leachability of pentachlorophenol (PCP) from soil. With a 20% (w/w) addition of organo-clays to soils, PCP concentrations in the soil solution dropped from 16.9 mg/L to below detection limits (0.2 mg/L). A large decrease in PCP concentration was also recorded with additions of as little as 2% organo-clay to contaminated soil.

Boyd *et al.* (1988a) found a linear uptake of benzene from water by HDTMA-smectite which they attribute to a partition process. Once the organic cations are fixed on the smectite clay surface, an organic phase forms that is derived from the alkyl hydrocarbon chains. This organic phase functions as a partition medium for NOC's which is very effective in removing certain organics from water. Chou *et al.* (1983) [cited in Jaynes and Boyd, 1991] state that the sorption process is similar to the dissolution of NOC in a bulk organic phase such as heptanol or octanol. Jaynes and Boyd (1991) found that the sorption isotherms of tetrachloromethane, benzene, toluene, ethylbenzene, propylbenzene, naphthalene and biphenyl on the HDTMA-clays indicated that sorption occurs by partition interactions. They note that the sorption coefficients demonstrate that adsorption of these compounds on the organo-clay complex was inversely proportional

to their aqueous solubilities. This means that benzene is sorbed to a lesser extent than biphenyl.

Lee *et al.* (1989a) measured increased sorptive capabilities of HDTMA-exchanged soils by examining several organic compounds that are representative of common groundwater contaminants. They found that the organic matter derived from exchanged HDTMA was 10 to 30 times more effective than natural soil organic matter in the partition uptake of toluene, ethylbenzene and benzene from water. They state that soil organic matter contains a higher polar group content and therefore is a less effective medium in solubilizing nonpolar compounds.

Lee *et al.* (1989b) [cited in Lee *et al.* (1990)] found that the sorption from water of aromatic compounds on TMA-smectite was different from the partition behaviour of aromatics onto HDTMA-smectite. The sorption isotherms of benzene, toluene and o-xylene were linear for HDTMA and nonlinear for TMA-smectite. The authors report a greater uptake of benzene from aqueous solutions on TMA-smectite despite the fact that HDTMA-smectite has a greater organic carbon content. Cadena (1989) also found TMA-smectite a very effective sorbent for benzene. Cadena (1989) states that the large surface areas in the interlayers is readily available to a planar molecule such as benzene which occupies the spaces between the TMA molecules vertically as opposed to lying flat (Figure 1.4). This orientation is preferred by the pi-electrons of the benzene ring. Cadena (1989) found that compounds related to benzene that have a nonplanar steric configuration or of greater size such as toluene do not fit into the spaces as well. The selectivity of TMA-smectite is benzene >> toluene > o-xylene. Lee *et al.* (1989b) [cited in Lee *et al.*, 1990] also determined the shape selectivity of TMA-smectite in the adsorption of aromatic compounds in water, as evidenced by a progressive reduction in uptake in going from benzene to larger aromatic compounds.

Results have shown that soils modified by exchange reactions of organic cations can be highly effective for enhancing the sorptive capabilities for NOCs. For organics of low water solubility such as biphenyl, organic cations with large (C₁₆) hydrocarbon groups are the most effective as they form a highly efficient partition medium for removing NOCs from water. Compounds of higher water solubility such as tetrachloromethane and

benzene appear to be more efficiently adsorbed by organic cations with small hydrocarbon chains.

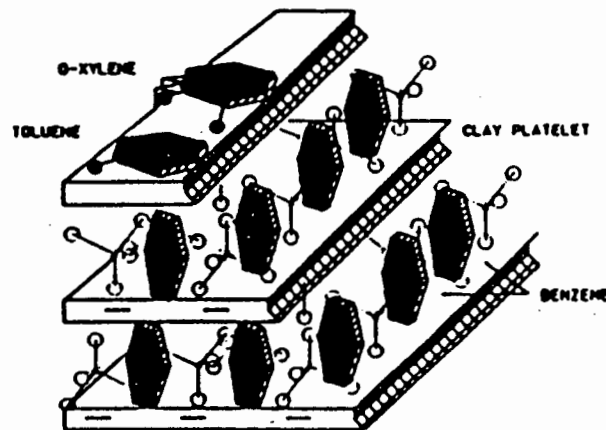


Fig. 1.4 Tailored clay with adsorbed benzene (Cadena, 1989).

1.5 General discussion

Chemical interactions can occur between clay and the contained liquid waste which alter the permeability of the clay liner. Using the Gouy-Chapman model of the electric double layer, predictions can be made as to how the clay liner will be altered when certain liquid wastes are introduced. For example, solutions with predominantly divalent ions will reduce the swelling capacity of Na-montmorillonite and solutions of high electrolyte concentration reduce the capacity of the clay particles to block soil micropores (Alther, 1987). With respect to organic permeants, studies have shown that pure organic liquids can increase the hydraulic conductivity of the clay but the magnitude of the increase varies for different studies (Budhu *et al.*, 1991; Fernandez and Quigley, 1985). However one should note that as landfill leachate often contains a mixture of organic compounds,

studies of the cooperative effects are more applicable than tests on pure organic liquids. Fernandez and Quigley (1985) found a 10 000-fold increase in hydraulic conductivity of initially water-wet samples when sequentially leached with alcohols and then certain aromatic compounds.

The sorptive capacity of clays for liquid organic wastes can be enhanced by exchanging the metal cations with quaternary ammonium cations. Lee *et al.* (1989a) and Boyd *et al.* (1988a) showed that smectites treated with HDTMA have a much greater sorptive capacity for benzene than soil organic matter. Jaynes and Boyd (1991) found that organics of low water solubility such as biphenyl are more effectively sorbed by organic cations with large (C_{16}) hydrocarbon groups than cations with small hydrocarbon groups such as TMA. This is because a highly efficient partition medium develops for removing these NOCs from water. Compounds of higher water solubility such as benzene appear to be more effectively removed by organic cations with small hydrocarbon chains (Lee *et al.*, 1989b). Cadena (1989) found that the selectivity of TMA-smectite for benzene and related aromatics is benzene > > toluene > o-xylene. Cadena (1989) attributes this to the fact that molecules that have a nonplanar steric configuration do not fit into the spaces between the TMA molecules as well as benzene and consequently are not as effectively sorbed. Brixie and Boyd (1994) recorded that organo-clays synthesized with large (C_{16}) alkyl groups were the most effective in reducing the leachability of PCP from soil where a 20% (w/w) addition of the organo-clay reduced PCP concentration from 16.9 mg/L to below detection limits (0.2 mg/L). A large reduction in PCP levels was observed with additions of as little as 2% (w/w) organo-clay to contaminated soil. One may conclude from these studies that organo-clays have the potential to remove organic contaminants from water and liquid wastes and in reducing leaching in contaminated soils.

2. Characterization of the Rensburg clay soil and commercial bentonite

2.1 Introduction

A thorough investigation into the properties of both the Rensburg soil and the commercial bentonite was required for assessing the potential suitability of the materials in the containment and treatment of petrochemical wastes. With respect to the containment of wastes, guidelines have been compiled for selecting appropriate soils to meet required specifications for liners (Benson *et al.*, 1994). The guidelines generally include minimum values or acceptable ranges for soil properties that describe soil composition, such as Atterberg limits and particle-size distribution. In this chapter, the results from various soil characterization procedures of the Rensburg soil and the bentonite are presented and discussed in the context of suitability of the materials as hydraulic barriers in waste-containment facilities.

The sorption capacity of both the Rensburg soil clay and the commercial bentonite for certain common organic pollutants will be discussed in Chapter 4. Certain soil and clay properties may directly affect the capacity of the materials to remove organics from an aqueous medium. These would include soil organic matter content, clay content and cation exchange capacity. Results from the characterization procedures are discussed in this chapter.

2.2 Materials and methods

2.2.1 Materials studied

The clay soil used in this study is of the Rensburg soil form (Soil Classification Working Group, 1991) which is common in the Eastern Highveld area. The soil can be described as a heavy, black clay soil similar to that described by Ginster (1993). A representative sample of the soil was collected from a pile which is being stored for use in a

rehabilitation project. The soil was air-dried and crushed to pass a 2 mm pore diameter sieve.

Characterization procedures were also performed on the commercial bentonite. This natural sodium-based bentonite is mined in the Western Cape and marketed by Cape Bentonite. No sample preparation was required as the bentonite was already in a fine powder form.

2.2.2 Methods used

Methods used in the characterization of the Rensburg soil and the bentonite are as follows:

- 1) organic matter content through dichromate oxidation of organic carbon (Walkley, 1935);
- 2) Atterberg limits using the method outlined by the American Standard Test Method (ASTM) (1993);
- 3) particle size analysis by the Lowy pipette method outlined by Gee and Bauder (1986);
- 4) BET specific surface area using nitrogen as the analytical gas (Carter *et al.*, 1986);
- 5) cation exchange capacity according to the LiCl method described in SSSSA (1990);
- 6) XRF elemental analysis (Willis, 1995);
- 7) clay mineralogy by X-ray diffractometry (Whittig and Allardice, 1986).

Results from the characterization procedures are presented in Table 2.1 and, where required, details of the methods used for the analyses are presented in Appendix A.

2.3 Results from characterization procedures

2.3.1 General analyses

The pH of the bentonite is high. This must be due to hydrolysis of the exchangeable sodium ions. Hydrolysis of basic cations is a primary source of soil alkalinity. This effect would also lead to the raised pH observed for the Rensburg soil which contains slightly more calcium but less sodium and magnesium than the bentonite.

The similarity in the organic carbon content of both the Rensburg soil and the bentonite is surprising as the bentonite did not have any visible signs of containing organic matter whereas the Rensburg soil was expected to contain some organic material. With respect to the sorption of nonpolar hydrocarbons, Lee *et al.* (1993) state that if organic matter is present in soils to the extent of 1% or more, it usually dominates sorption.

2.3.2 Atterberg limits

Atterberg limits are indices of the quantity of the clay-size particles and their mineralogical composition. A higher liquid limit and plasticity index are associated with soils having a greater quantity of clay particles. There exists a relationship between hydraulic conductivity and Atterberg limits such that the more plastic clays (having a higher liquid limit or plasticity index) should have a lower hydraulic conductivity (Benson *et al.*, 1994). The results from the Atterberg limit tests are presented in Table 2.1. Both the Rensburg soil and the commercial bentonite meet the required Atterberg limit values given by Benson *et al.* (1994) (Table 2.2) to achieve mean hydraulic conductivities of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$.

The Atterberg limit values for the commercial bentonite far exceed those for the Rensburg soil suggesting that a lower hydraulic conductivity could be attained using the pure bentonite. Natural sodium-base bentonites tend to be very high swelling. Clem (1985) states that the low permeability of sodium saturated bentonite is reflected in the Atterberg limit values for the bentonite. Alther (1987) states that the liquid limit of a typical Wyoming bentonite in sodium saturated form can range from 600 to 800%.

Table 2.1: Results from soil characterization procedures.

DETERMINATION	RENSBURG SOIL	BENTONITE
Soil organic matter (%)	1.29	1.12
Soil pH:		
H ₂ O	8.7	10.3
1M KCl	7.1	9.1
Cation exchange capacity (mmol _c /kg)	325	889
BET surface area (m ² /g)	75	41
Particle size distribution (%):		
Sand	40	2
Silt	11	17
Clay	50	85
Atterberg limits (%):		
liquid limit	59	381
plastic limit	24	46
plasticity index	13	53
linear shrinkage	35	335
Clay minerals		
dominant	smectite	smectite
minor	quartz kaolinite	
Elemental analysis		
Major oxides (%):		
SiO ₂	73.39	56.41
TiO ₂	0.965	0.187
Al ₂ O ₃	8.96	16.25
Fe ₂ O ₃	5.22	2.99
MnO	0.178	0.127
MgO	1.04	3.24
CaO	1.04	0.86
Na ₂ O	0.52	2.33
K ₂ O	1.13	0.734
P ₂ O ₅	0.03	0.03
LOI	4.01	5.83
Total	100.07	99.86
Trace elements (mg/kg):		
Zn	49	51
Cu	35	5.3
Ni	68	9.61

Table 2.2: Atterberg limits to achieve hydraulic conductivities (K) of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$ (from Benson *et al.*, 1994).

Property	Minimum for $K \leq 1 \times 10^{-7} \text{ cm.s}^{-1}$
liquid limit (%)	20
plasticity index (%)	7

Benson *et al.* (1994) add that it is not sufficient to solely regard the Atterberg limits as an indication of the suitability of the material as a liner as other factors, such as the chemical interactions between the hydraulic barrier and the waste being contained may greatly affect the hydraulic conductivity, and therefore, must be tested.

2.3.3 Particle size analysis

The percentage of sand, silt and clay (Table 2.1) was determined using the Lowy pipette method as outlined by Gee and Bauder (1986). This form of sedimentation analysis is based on the assumption that spherical particles settle at a velocity that can be calculated from Stokes Law. Non-spherical particles such as clay platelets bring a certain degree of error into the calculations. In addition, samples were not pre-treated for the removal of carbonates or organic matter. This may explain why total values of greater than 100% are obtained.

The particle size distribution of compacted soil affects hydraulic conductivity because the size of voids conducting flow is affected by the relative proportion of large and small particles. Low hydraulic conductivity is likely to be achieved when the soil is well graded and the clay fraction governs the hydraulic behaviour of the matrix (Benson *et al.*, 1994). Benson *et al.* (1994) report that hydraulic conductivity drops significantly when the bentonite in a sand-bentonite mixture is increased from 0 to 8%. Once the clay content reaches 12%, no further significant reduction in hydraulic conductivity occurs. The Rensburg soil has a clay fraction of 50% and the commercial bentonite has 85% clay which suggests that the clay content of both samples is sufficiently high to obtain low hydraulic conductivities.

2.3.4 Specific surface area

The surface area of a given material will greatly determine many of its chemical and physical properties. Water retention, cation exchange capacity, and the sorption of organic molecules are directly related to the specific surface which is defined as the surface area per unit mass of soil (Carter *et al.*, 1986).

Expanding layer silicates such as montmorillonite have extensive internal as well as external surface, giving specific surfaces up to 810 m²/g. Nonexpanding layer silicates such as kaolinite and some micas have only external surfaces and consequently the specific surface of these minerals ranges from 10 to 70 m²/g (Carter *et al.*, 1986).

Specific surface area was determined using the Brunauer, Emmett, and Teller (BET) equation which is derived from multimolecular adsorption theory and provides for the calculation of the number of adsorbate molecules in a monolayer (Carter *et al.*, 1986). Carter *et al.* (1986) note that the measured surface area of montmorillonites is largely dependent on the nature of the adsorbate used. Nitrogen does not penetrate the interlayer surfaces so the measurement obtained is only for external surfaces. Polar molecules such as ammonia, are strongly adsorbed and penetrate into the interlayer surfaces and therefore tend to give a better indication of the total surface area of montmorillonites.

Surface area of the Rensburg and commercial bentonite was determined using nitrogen as the analytical gas. The value obtained must be considered as a measurement of external surfaces only due to the inability of nonpolar nitrogen to penetrate the interlayers. Both samples contain predominantly smectite (as is shown in Section 2.4) and therefore the true value for specific surface should be much higher.

2.3.5 Cation exchange capacity determination

The cation exchange capacity (CEC) of the Rensburg soil and the commercial bentonite was determined according to the LiCl method described in SSSSA (1990). CEC is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil. It is directly related to the specific surface area (Wild, 1993).

Wild (1993) states that the approximate CEC for a pure smectite is 1000 mmol_c/kg. A value of 889 mmol_c/kg was obtained for the bentonite. The clay mineralogy (Section 2.4) indicates that the bentonite is of high purity. The particle size distribution analysis (Section 2.3.3) indicates that the bentonite is 85% clay and from the X-ray diffraction work (Section 2.4), the clay is high purity smectite. The CEC value for the bentonite is therefore close to the literature value. The CEC value obtained for the Rensburg soil is considerably lower. The clay content of the Rensburg soil is lower than the bentonite but can not be entirely responsible for the lower CEC. From the X-ray diffraction work of the Rensburg soil (Section 2.4), the clay fraction appears to contain predominantly smectite but also kaolinite and quartz. Wild (1993) reports the CEC of kaolinite to be between 20-60 mmol_c/kg. Less smectite in the clay fraction would lead to a lower CEC.

