DEPARTMENT OF TRANSPORT

TOWARDS SUCCESSFUL SPP TREATMENT OF LOCAL MATERIALS FOR ROAD BUILDING

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SYNOPSIS: This report discusses the use of certain proprietary soil stabilisers in low volume roads in South Africa. Although ionic soil stabilisers have been in use for many years, they have not been marketed to their fullest potential and in many cases have not performed up to expectation. Recent work has shown that, provided they are used in the right context with suitable natural soils, significant savings can be achieved, particularly in low volume roads. This could be particularly beneficial in view of the increasing need for improvement of the rural road network and of roads associated with the Reconstruction and Development Program (RDP). Recommendations for testing materials for compatibility with SPPs are provided. In addition, a detailed construction procedure and recommendations on quality control, which have been found to improve the success rate of the products significantly, are provided.	SINOPSIS: Die gebruik van ioniese grond stabiliseerders in lae volume paaie in Suid Afrika word in hierdie verslag bespreek. Alhoewel ioniese grond stabiliseerders reeds vir 'n geruime tyd gebruik word, is dit nog nie ten volle bemark nie. Onlangse werk het getoon dat aansienlike besparings moontlik is, veral op lae volume paaie, as dit in die regte konteks met toepaslike gronde gebruik word. Dit kan veral voordelig wees in die lig van die toenemende behoefte om die plattelandse paaienetwerk te verbeter en in paaie onder die Heropbou en Ontwikkelings Program (HOP). Aanbevelings word gemaak rakende die bepaling van die versoenbaarheid van die stabiliseerders en gronde. Verder word 'n konstruksiemetode voorgestel en aanbevelings word gemaak rakende kwaliteitsbeheer, wat die sukses met die gebruik van die produkte aansienlik verbeter.

TREFWOORDE: Lae volume paaie, stabilisering, gronde, stabiliseerders, ioniese grond stabiliseerders.
KEYWORDS: Low volume roads, materials, stabilisers, ionic soil stabilisers.

DISCLAIMER

The views and opinions expressed in this report are those of the authors and do not necessarily represent Department of Transport Policy.

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This report has been reviewed.

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SUMMARY

With the increasing necessity for reducing the cost of road construction, the innovative application of local materials is becoming more important. Mechanical methods of stabilisation have been used for many years but rely on the local availability of suitable materials for blending. Methods for stabilising soils by the addition of chemicals were already known and in use in ancient Mesopotamia and Egypt and lime stabilisation was used in the Roman Empire and in Greece. However, as traffic increased, roads needed to be developed quickly and to a high standard and only in the early twentieth century were cement, lime, bitumen and certain chemicals first routinely employed for road construction purposes. The advantage of chemical stabilisation is that only small volumes of stabilising agent are typically required and most materials can be stabilised with one or more of the available stabilising agents.

Traditionally, road construction materials have been specified and selected to meet certain criteria known to provide an adequate structural layer. As roads started carrying heavier traffic the necessary material requirements became stricter and the winning and processing of the materials became increasingly complex e.g. G1 materials. Standard design recommendations do not cater adequately for traffic volumes of less than 200 vpd. The material requirements for lightly trafficked roads can be substantially lower than that for heavily trafficked roads and as much recourse as possible should be made to the use of local or even in-situ materials. These materials may need to be blended, modified or improved, using a combination of blending and modification if necessary, to produce appropriate pavement materials. The use of local materials, particularly of in-situ soils, has the added advantage of reducing the environmental impact of road construction.

The main parameter of critical importance in any construction material is the influence of moisture on the strength properties. A cursory study of nearly any road materials manual or failure investigation will clearly show the consequences of excessive moisture in a road. One of the main reasons for moisture-related road failures is the moisture susceptibility of clay minerals, which, although not consciously built into roads, are frequently generated from partly weathered aggregates. Should local materials be used for structural layers in low volume roads, the probability that a greater percentage of clay minerals will be present increases significantly. This usually results in significantly increased moisture sensitivity of the material, with concomitant problems in retaining shear strength. In order to utilise clay-bearing natural materials with any degree of confidence some type of "water-proofing" mechanism is necessary.

The chemistry and physical structure of clays and the products is analysed in some detail in order to establish what processes are involved in the "stabilisation" reactions. This was considered necessary in order to be able to work from the basic principles and thus to develop test methods

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which identify and quantify these processes. The possible interrelationships between the product and soils is evaluated and recommendations regarding techniques for testing the products and their application and quality control are discussed.

This report discusses some of the background to the locally available products loosely termed "sulphonated petroleum products", or SPPs, all of which apparently evolved from the original Reynolds Road Packer produced in the United States in the early sixties. The behaviour of all the products under investigation, however, is apparently mainly related to their ability to influence the properties and moisture susceptibility of clayey materials.

The testing techniques and procedures currently used for material characterisation in road construction have generally proved to be unsuitable for testing SPP-treated materials. The only fully documented "specification" for SPPs has been produced in Hungary but is fairly general and does not appear to be satisfactory for southern African conditions. Standard engineering tests carried out locally on materials treated with SPP generally showed no improvements in the characteristics of the materials. The soaked CBR strength typically decreased. This was ascribed to the lubricating action of the SPP. Transportek thus thought it necessary to evaluate these products using more appropriate test methods. As the ion exchange reaction was considered to be the principal mechanism by which SPPs improved soils, basic research from first principles was directed in this direction. For this purpose the electro-chemical aspects of clays, specifically their cation exchange capacity, were researched. At the same time, the Natal Roads Department (particularly the Estcourt region) was carrying out field and laboratory testing. It developed a system by which the clay component of soils was investigated by means of X-ray diffraction methods and, based on these results, a more appropriate application rate for the SPP was selected. In this way marked increases in CBR strength could be obtained without the material being overdosed or excessive lubrication being caused. Subsequent research has involved the application of the test methods to various soils in an attempt to develop specifications for the successful use of SPPs.

Investigation and observation of numerous SPP-treated roads during construction and with time after construction have shown that the construction procedure and quality control during construction are critical for the successful performance of the road. Many of the problems on roads showing failures and poor performance can be attributed, firstly, to poor construction procedures and secondly to inadequate quality control during construction. Much of the reported poor performance of SPP-treated materials is the result of poor construction and, in fact, recent work has shown that even materials marginal in relation to the specifications listed above can perform well if proper construction techniques are used. A construction process is recommended and certain properties requiring careful control during construction are discussed.

1 INTRODUCTION

As South Africa approaches the twenty first century, its development potential and population continue to increase and the need for improving and upgrading roads in developing rural areas is becoming more important and urgent. A recent research project[1] has clearly indicated a significant backlog in the provision of appropriate roads to the poorer urban and rural sectors of the community.

With the increasing necessity for reducing the cost of road construction, the innovative application of local materials is becoming more important. Innovative methods of using local materials range from reducing the standard specifications to more appropriate limits for the level of traffic and the service required, thus allowing their use (albeit with a higher risk) to the modification and improvement of the local materials, which could be achieved either through mechanical or chemical means.

Mechanical methods of stabilisation have been used for many years but rely on the local availability of suitable materials for blending. Methods for stabilising soils by the addition of chemicals were already known and in use in ancient Mesopotamia and Egypt and lime stabilisation was used in the Roman Empire and in Greece[2]. However, as traffic increased, roads needed to be developed quickly and to a high standard and only in the early twentieth century were cement, lime, bitumen and certain chemicals first routinely employed for road construction purposes. The advantage of chemical stabilisation is that only small volumes of stabilising agent are typically required and most materials can be stabilised with one or more of the available stabilising agents.

Since the middle of the 1960s, a number of proprietary ionic soil stabilising products consisting primarily of strongly acidic sulphur based bituminous products have been marketed in various countries. The United States, the Federal Republic of Germany, Hungary, certain south American countries and South Africa appear to have been the focal areas for their development and use. Their use in the United States appears to have decreased in the 1970s and 80s but there has been a recent resurgence in their use, with a number of authorities laying experimental sections.

For some reason, possibly a lack of scientific backup and controlled experimentation as well as recorded unsuccessful projects, the products have never been seen as having great significance in the road building industry. Other "tried and tested" chemical stabilisers such as lime, cement and bituminous products have continued to enjoy wide support, despite the significant economic advantages of ionic soil stabilisers.

In recent years there has been greater appreciation of the possible use of these products, following numerous successful projects. It should be recorded that a number of unsuccessful projects and experiments have also been reported. However, despite the time that the materials have been

available, there is still very little scientifically-based information on their performance and capabilities.

It was for this reason that the Division of Roads and Transport Technology (Transportek), CSIR became involved, partly on its own account and partly in collaboration with the Natal Roads Department and subsequently, the Department of Transport, in investigating the use of certain of the proprietary products as an "honest broker". Great potential is seen for the use of this type of product in developing areas should its performance prove to be predictable and reliable.

This report discusses some of the background to the locally available products loosely termed "sulphonated petroleum products", or SPPs, all of which apparently evolved from the original Reynolds Road Packer produced by Zell Chemicals in the United States in the early sixties. It should be noted that there may be significant differences between the products, and the generic name SPP is used mainly for simplicity. The behaviour of all the products under investigation, however, is apparently mainly related to their ability to influence the properties and moisture susceptibility of clayey materials.

The chemistry and physical structure of clays and the products is analysed in some detail in order to establish what processes are involved in the "stabilisation" reactions[a]. This was considered necessary in order to be able to work from the basic principles and thus to develop test methods which identify and quantify these processes. The possible interrelationships between the product and soils is evaluated and recommendations regarding techniques for testing the products and their application and quality control are discussed.

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[a]   The term stabilisation is used in its widest sense i.e. improvement of the material. SPP stabilisation cannot be realistically compared with lime or cement stabilisation, for example, as no cementing products are formed.