2.3.6 Elemental analysis

Smectites are classified on the basis of cationic substitution. Dioctahedral smectites include montmorillonite - a Mg rich smectite, beidellite - an Al rich smectite, and nontronite - an Fe rich smectite (Figure 1.1). They are often collectively called montmorillonites as they all contain at least a small amount of Fe and varying amounts of tetrahedral Al (Borchardt, 1989). Borchardt (1989) states that soil smectites tend to form a continuous series between montmorillonite and beidellite.

The XRF elemental analysis was done on the whole Rensburg soil and the bentonite and not on the isolated clay fractions. However, certain inferences may be made on the type of smectite in the samples based on the chemical data. The bentonite sample contains significantly more Mg and Al than the Rensburg soil. This suggests that the bentonite is composed of a montmorillonite/beidellite smectite. The Rensburg soil contains more Fe than the bentonite. The Rensburg soil itself gives no indication (from a visual perspective) of the presence of iron oxides in the soil. The Fe measured by XRF may be due to the presence of nontronitic smectite in the soil. It should be noted, however, that most soil environments seldom contain so little Al that nontronite instead of montmorillonite or beidellite is the more stable product. On the other hand, all soil smectites discovered so far contain at least small amounts of Fe, the octahedral sheet containing, on average, three Al for every Fe (Borchardt, 1989).

2.4 Clay mineralogical characteristics

To distinguish the smectite group of minerals from other 1.4 nm clay minerals such as chlorite and vermiculite, Buhmann *et al.* (1985) suggest rendering the clay homoionic with either Mg^{2+} and solvating (with either glycerol or glycol) or K^+ and heating, and then observing the shifts in (001) spacings.

The similarity in basal spacing of Mg-saturated vermiculite or smectite necessitates differentiation to distinguish between these two minerals. Smectite is able to adsorb double sheets of glycerol molecules, consequently expanding the basal spacings to approximately 1.77 nm (Whittig and Allardice, 1986). This can be clearly seen in Figure 2.1 where the 1.58 nm peak of Mg-saturated bentonite shifts to 1.83 nm after glycerol solvation indicating the presence of smectite. The 1.58 nm peak of Mg-saturated Rensburg soil clay also shifts to 1.83 nm after glycerol solvation as shown in Figure 2.2. Mills and Zwarich (1972) (cited in Buhmann, 1986) state that broad shouldered peaks are an indication of interstratification. The 1.58 nm peak in the Mg-saturated Rensburg soil clay has a definite broad shoulder unlike the sharp peak for the Mg-saturated bentonite, indicating the presence of interstratified material.

Barnishel and Bertsch (1989) propose that the differentiation between chlorite and vermiculite can be achieved with K-saturation as vermiculites will collapse to essentially non-expanded structures (1.0 nm) when saturated with K and heated to 110°C whereas chlorites will be unaffected by this heating. The collapse of vermiculite should be substantially complete at 100°C heating. The collapse of the peak to 1.0 nm upon heating to 300°C indicates either smectite and/or vermiculite. A basal spacing of 1.52 nm for a K-saturated, air dried smectite can be taken to indicate montmorillonite (Buhmann *et al.*, 1985). The K-saturated bentonite (Figure 2.3) has a sharp peak at 1.52 nm indicating montmorillonite. The 1.52 nm peak does not collapse upon heating to 100°C but collapses to 1.00 nm upon heating to 300°C which indicates smectite in the sample and the absence of vermiculite. This test therefore confirms that the bentonite is predominantly smectite, and as the K-saturated peak occurs at 1.52 nm, it appears as if the sample is predominantly montmorillonite.

The K-saturated Rensburg soil clay shows a very slight collapsing of the peak when the sample was heated to only 100°C (Figure 2.4) and a stronger tendency to collapse upon

heating to 300°C. The collapse at 300°C confirms the presence of smectite in the sample. There appears to be small amounts of vermiculite in the Rensburg soil clay and, due to the seemingly incomplete collapse at 300°C, this sample also appears to also contain some chlorite. The broadness of the peaks for the Rensburg soil clay sample indicates interstratified material which probably includes vermiculite, chlorite and organic matter. The Rensburg soil clay also contains kaolinite and quartz as minor constituents.

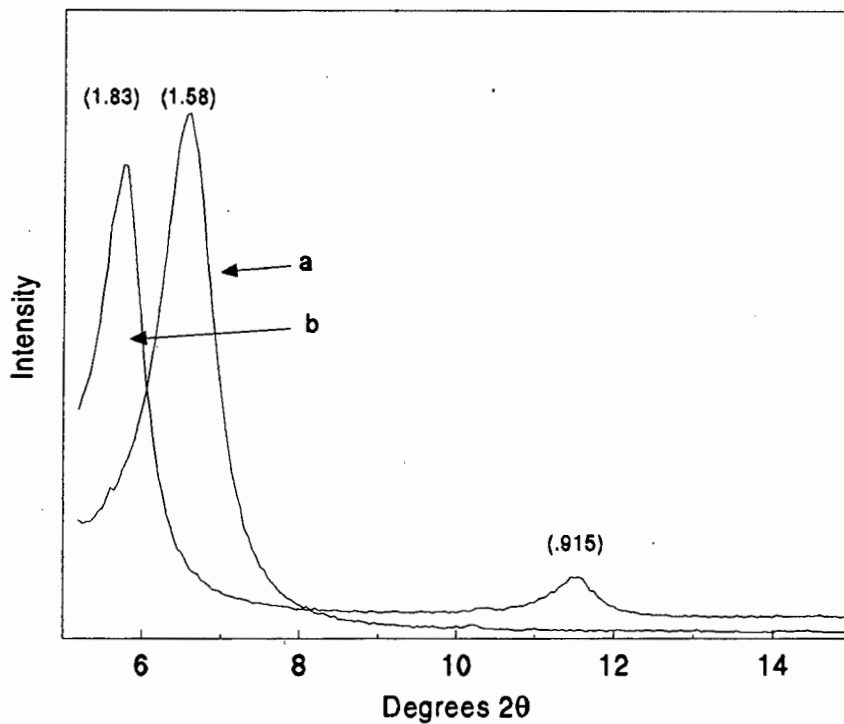


Figure 2.1: X-ray diffractogram (CoK α radiation) for Mg-saturated bentonite: a=air-dried; b=glycerol solvated: d-spacings in parentheses are given in nm.

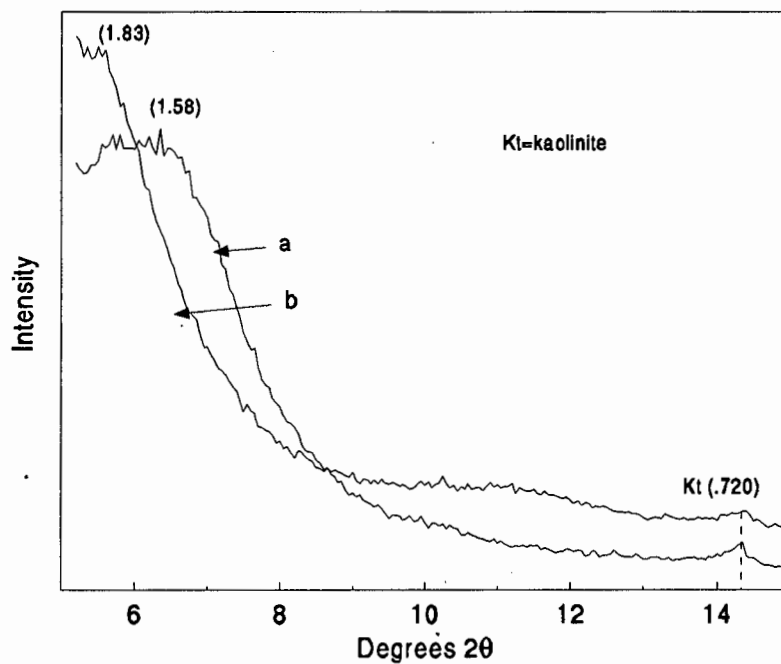


Figure 2.2: X-ray diffractogram (CoK α radiation) for Mg-saturated Rensburg soil clay: a=air-dried; b=glycerol solvated: d-spacings in parentheses are given in nm.

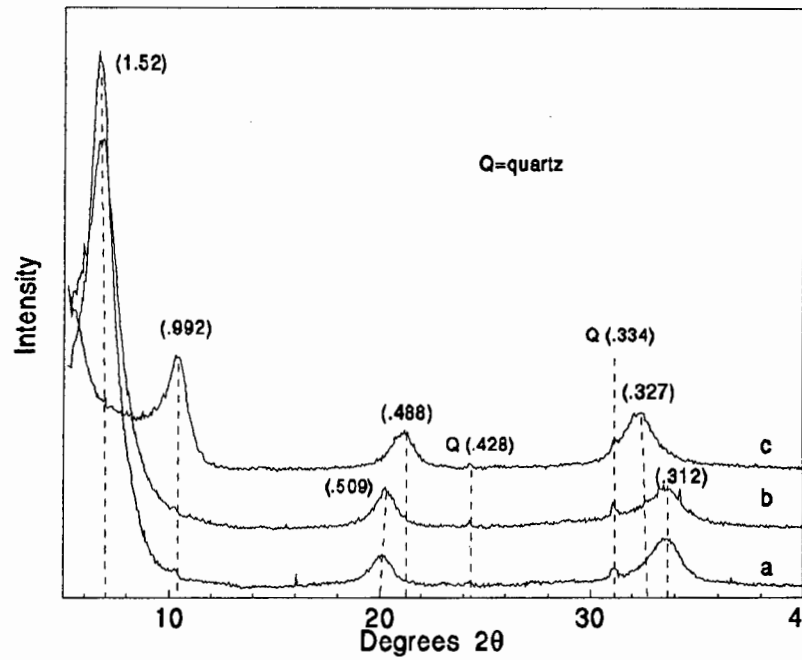


Figure 2.3: X-ray diffractogram (Co $K\alpha$ radiation) for K-saturated bentonite: a=air-dried; b=100°C; c=300°C: d-spacings in parentheses are given in nm.

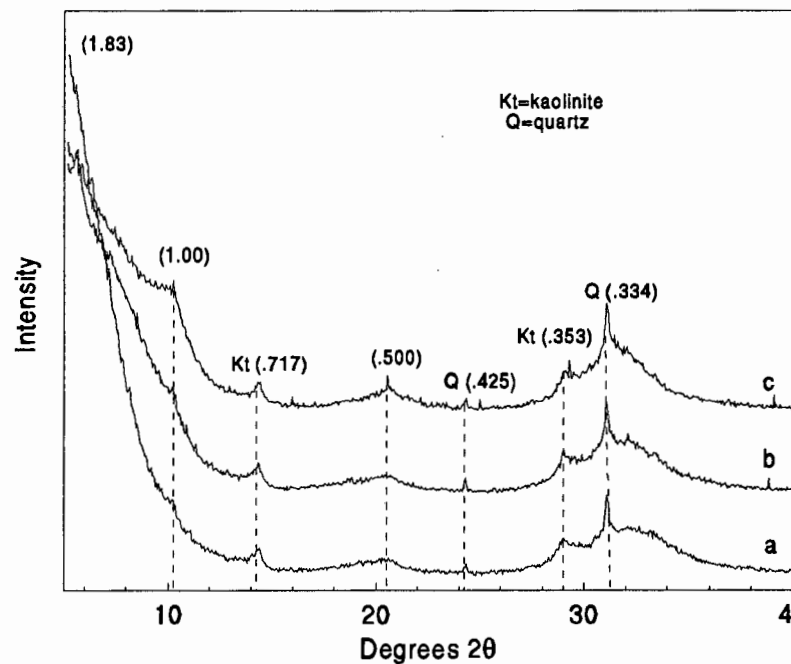


Figure 2.4: X-ray diffractogram (Co $K\alpha$ radiation) for K-saturated Rensburg soil clay: a=air-dried; b= 100°C; c=300°C: d-spacings in parentheses are given in nm.

2.5 Conclusions

Both the Rensburg soil and the commercial bentonite meet the minimum values for the Atterberg limits for achieving $K \leq 1 \times 10^{-7} \text{ cm.s}^{-1}$. In addition, the clay content of both the Rensburg soil and the bentonite is relatively high and dominated by smectitic clay. From these results one may predict that both materials would make good hydraulic barriers for containing waste and would constitute effective adsorbents for solutes when contacted with various liquids. However, the hydraulic conductivity of a material must be tested with the proposed contaminant to be contained, as physical, chemical and biological interactions between the liner and waste can significantly alter the hydraulic conductivity. The results from permeability tests are discussed in Chapter 3.

With respect to the adsorption of nonpolar organic contaminants, the organic carbon content of both the soil and the bentonite is likely to contribute to the sorption capacity. Clays, organic matter and other soil mineral surfaces provide sites for the sorption of polar and ionic organic compounds. Clays may be modified to increase their sorptive capacities for certain common organic pollutants. The sorptive capacity of untreated and chemically treated clays for certain organic compounds is discussed in greater detail in Chapter 4.

3. Hydraulic conductivity of smectitic clay soil with respect to liquid organic waste

3.1 Introduction

According to Anderson (1982), clay liners should never be described as impermeable and, since all clay liners are permeable, the questions to ask are "at what rate are they leaking" and "to what extent do they resist permeability increases upon exposure to leachate?". In this chapter, an attempt will be made to address these (and other) questions with respect to the containment of two samples of petrochemical waste in smectitic clay rich soil.

Soils with high clay contents and consequently low permeabilities are frequently used as natural and artificial barriers for the containment of hazardous waste. It has been well established that solutions of high electrolyte concentration will reduce the thickness of the electric double layer and consequently reduce the capacity of the clay particles to block soil micropores (Alther, 1987). With respect to organic permeants, studies have shown that pure organic liquids can increase the hydraulic conductivity of clay but the magnitude of the increase varies for different studies (Budhu *et al.*, 1991; Fernandez and Quigley, 1985). The nature of the different organic chemicals in toxic landfills is so variable that cooperative effects among different chemicals may render measurements on pure organic liquids of little use in predicting permeability of mixtures. It is therefore essential that the actual hydraulic conductivity of the organic waste to be contained is determined with respect to the potential soil clay barrier.

3.2 Materials and methods

3.2.1 Organic waste studied

Samples of Unutilized Petroleum Products (UPP) were collected in 5 L tins from the edge of the dams where they are currently stored, adjacent to a petrochemical plant at Secunda, South Africa. BP10 is predominantly an aqueous phenolic waste but an organic emulsion is clearly visible when the sample is shaken. Suspended solids are also present in the

sample. BP10 has a pH of 9.63 and an EC of 26.4 dS/m. Details of some of the organic constituents found in BP10 are presented in Table 4.1. BP10 was used in both the column work and the sorption experiments to be discussed.

BP2 is a mixture of predominantly thick oil with some water which was collected off the surface of a dam which contained an aqueous organic waste. BP2 has a density less than water and has a viscosity similar to a thick syrup. No organic analysis was conducted on BP2 which, on account of its tar-like consistency, was not used in sorption experiments and was used in only one column leaching experiment.

3.2.2 Column leaching apparatus

Leaching columns were packed with air-dried Rensburg soil which had been passed through a 2 mm sieve. Perspex rigid-wall columns with a diameter of 5.5 cm were uniformly packed (passing the soil through a funnel into the column for even distribution of soil particles) to a height of 9 cm using a mass of 265 g of Rensburg soil. The liquid to be leached through the soil columns was contained in a mariotte bottle at a constant head of 90.0 cm following the experimental setup as described by Nowicki and Fey (1994). The experimental design is illustrated in Figure 3.1.

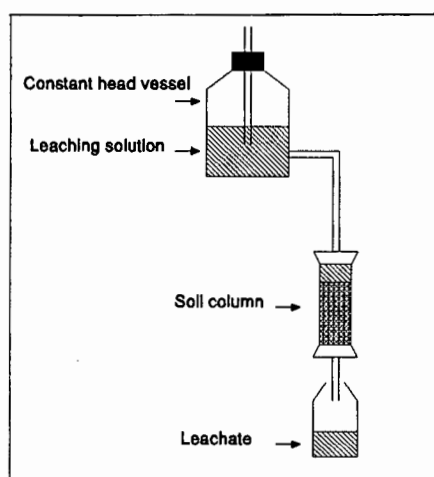


Figure 3.1: Schematic representation of column leaching apparatus.

Leachate was collected from the time the first drop of leachate came out of the bottom of the soil column, or as soon as possible thereafter. Measurements of leachate were taken by recording the time at which incremental volumes of leachate had passed through the column. The times and volumes were entered into a spreadsheet (shown in Appendix B) and hydraulic conductivity (K) was calculated according to the following equation:

$$K = \frac{(V \cdot L)}{(t \cdot h \cdot A)} \dots\dots\dots(1)$$

Where K = hydraulic conductivity ($\text{cm} \cdot \text{s}^{-1}$)
 V = incremental volume (cm^3)
 t = time per incremental volume (s)
 A = cross-sectional area of soil column (cm^2)
 h = hydraulic head (cm)
 L = length of soil column (cm).

In equation (1), A and h are known and are constant, such that $(1/Ah)$ is fixed at a value of 4.61×10^{-4} , allowing equation (1) to be simplified to:

$$K = \left(\frac{V \cdot L}{t} \right) \cdot 4.61 \times 10^{-4} \dots\dots\dots(2)$$

L varied with the amount of swelling and was considered constant after pre-wetting of the columns. Pre-wetting of the columns was done by connecting the constant head leaching bottle to the bottom of the packed column and starting with a head of 10 cm, increasing the head to 90 cm over the pre-wetting time. CaSO_4 pre-wetted columns were given 48 hours to wet, and after that time, CaSO_4 solution was accumulating at the top of the soil column. Na_2CO_3 and distilled water pre-wetted columns required a longer time to wet. Columns undergoing pre-wetting with Na_2CO_3 were left for 242 hours before commencing leaching experiments. The distilled water pre-wetting columns were also left for 242 hours, for convenience, but appeared to wet up slightly quicker than the Na_2CO_3 columns.

Once the column had been pre-wetted, the constant head leaching bottle was detached from under the column and connected to the top of the column. If required, the solution in the leaching bottle was changed.

3.3 Results and discussion

3.3.1 Comparison of the Rensburg soil clay and commercial bentonite

In order to establish the suitability of the Rensburg soil as a liner material, the same column experiments to be run on the Rensburg soil were also to be run using the commercial bentonite, which is sold for use as a liner material. However, it was found that the pure bentonite, once packed into a column, was extremely difficult to wet. This is attributed to the extreme hydrophilic nature of the bentonite. Once the surface of the clay column is in contact with water, the bentonite swells to such an extent that no further water can pass into the column to saturate the rest of the clay.

Due to the difficulties experienced in pre-wetting the bentonite columns it was decided that the Atterberg limits would have to be used instead of column experiments, to compare the suitability of the two materials as possible liners. The results from the Atterberg limit tests presented in Table 2.1 (Chapter 2) indicate that both the Rensburg soil and the commercial bentonite meet the required Atterberg limit values given by Benson et al. (1994) (Table 2.2) to achieve mean hydraulic conductivities of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$. The Atterberg limit values for the commercial bentonite far exceed those for the Rensburg soil, suggesting that a lower hydraulic conductivity could be attained using the pure bentonite.

It is important to note that as other factors such as interactions of the liner material with the waste being contained also affect hydraulic conductivity, it is not sufficient to solely regard the Atterberg limits as an indication of the suitability of the material as a liner. In this project, an attempt was made to establish how the Rensburg soil interacted with two samples of petrochemical waste. This would also have to be established if the bentonite was to be used as a liner.

An additional factor to be considered is cost of the commercial bentonite in comparison to the Rensburg soil. Commercial bentonite currently has a retail value of approximately R 50 (~ 14 US\$)/ton not including transport. The abundance of the Rensburg soil in the Highveld area may justify the use of this material over the bentonite if the Rensburg soil meets guideline specifications.

3.3.2 Reproducibility

To test the assumption that the method of packing used would result in reproducible columns, five columns were packed in the method described in Section 3.2.2, pre-wetted with a 0.005M CaSO₄ solution (refer to Section 3.3.3.1 for discussion on choice of leaching solution) and then subsequently leached with the same solution.

The hydraulic conductivities of all five columns dropped initially, perhaps indicating that the clay was not initially swollen to its full capacity although, after pre-wetting, no additional swelling was observed through measuring the height of the soil column. All five columns stabilized within the range of 2.1 to 7.2x10⁻⁵ cm.s⁻¹ giving a mean value of 4.0x10⁻⁵ cm.s⁻¹ and standard deviation of 1.7x10⁻⁵ cm.s⁻¹. A plot of hydraulic conductivity values against cumulative volume is given in Figure 3.2.

All five columns behaved in a similar manner, decreasing to hydraulic conductivities within the same order of magnitude. It was concluded that the packing of the columns could be conducted in a reproducible manner.

3.3.3 Baseline measurements with simple aqueous solutions

3.3.3.1 CaSO₄

Careful consideration should be given to the choice of test fluids used for hydraulic conductivity measurements, as various biological, chemical and physical processes may occur in the system that change the hydraulic conductivity. For example, if there are swelling clay minerals in the soil samples, a change in the chemical composition of the soil solution may have large effects on hydraulic conductivity. If the solution causes dispersion of the clays, the fine particles may migrate within the sample and block pores, thereby reducing the hydraulic conductivity. Klute and Dirksen (1986) recommend the use of 0.005M CaSO₄ as a test fluid as the Ca ion will reduce the dispersion of clays within a sample, allowing a measurable hydraulic conductivity.

The soil columns that were leached with 0.005M CaSO₄ showed swelling. The soil columns were all packed to a height of 9.0 cm, but after saturation with the 0.005M CaSO₄ solution

the columns had swelled, on average for the five columns, an additional 2.7 cm. The soil in the columns appeared to remain in aggregates and flocculated.

The values of the determined hydraulic conductivities are presented in Appendix B and illustrated in Figure 3.2. Using 0.005M CaSO₄ as the test fluid did result in a measurable hydraulic conductivity as predicted by Klute and Dirksen (1986). It did not, however, result in a hydraulic conductivity of $\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, the threshold widely considered to be acceptable for clay liners (Benson et al, 1994). From these results, it appears as if a solution which flocculates the soil clay, such as 0.005M CaSO₄, would not be suitable for the pre-wetting of this soil if it was to be used as a clay liner. Testing with the fluid to be contained by the clay liner is also necessary, however, as chemical and physical interactions may greatly change the hydraulic conductivity of the soil with respect to the waste. This is discussed in Section 3.3.4.

3.3.3.2 *Distilled water*

Klute and Dirksen (1986) do not recommend the use of deionized or distilled water for hydraulic conductivity determinations as the soil structure may change when the ambient soil solution is replaced by distilled water. Such water tends to be dispersive and consequently the hydraulic conductivity should be reduced when a clay soil is percolated with distilled water as opposed to 0.005M CaSO₄. However, when testing the suitability of a material for its possible use as a liner, it is important to get an indication of which solutions result in low hydraulic conductivity measurements. These solutions may then possibly be used to pre-wet the liner. Tap water was not used since its composition is variable.

The two columns that were pre-wetted with distilled water swelled on average 2.9 cm which was slightly more than for CaSO₄. The soil lost the individual aggregate structure and the clay appeared to disperse slightly. A plot of all K measurements against cumulative volume is presented as Figure 3.3. A record of all measurements taken is provided in Appendix B. It appears from the graph that the columns had already approximately reached equilibrium due to the long period (242 hours) allowed for the pre-wetting of the columns. Although distilled water disperses clay, the hydraulic conductivity is lower than the CaSO₄ leached columns by only a factor of 2. Alther (1987), when comparing different test fluids, considers

a hydraulic conductivity increase (or decrease) of a factor of about 2 to be an insignificant change.

The visible disaggregation in the presence of distilled water appears not to have significantly lowered the hydraulic conductivity, but a considerable decrease in hydraulic conductivity was observed when the soil was leached with Na_2CO_3 (Section 3.3.3.3).

3.3.3.3 Na_2CO_3

The five columns which were initially leached with 0.005M CaSO_4 were then subsequently leached with a 0.02M solution of Na_2CO_3 . A Na_2CO_3 solution of this concentration is dispersive and this was clearly visible from the textural alteration of the soil. The soil clay in the columns did not appear to undergo any additional swelling from the initial swollen state. Additional swelling within the soil column to fill the pore spaces may have occurred, but not vertical swelling of the soil columns as observed with CaSO_4 and distilled water pre-wetting. The texture of the top 5 cm of each column changed from granular to a smooth, creamy appearance, signifying a breakdown in structure.

Sharp decreases in hydraulic conductivities were recorded upon leaching with the dilute Na_2CO_3 solution following the 0.005M CaSO_4 leaching (Figure 3.4). The last hydraulic conductivity readings for the five columns ranged between 2.4×10^{-7} and $1.5 \times 10^{-6} \text{ cm.s}^{-1}$ with an average value of $5 \times 10^{-7} \text{ cm.s}^{-1}$. Two dry soil columns were set up and pre-wetted with 0.02M Na_2CO_3 (which required 242 hours for apparent saturation) and then leached with the same fluid. The hydraulic conductivity was very low with less than 5ml of leachate being collected in a 24 hour period, corresponding to a hydraulic conductivity of $< 3 \times 10^{-7} \text{ cm.s}^{-1}$. As the hydraulic conductivity of the distilled water leached columns was not significantly lower than the CaSO_4 leached columns, dispersion of clay particles from distilled water does not appear to significantly decrease the hydraulic conductivity. The decrease observed for Na_2CO_3 leached columns is possibly due to additional swelling. This conflicts with results

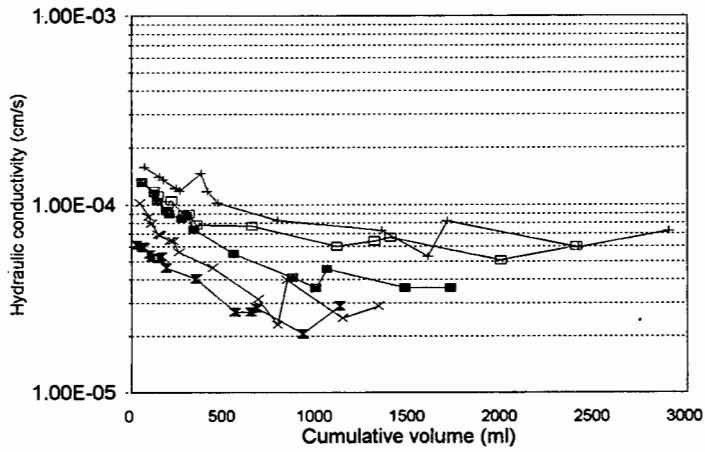


Figure 3.2: Hydraulic conductivity of five identically packed columns of Rensburg soil leached with 0.005M CaSO₄

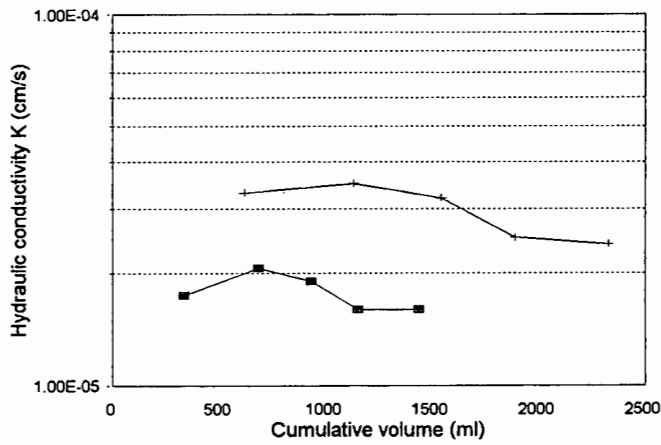


Figure 3.3: Hydraulic conductivity of two columns of Rensburg soil leached with distilled water.

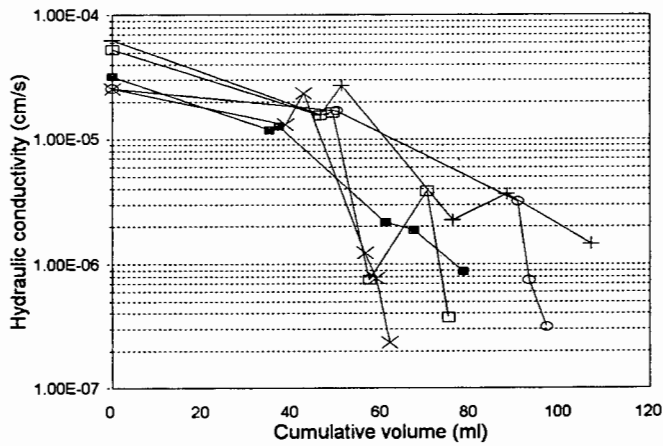


Figure 3.4: Hydraulic conductivity of five columns of Rensburg soil leached with 0.02M Na₂CO₃ after leaching with 0.005M CaSO₄ (see Figure 3.2).

of Frenkel *et al.* (1977) who found that clay dispersion and plugging from the use of distilled water was primarily responsible for reductions in hydraulic conductivity. Frenkel *et al.* (1977) report that the additional swelling of montmorillonitic soils leached with a dilute Na solution had a negligible effect on hydraulic conductivity. Clem (1985), on the other hand, states that the swelling capacity of smectitic clays, in particular Na-montmorillonite, has a marked effect on hydraulic conductivity as swollen clay particles effectively block off macropores. The swelling capacity of montmorillonites based on their exchangeable cation composition affects their suitability as liner materials. Na-saturated montmorillonites, due to their high swelling capacity, are generally most suitable for landfill liners. Mixed Ca-Na saturated montmorillonites are considered less suitable but can be activated by Na_2CO_3 treatment which enhances the swelling capacity but apparently not to the same extent as natural Na-montmorillonites.

From the results obtained in this experiment, it appears as if the swelling capacity of the clay has been significantly enhanced by leaching with dilute Na_2CO_3 . The resulting hydraulic conductivities are approximately two orders of magnitude lower than when leached with CaSO_4 .

3.3.4 Measurements with waste organic liquids

3.3.4.1 BP10 aqueous organic waste

The hydraulic conductivity of BP10, a predominantly aqueous organic waste, was determined by leaching the BP10 through the soil columns (Figure 3.5). The soil columns were either pre-wetted with 0.005M CaSO_4 , distilled water or 0.02M Na_2CO_3 . The leaching experiments were also performed on dry columns. A record of all measurements taken is provided in Appendix B.