2   TRADITIONAL ROAD CONSTRUCTION MATERIALS

Traditionally road construction materials have been specified and selected to meet certain criteria known to provide an adequate structural layer. As roads started carrying heavier traffic the necessary material requirements became stricter and the winning and processing of the materials became increasingly complex e.g. G1 materials. The bulk of the road network currently required to meet the increased need for mobility and access, particularly in developing areas can, however, be considered to be lightly trafficked, carrying on average less than 200 vehicles per day. Standard design recommendations, such as the TRH series of documents[3,4] and the CSRA specifications,[5] do not cater adequately for this type of traffic, as they are based on a minimum design traffic of 200 000 standard axles per lane over the design life of the road. It should be borne in mind that even these designs are probably slightly conservative in order to ensure that the design lives of roads constructed in accordance with them are achieved.

The material requirements for lightly trafficked roads[6] can be substantially lower than, for example, those given in TRH4,[3] and as much recourse as possible should be made to the use of local or even in-situ materials. These materials may need to be blended, modified or improved, using a combination of blending and modification if necessary, to produce appropriate pavement materials. The use of local materials, particularly of in-situ soils, has the added advantage of reducing the environmental impact of road construction.

Traditional material requirements are typically based on standard indicator tests, such as particle size distribution, limits of consistency and laboratory strength under extreme conditions[4,7]. These tests and specifications have resulted from many years of experience (since the early part of the century) by trial and error, empirical studies, and more recently, from performance-related evaluations and full-scale controlled experimental sections.

This experience has resulted in a number of criteria which ensure that the materials develop adequate in-situ strength and retain this strength under the worst conditions likely to prevail in the road. These worst conditions are normally associated with high moisture contents at which materials with a clay-mineral (phyllosilicate) component may decrease significantly in strength. An approximate indication of the clay mineral component of a material can usually be obtained from the Atterberg limit tests, whilst its particle size distribution is an indicator of its densification and interlocking properties (with reference to a Fuller-type grading), its permeability and workability in terms of construction processes. The strength of the material is strongly dependent on these same properties but is typically measured directly (e.g. CBR test).

The main parameter of critical importance in any construction material is the influence of moisture on the strength properties. A cursory study of nearly any road materials manual or failure

investigation will clearly show the consequences of excessive moisture in a road. One of the main reasons for moisture-related road failures is the moisture susceptibility of clay minerals, which, although not consciously built into roads, are frequently generated from partly weathered aggregates[8].

Should local materials be used for structural layers in low volume roads, the probability that a greater percentage of clay minerals will be present increases significantly. This usually results in significantly increased moisture sensitivity of the material, with concomitant problems in retaining shear strength. This is one of the main factors currently mitigating against the use of many local materials as structural layers in roads.

In order to utilise clay-bearing natural materials with any degree of confidence some type of "water-proofing" mechanism is necessary. One of the objectives of this project is to determine whether the process of "water-proofing" described by the suppliers/manufacturers of these products does in fact occur. Preliminary evaluations of these products in other projects has shown that this does indeed occur in certain instances[9].

It should be noted that the term "water-proofing" in this report refers to the action of making their strength less moisture dependent by inhibiting the adsorption of water onto the clay particles.
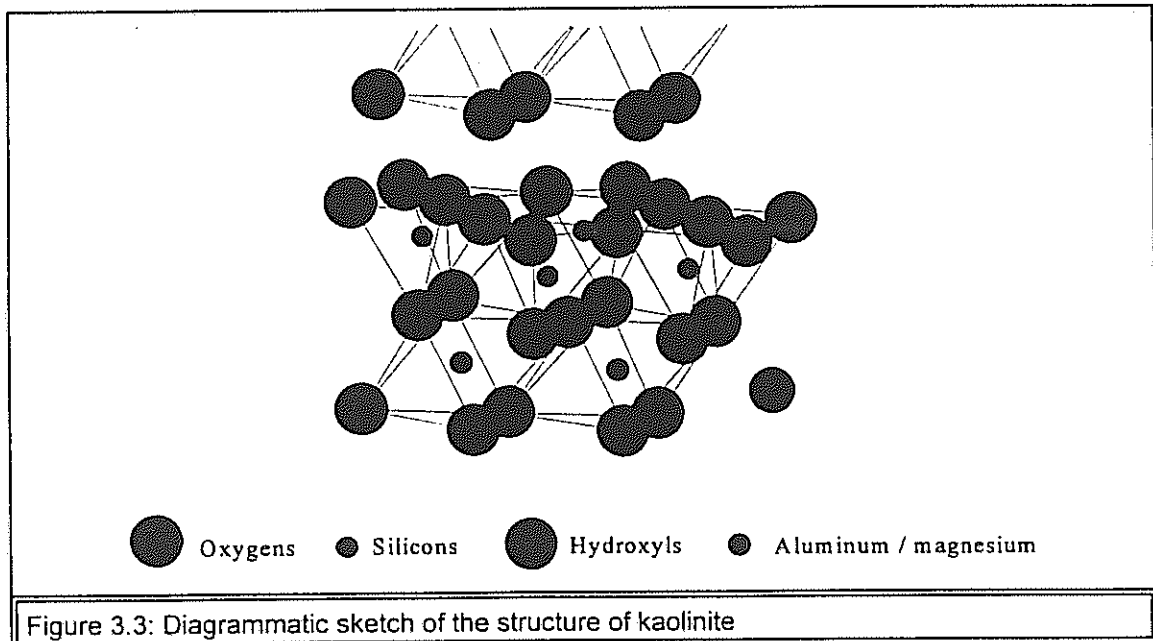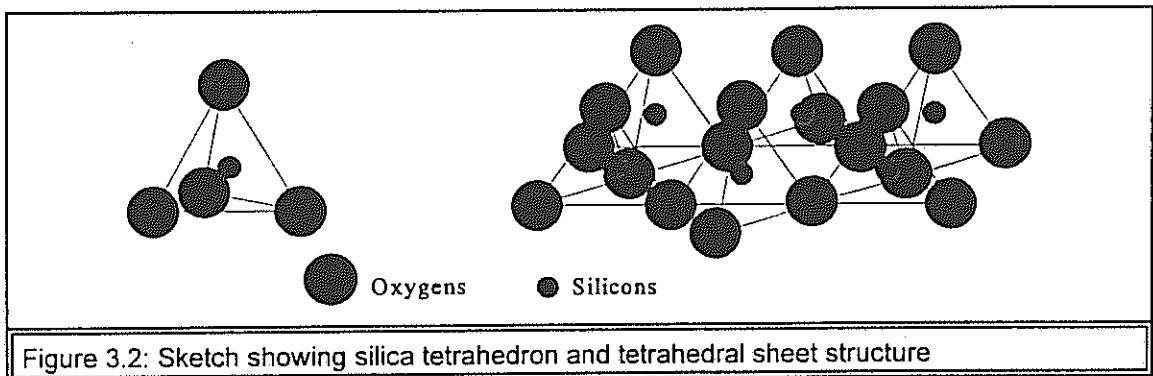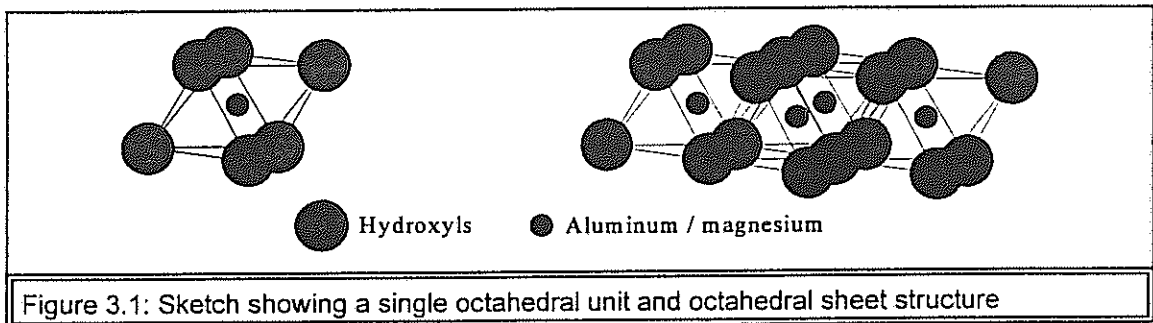
3   PROPERTIES OF CLAY MINERALS