In determining how the BP10 will interact with the Rensburg soil it is important to consider the chemical composition of the waste. BP10 is primarily an aqueous organic waste with some non-aqueous organics present as an emulsion. The low dielectric constants of organic liquids tends to cause a contraction of the diffuse double layer that surrounds soil particles. Bowers and Daniel (1987) state that, in compacted clay, particles tend to flocculate or aggregate when a concentrated organic liquid is introduced, which can lead to formation of

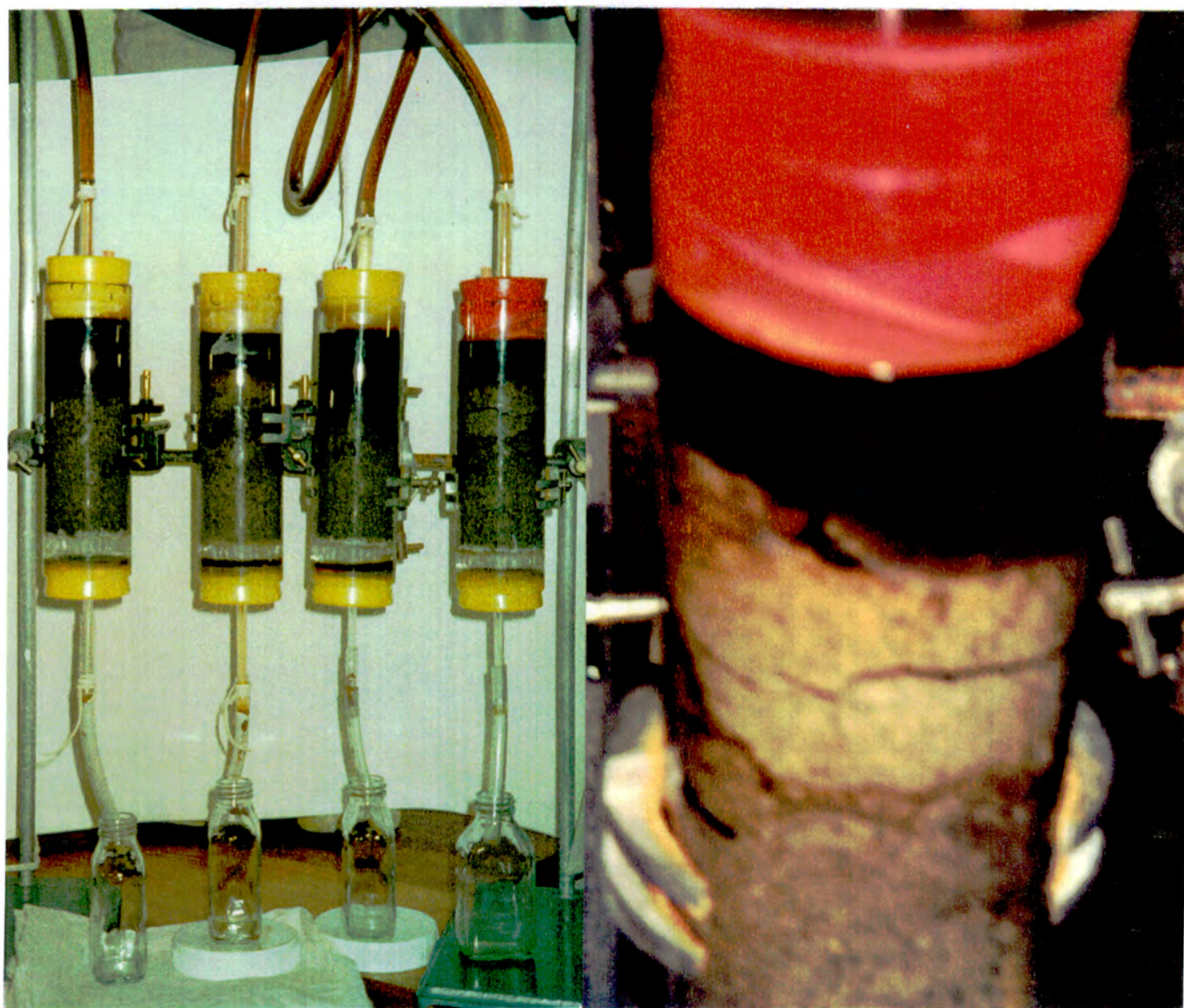


Figure 3.5: Four Rensburg soil columns with BP10 as the leaching solution. Cracks in $\text{CaSO}_4\text{-Na}_2\text{CO}_3$ pre-treated column when leached with BP10 can be seen in the right-hand column and enlarged on the right.

macropores or shrinkage cracks. Bowders and Daniel (1987) found that, on tests with methanol, heptane and trichloroethylene, organic liquids had little effect on the hydraulic conductivity, unless the concentration of the organic liquid was greater than 80% by volume. These authors suggest that if an organic liquid does not cause soil particles to flocculate in suspension, it will not cause an alteration in the fabric of the compacted clay or an increase in hydraulic conductivity. Unfortunately, this hypothesis could not be tested on BP10 due to the high salinity of the waste which would automatically cause flocculation of the clay particles.

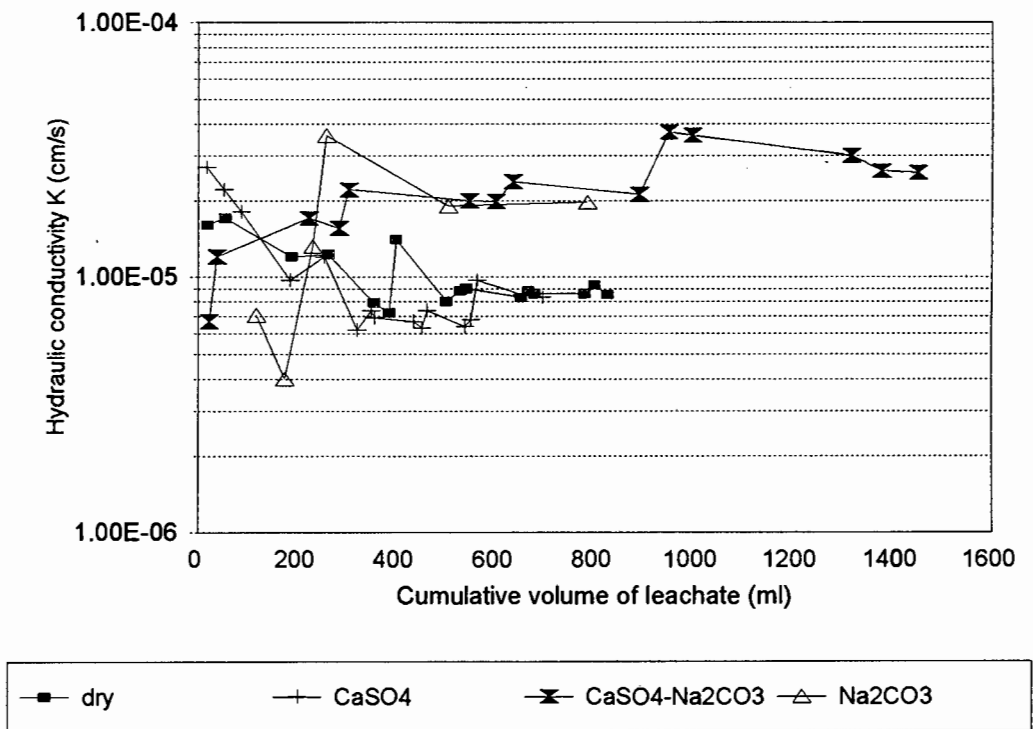
The high salinity (EC of 26.4dS/m) of BP10 must also be considered as a possible major influence on hydraulic conductivity measurements. Alther (1987) states that if properly hydrated with fresh water, a good bentonite is capable of withstanding severe salt contamination. On tests using a municipal landfill leachate (TDS = 36840 mg/L) Alther (1987) found no significant increases in hydraulic conductivity of bentonite but suggested that, when used to contain brines, it may be advisable to use a calcium bentonite and achieve low permeability by filling pore spaces with fine particles.

The choice of solution used to pre-wet the columns appears to have a marked effect on the hydraulic conductivity measurements. The results for each will be discussed separately in this section.

Duplicate dry columns (a and b) were leached with BP10 and though initially there was some variation between the two columns, the hydraulic conductivity readings for both columns decreased to below $1 \times 10^{-5} \text{ cm.s}^{-1}$ (Table 3.1 and Figures 3.6 a and b). The two columns swelled on average an additional 1.7 cm upon leaching with BP10 and no dispersion of the clay particles was apparent. It was interesting to note that the suspended solids present in the BP10 visibly accumulated in the top 3 cm of the soil column.

The CaSO_4 pre-wetted column behaved in a similar fashion to the dry columns, equilibrating at hydraulic conductivity measurements of $< 1 \times 10^{-5} \text{ cm/s}$ (Table 3.1 and Figure 3.6a). The soil aggregates did not change in appearance from the CaSO_4 leaching and the clay appeared to remain flocculated as one might expect when leaching with a solution of high salinity. As with the dry columns, solids accumulated towards the top of the soil column, this time appearing to penetrate only the top 1cm of the soil column.

a)



b)

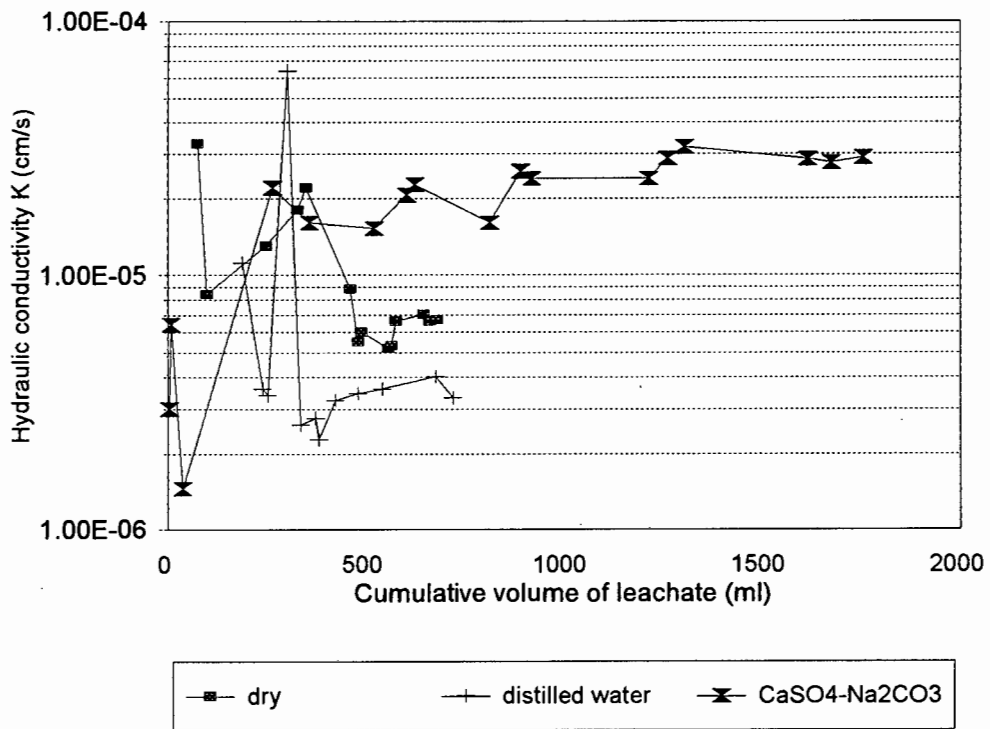


Figure 3.6 (a and b): Hydraulic conductivity measurements for columns leached with BP10. The legend indicates the various pre-treatments.

Table 3.1: Hydraulic conductivity measurements for columns leached with BP10

Column pretreatments	Final hydraulic conductivity (cm.s ⁻¹)
Dry-a	8.5x10 ⁻⁶
Dry-b	6.6x10 ⁻⁶
CaSO ₄	8.5x10 ⁻⁶
Distilled water	3.3x10 ⁻⁶

The distilled water pre-wetted column resulted in a lower equilibration hydraulic conductivity than for the CaSO₄ pre-wetted or dry columns (Figure 3.6b). There was no apparent sign of a change in the soil structure when leached with BP10 despite the fact that the soil was initially dispersed and BP10 has a flocculating effect on account of its high salinity. BP10 suspended solids accumulated in the top 0.5cm of the soil column only, possibly unable to penetrate further as dispersed clay particles occupy the pore spaces.

The lowering of hydraulic conductivity noted in the above three situations may be attributed to the suspended solids which visibly accumulate at the top of the soil column and which may act to block pores in the soil. Other factors such as microbial growth in the pores and the precipitation of salts within the pores may also contribute to the lowering hydraulic conductivity recorded in these experiments.

The Na₂CO₃ pre-wetted columns exhibited sharp increases in hydraulic conductivity upon leaching with BP10 (Figure 3.6 a and b). Three columns were run, two being treated with CaSO₄ and then 0.02M Na₂CO₃ and the third pre-wetted with 0.02M Na₂CO₃ only. All three exhibited similar behaviour with the hydraulic conductivity increasing by almost two orders of magnitude. Within 24 hours of leaching the columns with BP10, narrow bands of suspended solids were clearly visible throughout the top 5cm of the columns. Within 48 hours, in place of the bands, large cracks had appeared in the soil columns (Figure 3.5). The increase in hydraulic conductivity is attributed to this cracking. A possible explanation for this cracking is discussed later in section 3.3.4.3.

From these preliminary experiments, BP10 would appear to be best contained by the Rensburg soil when it is pre-wetted with distilled water. The dry and CaSO₄ pre-wetted columns were almost as effective. However, with respect to the containment of BP10 by the Rensburg soil, the hydraulic conductivity measurements obtained exceed the acceptable threshold for the containment of hazardous waste ($\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, DWAF, 1994a), irrespective of the pre-treatment. Using DWAF guidelines, the Rensburg soil would not appear to make a suitable lining material for the containment of BP10. However, certain experimental factors such as possible side-wall seepage from the rigid wall columns could lead to increases in measured hydraulic conductivity. In addition, soil columns left to run over a longer time period may exhibit different hydraulic conductivities from those measured in this experimental work.

3.3.4.2 BP2 oil organic waste

The BP2 liquid was too viscous to pass through the tubing between the constant head bottle and the soil columns. A 50 cm Perspex rigid-wall column was therefore used instead of leaching the test fluid from a constant head bottle. The column was packed with 265 g of dry Rensburg soil to a height of 9 cm (as in previous experiments) and BP2 was poured into the column to give a head of 30 cm of BP2.

The column was allowed to stand for 36 days and during that time the BP2 had migrated only 2.6 cm down the soil column. This means that the hydraulic conductivity of BP2 with respect to the dry Rensburg soil is $< 1 \times 10^{-7} \text{ cm.s}^{-1}$, suggesting that BP2 could be contained by this clay soil to an extent conforming to the acceptable threshold ($\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, Benson *et al.*, 1994, DWAF, 1994a) for clay liners.

3.3.4.3 Salinity effects on Na₂CO₃ pre-treated columns

In an attempt to ascertain the cause of the cracking of the Na₂CO₃ pre-treated columns when leached with BP10 (described in Section 3.3.3.3), additional columns were set up. Na₂CO₃ and distilled water pre-treated columns were leached with a NaCl solution of equivalent EC to the BP10 (26.4 dS/m), in order to test the hypothesis that the cracking behaviour was related to the salinity increase after contacting the soil with BP10.

Small cracks were observed in the Na_2CO_3 pre-treated columns after approximately 96 hours of leaching with the concentrated salt solution. No cracks appeared in the distilled water pre-treated column.

As suggested by observations reported earlier, soil pre-treated with Na_2CO_3 undergoes additional swelling to that caused by distilled water alone. McBride (1989) states that the initial swelling of smectites is due to the hydration of interlayer cations and as a result of this hydration, up to four layers of H_2O molecules can be adsorbed. McBride (1989) attributes the additional Na-saturation induced swelling capacity of montmorillonites to the weak attractive forces between layers, as a result of the large hydration radius of the Na^+ ion. Expansion is thus facilitated as water molecules migrate into the interlayers of the clay in response to an osmotic potential gradient between the interlayer solution and the more dilute bulk solution. It can be postulated, therefore, that when BP10 or a concentrated NaCl solution is passed through the soil column, the water molecules which have previously migrated into the interlayers respond to the new osmotic gradient by migrating out into the saline solution. This results in contraction of the clay particles and ultimately, cracking of the soil columns.

The possibility of cracks forming in a liner which has been constructed to contain potentially hazardous contaminants must be avoided. From this experimental work, cracks appear to form in Rensburg soil columns pre-wetted with Na_2CO_3 and then leached with BP10. Therefore, a solution likely to cause additional swelling such as a dilute Na solution should not be used to pre-wet a Rensburg soil liner being constructed to contain a highly saline waste such as BP10. If tapwater is to be used to pre-wet the soil, then it should be analyzed to ensure that it is not similar in composition to a dilute Na solution. As the commercial Na-saturated bentonite also undergoes additional osmotic swelling when saturated with water, it may also prove to be an unsuitable lining material for the containment of BP10. Testing of the commercial bentonite with a saline waste such as BP10 would be essential before containment of the waste in liners constructed of the bentonite.

3.3.5 BP10 leachate composition

pH and EC measurements of the BP10 leachate fractions are discussed in this section. The organic composition of BP10 and BP10 leachate fractions is discussed in Chapter 4.

3.3.5.1 pH

Plots of pH and EC breakthrough for the Dry-a and the CaSO₄ pre-treated columns are provided (Figures 3.7 and 3.8). The initial pH of the leachate from the CaSO₄ pre-treated column is approximately 8. This is the residual CaSO₄ solution leaching through the column. It is interesting to note the drop in pH in the CaSO₄ leachate fractions which correspond to an increase in EC readings. This may be due to the increase in salts from BP10 passing through the soil which replace hydrogen ions on exchange sites. It is essentially the same effect as the drop in pH that was recorded in the soil characterization (Table 2.1) when the pH of the soil was measured in KCl as opposed to water. The added salts replace the H⁺ ions on the exchange sites, resulting in a reduction in pH.

3.3.5.2 Electrical conductivity

The breakthrough of BP10 pH through the soil columns appears at approximately the same cumulative volume measurement as the breakthrough in EC measurements. This suggests that the soil does not have a stronger pH buffering capacity than EC buffering capacity and vice versa. It is clear from these measurements that both pH and EC could be used in monitoring the containment of BP10 as both pH and EC measurements of surface and groundwater would give a clear indication of leakage of the liner.