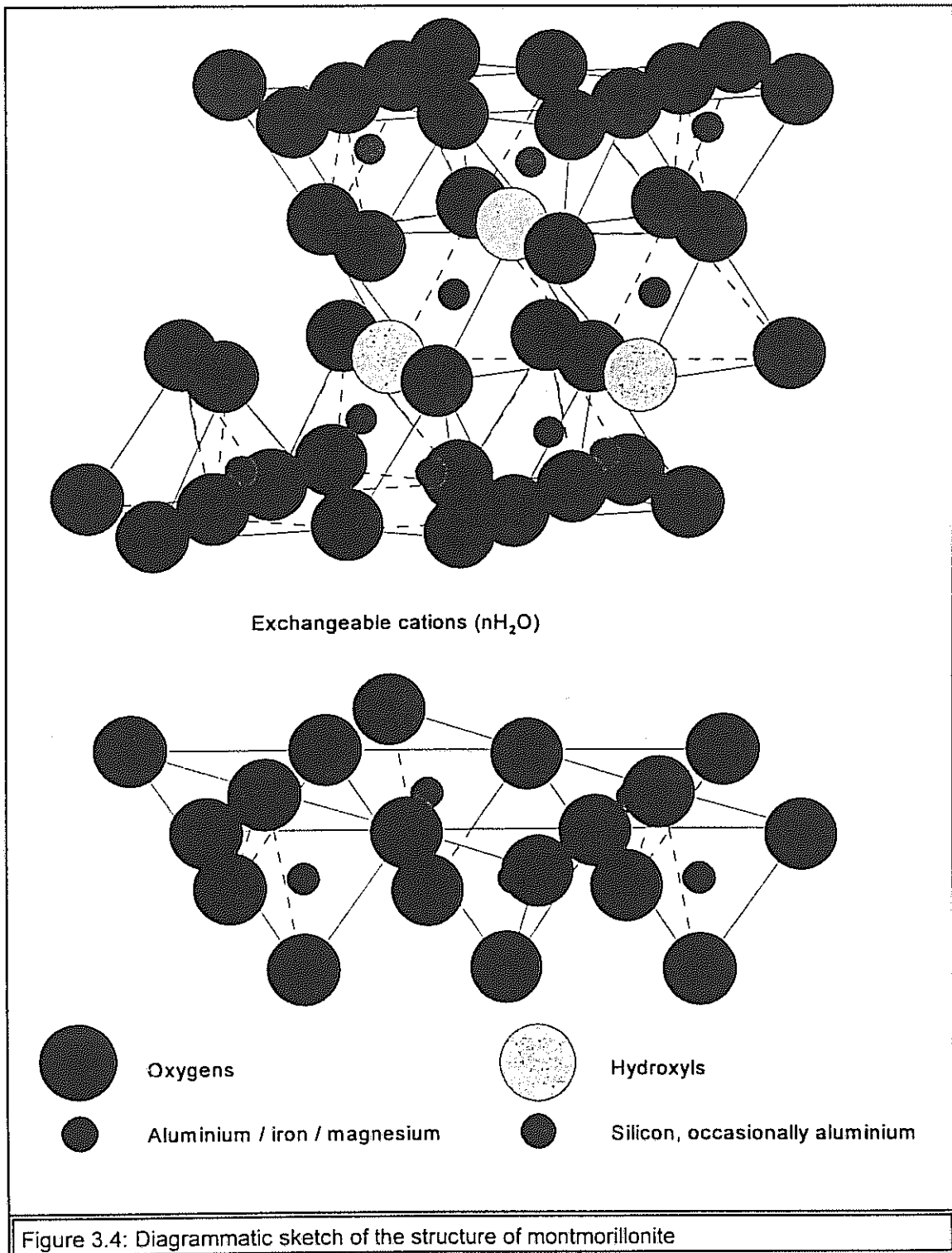## 3.1   CHEMICAL AND PHYSICAL CHARACTERISTICS OF CLAYS

Clays are a specific group of silicate minerals (phyllosilicates) consisting primarily of hydrous alumino-silicates. Clays are developed most abundantly from the weathering of minerals such as feldspars, amphiboles, pyroxenes and micas. They are very fine-grained (by definition less than 0,002 mm) and have structures composed of various combinations of sheets of alumina octahedra and silica tetrahedra which are polymerised in two directions (Figures 3.1 and 3.2). The sheets or layers are held together by different forces in different minerals but the interlayer bonding is always weaker than that within the layers[10]. This results in a pronounced cleavage in the plane parallel to the sheets. Depending on the relative sequence of these sheets, different clay minerals with unique properties are formed. For example, in minerals of the kaolinite group (kaolinite, dickite, halloysite) one tetrahedral sheet is combined with one octahedral sheet (a 1:1 type mineral) (Figure 3.3). The combination results in the replacement of two thirds of the hydroxyl ions in one plane of the octahedral sheet by the apical oxygens of the tetrahedral sheet.

A 2:1 type of layer structure results when a second tetrahedral layer is added in a similar manner with replacement of the hydroxyl ions in the sheet on the opposite side of the octahedral sheet. This results in two tetrahedral sheets which sandwich an octahedral sheet and is the basic structure of the smectite, vermiculite and mica groups of clay minerals (Figure 3.4). The chlorite group of minerals has an additional octahedral layer between successive 2:1 sheets. The clay minerals themselves are formed by stacking the basic clay structures (theoretically infinite in size in the x and y planes) in the z plane, with weak bonds between the oxygen atoms at the top of one layer and either the oxygen or hydroxyls beneath the overlying layer.

There is a slight difference in size between the octahedral and tetrahedral sheets which results in some misfit in the interlocking process and causes internal stress within the clay structure. Relief from this may be sought internally through ionic substitution or even by rotation of the tetrahedra. It is also possible for isomorphic substitution of the constituent metal ions to take place, e.g. aluminium may replace some of the silicon and magnesium may replace aluminium, etc. This results in charge imbalances which are typically compensated for by the adsorption of exchangeable ions and water molecules in interlayers and on particle surfaces. The small size and platy or sheet-like structure of clays results in a very high specific surface (surface area per unit mass) and, by definition, places them within the limits of the colloidal state. Because of their small size, their composition and structure has been determined largely by X-ray diffraction methods and electron microscopic work. The charge is thought to occur as discrete charges rather than as a uniform distribution over the surface[10]. Quantification of the charges in this type of situation is usually best

done by calculation but the heterogeneity of clay minerals means that in practice measurement of the cation exchange capacity is the only feasible method.

Figure 3.1: Sketch showing a single octahedral unit and octahedral sheet structure

Figure 3.2: Sketch showing silica tetrahedron and tetrahedral sheet structure

Figure 3.3: Diagrammatic sketch of the structure of kaolinite

Exchangeable cations (nH$_2$O)

Oxygens

Hydroxyls

Aluminium / iron / magnesium

Silicon, occasionally aluminium

Figure 3.4: Diagrammatic sketch of the structure of montmorillonite

The surfaces of all materials have distinctive physico-chemical properties caused by surface strain resulting from the imbalance of "nearest neighbours" at the material surface[10] i.e. one direction is bounded by space and surface atoms are thus pulled by attractive forces most strongly on the side facing inwards. This is particularly important when the individual particles are very small. It has also

been found that negative charges tend to be concentrated on the flat surfaces of the clays whilst the positive charges are apparently concentrated on the edges[10].

It should be noted that the complex ionic structures and the charge imbalances of clay minerals result in the minerals being effectively polar. When they are in contact with liquids, solutions or suspensions containing other polar substances, both positive and negative electrical attractions can occur[11].

3.2   CLAY-WATER SYSTEM

The weak bond between the stacked clay sheets and the ionic charge associated with them is responsible for one of the most important features of clay minerals, namely their ability to attract water and other polar molecules into the gaps between the unit layers. The movement of water to and from these layers results in volumetric changes within the clays, particularly montmorillonite or smectite clay minerals. Two types of water are important in the study of clay-water interaction:

a)   Absorbed water

b)   Adsorbed water

3.2.1 Absorbed water

Absorbed water is typically found in the voids and capillaries of soils. It is held in place by gravity and capillary suction (or surface tension effects). It is usually this water which is measured in oven-dried gravimetric moisture determinations. It can simply be described as an indication of the sponge-like properties of the material. This water affects the total strength of the material through the pore water pressure and the effective stress developed under loading. The rate of dissipation of pore water pressure is a function of the permeability of the material.

3.2.2 Adsorbed water

Adsorption is the phenomenon in which matter concentrates at a surface or interface such that the concentration can relieve unfavourable energy situations. This is typically the case when water is adsorbed to the edges or faces of clay minerals to alleviate charge imbalances.

Adsorbed water has a microscopic effect on the behaviour of soil. This water is attached by electro-chemical means to the clay mineral surfaces and edges and in the interlayers between the clay sheet units and considerable energy is required to drive it off. Although the loss of adsorbed water is initiated at temperatures below, but approaching 100°C, it continues until the last interlayer water is removed at temperatures usually in excess of 300°C, after which dehydroxylation (decomposition of the hydroxyl molecules) is initiated. In smectites, vermiculites and attapulgites, this water may occur in interlayer positions or within structural channels. Much of the adsorbed water can be

regained at ordinary temperatures. It is generally agreed that this adsorbed water, directly adjacent to the clay mineral surfaces, has a structure other than that of liquid water. Because of the polar nature of the water molecule and the mode of attachment to the clay particles, strong density gradients occur within the water molecules near the clay particle and the water is often described as non-liquid[11]. The non-liquid water may extend out from the clay mineral surfaces by as much as 60 to 100 Å[12]. However, as the thickness of the adsorbed water increases outward from the surface, the nature of the water changes, sometimes abruptly, other times gradually, to that of liquid water. Ions and molecules adsorbed on the clay mineral surface exert a major influence on the thickness of the adsorbed water layers and on the nature of this water.

The adsorbed water, together with the associated counter ions (balancing the overall negative charge on the particle) typically surrounds the colloidal clay particles and is referred to as the electrical double layer or diffuse double layer. This "solution" consists of highly mobile ions surrounded by water molecules and is referred to as the micellar solution and the whole clay system as the colloidal micelle. A concentration gradient exists within the double layer, decreasing outwards. The study of the effects and consequences of the double layer is highly complex and is not entered into in great detail in this report. A full discussion is given by Gillott[10]. The thickness and nature of this layer is, however, critical with respect to the properties of the clay mineral, providing a lubrication effect in terms of shear strength and compaction (through the plasticity), but resisting densification because of the incompressibility and elastic response of the water.

Water may also be attached to the clay minerals through direct hydration of the exchangeable cations associated with the mineral. Since the cations cannot escape from the clay particle, neither can the water of hydration. This mechanism is particularly important at low water contents[13].

It has also been shown that the water adsorption of many clay minerals can be significantly reduced by the treatment of the clay minerals with various organic molecules[11,13].

3.3 CATION EXCHANGE CAPACITY

As discussed earlier, the unique structure and composition of clays result in an imbalance in the electrical charge of the clay minerals. This is mostly compensated for by the adsorption of cations and anions onto the clay surface in an exchangeable state. The nature and number of the ions on the clays affect the properties of the material, especially its plasticity and water retention properties. This is clearly illustrated if the sodium ions in a montmorillonite clay with a plasticity index (PI) of 600 are exchanged with calcium ions. The plasticity index decreases to about 50[13]. Many examples of these changes, which indicate the importance of cations in clays, are cited in the literature and this phenomenon is clearly illustrated by reduction in the plasticity of most soils treated with hydrated lime ($Ca(OH)_2$).