3.4 DWAF requirements for waste disposal

The phenol content of BP10 waste (Table 4.1) will be the only organic constituent of BP10 considered in this discussion of the toxicity of the BP10 waste and the required liner design for the containment of the waste. The U.S. Environmental Protection Agency classify phenol as being an acute toxin (both human and environmental) causing developmental effects in humans (World Resources Institute, 1994). In the Minimum Requirements document (DWAF, 1994b) phenol is classified into Class 6.1 with a Hazard Rating of 3. Class 6.1 includes substances liable to cause death or serious injury or to endanger human health if swallowed or inhaled, or by skin contact. Various other factors, in addition to the potential of a substance to endanger human health, are considered for Class 6. Class 6 has been extended to include ecotoxicity and environmental fate. Phenol is in moderate Hazard

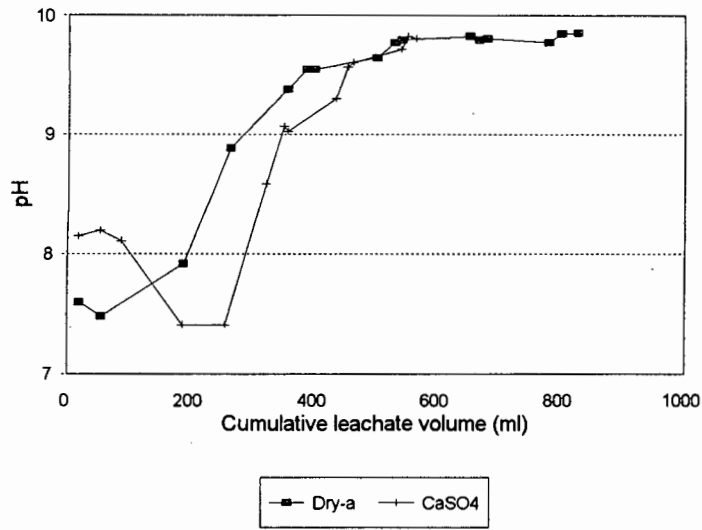


Figure 3.7: pH breakthrough of BP10 leachate through Rensburg soil columns. The legend indicates the various pre-treatments.

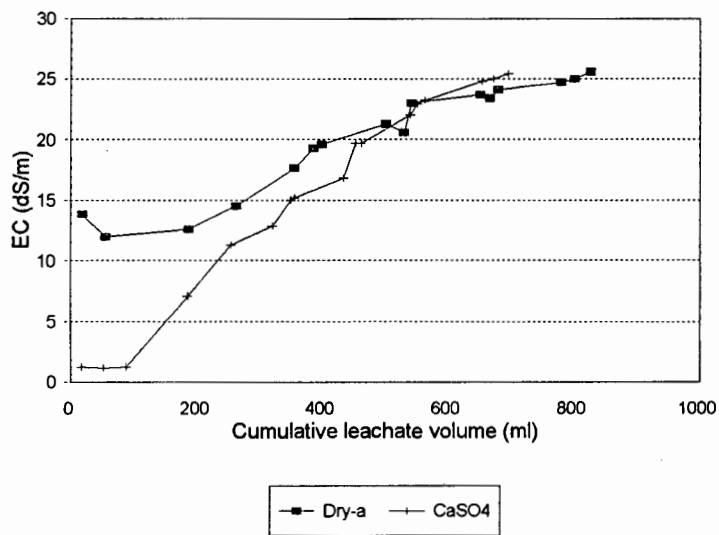


Figure 3.8: EC (dS/m) breakthrough of BP10 leachate through Rensburg soil columns. The legend indicates the various pre-treatments.

Group 3 as it is potentially biodegradable but it also generally highly mobile. It is therefore a constituent which is potentially highly harmful to human health or to the environment but is not persistent. The biodegradability of phenol is an important consideration in the disposal of this waste but it will not be discussed in the context of this study.

The total load capacity (TLC), given in grams/hectare, is based upon the risk posed by a volume/mass of waste if disposed directly into a water body. It can be used to determine the amount of waste that can be disposed (following DWAF guidelines) before the substance begins to pose a threat to humans or the environment. The TLC of a waste is influenced by the inherent hazardousness of the waste, by mobility (leachability) of the waste and by the landfill design (DWAF, 1994b). The TLC of phenol for any given approved landfill disposal site (according to DWAF (1994b) calculations) is 117300 g/h.

Applying the TLC of phenol to BP10 waste which has a phenol concentration of 822 mg/L, and assuming the volume of BP10 to be disposed was 12×10^6 L, then the site would have to cover an area of 84 hectares (or approximately 1 km²) to not exceed the TLC.

The Minimum Requirements (DWAF, 1994a) require a liner for every hazardous (H) waste site, regardless of whether it generates significant leachate or not, or whether it is classified as H:h or H:H. Toxic substances with a Hazard Rating of 1 or 2 must be disposed of at an H:H permitted sites whereas toxic substances with a lower Hazard Rating of 3 or 4 can be disposed of at permitted H:H or H:h sites.

The lining system required in these sites is additional to the unsaturated zone comprising soil or rock between the phreatic surface of the groundwater and the landfill. Any soil used for a compacted soil liner must have a minimum Plasticity Index of 10 and a maximum particle size of 25 mm (DWAF, 1994a). The Rensburg soil and the commercial bentonite meet these requirements.

A lining layer, constructed of compacted soil of low permeability, must meet certain requirements with respect to the flow of leachate. The maximum allowable outflow rates as given by DWAF (1994a) are as follows:

Class H:h landfills: measured outflow rate must not exceed 3×10^{-7} cm/s

Class H:H landfills: measured outflow rate must not exceed 1×10^{-7} cm/s.

The design of the liner is based on estimated permeability coefficients measured in the laboratory but these estimates must be validated in the field using *in situ* permeability tests such as the double ring infiltrometer (DWAF, 1994a). The Minimum Requirements document (DWAF, 1994a) specifies that in permeability tests, "ordinary clear" water should normally be used, unless a sample of leachate from similar waste or a sample of the liquid waste is available. In the case of H sites, it must be known that the waste will not significantly increase the permeability of the liner.

The results from the permeability tests with the BP10 discussed in this chapter emphasize the importance of conducting permeability tests with the proposed waste to be contained. It was shown that the salinity of BP10 causes cracking of the Na_2CO_3 pre-wetted Rensburg soil resulting in a marked increase in permeability. With respect to the containment of BP10 by the Rensburg soil, the hydraulic conductivity measurements from this experimental work exceed the acceptable threshold for the containment of hazardous waste as given by the DWAF (1994a), irrespective of the pre-treatment. Using DWAF guidelines, the Rensburg soil would not appear to make a suitable lining material for the containment of BP10 despite meeting the requirements for minimum Plasticity Index and maximum particle size.

The DWAF preferred treatment disposal technology for phenolic waste is biological treatment and incineration whilst land-fill codisposal and conditional encapsulation are allowed technologies (DWAF, 1994b). The smectitic clay soil could possibly be used as a liner to contain BP10 in a dam during biological treatment of BP10 if bioremediation was proven to be a suitable treatment.

3.5 Conclusions

The results from the preliminary permeability tests of the Rensburg soil indicate that additional osmotic swelling of the smectite in the soil from leaching with dilute Na_2CO_3 leads to reductions in hydraulic conductivity compared to when the soil is leached with 0.005M CaSO_4 or distilled water. However, this additional swelling appears to lead to the formation of cracks within the soil column when Na_2CO_3 pre-treated columns are

subsequently leached with BP10, a petrochemical waste of high salinity. The cracking, which gives rise to sharp increases in hydraulic conductivity, is attributed to interlayer water responding to the osmotic gradient by migrating out into the test fluid. As the commercial Na-saturated bentonite also undergoes additional osmotic swelling, it is possible that it would respond in a similar manner to the Na_2CO_3 pre-treated columns when leached with BP10, rendering the bentonite unsuitable for the containment of BP10 leachate.

Permeability tests using BP10 confirm the need to test all potential liners with the waste to be contained. From these preliminary experiments, BP10 would appear to be best contained by the Rensburg soil when it is pre-wetted with distilled water. The dry and CaSO_4 pre-wetted columns were almost as effective. However, with respect to the containment of BP10 by the Rensburg soil, the hydraulic conductivity measurements obtained exceed the acceptable threshold for the containment of hazardous waste ($\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, DWAF, 1994a) irrespective of the pre-treatment. Using DWAF guidelines, the Rensburg soil would not appear to make a suitable lining material for the containment of BP10 despite meeting guideline values for Plasticity Index and maximum particle size. However, certain experimental factors such as possible side-wall seepage from the rigid wall columns may have led to increases in measured hydraulic conductivity. In addition, soil columns left to run over a longer time period may exhibit different hydraulic conductivities from those reported in this chapter.

The hydraulic conductivity of BP2 with respect to the dry Rensburg soil is $< 1 \times 10^{-7} \text{ cm.s}^{-1}$, suggesting that BP2 could be contained by this clay soil to an extent conforming to the acceptable threshold ($\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$, Benson *et al.*, 1994; DWAF, 1994a) for clay liners.

Monitoring for leakage of liners containing BP10 could be achieved through pH and EC measurements of surrounding ground and surface water. This is quicker and cheaper than monitoring for specific organic pollutants contained in BP10.

4. An investigation into the sorption of organic compounds by Rensburg soil and chemically treated clays

4.1 Introduction

By exchanging the neutral metal cations with large organic cations, clay can be made more organophilic and the sorptive capacity of the clay for certain organic compounds enhanced (Boyd *et al.*, (1988a); Mortland *et al.*, (1986); Lee *et al.*, 1989). Boyd *et al.* (1988a) found that when the metal cations in smectites are replaced with the hexadecyltrimethylammonium (HDTMA) ion, the sorptive property of the clay is greatly modified and the HDTMA-clay becomes a powerful partition medium in the uptake of benzene. Lee *et al.* (1989) report that the sorption coefficients (K values) of certain common organic groundwater contaminants on HDTMA-treated soils increased by approximately 200 times from sorption on untreated soils. Mortland *et al.* (1986) report that HDTMA-treated smectite adsorbs phenols and chlorophenols in proportion to their hydrophobicities with phenol, the most hydrophobic, being the least sorbed. The use of organo-treated clays has potential in the treatment of water and liquid wastes contaminated by organic pollutants. In this chapter, the sorptive capacity of the chemically treated bentonite and Rensburg soil clay for benzene and phenol is investigated and discussed in the context of the potential for using treated clays for decontaminating the BP10 liquid waste investigated in Chapter 3.

In addition to the batch equilibration experiments, the characterization of the BP10 leachate composition after passage through the Rensburg soil is discussed in this chapter. The leachate fractions were analyzed for specific organic compounds in an attempt to determine which compounds are preferentially attenuated by the Rensburg soil. Of particular interest in BP10 waste are the phenolics which generally are very mobile through soil materials. When the sorptive capacity of a soil material for a specific compound is low, the risk associated with storing the compound is enhanced.

4.2 Materials and methods

4.2.1 Clay preparation

The clay fraction was isolated from both the Rensburg soil and the commercial bentonite by dispersing the samples in a dilute Na_2CO_3 solution and repeatedly collecting the supernatant after the settling of the $> 2 \mu\text{m}$ fraction. The clay was then flocculated using CaCl_2 and dialysed against distilled water for approximately 48 hours to remove accumulated salts. The treated clay was then prepared using the method described by Boyd *et al.* (1988a). The Ca-saturated clay suspensions of both the Rensburg soil and commercial bentonite were freeze-dried in order to facilitate subsequent resuspension of the clay in aqueous solutions.

To exchange the Ca cations on the clay with the quaternary ammonium cation (QAC), a sample of freeze-dried Ca-saturated clay was placed in a beaker and a solution of hexadecyltrimethylammonium (HDTMA) chloride was added such that the number of moles of HDTMA was equivalent to the CEC of the clay. Smith *et al.* (1990) reported a strong (95%) uptake of HDTMA by clay when added at 100% of the CEC. The clay suspension initially had froth on the surface, presumably due to the surfactant nature of the QAC. According to Smith and Galan (1995), the exchange is rapid, reaching completion in 30 minutes. In this experiment, the clay-water slurry was stirred for 1 hour. HDTMA was very effective in flocculating the clay, giving the clay the appearance of curdled milk. The clay suspension was then freeze-dried. The consistency of the freeze-dried HDTMA-saturated clay was considerably different from the freeze-dried Ca-saturated clay, taking the form of fine powder as opposed to the soft, porous, massive structure of the latter.

4.2.2 Sorption experiments

The uptake of phenol and benzene from water was determined using the batch equilibration technique following closely the method outlined by Boyd *et al.* (1988a). Samples of QAC-treated and Ca-saturated bentonite and Rensburg soil clay and of the original Rensburg soil (air-dried, $< 2 \text{ mm}$) were used for both the benzene and phenol experiments in an attempt to establish sorptive capacities. Samples of clay (0.1-0.5 g) and Rensburg soil (1.0 g) were weighed into 30 ml glass centrifuge tubes, and 25 ml of distilled water was added. Benzene

or an aqueous phenol solution was added quantitatively to the tubes using a graduated syringe. For benzene, between 4 and 25 μl were added. For phenol trials, aliquots of a phenol solution was added corresponding to between 0.096 and 3.84 mg of phenol. Blanks were made up using the same method but without the clay or soil. The centrifuge tubes were immediately closed with Al foil-lined corks and then shaken for 18 hours at room temperature on a reciprocating shaker. Boyd *et al.* (1988a) established that equilibrium in such experiments was reached within 18 hours. The tubes were then covered with Parafilm and centrifuged at 6000 rpm for 45 minutes to remove suspended clay particles from the supernatant. The supernatant was then analyzed to determine the equilibrium benzene or phenol concentration of the supernatant.

Phenol was determined by gas chromatography (GC) using flame ionization detection (FID). Quantification was achieved via external calibration. Benzene measurements were made using a Beckman DU650 spectrophotometer, reading absorbance at a wavelength of 264 nm.

4.3 Results and discussion

4.3.1 Phenol sorption

An initial attempt was made to determine the equilibrium phenol concentration using a UV spectrophotometer, utilizing the appropriate absorption band at 269 nm in the ultraviolet region, as this could prove to be a simpler method than analysis by GC. Despite centrifuging and filtering the supernatants through a 0.2 μm filter, there was a large background to the phenol peak at 269 nm for all samples which had been equilibrated with clay. The background was probably caused by the presence of small clay particles which could not be removed through gravitational or filtration methods, since preliminary tests indicated that the magnitude of the background was influenced by filtration. As the phenol peak at 269 nm is not a sharp peak and the background interference was not constant, the analytical error associated with using this method was very high. UV spectrophotometry was therefore discarded as being an unsatisfactory method for phenol determination in the batch equilibration supernatants. Recourse was made to GC. Mortland *et al.* (1986) used UV spectrophotometry for the analysis of phenol and chlorophenol after equilibration with clays, but reported no interferences of the kind observed here.

The data obtained from these experiments are presented in Appendix C. The data suggest that negligible amounts of phenol are removed from the aqueous solution and sorbed by either the QAC-treated clay, the Ca-saturated clay or the Rensburg soil. However, inconsistencies in the data make it unsuitable for presentation as sorption isotherms. The apparent range of error associated with each data point exceeds the amount of phenol sorbed by each sample and therefore it is not possible to determine the amount of phenol sorbed. Possible sources of error are discussed later in this section. The data do, however, suggest that insignificant amounts of phenol are removed from the aqueous solution by the QAC treated clay, Ca-saturated clay or the Rensburg soil, confirming the results of Mortland *et al.* (1986), who reported that phenol was not significantly removed from an aqueous solution by HDTMA treated clay, ostensibly due to the hydrophilic nature of phenol. The authors attribute this to phenol interacting strongly with water through hydrogen bonding and therefore not being sufficiently attracted to the hydrophobic surfaces of the HDTMA-smectite. With respect to the untreated clay samples and the Rensburg soil, McBride (1994) states that acidic organic molecules are generally very weakly adsorbed, if at all, on soil material. According to McBride (1994), phenol sorption is pH-dependent, the neutral form being weakly retained by physical adsorption (on organic matter in particular) and the anionic form adsorbing very little on soil organic matter and layer silicate clays because of electrostatic repulsion between the molecules and the negative surface charge of these colloids. The pH of all the supernatants was found to be between 8.2 and 9.0. As the pK_a of phenol is 9.98, approximately 50% of the phenol molecules in the supernatants would have been in the dissociated form.

In the phenol-sorption experiment, between 0.1 and 0.5g of clay was used in each centrifuge tube. As the sorption capacity of clay for phenol is relatively low, more consistent results might have been obtained through replication and by increasing the amount of clay used to at least 1g. Whenever possible, supernatant samples were refrigerated to limit the possible biodegradation of phenol. However, the samples were not refrigerated whilst *en route* to the analyst (a period of approximately 36 hours). During this period, some alteration in the phenol concentration may have occurred. All the above mentioned factors may have contributed to the apparent error in the results of this sorption work.