The cation exchange capacity of a soil (a measure of the potential of the clay components of a soil to exchange cations) depends on a number of factors:

- **Quantity of clay and silt fractions**: The absolute quantity of clay minerals as well as the relative proportions of the different clay mineral types. Silt fractions may also have an appreciable exchange capacity caused mostly by surface effects. Finer textured soils tend to have higher cation exchange capacities than sandy soils.

- **Type of clay mineral present**: A small quantity of montmorillonite or vermiculite will have a greater exchange capacity than a much larger amount of kaolinite or illite. Interlayering of the clays can also have a profound effect. The ion-exchange capacity figures for the clay fractions are only an indication of the clay minerals present when mixtures of clay minerals occur. Because of this, the exchange-capacity figure should not be used for identification of the clay minerals. The data should be supplemented by X-ray diffraction study. A marked difference between the cation exchange capacities of clay soils can be caused by the dominance of either 1:1-type clays or of 2:1-type clays[14].

- **Physico-chemical properties of the clays**: This includes such aspects as the degree of crystallisation of the clay minerals, the incumbent cations, the hydration and dehydration history of the soil and the pH of the material. This latter aspect is particularly important when the cation exchange capacity is measured, as variations in the pH of a soil or any additives to it may alter the cation exchange capacity significantly. It is important therefore that the parameter is measured at an appropriate pH.

- **Amount of organic and amorphous matter present**: The presence of organic matter and amorphous material increases the exchange capacity irrespective of the clay minerals present. Within a given soil textural group, organic matter content, together with the amount and kind of clay, influence the exchange capacity.

Typical cation exchange capacities of various clay minerals are summarised in Table 3.1[15].

Variation in the exchange capacity of the individual minerals is caused by differences in the availability of exchange sites (i.e. the position of negatively charged spots on the particles) and by the chemical composition initiating the negative charges. Irregularities in the lattice structure and variation in grain size increase the ion-exchange capacity by providing a greater number of unsatisfied bonds at the edges. This is particularly noticeable in kaolinite and halloysite.

Mineral	Structural control	Exchange capacity, meq/100g at pH=7
Kaolinite	Unsatisfied valences on edges of structural units.	3-15
Halloysite (2H$_2$O)	Unsatisfied valences on edges of structural units.	5-10
Halloysite (4H$_2$O)	Unsatisfied valences on edges of structural units and on internal surface between the layers.	40-50
Montmorillonite group	Substitutions in the octahedral and tetrahedral units giving excess negative charge, unsatisfied valences on edges of units.	70-100
Illites (hydrous micas)	As in montmorillonite, plus deficiency of K$^+$ between the layers.	10-40
Vermiculite	Replacement of interlayer cations, substitution within the units, and unsatisfied valences on edges of units	100-150
Chlorite	No data. Possible deficiency of charge due to substitution in the brucite layer	10-40
Glauconite	As in illites	11-20+
Palygorskite group	Substitution of Al^{+3} for Si^{+4} in structural units, unsatisfied exchange sites within channels in the structure	20-30
Allophane	Porous amorphous structure with unsatisfied valences	70

Table 3.1: Cation exchange capacity of clay minerals[15]

The cation exchange capacity increases as the grain size of a clay mineral decreases, as the surface area is larger and there are more broken bonds. The exchange capacity of kaolinite with a specific surface area of 10 square metres per gram (m^2/g), increases from about 2 milliequivalents per 100 gram (meq/100g) to 8 meq/100g when the specific surface area is 40 m^2/g. Further reduction in grain size, which often goes together with disordered lattice structure, tends to produce a mineral amorphous to X-rays. Minerals with a disordered lattice structure have higher exchange capacities than larger, better crystallized grains of similar composition because of increased surface area and more broken bonds. Materials like silica gel have exchange capacities in the range of 70 to 100 meq/100g. However, such exchange is related more to adsorption than to true cation exchange.

In the inorganic part of most soils, the figures obtained for cation exchange are those produced by mixtures of clay minerals. Attempts have been made to characterize such clays from X-ray diffraction data.

Ion exchange takes place when a solution containing cations and anions comes into contact with a mineral surface. The reactions are the result of the chemical elements in the solution coming into contact with the mineral. The structural causes of cation exchange in the clay minerals are:

- Unsatisfied valences produced by "broken bonds" at surfaces and edges of particles
- Unbalanced charges caused by isomorphous substitution of cations - for example, Al^{+3} substituted for Si^{+4}
- Dissociation of structural OH^- radicals, the H^+ of which may be replaced by metallic cations
- Accessibility of structural cations other than H^+, which become exchangeable under certain conditions; e.g. at low pH values Al^{+3} ions move from the octahedral units to the exchange positions.

The principal cause of cation exchange in montmorillonites, illites and vermiculites is isomorphous replacement. "Broken bonds" are the most important cause of cation exchange in kaolinite, halloysite, and in fine particles of other minerals such as quartz.

The micelles of clay minerals present a number of charged spots which attract cations and anions in a solution surrounding the micelles. Ion exchange is thus, in part at least, a surface phenomenon, as even the interlayer cations can be considered as part of an extended surface. The fact that there are different positions for the negative charges on the clay micelles, which are themselves electrically charged colloidal particles, causes replacement to take place at different levels. Thus, in montmorillonite, exchange takes place at three sites: on the flat surfaces, at the edges, and between the silica and alumina layers where ions are loosely held to neutralize deficiencies in these layers caused by isomorphous replacements. The excess negative charge on the mineral is neutralised by an equivalent quantity of positive ions. In nature the most common exchangeable cations are Ca^{+2}, Mg^{+2}, H^+, Na^+ and K^+. Calcium is the dominant cation in soil clay minerals.

Ion exchange takes place in a water film which surrounds a micelle of clay or a mineral grain. As discussed in an earlier section, this water film is considered to be a diffuse double layer. The double layer is a space containing water and an ion swarm which is dependent on the surface-charge density of the mineral surface (the surface of the clay micelle), the kinds of exchangeable cations, the concentration of electrolytes in the solution, and to a lesser extent, on the temperature. The charge density of the clay-mineral surface depends on the kind of mineral and on the cations (and anions) already present. The exchangeable cations are held to the mineral surface by coulomb forces.

There are a number of theories for the distribution of positive and negative ions in the double layer. It is considered that the diffuse double layer at a plane surface (the surface of the material) has a

negative charge. The concentration of the exchangeable ions is highest in the immediate vicinity of the surface and decreases towards the intermicellar surface of uniform composition. The double layer contains ions with negative as well as those with positive charges, which come from the free electrolyte (the solution in contact with the mineral).

It has been shown that the clay minerals vary, because of their structure, in the amount of inherent and accidental charges. It has also been pointed out that particle size, porous structure and charged framework are all important features of ion exchange. Minerals with a charged framework, such as montmorillonite, have a high exchange capacity because of substitutions within the tetrahedral and octahedral layers producing a strong negative charge which holds exchangeable cations between the structural composition with little or no substitution in the units. This charge is solely due to unsatisfied valences at the edges of the micelles. The number of such broken bonds depends on the particle size. Thus a kaolinite separated from soil was found to have a surface area of 80 m^2/g. With an exchange capacity of 0,12 meq/100g there is an area of about 20 $Å^2$ for each univalent cation.

Cation-exchange reactions in natural situations are more complex, as neither the concentration of cations and anions in waters percolating through rocks and soils, nor the initial reactions of the silicate minerals in releasing cations by exchange or by solution, are seldom known.

The replaceability of an exchangeable cation on a clay mineral differs with type of mineral, nature of other adsorbed cations, concentration of cations in solution and pH[15].

In summary it should be noted that studies of the cation exchange capacity are very difficult to carry out because of the number of factors affecting the property and the atomic scale at which the process occurs. It is unlikely that all of the factors involved have actually been identified and it is clear that the process is not yet fully understood.

3.4 pH-DEPENDENCE OF CATION EXCHANGE CAPACITY

The negative charges on clays (CEC) are of two types: permanent charges and pH-dependent charges. Permanent charges are those arising from isomorphous substitution within the clay structure whilst pH- dependent charges are those associated with edge effects of broken clay minerals.

It should be pointed out that cation exchange in most soils increases as its pH increases. At a very low pH value, only the "permanent" charges (cations subject to replacement at all common pH levels) and a small portion of the charges of organic colloids hold ions that can be replaced by cation exchange. On the majority of the organic colloid exchange sites and on some of those of the

inorganic fraction, hydrogen and perhaps aluminium hydroxyl ions are held so tightly as to resist replacement. The cation exchange capacity is therefore relatively lower than that at a high pH[14].

As the pH is raised, the hydrogen held by the remainder of the organic and inorganic colloids becomes ionized and is replaceable. Also, the adsorbed aluminium hydroxyl ions are removed, forming $Al(OH)_3$, thereby releasing additional exchange sites on the mineral colloids. The net result is an increase in the cation exchange capacity. In order to minimise this effect, the cation exchange capacity is usually determined at a pH of 7,0 or above. The method currently in use at Transportek is carried out at a pH of 8,1[16].

This means that it includes most of the exchange capacity dependent on pH as well as the permanent exchange capacity. Carroll[15] noted that a variation in pH will cause a variation in the ratios of exchangeable cations in a clay mineral.

The importance of the ratio of pH-dependent charge to permanent charge is greater in 1:1 layer silicates than in 2:1 layer silicates. For montmorillonites the pH-dependent cation exchange capacity may be 20 per cent of the total cation exchange capacity; for illite it may be 40 per cent, while for kaolinite and allophane it is essentially 100 per cent[17].

3.5 ANION EXCHANGE

Anion exchange involves the exchange of an anion adsorbed to a clay mineral with an anion in a solution in contact with the mineral. It has been found that the adsorption of anions by clay minerals in some cases involves replacement and in others, addition. The anion exchange capacity of a soil is, however, a difficult parameter to measure.

The anion exchange capacity of kaolinite and halloysite is similar to their cation exchange capacity, but the anion exchange capacity of other clay minerals is much less than their cation exchange capacity[15].

Because of the frequent presence of hydrous ferric and aluminous oxides in certain soils, particularly in tropical and subtropical soils, their anion exchange capacity is greater than that contributed by the clay minerals.

Some clay minerals exhibit positive as well as negative surface charges. This makes anion exchange possible between surface hydroxyl units and, for example, the phosphate, sulphate, chloride and nitrate anions.

Under certain conditions, hydrous oxides of iron and aluminium, allophane (an amorphous clayey material) and even kaolinite show evidence of having positive charges on their crystal surfaces. These charges are thought to have two sources:

(a) The protonation or adding of hydrogen ions to hydroxyl groups on the edges of these minerals; and

(b) The exchange of the hydroxyl groups for other anions, such as phosphate.

At high pH values the hydrogen ion tends to dissociate from the oxygen, leaving a negative charge on the surface (source (a) above). As the pH is lowered an additional hydrogen ion associates with the hydroxyl, leaving a net positive charge. This charge attracts anions such as $H_2PO_4^-$, SO_4^{-2}, NO_3^- and Cl^-. These ions can exchange with each other, giving rise to anion exchange[14].

The second mechanism (source (b) above) that shows a positive charge on certain colloids is that in which phosphates and similar ions exchange for hydroxyl. This reaction also occurs primarily at low pH values, the negative hydroxyl ion being replaced by positively charged aluminum ions in the crystal.

By one of the two mechanisms of anion exchange, SO_4^{-2}, NO_3^-, and Cl^- ions as well as phosphates, typically become adsorbed by allophane, the hydrous oxides and to some extent, by the kaolinite group. The reactions are most significant for phosphates since these ions tend to be quite tightly adsorbed.

In anion exchange negatively charged ions on the clay mineral are replaced by anions in the intermicellar solution. The anion exchange capacity of the 2:1 layer structure minerals is much less than their cation exchange capacity. In smectites, for example, it is generally less than 5 meq/100g[10] although higher values are given by other workers[11] (Table 3.2). Kaolinite has similar values for both types of exchange capacity.

Table 3.2: Typical anion exchange capacities of various clays (meq/100g)[11]	
Mineral	Anion exchange capacity (meq/100g)
Smectites	12 - 23
Vermiculite	4
Kaolinites	6 - 20

It has been suggested that the exchange capacity for anions shown by kaolinite in acid solution results from aluminum ions on the crystal edges which acquire a positive potential. This is balanced by exchangeable anions which act as counter ions. Hydrous oxides of iron and aluminum probably contribute to the anion exchange capacity of acid soils. This type of exchange is essentially a non-specific adsorption phenomenon resulting from electrostatic attraction between anions and surfaces with a positive pH dependent charge. Specific adsorption is also known, most typically involving weakly acidic anions such as phosphate and silicate; similar reactions with sulphates and fluorides have also been reported. The formation of partly covalent bonds, coordination by cations or anionic decomposition of non-crystalline alumino-silicates are suggested mechanisms of attachment. Allophane and imogolite strongly interact with anions and in Japan high phosphate uptake has been used as a quick method for recognition of allophane in soils. Engineering uses of anion exchange include treatment of drilling muds and of clays used as liners in reservoirs[10].

It is significant that anions are larger than cations (in their crystal-lattice radii) and that they interact with water in a different way. Instead of attracting dipolar water molecules around them, anions tend to break up the hydrogen-bonded structure of liquid water, with the result that the bigger they are, the more difficult it is for them to enter the water[12].

3.6   GENERAL

The chemical and physical properties of clay minerals are obviously highly variable and complex and are only very briefly described above in order to provide background for the further discussion in this report. Further details on clay mineralogy can be found in standard text books[10,11] from which much of the foregoing discussion has been extracted.

It is, however, clear that the basic chemical and physical structure of clay minerals results in a number of unique properties which typically make excessive clay contents a major problem in road construction materials. Two of the most important properties of clay minerals in construction materials are their high specific surface and the electrical charges in their crystal structure. It is these properties in association with the electrical double layer and the presence of gravimetric water which affect all of their characteristics such as plasticity, friction, cohesion and hence their engineering behaviour. The quantity and type of exchangeable cations adsorbed onto the clay surfaces also affect the properties of the material and the susceptibility of the properties to change after treatment with other cations.

In addition to the ion exchange properties of the clay minerals described above, the influence of other soil components should not be overlooked. Hydrous ferrous and alumina oxides, organic matter and amorphous materials also have significant effects which need to be recognised during interpretation of ion exchange testing.

The rate of ion exchange varies with clay mineral type and with the nature and concentration of the ions. In general, the reaction for kaolinite is most rapid, being almost instantaneous. It is slower for smectite and for attapulgite, and, in the case of illites, requires even longer time, perhaps hours or days, to reach completion.

One of the major problems affecting the properties of clays is their high variability. There is a strong interrelationship between the various properties, with the result that a small change in one property affects a number of other properties which in turn disturb the physico-chemical equilibrium and may affect the pH. This makes quantification of many of the properties very difficult.

The large effort required to compact soil materials containing high clay and silt contents is a significant construction problem when using local materials. Two processes are involved:

a)   The clods of soil held together by soil suction and clay electro-chemical effects need to be broken down. (In laboratory compaction work prior to construction, the clods are broken down manually before the maximum dry density and optimum moisture content are determined). Some sort of soil dispersion effect is thus required in practice to disaggregate the soil clods in order to achieve the same effect.

b)   The soil suction forces between unsaturated soil particles are a function of the particle size and of the surface tension of the adjacent solution. Thus the finer the material, the greater the suction forces and the greater the energy required to overcome these during compaction of the material.

It is common knowledge that, up to the optimum moisture content of a soil, the addition of water results in better lubrication of the particles and decreasing difficulty with compaction[18]. In clayey soils this is partly true as increasing water reduces ionic attractions and negative pressure i.e. soil suction. This reduction, however, only affects the normal force between particles and not the coefficient of sliding friction. In order to reduce sliding friction, modification of electrical double-layer interactions, i.e. those which contribute to flocculation as opposed to dispersion, are necessary.

4   BACKGROUND AND PROPERTIES OF IONIC STABILISERS

4.1   BACKGROUND

All the "stabilisers" discussed in this report rely on ionic exchange reactions to perform their expected functions satisfactorily. As they are all proprietary products, it is not possible to establish their exact compositions. It would appear, however, that their active "ingredients" are mostly mineral oils (hydrocarbon chains) modified with sulphuric acid to form a sulphonic acid. The mineral oil may be a natural petroleum derivative (oil or bitumen) or an artificial oil. It should be borne in mind that the sulphonated oil is only the basis of these products and that each proprietary brand has specific additives to improve the reactivity. It is apparently possible to adjust the formulation of some of these products to increase their reactivity with certain material types.

Sulphonated petroleum products are all "surface active agents" (surfactants) and have been used for many decades as the bases for detergents, lubricating oils and cutting fluids[19] and in the treatment of hard water[20]. They have also been used as chemical filters. Their ability to form micelles in solution gives them their soap-like or detergent action.

The most important aspect concerning the composition of these products with respect to soil stabilisation is their chemical nature. The molecules can be described as consisting of a sulphonic moiety which is soluble in water (and is hydrophilic) attached to an aromatic hydrocarbon ring and aliphatic hydrocarbon chain. The hydrocarbon component can be considered as a hydrophobic tail attached to the sulphonic acid head[21]. This type of structure is typical of many surfactants, the sulphonic acid derivative being recognised as one of the strongest acidic cation exchangers[20].

Two specific properties theoretically make SPPs extremely useful for soil stabilisation:

- their ability to fix, displace or replace exchange cations in clays;
- their ability to make the soil materials (particularly clays but not necessarily clays only) hydrophobic by displacing adsorbed water and water of hydration and preventing re-adsorption of this water.

Very little reference to these proprietary sulphonated petroleum products has been published, although a small laboratory evaluation of Reynolds Road Packer (RRP) was carried out by the Federal Highway Administration in the early 1970s[22]. It was concluded from the results of a limited testing programme involving four acidic materials that no improvement in the engineering properties (Atterberg limits, moisture/density relationships, CBR and compressive strength) was achieved. The failure of the product to perform was attributed by the researcher to the acidity of the materials.

Interesting research has been carried out, also by the Federal Highway Administration, on the use of compaction aids for fine materials[18]. One of the compaction aids used was RRP, then produced in the United States. The effect of RRP in increasing the maximum dry density of two of the six soils tested was noted, these being a kaolinitic material and acidic montmorillonitic soil (this was at a low concentration of RRP). Measurements of the surface tension of the product at different concentrations indicated that at the concentrations typically used, no significant reduction in surface tension over distilled water was obtained.

4.2   CATION EXCHANGE

SPPs can be considered as anionic surface active agents. They are highly susceptible to ion exchange reactions in which appropriate inorganic ions present on mineral surfaces (particularly clays) and in clay interlayers are replaced by, or attached to, the organic molecules. This reduces the mobility of the ions and functionally reduces the plasticity of the material. The bonding of the sulphonic molecule may be through a number of mechanisms, such as direct chemical bonds (between the SO_3^- anionic head of the SPP and a metal cation at the surface), inductive bonds (between an uncharged oxygen ion in the sulphonic group and a metal cation), occupation of a vacant ionic site in the mineral structure by the SPP or dissolution of the SPP head in the diffuse double layer[21]. These processes are given in a generally decreasing order of bond strength. Various chemical factors, such as the valence, hydration state and ionic radius of the incumbent cations and the pH of the solution, affect the tendency for the various exchange reactions and bonding processes to take place. Sulphonated petroleum products are, however, particularly active ion exchangers because of their surfactant properties and large molecular size and can displace most inorganic cations.

4.3   "WATERPROOFING" CAPABILITY

Once an ion exchange reaction has occurred and the sulphonic acid moiety has attached to a mineral particle, the so-called hydrophobic tails of the SPPs are directed away from the particle and form an oily protective layer around it. In theory, this has the effect of reducing the thickness of the electrical double layer or hydration layer and of preventing water from gaining access to the mineral particle. With this reduced double layer thickness, it now becomes theoretically possible to achieve a greater degree of compaction in the material and also to reduce the possible water adsorption of the material in the long term.