4.3.2 Benzene sorption

An attempt was made to investigate the sorptive capacity for benzene of the Rensburg soil, Ca-saturated Rensburg soil clay and bentonite and HDTMA-treated Rensburg soil clay and bentonite. The method used in this experiment was the same as the method outlined by Boyd *et al.* (1988a), except that 0.1 to 0.5 g of clay was used instead of 0.5 to 1.0 g as described by Boyd *et al.* (1988a), and the analysis was performed using UV spectrophotometry instead of GC. When working with benzene it is important to bear in mind the relatively low solubility of benzene in water. A preliminary calibration curve of 4 to 25 μl of benzene in 25 ml of distilled water was linear, suggesting that this was within the solubility range of benzene. This calibration curve was prepared from absorbance measurements at 264 nm.

Boyd *et al.* (1988a) report centrifuging samples to separate the liquid and solid phases (for 45 minutes at 8000 X g) and then withdrawing 10ml aqueous phase samples from the supernatant by pipette. For GC analysis, the benzene in the 10 ml of supernatant was extracted with hexane. For UV spectrophotometry, approximately 10 ml of the supernatant was withdrawn with a pipette, following centrifugation, and the absorbance at 264 nm was read directly.

It was found that the recovery of benzene was very low even in samples which contained no clay or soil. Various possibilities were explored to explain the loss of benzene such as the possibility that benzene was sorbing to the Al foil-lined corks or being removed through filtration. A standard solution (giving a known absorbance) was placed in a glass centrifuge tube without clay or soil, covered with Parafilm, and centrifuged for the same time period as the samples. When an aliquot of the standard solution was withdrawn and analyzed, it was found to have an absorbance of only 14% of the original standard solution value. Centrifugation of the samples appeared to be forcing the benzene out of solution. The heating of the solutions during centrifugation, resulting in volatilization, and a tendency for the benzene to demix from the aqueous phase, are two possible explanations for the loss of benzene from the supernatants. Boyd *et al.* (1988a) used a similar method but do not report difficulties of this kind. They did not specifically report any attempt to check whether centrifugation affected the stability of benzene solutions in the absence of an adsorbing solid, and it is therefore possible that their adsorption results are in error.

4.3.3 The use of chemically treated clays for the decontamination of BP10

It has been suggested that soils modified by exchange reactions of organic cations have potential for the removal of nonionic organic contaminants (NOC) from aqueous solutions (Boyd *et al.*, 1988a; Smith *et al.*, 1990; Lee *et al.*, 1989). According to Boyd *et al.* (1988a), the use of HDTMA-treated clay may be an effective way of enhancing the removal of organic contaminants present in leachate water, and may find use in the construction of clay liners for disposal reservoirs. These authors found HDTMA-smectite to be an effective sorbent for removing benzene and trichloroethene from water. The use of these chemically treated clays appears, however, to be limited with respect to the removal of more hydrophilic compounds such as phenol (Mortland *et al.*, (1986); this study).

When considering possible methods of decontaminating BP10, there may be constituents present in BP10 which respond to treatment by QAC-treated clay. The phenol concentration of BP10 must, however, also be taken into consideration and it is not likely to respond to QAC-treated clay. Therefore, the use of QAC-treated smectite is not recommended for the decontamination of BP10; an alternative method such as bioremediation is likely to be more effective (DWAF, 1994b).

4.4 BP10 leachate composition

Leachate fractions from columns of Rensburg soil leached with BP10 liquid were collected and analyzed for various organic constituents in an attempt to determine which compounds are preferentially attenuated by the soil. This analysis was carried out on the fractions of leachate from the CaSO₄ pre-treated and the Dry-a columns. The organic analysis was performed using GC with FID. Further details of the analysis are provided in Appendix C.

It is interesting to note, from a visual assessment of leachate fractions, that none of the leachate samples collected throughout this experiment contained the non-aqueous phase organics present in the original BP10. The BP10 aqueous and non-aqueous phases do not appear to separate whilst passing through the tubing to the soil column as a sample of the original BP10 was collected from the top of the soil column which contained both phases. The emulsion, which is clearly visible in BP10 when shaken, is not apparent in any of the leachate fractions. The nonaqueous phase could consist of organics present in the BP10 at

concentrations which exceed their solubility limit, or organics which are not significantly soluble in water such as neutral nonpolar compounds. Schwarzenbach *et al.* (1993) state that neutral nonpolar organics are more similar to the natural organic matter of soils than to water and consequently weak physical adsorption by soils of nonpolar organics can take place. The "bonds" that are made between the sorbate and the natural organic sorbent are relatively weak intermolecular attractions which require only small activation energies to remove the compounds from their points of solid attachment. The organic matter of the Rensburg soil could be acting as an organic partitioning phase for the BP10 nonaqueous organics, consequently removing them from the waste. Soil particles are possibly being coated with the non-aqueous phase organics from the BP10 due to the greater affinity of the non-aqueous phase organics for soil organic matter and mineral surfaces than for polar water.

This may in fact be an additional contributing factor to the reductions in hydraulic conductivity which were observed for most of the soil columns when leached with BP10. The coating of soil particles with hydrophobic organics may lead to a more organophilic environment in the pore spaces. Fernandez and Quigley (1985) state that for an immiscible liquid such as benzene to replace water from the pores, energy is required to overcome the interfacial tension. In this situation, once the organics coat the soil particles, more energy is required for the predominantly aqueous BP10 to pass through the pores as the environment is now more organophilic than hydrophilic.

From a visual assessment of the leachate fractions, it is clear that certain organics are being retained by the Rensburg soil. The leachate fractions collected from the Dry-a column have undergone no dilution and yet the earlier fractions are significantly lighter, with the colour increasing with each fraction collected (Figure 4.1).

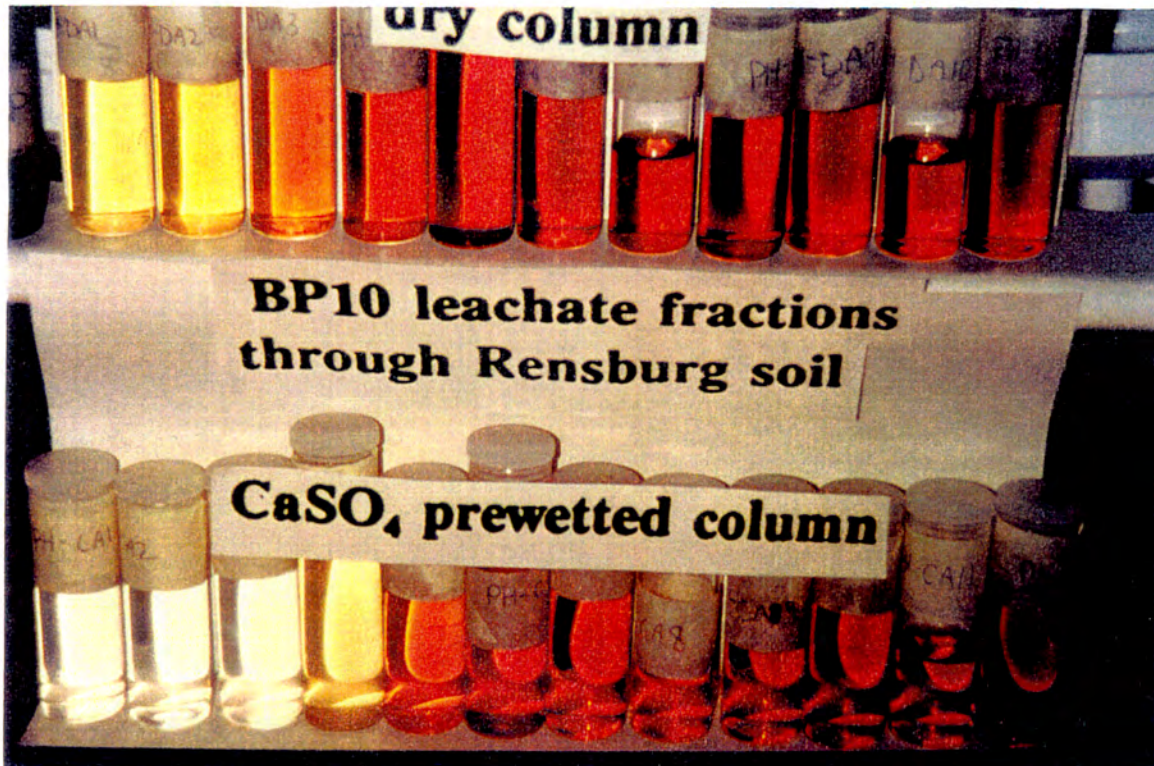


Figure 4.1: BP10 leachate fractions collected from the Dry-a (top row) and the CaSO₄ pre-treated (bottom row) Rensburg soil columns. The sample just visible in the top left hand corner is the original BP10. The colour of the original BP10 can be clearly seen at the head of each soil column in Figure 3.5.

Table 4.1: Concentrations (mg/L) of organic constituents in BP10 liquid waste and in successive fractions of BP10 leached through the Rensburg soil.

Organic constituents	original BP10	BP10 leachate fraction number (cumulative volume in parentheses)						
		1 (19ml)	2 (55ml)	3 (188ml)	5 (355ml)	6 (386ml)	8 (501ml)	11 (652ml)
phenol	882	539	563	590	589	602	669	600
o-cresol	81	25	28	35	36	34	35	27
butanone and propanone	110	97	109	86	74	117	98	122
2-pentanol	13	14	12	11	13	13	14	14
1-butanol	142	150	145	121	126	143	145	146

The analysis of certain oxygenated organics in the leachate suggests an attenuation of phenol and cresol by the Rensburg soil. All other alcohols and oxygenates measured appear to pass directly through the soil column. The results from the analysis are presented in Table 4.1. The leachate fraction numbers represent the order in which the fractions were collected (1 represents the first fraction, 8 the eighth).

Phenol is a fairly weak acid with a pK_a of 9.98. Alcohols such as pentanol are even weaker acids than phenol. McBride (1994) states that, in general, organic acids are highly mobile and susceptible to leaching in soils. Acidic molecules are adsorbed most effectively when the soil pH is low and the organic carbon content is high. In their neutral form, these molecules are weakly retained through physical adsorption (primarily on organic matter) and the anions adsorb very little on soil organic matter and layer silicates due to electrostatic repulsion.

A possible explanation for the apparent attenuation of phenol and cresol by the Rensburg soil when the soil is leached with BP10 is that the non-aqueous phase organics coat the soil particles, providing a more organophilic environment in the pore spaces. This would act to increase the organic carbon content of the sorbent which, according to McBride (1994), results in more effective sorption of acidic organic molecules such as phenol. However, Mortland *et al.* (1986) report that phenol is not significantly removed from an aqueous environment by clay treated with the HDTMA cation which acts to increase the carbon content of the clay. The organophilic environment created by the HDTMA is nonpolar and, according to Mortland *et al.* (1986), phenol interacts more strongly with water through hydrogen bonding than with the nonpolar environment created by the HDTMA cation. The possible coating of soil organic matter by the non-aqueous phase organics in BP10 may provide a medium which is capable of attenuating some phenol and cresol. This possible cooperative effect in the attenuation of phenol and cresol requires further investigation.

In addition, biodegradation of phenol and cresol by microbes present in the soil may be a contributing factor to the apparent removal of these constituents from BP10. The degradation would have to be fairly rapid due to rate at which BP10 is passing through the soil column. This possible biodegradation could be confirmed by setting up two soil columns, sterilizing one of the columns, and then leaching both with BP10.

4.5 Conclusions

In general, the sorptive capacity of soil materials for phenol is low (McBride, 1994) and therefore, the leachability of phenol enhances the risk associated with storing phenolic waste. The exchange of the base cations of clay for HDTMA does not appear to significantly enhance the sorptive capacity of clay for phenol (Mortland *et al.*, 1986; this study). The use of QAC-treated clays, therefore, does not represent an effective method for decontaminating BP10. The use of QAC-treated clays has greater potential in the treatment of less water soluble organic compounds such as benzene (Boyd *et al.*, 1988a; Lee *et al.*, 1989). Unfortunately, the results for benzene were not amenable to a similar interpretation due to difficulties encountered with the method. There appeared to be some attenuation of phenol and cresol by the Rensburg soil during column leaching experiments with BP10. This may be due to other constituents in BP10 providing a medium on soil surfaces for sorption and/or biodegradation of phenol and cresol, but further investigation in this area is required.

The implications of the results from the batch equilibration experiments are discussed in greater detail in Chapter 5.

5. General discussion and conclusions

One of the primary objectives of this project was to determine whether a smectitic clay rich soil (Rensburg form), which is abundant in the vicinity of a petrochemical plant, could be used to contain two samples of petrochemical waste (BP10-aqueous and BP2-nonaqueous) within specified guideline values for hydraulic conductivity. Based on the soil characterization results obtained, both the Rensburg soil and the commercial bentonite meet the minimum values for the Atterberg limits for achieving $K < 1 \times 10^{-7} \text{ cm.s}^{-1}$ as given by Benson *et al.* (1984). In addition, the clay content of both the Rensburg soil and the bentonite is high and dominated by smectitic clay. It might consequently be expected that both materials would make effective hydraulic barriers for containing waste. Atterberg limits, however, are index property tests of the liner material only and therefore cannot be used to predict how the material will interact with the waste being contained. Column leaching experiments were set up in an attempt to determine the hydraulic conductivity of both the Rensburg soil and the commercial bentonite with respect to the two samples of petrochemical waste.

In order to establish the suitability of the Rensburg soil as a liner material, the same column leaching experiments using the Rensburg soil were also to be run using the commercial bentonite, which is sold for use as a liner material. Due to difficulties experienced in pre-wetting the bentonite columns because of pronounced swelling behaviour, it was decided that the Atterberg limits would have to be used instead of column experiments to compare the suitability of the two materials as liners. The Atterberg limit values for the commercial bentonite far exceed those for the Rensburg soil, suggesting that a lower hydraulic conductivity could be attained using the pure bentonite. However, this would have to be established with leaching experiments.

Baseline measurements using simple aqueous solutions (0.005M CaSO_4 , distilled water and 0.02M Na_2CO_3) were made on the Rensburg soil before testing with BP10 and BP2. Hydraulic conductivity values for the columns treated with CaSO_4 solution and distilled water were within the same order of magnitude despite the increased dispersion of the clay in the distilled water pre-treated columns. Hydraulic conductivity dropped sharply when the CaSO_4 -leached columns were subsequently leached with Na_2CO_3 solution. The decrease in

hydraulic conductivity is attributed to the increased swelling capacity of Na-treated smectite. This conflicts with the results of Frenkel *et al.* (1977) who report that additional swelling of montmorillonitic soils leached with a dilute Na solution had a negligible effect on hydraulic conductivity, and that dispersion and plugging from the use of distilled water was primarily responsible for reductions in hydraulic conductivity.

Once baseline measurements were obtained, the hydraulic conductivity of BP10, a predominantly aqueous waste, was determined by leaching the BP10 through soil columns pre-wetted with either CaSO₄, distilled water, or Na₂CO₃. The leaching experiments were also performed on dry columns. In determining how the BP10 would interact with the Rensburg soil it was important to consider the chemical composition of the waste. BP10 is primarily an aqueous organic waste with some non-aqueous organics. The EC and pH of BP10 are both high (26.4 dS/m and 9.63, respectively). From preliminary experiments, BP10 appeared to be best contained by the Rensburg soil when it is pre-wetted with distilled water. The dry and the CaSO₄ pre-wetted columns were almost as effective. With respect to the containment of BP10 by the Rensburg soil, however, the measured hydraulic conductivities exceed the acceptable threshold values for the containment of hazardous waste ($\leq 1 \times 10^{-7} \text{ cm.s}^{-1}$) (DWAF, 1994a), irrespective of the pre-treatment.

Certain experimental factors such as side-wall seepage from the rigid wall columns could lead to increases in hydraulic conductivity. Flexible wall permeameters are considered by some (Budhu *et al.*, 1990) to be superior to the rigid wall permeameters as side-wall seepage is usually not a problem with the former. Flexible wall permeameters do not, however, allow one to observe the effects of shrinking of the soil column as the permeameter wall shrinks with the soil column. Hence, situations such as the shrinking and cracking of the Na₂CO₃ pre-treated columns when leached with BP10 may not lead to measurable increases in hydraulic conductivity. Boynton and Daniel (1985) compared both and found little variation in measured hydraulic conductivities but stress that great care must be taken in preparing the columns. An additional experimental factor to consider is the time period over which soil columns were equilibrating. Soil columns left to run over a longer period of time may exhibit different hydraulic conductivities from those reported in this thesis.