4.4   SURFACTANT PROPERTIES

SPPs are described as surfactants with the property of being able to reduce the surface tension of the solution in which they are emulsified. A number of tests were carried out on the products diluted at the rate typically recommended ($0,03\ell/m^2$) and the surface tension measurements given below were obtained (Table 4.1).

Table 4.1: Measured surface tensions of SPPs (dynes/cm)	
Product	Surface tension (dynes/cm)
Water	71,2
Conaid	29,4
ISS 2500	67,5
Roadamine	29,4

It is clear that Conaid and Roadamine result in a significant reduction in the surface tension of water on their addition. ISS 2500, on the other hand, does not have the same surfactant properties as the other two and may thus not act in an identical manner in all cases. It would appear from these results that the composition of ISS 2500 has changed little from the original RRP formula by comparison with the significant differences in properties and appearance of Conaid and Roadamine[18].

4.5   GENERAL

It is interesting to note that for effective compaction of soils with high fines contents, the process of breaking down soil clods is a major energy consumer. Any chemical which assists with this process would result in either a higher density for a given compactive effort or the same density for a lower effort. This reduction of clod strength could be achieved either by reduced surface tension, by increased dispersion or both mechanisms[18].

For a compaction aid to be effective it should reduce the strength of the material in some way[18]. However, this reduction should be temporary in order to render the long term strength adequate. If the loss of strength is temporary and this effect is lost through biological activity, oxidation or adsorption onto clay particles, the compaction aid can be considered to be of benefit.

5 ACTION OF STABILISERS

In the context of soil stabilisation with SPPs it is has generally been considered that, for them to have any effect, the material to be treated shall have an adequate quantity of suitable clay mineral (not necessarily clay-sized fraction). This clay shall have an appropriate cation exchange capacity and the cations should be capable of being exchanged (some clays, particularly micas and illites, "fix" potassium, which is then not easily displaced or removed). In addition, the material shall have an appropriate pH, bearing in mind that the SPPs are typically highly acidic, even after extreme dilution.

It should be noted that it is the clay minerals with their unique plasticity and water adsorption characteristics which tend to render many materials inappropriate for road construction and that neutralisation of their water susceptibility is probably the main priority.

However, recent observations during this resaerch have shown that, apart from the actions of SPPs on clay minerals described above, a number of other reactions may take place. This means that certain materials which are inherently weak, not necessarily as a result of their clay content, could also be improved.

Soils containing hydrous iron and aluminium oxides

The amphoteric nature of these metal oxides (i.e. variation of charge with pH) results in the potential for ionic exchange to occur. These materials are very common in tropical and sub-tropical soils. There is a very good possibility of some SPP being adsorbed onto them. Although iron and aluminium oxides in themselves do not contribute to plasticity as defined, they do have the susceptibility to hydrate by adsorbing water. This results in a reduction in their shear strength (although compaction efforts are reduced). It is also suspected that drying of iron and aluminium oxides treated with an SPP would result in higher surface tension effects, resulting in an effective strengthening of the materials.

Field observations have shown that the strength of many soils with a high iron content can apparently be significantly improved by treatment with SPPs. One of the strongest bonds affecting the attachment of SPP molecules to soil particles is the direct ionic bond between the anionic SO_3^- head of the SPP and metal cations at the surface of the soil particle. Many of the iron-rich soils in South Africa have limonite as the predominant iron component. This is an amorphous, crypto-crystalline mineral consisting of various components, goethite and hydrated haematite being predominant. The bonding of SPPs directly onto these particles reduces their propensity for hydration and thus should improve the shear characteristics of these soils when wet. A similar process affects alumina.

Calcareous materials

Calcium is typically found in soils in South Africa as the exchange cation on clays, as described earlier, and very commonly in semi-arid to arid areas as a carbonate (mostly as calcite in calcretes). Calcium is a relatively stable mineral which is known for its self-cementation properties[23]. Cyclic wetting and drying dissolves and re-precipitates calcium carbonate with a resulting cementation action. Calcite in itself is thus a relatively stable material which is probably unlikely to be improved directly with an SPP.

However, many calcareous materials have been treated effectively with SPPs. Some of these have relatively high clay contents (not the usual reactive clays, but sepiolite and palygorskite) and it is assumed that the ionic reaction with these is successful. These are unusual clays whose properties have not yet been fully investigated or described. Other calcareous materials contain very little clay but the addition of phosphate ions appears to result in a good reaction. It is considered by some SPP suppliers that this addition of phosphate ions may act on the calcite to form apatite (a significantly harder mineral than calcite). However, the low concentrations of phosphate added would appear unlikely to have a dominant effect on the calcite. It is known that phosphates can replace hydroxyl ions (usually attached to aluminium) under moderately acid conditions[14]. This is considered to be a possible mechanism for phosphate ions included in the SPP to attach to calcium ions in the same way. It is known also that phosphoric acid can have a beneficial effect on certain clays[18].

One aspect which should be considered is that many calcretes contain amorphous silica[24]. The following discussion may thus be relevant to calcretes.

Soils containing amorphous silica

It is known that amorphous silica can have a monolayer of hydroxide ions surrounding its surface (silanol layer)[10]. These hydroxyl groups may be the sites of adsorption for water, polar compounds and cations. It is thus possible for the amorphous silica present in a soil to influence the results of cation exchange capacity determinations. The possibility of amorphous silica being present in a soil is best determined by X-ray diffraction techniques.

Soils containing organic material

Caution is necessary when determining the cation exchange capacity of materials containing excessive organic matter. The cation exchange capacity of organic material is typically very high.

The average cation exchange capacities of typical silicate clays are about 0,5 meq for each one per cent of clay whilst for organic matter the average is about 2,0 meq for each one per cent of clay.

Soils containing other amorphous materials

Other amorphous material, particularly allophane which is a hydrous allumino-silicate of variable composition and difficult to identify, may have relatively high cation exchange capacities (25 to 50 meq/100g for allophane) but may not have the same consequences in terms of the effect of water on its particles. It would appear that the liquid limit, for instance, is closely related to the composition of the associated clay minerals[25].

Environmental aspects

SPPs are used in a highly dilute form (0,01 to 0,03 litres/m^2) and are environmentally acceptable. Although highly acidic in their undiluted form (skin contact should be avoided), once diluted they are unlikely to affect sites adjacent to their use. It has, however, been noted that vegetation does not easily establish on compacted materials treated with SPPs. This is probably the result of the material being retained at a moisture content less than the wilting point of most plants.

6 LABORATORY TESTING

6.1 BACKGROUND AND PROBLEMS

The testing techniques and procedures currently used for material characterisation in road construction (e.g. TMH1[7]) have generally proved to be unsuitable for testing SPP treated materials when the latter are used at the standard dilution recommended by the suppliers. It has been found that the reaction time of the SPP treatment may take up to 60 days[26] although theoretical soil chemistry states that ion exchange reactions are very rapid, being affected only by the permeability of the material, the concentration of the solutions and the accessibility of the clays to the cations. This is supported by the findings of Hoover et al[18] who note that the increase in maximum dry density, which is typically obtained from surfactant waterproofers (cationic, anionic or non-ionic), is due to the rapid exchange of inorganic for large organic ions. This results in an almost instantaneous hydrophobic effect which is described as fair to excellent.

The only fully documented "specification" for SPPs (Reynolds Road Packer in particular) has been produced in Hungary[2] but is fairly general and does not appear to be satisfactory for southern African conditions. This requires a drop in the liquid limit (not usually recorded using the local test method), changes in the compactability (increased MDD and OMC), increased CBR and a maximum pH of 7,5. Only the latter requirement seems to have any merit locally, although materials with higher pHs (mostly calcretes) have been successfully treated.

Standard engineering tests carried out locally on materials treated with SPP at 0,03 ℓ/m^2 (the standard dilution rate for SPPs) generally showed no improvements in the characteristics of the materials. The soaked CBR strength typically decreased. This was ascribed to the detergent (lubricating) action of the SPP. Transportek thus thought it necessary to evaluate these products using more appropriate test methods.

As the ion exchange reaction was considered to be the principal mechanism by which SPPs improved soils, basic research from first principles was directed in this direction. For this purpose the electro-chemical aspects of clays, specifically their cation exchange capacity, were researched in relation to the various SPPs and a tentative test procedure was developed[27]. At the same time, the Natal Roads Department (particularly the Estcourt region) was carrying out field and laboratory testing. It developed a system[27] by which the clay component of soils was investigated by means of X-ray diffraction methods and, based on these results, a more appropriate application rate for the SPP was selected. In this way marked increases in CBR strength could be obtained without the material being overdosed or excessive lubrication being caused.

Subsequent research has involved the application of the test methods to various soils in an attempt to develop specifications for the successful use of SPPs.

6.2 RESULTS AND DISCUSSION

The principal testing technique proposed by Transportek is to evaluate the effect of the product on the electro-chemical properties of the materials. Test procedures have been developed in the Division to evaluate various materials with different SPPs to determine which, if any, are likely to react satisfactorily with any specific material. Examples of some results obtained during the early stages of the project are shown in Table 6.1, in which the cation exchange capacities for various materials, both treated and untreated with different stabilisers, are given.

Table 6.1: Effect of SPPs on cation exchange capacities (CEC) of some soils

Sample	Cation exchange capacity (meq/100 g)			
	Untreated	Product A	Product B	Product C
A	21	13	21	16
B	11	12	12	12
C	13	6	7	6
D	12	13	14	25
E	57	29	7	9
F	59	36	63	17
G	54	7	14	2

It is clear that the CEC of certain materials is significantly affected by certain SPPs whilst for other materials no affect is recorded. In some cases the values increase after treatment. This was considered to be a spurious effect of pH variations in the soils, which was exacerbated by the various pH characteristics of the products. The results of testing using this method on various soils with differing SPP compositions were compared with the results of in-house testing by a supplier of SPP and the rating of effectiveness apparently correlated very closely with the results obtained by the supplier.

The results of the CEC testing were plotted on a diagram which showed whether the material would be suitable for treatment with an SPP or not (Figure 4.4 in reference 28). The basis of this figure was that a minimum CEC of 15 meq/100g was necessary to ensure that an adequate quantity of the correct clay minerals were present and a minimum reduction in CEC after treatment was necessary to ensure that the reaction would occur.

A plot of all the results obtained since this was developed is provided as Figure 6.1.

The varying pH values of the different natural materials had to be taken into account, as the test was carried out in a slightly alkaline environment. This resulted in some unquantifiable variation as some of the acidity of the SPP and of any acidic soil tested was neutralised before the cation exchange reaction could take place. From time to time spurious results were obtained (Figure 6.1) which had to be interpreted very carefully. Attempts to find suitable test methods for the cation exchange capacity at different pH values have met with little success to date. As stated earlier, the presence of excessive quantities of organic material is also known to affect the determination of the electro-chemical properties and shall be accounted for. The standard procedure is to remove any organic material with hydrogen peroxide prior to CEC testing.
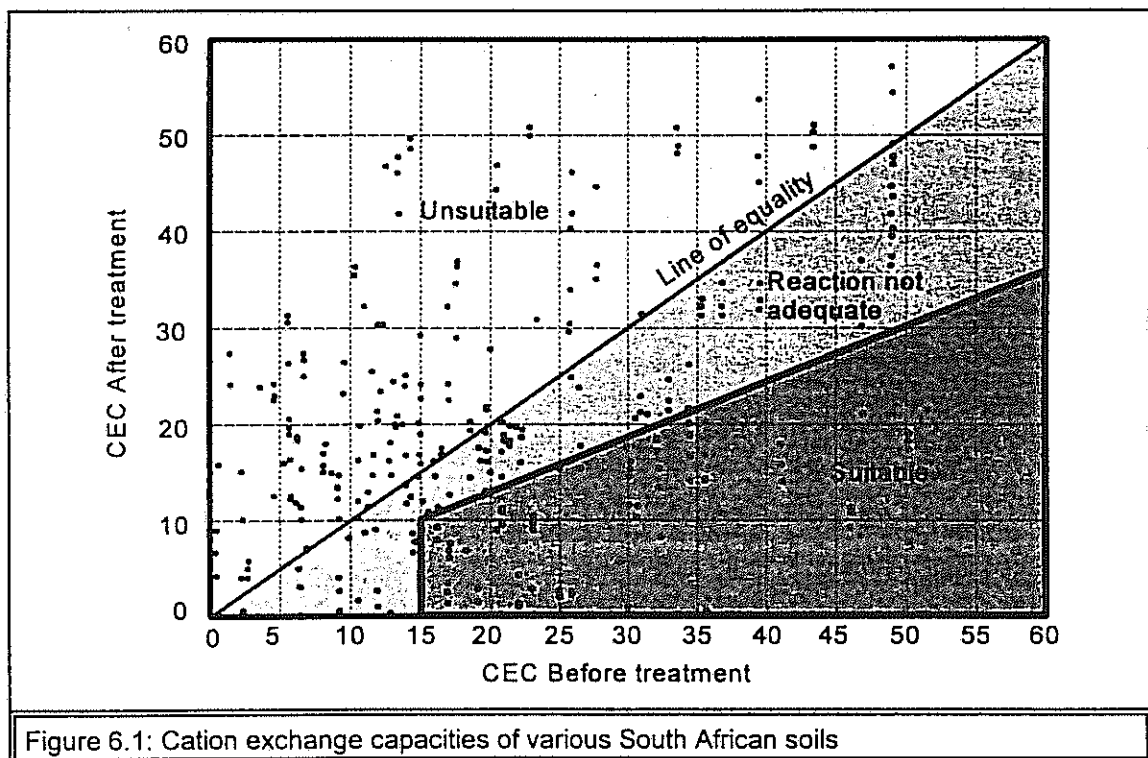
Figure 6.1: Cation exchange capacities of various South African soils

As the research continued, measurement of the CEC after various curing periods was carried out. This work led to the conclusion that, despite the laboratory work being carried out by a single operator, the repeatability of the CEC test was very poor, generally as a result of time effects. Provided all samples were cured for identical periods, repeatable results could be obtained. As this was a major logistical problem, other techniques for testing were investigated.

A simple method of determining the cation exchange capacity using Methylene Blue Adsorption (MBA)[29] was investigated. Methylene blue is a traditional chemical indicator which is adsorbed by clay minerals in proportion to their cation exchange capacity. The test was carried out on a number

of soils. The results are given in Table 6.2. A description of the procedure followed is given in Appendix A.

Comparative studies were carried out using the traditional titration method, the MBA method and a photospectrographic method. The results are given in Table 6.2.

Table 6.2: Results from cation exchange capacity tests.			
Sample	Cation Exchange Capacity (meq/100g)		
	MBA	BaCl$_2$	Photo*
A	0	-	1
B	11	33	21
C	30	26	20
D	2	10	30
E	4	23	16
F	6	18	27
G	56	89	22
H	1	6	3
I	4	-	5
J	5	-	5
K	6	-	7
Note: * Photospectrographic method.			

It was concluded from this work that the MBA method was a simple, yet effective method of determining the CEC which gave sufficiently accurate results for SPP work, provided the operator's interpretations of the results are consistent.

Work previously carried out during a small investigation of roads constructed locally with Conaid for Conaid Asia Pty (Ltd)[30] indicated that there was a significant change in the pH over time in the road. The pH of samples removed from both the treated and the control sections was measured. The average pH of all the samples decreased by 1,30 per cent after treatment with Conaid. This decrease was mainly due to the decrease in the pH of every sample with which the Conaid apparently did not react beneficially (i.e. the maximum dry density (MDD) decreased). The decrease in pH may possibly be attributed to the fact that the pH of Conaid is very low and that when it is added and does not react with the material, an excess of "free" Conaid is present in the material. This would lead to a decrease in the total pH of the material. In 63 per cent of the cases where the Conaid had a beneficial effect (i.e. where the MDD increased), the pH also increased after treatment. In these cases the Conaid was apparently mostly "adsorbed" by the material. This would

result in the displacement of the prevailing cations in the soil, which appear to neutralise some of the remaining acidity by combining with other molecules in the material or product and forming an alkaline material. It is also possible that some of the hydroxyl ions in the clays are also displaced. This was an unexpected and interesting finding.

This led to laboratory investigations into the changes in pH with time. A test routine in which the change in pH with time is monitored was developed. In this the pH of the natural material and the material treated with the standard concentration of the three SPPs is measured. The four samples are then allowed to stand for 7 days and the pH is re-measured. Invariably the control (natural material treated with distilled water) shows a small change in pH value but the materials treated with SPPs show either an increase or decrease with time. Those materials showing a decrease in pH (taking into account the results of X-ray diffraction studies and CEC testing) are considered to be unsuitable for treatment, whilst those in which the pH increases, are considered suitable. The product showing the highest increase in pH is taken as that which will react best.

Investigations into the use of pH measurements for predicting the reaction potential of SPPs revealed that the long-term pH test as traditionally carried out shows very poor repeatability. Figure 6.2 clearly shows that the variation in measurements over time is significantly larger than the variation in pH attributed to the electrochemical reaction. Although general trends are clear, the pH scatter was considered too large to allow this test to be used as a routine test.

The problems with pH measurements were investigated further and additional long-term tests carried out with a slightly modified procedure. The soil samples (clay fractions) were sealed in glass bottles during the "curing" periods. This resulted in far less variation in the pH readings (Figures 6.3, 6.4 and 6.5) but still showed unacceptable variations for routine testing purposes. It was thus decided that the use of pH as an indicator was only practicable for research purposes.