The DWAF recommends bioremediation for phenolic wastes with co-disposal as an accepted technology (DWAF, 1994a). If BP10 was found to be amenable to bioremediation,

the Rensburg soil could perhaps be used to contain the waste during the period of treatment.

The hydraulic conductivity of BP2 with respect to the dry Rensburg soil is $< 1 \times 10^{-7} \text{cm.s}^{-1}$, suggesting that BP2 could be contained by this clay soil to an extent conforming to the acceptable threshold.

The additional osmotic swelling of Na_2CO_3 pre-treated columns led to the formation of cracks within the soil column when the columns are subsequently leached with BP10. The cracking, which gives rise to an increase in hydraulic conductivity, is attributed to interlayer water responding to the osmotic gradient established by the high salinity of BP10 by migrating out into the test fluid. As the commercial bentonite also undergoes additional osmotic swelling, it is possible that it would respond in a similar manner to the Na_2CO_3 pre-treated columns when leached with BP10, rendering the bentonite unsuitable for the containment of BP10 leachate. This would have to be confirmed with tests on the bentonite employing BP10 or any other liquid waste of high salinity.

Anticipating that, no matter how effectively the liquid waste is retained by the clay liner, there will always be some leachate generated during storage, it was necessary to assess the degree of chemical alteration of the waste as a result of permeating the smectitic soil. pH and EC measurements were made on leachate fractions collected from columns leached with BP10. The measurements suggest that monitoring for leakage of liners containing BP10 could be adequately achieved through pH and/or EC measurements of surrounding ground and surface water, which would be quicker and cheaper than monitoring for specific organic pollutants contained in BP10.

A visual assessment of the original BP10 and the corresponding leachate from columns of Rensburg soil pointed to the removal of certain organic constituents from BP10 corresponding to the apparent removal of the oily phase and to a change in colour of the leachate fractions. Chemical analysis of the leachate fractions indicated some attenuation of phenol and cresol by the Rensburg soil. McBride (1994) states that the sorptive capacity of soil materials for organic acids, including phenols, is generally low. The mobility of these compounds enhances the risk associated with storing such wastes. The apparent attenuation of phenol and cresol by the Rensburg soil during column leaching experiments with BP10 may be due to other constituents in BP10 providing a medium for adsorption on soil

surfaces, but this possible cooperative effect requires further investigation. Biodegradation of phenol and cresol by soil microbes may also be a contributing factor to the apparent removal of these constituents from BP10. This could be tested by setting up two soil columns, sterilizing one of the columns, and then leaching both with BP10.

The environmental impact associated with waste disposal can be reduced through treatment of waste as an alternative to, or prior to, disposal to remove the more hazardous constituents of the waste. A review of recent literature revealed growing interest in the use of treated clays for the removal of specific organic pollutants from water (Boyd *et al.*, 1988a; Mortland *et al.*, 1986; Lee *et al.*, 1990). One of the aims of this work was to investigate the sorptive capacity of the chemically treated bentonite and Rensburg soil clay for benzene and phenol, in the context of the potential for using treated clays for decontaminating the BP10 waste. The replacement of the basic cations on the clay by the hexadecyltrimethylammonium (HDTMA) cation does not appear to enhance the sorptive capacity of clay for phenol, in agreement with the results of Mortland *et al.* (1986). The use of quaternary ammonium cation (QAC)-treated clays does not appear, therefore, to represent an effective method for removing the phenolics from BP10. The use of QAC-treated clays may have greater potential in the treatment of less soluble organic compounds such as benzene (Boyd *et al.*, 1988a; Lee *et al.*, 1989). Unfortunately, the results of benzene sorption tests were unreliable due to difficulties encountered with the method.

From the investigation into the sorptive capacity of clays for phenol and benzene on treated clays, various recommendations can be made with respect to the method. Firstly, the use of UV spectrophotometry as the method of analysis is not recommended due to potential interference from extremely fine dispersed clay particles which cannot be removed from the liquid phase by either centrifugation or filtration through a $0.2\mu\text{m}$ filter. Secondly, when working with compounds which are not expected to sorb significantly, the clay:water ratio should be large enough for sorption to be measurable within an acceptable degree of accuracy. Thirdly, the volatility and low solubility of benzene cast doubt on the results obtained from sorption experiments which employ centrifugation prior to analysis. Working conditions need first to be sought which will give full recovery of benzene in the absence of an adsorbing solid phase.

In conclusion, the aim of this study was to investigate the potential of Rensburg soil for the containment and treatment of petrochemical waste. The permeability of BP2, an oily organic

waste, was found to be $< 1 \times 10^{-7} \text{ cm.s}^{-1}$ with respect to the smectitic clay rich Rensburg soil. With respect to the containment of BP10 aqueous organic waste by the Rensburg soil, the hydraulic conductivity measurements obtained exceed the acceptable threshold for the containment of hazardous waste irrespective of the pre-treatment. The high salinity of BP10 resulted in the formation of cracks in Rensburg soil columns pre-treated with Na_2CO_3 , and it is possible that similar shrinkage could occur in any Na-saturated smectitic clay liner used to contain BP10.

The BP10 liquid waste would not be amenable to the removal of phenols by contact with the Rensburg soil clay, even when pre-treated with a quaternary ammonium salt. Bioremediation is likely to represent a more suitable method of decontaminating the waste. The literature suggests that QAC-treated clays have potential in the removal of less soluble organic compounds such as benzene from water. Experiments designed to quantitatively test this removal, however, should make use of special precautions to avoid misinterpretation through loss of the organic constituent from the aqueous phase during separation of the adsorbing solid.

6. References

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Appendix A

Soil characterization procedures

A.1 Cation exchange capacity (CEC) determination

The CEC of the Rensburg soil and the commercial bentonite was determined according to the LiCl method described in SSSSA (1990). The analysis was done by the Institute for Soil, Climate and Water in Pretoria.

A.2 Specific surface area

Specific surface area was determined using the Brunauer, Emmett, and Teller (BET) equation which is derived from multimolecular adsorption theory and provides for the calculation of the number of adsorbate molecules in a monolayer (Carter *et al.*, 1986). Carter *et al.* (1986) note that the measured surface area of montmorillonites is largely dependant on the nature of the adsorbate used. Nitrogen does not penetrate the interlayer surfaces so the measurement obtained is only for external surfaces. Polar molecules such as ammonia are strongly adsorbed and penetrate into the interlayer surfaces and therefore tends to give a better indication of the total surface area of montmorillonites. Carter *et al.* (1986) give 810 m₂/g as the theoretical specific surface area for montmorillonites.

Surface area of the Rensburg and commercial bentonite was determined at the Department of Chemical Engineering (UCT) using a Micrometrics ASAP 2000 instrument and nitrogen was used as the analytical gas under standard operating conditions. In the procedure, a sample is evacuated and then purged with helium in order to replace any gas molecules adsorbed onto the sample surface. The sample is then weighed followed by equilibration with nitrogen gas at some pressure P. The change in mass of the sample can then be used to determine the number of N₂ gas molecules adsorbed onto the surface of the sample. As

the cross-sectional area occupied by an N_2 molecule is known, if a simple monolayer of gas has formed on the surface, the surface area of the sample can be calculated.

A.3 Clay mineralogy

The clay fraction of both the Rensburg soil and the bentonite was isolated by dispersing the samples in a dilute Na_2CO_3 solution and then collecting the supernatant after the settling of the $> 2\mu m$ fraction. The collected clay was then flocculated with either KCl or $MgCl_2$ and dialysed to remove excess salts. A 2ml aliquot of the dialysed suspension was then pipetted onto a glass slide, allowing the clay particles to settle out with a preferred orientation and allowed to dry at room temperature. The K-saturated slides were first scanned after being air-dried. They were then heated first to $100^\circ C$ and then to $300^\circ C$, being scanned after each treatment. The Mg-saturated slides were run after being air-dried and then after Mg solvation of the samples. The Mg-saturated slides were glycerol solvated using a fine aerosol spray of 15% glycerol in water solution.

The clay mineralogy of the Rensburg and bentonite samples was determined by scanning the slides using a Philips PW 1390 X-ray diffractometer. A cobalt tube ($Co K\alpha = 1.790\text{\AA}$) operating at 40kV and 25mA was used and the samples were scanned through the range of $5.2-40^\circ 2\theta$, with a step size of $0.05^\circ 2\theta$ and a step duration of 1 second.

The results for the XRD analysis are discussed in detail in Section 2.2.2 and the spectrum are provided.

A.4 Soil organic matter content

Soil organic carbon was determined by means of the Walkley-Black method (Walkley, 1935). This standard method for the determination of soil organic matter involves the rapid dichromate oxidation of organic carbon without heating of the samples.

A.5 Particle size distribution analysis

A standard method using a Lowy pipette was used, as outlined by the SSSSA (1990). Carbonate, organic binding materials and iron oxides were not removed from the samples prior to analysis. An aliquot (10g) of dispersed sample was placed in a plastic cylinder for sedimentation and withdrawal at the appropriate time and depth as prescribed by Gee and Bauder (1986). The sand fraction of the sample consisted of all material collected in a 0.053mm pore diameter sieve.

A.6 Calcium carbonate determination

The CO_3^{2-} content of the Rensburg soil and the bentonite sample was determined by means of the "Karbonat-bombe", using the method of Birch (1981). This involves treating the samples with concentrated HCl which reacts with the CaCO_3 present in the sample, resulting in the evolution of CO_2 . The volume of CO_2 evolved is measured by a pressure gauge on the "Karbonat Bombe". Despite the presence of CaCO_3 concretions in the Rensburg soil, this method was not sensitive enough to measure the effervescence which was visible during the testing of the Rensburg soil. No CaCO_3 was measured in the bentonite sample.

A.7 Measurement of soil pH

2.5g aliquots of sample were placed in 3 centrifuge tubes and suspended in 25ml of either distilled water or 1M KCl. After shaking on a horizontal shaker for 10 minutes, the tubes were centrifuged for 5 minutes at 6000 rpm and the pH of the supernatant was determined using a Crison micro pH 2001 meter.

A.8 Atterberg limits

Atterberg limits are indices of the quantity of clay-size particles and their mineralogical composition. Higher liquid limit and plasticity index are associated with soils having a greater quantity of clay or clay particles having a higher surface activity. More plastic clays (having a higher liquid limit or plasticity index) should have a lower hydraulic conductivity (Benson *et al.*, 1994).

Measurements of the Atterberg limits of the Rensburg soil and the bentonite were done at Geoscience Laboratories, Cape Town using the American Standard Test Method (1993).

A.9 Soil elemental analysis

Dry samples were crushed to a fine powder using a ball and ring sieb mill. Powder briquettes were prepared by compressing an aliquot of the milled soil surrounded by boric acid powder, under an applied pressure of 10 tonnes. Fusion discs were prepared according to the Norrish Fusion method (Norrish and Hutton, 1969).

Nine major elements, Fe, Mn, Ti, Ca, K, P, Si, Al and Mg (with Ni and Cr when Ni and Cr concentrations exceed ~2000 ppm) are determined using fusion disks. The disks are analyzed on a Philips PW1480 wavelength dispersive XRF spectrometer with a Mo/Sc x-ray tube. Fe, Mn and Ti are measured with the tube at 100 kV, 25 mA. The other elements are determined with the tube at 40 kV, 65 mA. Peak only measurements are made on the elements Fe through Mg. Sodium is determined using powder briquettes, the x-ray tube at 40 kV, 65 mA, and with backgrounds measured at -2.00 and $+2.00^{\circ}2\theta$ from the peak position (Willis, 1995).

Trace elements are determined on powder briquettes using a series of x-ray tubes. Analytical conditions are listed in Willis, 1995.

Appendix B- Raw data from hydraulic conductivity trials

Reproducibility trials for 5 columns pre-wetted and leached with 0.005M CaSO4

Column	Date	DAY	HOUR	MIN	VOLUME (ml)	CUMULATIVE VOLUME (ml)	CUMULATIVE TIME (hrs.)	HYDRAULIC CONDUCTIVITY (cm/s)	logK	
a	14/9/95	1	11	25	0	0	0	0		
		1	12	5	59.27	59.27	0.67	0.000133	-3.875	
		1	12	54	63.87	123.14	1.48	0.000117	-3.931	
		1	13	9	17.67	140.81	1.73	0.000106	-3.975	
		1	13	57	50.54	191.35	2.53	9.5E-05	-4.024	
		1	14	13	16.19	207.54	2.80	9.1E-05	-4.041	
		1	15	22	65.94	273.48	3.95	8.6E-05	-4.066	
		1	15	48	25.76	299.24	4.38	8.9E-05	-4.050	
		1	16	36	40.13	339.37	5.18	7.5E-05	-4.124	
		1	22	24	215.15	554.52	10.98	5.6E-05	-4.255	
		15/9/95	2	9	47	316.19	870.71	22.37	4.2E-05	-4.381
			2	13	32	62.55	998.39	26.12	3.6E-05	-4.444
	2		15	25	58.06	1056.45	28.00	4.6E-05	-4.335	
	16/9/95	3	9	3	422.69	1479.14	45.63	3.6E-05	-4.445	
		3	20	27	247.22	1726.36	55.82	3.6E-05	-4.439	
	b	14/9/95	1	11	25	0	0	0.00		
			1	12	5	71.59	71.59	0.67	0.000161	-3.793
			1	12	54	78.18	149.77	1.48	0.000143	-3.843
			1	13	9	22.97	172.74	1.73	0.000138	-3.861
			1	13	57	66.44	239.18	2.53	0.000124	-3.905
			1	14	13	21.48	260.66	2.80	0.000121	-3.918
			1	15	22	114.54	375.2	3.95	0.000149	-3.826
1			15	48	34.63	409.83	4.38	0.00012	-3.922	
1			16	36	55.78	465.61	5.18	0.000104	-3.981	
1			22	24	325.08	790.69	10.98	8.4E-05	-4.076	
15/9/95			2	9	47	562.65	1353.34	22.37	7.4E-05	-4.130
			2	13	32	133.66	1603.77	26.12	5.3E-05	-4.273
		2	15	25	104.41	1708.18	28.00	8.3E-05	-4.080	
16/9/95		3	9	3	707.15	2415.33	45.63	6E-05	-4.221	
		3	20	27	488.15	2903.48	55.82	7.2E-05	-4.200	
c		14/9/95	1	11	25	0	0	0.00		
			1	12	5	27.84	27.84	0.67	6.3E-05	-4.204
			1	12	54	33.04	60.88	1.48	6.1E-05	-4.217
			1	13	9	10.06	70.94	1.73	6E-05	-4.220
			1	13	57	29.63	100.57	2.53	5.5E-05	-4.256
			1	14	13	9.5	110.07	2.80	5.3E-05	-4.273
			1	15	22	40.59	150.66	3.95	5.3E-05	-4.277
	1		15	48	15.58	166.24	4.38	5.4E-05	-4.269	
	1		16	36	25.05	191.29	5.18	4.7E-05	-4.329	
	1		22	24	159.17	350.46	10.98	4.1E-05	-4.386	
	15/9/95		2	9	47	208.36	558.82	22.37	2.7E-05	-4.562
			2	13	32	46.07	645.02	26.12	2.7E-05	-4.569
		2	15	25	36.01	681.03	28.00	2.9E-05	-4.542	
	16/9/95	3	9	3	246.84	927.87	45.63	2.1E-05	-4.678	
		3	20	27	198.16	1126.03	55.82	2.9E-05	-4.536	
	d	14/9/95	1	11	25	0	0	0.00		
			1	12	5	59.3	59.3	0.67	0.000133	-3.875
			1	12	54	65	124.3	1.48	0.000119	-3.924
			1	13	9	18.84	143.14	1.73	0.000113	-3.947
			1	13	57	53.76	196.9	2.53	0.000101	-3.997
			1	14	13	19	215.9	2.80	0.000107	-3.972
			1	15	22	68.86	284.76	3.95	9E-05	-4.047
1			15	48	26.13	310.89	4.38	9E-05	-4.044	
1			16	36	42.16	353.05	5.18	7.9E-05	-4.103	
1			22	24	299.37	652.42	10.98	7.7E-05	-4.112	
15/9/95			2	9	47	457.36	1109.78	22.37	6E-05	-4.220
			2	13	32	109.32	1313.95	26.12	6.4E-05	-4.194
		2	15	25	84.91	1398.86	28.00	6.8E-05	-4.170	
16/9/95		3	9	3	598.13	1996.99	45.63	5.1E-05	-4.294	
		3	20	27	407.54	2404.53	55.82	6E-05	-4.222	
e		14/9/95	1	11	25	0	0	0.00		
			1	12	5	46.32	46.32	0.67	0.000104	-3.983
			1	12	54	48.18	94.5	1.48	8.8E-05	-4.054
			1	13	9	13.51	108.01	1.73	8.1E-05	-4.092
			1	13	57	37.8	145.81	2.53	7.1E-05	-4.150
			1	14	13	12.48	158.29	2.80	7E-05	-4.154
			1	15	22	50.3	208.59	3.95	6.6E-05	-4.184
	1		15	48	18.96	227.55	4.38	6.6E-05	-4.183	
	1		16	36	30.35	257.9	5.18	5.7E-05	-4.245	
	1		22	24	181.85	439.75	10.98	4.7E-05	-4.328	
	15/9/95		2	9	47	243.93	683.68	22.37	3.2E-05	-4.493
			2	13	32	57.12	790.64	26.12	2.3E-05	-4.642
		2	15	25	51	841.64	28.00	4.1E-05	-4.392	
	16/9/95	3	9	3	299.55	1141.19	45.63	2.5E-05	-4.594	
		3	20	27	195.45	1336.64	55.82	2.9E-05	-4.541	

Column	Date	DAY	HOUR	MIN	VOLUME CUMULATIVE (ml)	VOLUME CUMULATIVE (ml)	CUMULATIVE TIME (hrs.)	HYDRAULIC CONDUCTIVITY (cm/s)	logK
a	26/9/95	1	11	0	0	0	0	0	
	27/9/95	2	15	15	335	335	28.25	1.8E-05	-4.743
	28/9/95	3	16	20	352	687	53.33	2.1E-05	-4.670
	29/9/95	4	12	15	246	933	73.25	1.9E-05	-4.725
	30/9/95	5	9	35	221	1154	94.25	1.6E-05	-4.795
	1/10/95	6	13	27	287	1441	122.45	1.6E-05	-4.809
b	26/9/95	1	11	0	0	0	0		
	27/9/95	2	15	15	620	620	28.25	3.3E-05	-4.476
	28/9/95	3	16	20	573	1133	53.33	3.5E-05	-4.458
	29/9/95	4	12	15	412	1545	73.25	3.2E-05	-4.501
	30/9/95	5	9	35	349	1894	94.25	2.5E-05	-4.596
	1/10/95	6	13	27	435	2329	122.45	2.4E-05	-4.629

0.02M Na2CO3 leached columns (previously leached with 0.005M CaSO4)

A-7

COLUMN	DATE	DAY	HOUR	MIN	VOLUME (ml)	CUMULATIVE VOLUME (ml)	CUMULATIVE TIME (hrs)	HYDRAULIC CONDUCTIVITY (cm/s)	logK
a	18/09/95	1	11	53	0	0	0.00		
		1	16	15	35.1	35.1	4.37	1.2E-05	-4.91959
		1	16	30	2.15	37.25	4.62	1.3E-05	-4.88992
	19/09/95	2	8	50	23.78	61.03	20.95	2.2E-06	-5.66119
		2	13	45	6.27	67.3	25.87	1.9E-06	-5.71911
	20/09/95	3	8	43	11.16	78.46	44.83	8.8E-07	-6.05459
	b	18/09/95	1	11	53	0	0	0.00	
1			16	15	46.52	46.52	4.37	1.6E-05	-4.79726
1			16	30	4.61	51.13	4.62	2.8E-05	-4.55865
19/09/95		2	8	50	24.86	75.99	20.95	2.3E-06	-5.6419
		2	13	45	12.13	88.12	25.87	3.7E-06	-5.43252
20/09/95		3	8	43	18.84	106.96	44.83	1.5E-06	-5.82717
c		18/09/95	1	11	53	0	0	0.00	
	1		16	15	50.12	50.12	4.37	1.7E-05	-4.76489
	1		16	30	5.42	55.54	4.62	3.2E-05	-4.48836
	19/09/95	2	8	50	35.09	90.63	20.95	3.2E-06	-5.49222
		2	13	45	2.46	93.09	25.87	7.5E-07	-6.12545
	20/09/95	3	8	43	4	97.09	44.83	3.2E-07	-6.50019
	d	18/09/95	1	11	53	0	0	0.00	
1			16	15	46.33	46.33	4.37	1.6E-05	-4.79903
1			16	30	2.8	49.13	4.62	1.7E-05	-4.7752
19/09/95		2	8	50	8.32	57.45	20.95	7.6E-07	-6.11728
		2	13	45	12.83	70.28	25.87	3.9E-06	-5.40815
20/09/95		3	8	43	4.81	75.09	44.83	3.8E-07	-6.42011
e		18/09/95	1	11	53	0	0	0.00	
	1		16	15	38.74	38.74	4.37	1.3E-05	-4.87674
	1		16	30	3.98	42.72	4.62	2.4E-05	-4.62247
	19/09/95	2	8	50	13.7	56.42	20.95	1.3E-06	-5.90068
		2	13	45	2.58	59	25.87	7.9E-07	-6.10476

Hydraulic conductivity measurements for columns leached with BP10

COLUMN	DATE	DAY	HOUR	MINUTE	VOLUME (ml)	CUMULATIVE VOLUME (ml)	CUMULATIVE TIME (hrs.)	HYDRAULIC CONDUCTIVITY (cm/s)	log(K)	pH	EC(dS/m)		
BP10- drya	26/09/95	1	12	45	0	0	0						
		1	14	23	19	19	1.63	1.6E-05	-4.798	7.6	13.81		
		1	17	20	36	55	4.58	1.7E-05	-4.777	7.48	11.94		
	27/09/95	2	8	30	133	188	19.75	1.2E-05	-4.920	7.92	12.6		
		2	17	25	75	263	28.67	1.2E-05	-4.938	8.89	14.52		
	28/09/95	3	9	20	92	355	44.58	7.9E-06	-5.101	9.38	17.63		
		3	15	12	31	386	50.45	7.2E-06	-5.140	9.55	19.29		
	29/09/95	3	16	30	13	399	51.75	1.4E-05	-4.863	9.55	19.58		
		4	10	0	102	501	69.25	8E-06	-5.098	9.65	21.3		
	30/09/95	4	14	30	29	530	73.75	8.8E-06	-5.054	9.78	20.6		
		4	16	20	12	542	75.58	9E-06	-5.047	9.8	23		
	3/10/95	5	10	30	110	652	93.75	8.3E-06	-5.081	9.83	23.7		
		8	12	15	0	652	167.50						
	4/09/95	8	14	35	15	667	169.83	8.8E-06	-5.055	9.8	23.4		
		8	16	40	13	680	171.92	8.6E-06	-5.068	9.81	24.1		
		9	8	40	100	780	187.92	8.6E-06	-5.067	9.78	24.7		
		9	11	45	21	801	191.00	9.3E-06	-5.030	9.85	25		
		9	16	0	26.5	827.5	195.25	8.5E-06	-5.068	9.86	25.6		
		BP10 dryb	27/09/95	1	10	25	0	0	0.00				
1				13	30	75	75	3.08	3.3E-05	-4.477	7.33	12.83	
1				17	25	24	99	7.00	8.4E-06	-5.076	7.43	11.79	
28/09/95			2	9	20	150	249	22.92	1.3E-05	-4.889	8.96	14.92	
	2		15	12	79	328	28.78	1.8E-05	-4.734	9.39	19.2		
29/09/95	2		16	30	21	349	30.08	2.2E-05	-4.655	9.44	19.5		
	3		10	0	113	462	47.58	8.8E-06	-5.053	9.63	21.7		
30/09/95	3		14	30	18	480	52.08	5.5E-06	-5.261	9.83	23.3		
	3		16	20	8	488	53.92	6E-06	-5.223	9.83	23.5		
3/10/95	4		10	30	69	557	72.08	5.2E-06	-5.284	9.85	24.5		
	7		12	15	0	557	145.83						
4/09/95	7		14	35	9	566	148.17	5.3E-06	-5.277				
	7		16	40	10	576	150.25	6.6E-06	-5.182				
	8		8	40	71	647	164.17	7E-06	-5.155				
	8		11	45	14.8	661.8	167.25	6.6E-06	-5.182				
	BP10-CaSO4a		26/09/95	1	10	57	0	0	0.00				
				1	11	58	18	18	1.01	2.7E-05	-4.573	8.15	1.25
				1	14	23	35	53	3.43	2.2E-05	-4.664	8.2	1.18
			27/09/95	1	17	20	35	88	6.38	1.8E-05	-4.750	8.11	1.28
2		8		30	98	186	21.54	9.7E-06	-5.014	7.41	7.09		
28/09/95		2	17	25	69	255	30.46	1.2E-05	-4.936	7.41	11.27		
		3	9	20	66	321	46.38	6.2E-06	-5.207	8.59	12.82		
29/09/95		3	15	12	29	350	52.24	7.4E-06	-5.130	9.07	15		
		3	16	30	6	356	53.54	6.9E-06	-5.160	9.03	15.21		
30/09/95		4	10	0	78	434	71.04	6.7E-06	-5.175	9.3	16.83		
		4	14	30	19	453	75.54	6.3E-06	-5.199	9.57	19.7		
3/10/95		4	16	20	9	462	77.38	7.4E-06	-5.133	9.61	19.7		
		5	10	30	78	540	95.54	6.4E-06	-5.192	9.72	22		
4/09/95		8	12	15	0	540	169.29						
		8	14	39	10.9	550.9	171.69	6.8E-06	-5.167	9.83	22.9		
		8	16	40	13	563.9	173.71	9.7E-06	-5.015	9.81	23.2		
		9	8	40	90.5	654.4	189.71	8.5E-06	-5.072		24.8		
		9	11	45	18	672.4	192.79	8.7E-06	-5.058		25		
		9	16	0	23.6	696	197.04	8.3E-06	-5.080		25.4		

Hydraulic conductivity measurements for columns leached with BP10 (continued)

COLUMN	DATE	DAY	HOUR	MINUTE	VOLUME (ml)	CUMULATIVE VOLUME (ml)	CUMULATIVE TIME (ml)	HYDRAULIC CONDUCTIVITY (cm/s)	log K	pH	EC(dS/m)	
BP10- distilled water	10/10/95	1	10	25	0	0	0					
	11/10/95	2	11	0	187	187	24.58	1.1E-05	-4.943			
	12/10/95	3	8	55	52	239	46.5	3.6E-06	-5.449			
		3	15	10	14	253	52.75	3.4E-06	-5.474			
		3	16	15	48.5	301.5	53.88	6.4E-05	-4.192			
	13/10/95	4	12	12	34	335.5	73.78	2.6E-06	-5.592			
	14/10/95	5	9	17	39	347.5	94.87	2.8E-06	-5.557			
	14/10/95	5	13	49	7	381.5	99.31	2.4E-06	-5.627			
	15/10/95	6	8	55	42	423.5	118.41	3.3E-06	-5.482			
	16/10/95	7	9	15	557	480.5	142.74	3.4E-05	-4.465			
	17/10/95	8	10	45	62	542.5	168.24	3.6E-06	-5.439			
19/10/95	10	13	30	135	677.5	218.99	4E-06	-5.400				
20/10/95	11	9	12	43	720.5	238.69	3.3E-06	-5.485				
BP10- Na ₂ CO ₃	10/10/95	1	10	25	0	0	0					
	11/10/95	2	11	0	117	117	24.58	7.1E-06	-5.147			
	12/10/95	3	8	55	58	175	46.5	4E-06	-5.402			
		3	15	10	56	237	52.75	1.3E-05	-4.872			
		3	16	15	27	258	53.88	3.6E-05	-4.446			
	13/10/95	4	12	12	248	506	73.78	1.9E-05	-4.729			
	14/10/95	5	9	17	281	787	94.87	2E-05	-4.700			
BP10-Na ₂ CO ₃ a	27/09/95	1	10	25	0	0	0					
		1	15	20	22	22	4.92	6.7E-06	-5.174	8.27	0.811	
		1	17	25	16	38	7.00	1.2E-05	-4.939	7.42	3.83	
	28/09/95	2	9	20	185	223	22.92	1.7E-05	-4.759	7.29	8.96	
		2	15	12	62	285	28.78	1.6E-05	-4.800	7.33	10.01	
		2	16	30	19.4	304.4	30.08	2.2E-05	-4.651	8.45	12.49	
	29/09/95	3	10	30	244	548.4	48.08	2E-05	-4.692	9.19	18.7	
		3	14	30	53.8	602.2	52.08	2E-05	-4.696	9.22	21.3	
		3	16	35	33.5	635.7	54.17	2.4E-05	-4.618	9.28	22.6	
	30/09/95	4	10	28	256	891.7	72.05	2.1E-05	-4.669		24.8	
		3/10/95	7	12	15	0	891.7	145.83				
			7	14	39	59.1	950.8	148.23	3.7E-05	-4.433		
			7	16	40	48	998.8	150.25	3.6E-05	-4.448		
		4/09/95	8	8	40	320	1318.8	166.25	3E-05	-4.523		
			8	11	45	59.5	1378.3	169.33	2.9E-05	-4.539		
			8	16	0	74.2	1452.5	173.58	2.6E-05	-4.582		
	BP10-Na ₂ CO ₃ b	26/09/95	1	10	57	0	0	0				
		1	13	27	5	5	2.50	3E-06	-5.523	7.98	0.948	
		1	14	23	4	9	3.43	6.4E-06	-5.192	7.96	2.06	
		1	17	20	29	38	6.38	1.5E-06	-4.832	7.7	4.09	
27/09/95		2	8	30	227	265	21.55	2.2E-05	-4.649	7.5	8.91	
		2	17	25	93	358	30.47	1.6E-05	-4.806	8.57	13.38	
28/09/95		3	9	20	164	522	46.38	1.5E-05	-4.811	9.48	17.45	
		3	15	12	82	604	52.25	2.1E-05	-4.679	9.58	18.72	
		3	16	30	20	624	53.55	2.3E-05	-4.637	9.57	19.56	
29/09/95		4	10	0	190	814	71.05	1.6E-05	-4.789	9.69	21.7	
		4	14	30	78	892	75.55	2.6E-05	-4.586	9.79	22.3	
		4	16	20	29	921	77.38	2.4E-05	-4.625	9.82	23	
30/09/95		5	10	30	296	1217	95.55	2.4E-05	-4.612	9.83	23.4	
		3/10/95	8	12	15	0	1217	169.30				
			8	14	39	47	1264	171.70	2.9E-05	-4.533		
			8	16	40	43	1307	173.72	3.2E-05	-4.496		
		4/09/95	9	8	40	311	1618	189.72	2.9E-05	-4.536		
		9	11	45	58	1676	192.80	2.8E-05	-4.550			
		9	16	0	81	1757	197.05	2.9E-05	-4.544			

Appendix C

Details of organic analysis and raw data from sorption trials

Analysis of organic constituents of BP10 and synthetic aqueous phenol solutions was performed by SASOL Chromatographic Services at Secunda. The analysis was done gas chromatographically via GC/FID using a 60m Carbowax 20M macropore capillary column. Quantification was achieved via external calibration.

The results of the phenol sorption experiments on treated clays using synthetic aqueous phenol solutions are as follows:

Table A.1 Results from phenol sorption experiments

Sorbing medium	phenol added (mg)	phenol remaining (mg)	phenol sorbed (mg/kg)	equilibrium conc. (mmol/L)
HDTMA Rensburg	0.096	0.08	183.9	.034
	.192	.153	454	.065
	.293	.270	264.4	.115
	.823	.578	2816	.245
HDTMA bentonite	.096	.083	161	.035
	.192	.163	351	.070
	.293	.308	0	.131
	.823	.668	1845	.284
	1.53	1.55	0	.661
	3.84	3.69	1726	1.57
Ca bentonite	.192	.19	0	.079
	.293	.405	0	.172
	.823	.893	0	.379
Ca Rensburg	.096	.083	49	.014
	.192	.173	80.2	.073
	.293	.35	0	.148
	.823	.85	0	.361
	1.53	1.58	0	.671
Rensburg soil	.293	.35	0	.149
	.823	.73	102	.308
	1.53	1.15	10.3	.487
	3.84	4.22	0	1.79