Discussions with officials from the various roads departments and some suppliers of SPPs indicated that the procedure for evaluating SPPs which had been published previously[27] and which was being implemented was showing good results. The investigations thus continued along this path.
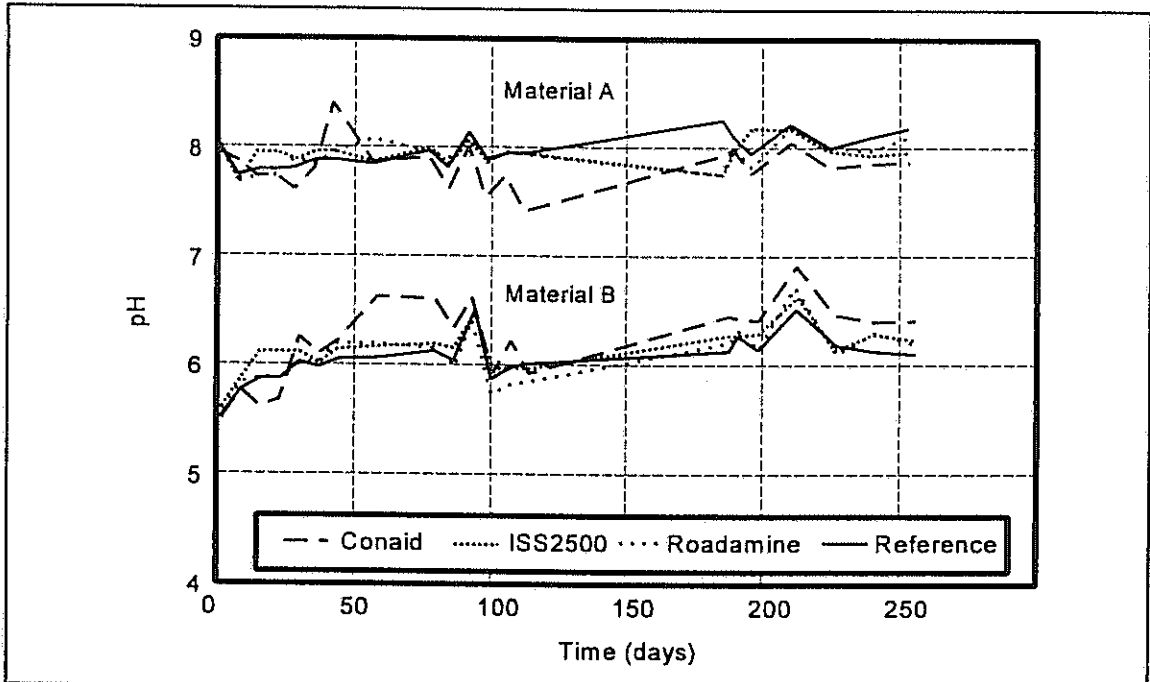
Figure 6.2: Variations in initial long term pH results.
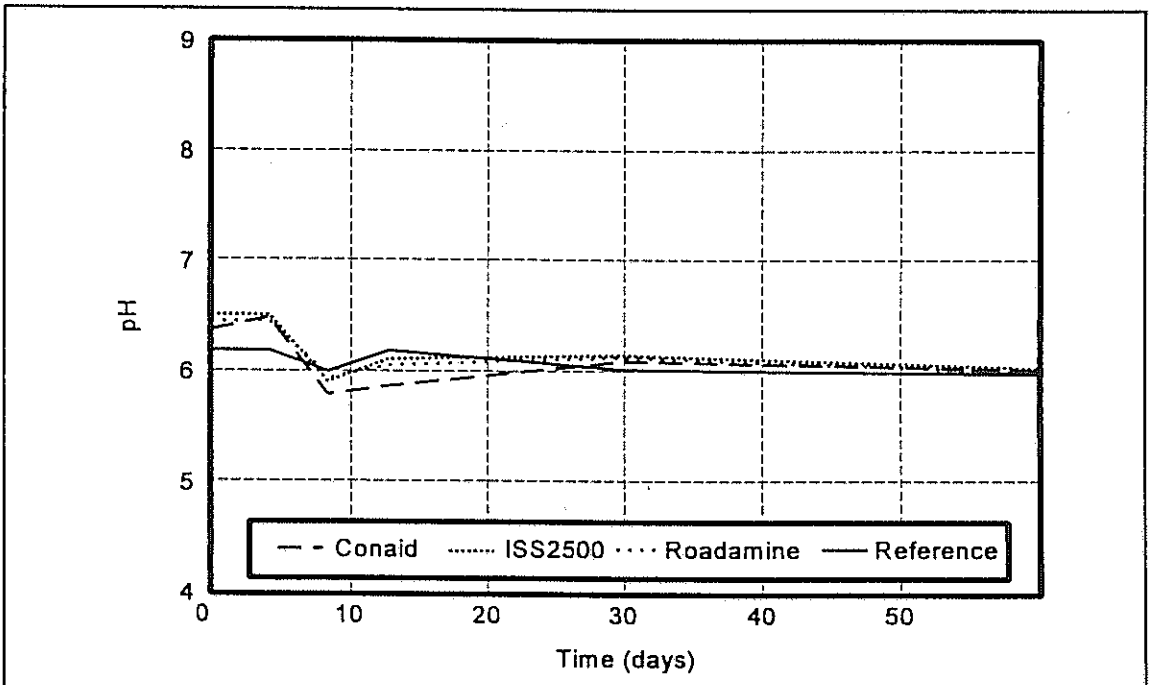
Figure 6.3: Long term pH results (material A).

Figure 6.4: Long term pH results (material B).

Figure 6.5: Long term pH results (material C).
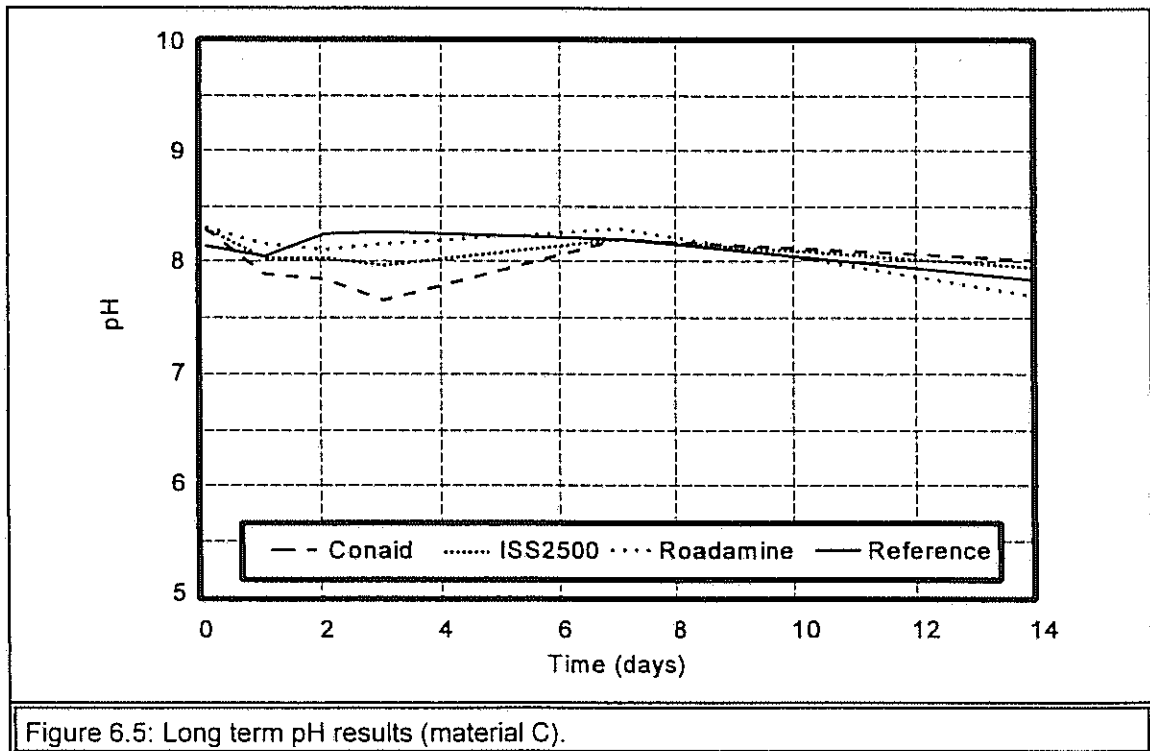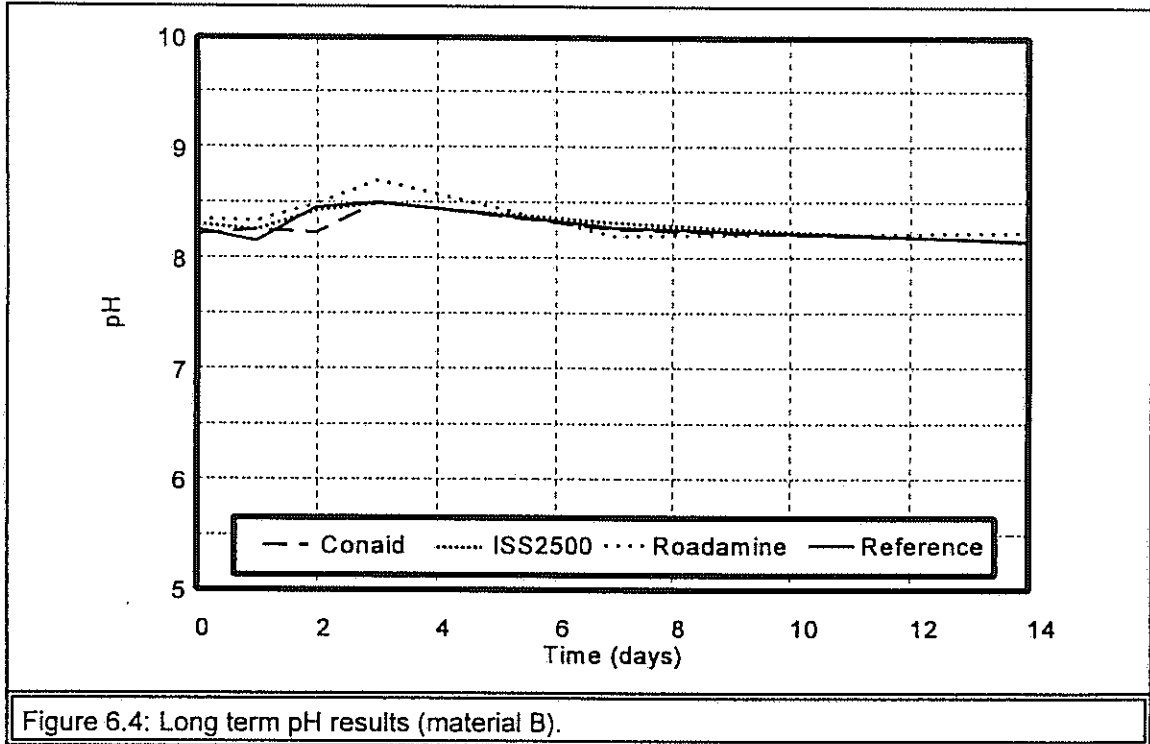
Work by the Natal Roads Department[27] had shown that, provided the concentrations of the products are correct for the material being tested, it is possible to enhance the CBR values. The concentration is based on the type of clay present as determined from X-ray diffraction studies.

No estimate of the strength improvement in a soil after treatment with an SPP can yet be made on the basis of the electro-chemical testing. It is, however, safe to assume that a significant increase will occur when the electro-chemical tests indicate a reaction. This is supported by limited field evidence.

No method currently exists for the specification of the SPP or for quality control purposes. Research carried out indicated that, if it is not known what the products contain, it would be difficult to specify limits which could be applied to a range of products without possibly disadvantaging or benefitting the various suppliers. It is recommended that each supplier provides approved certificates of quality from his manufacturing plants with each batch of material supplied. This places the onus on the individual suppliers to develop quality control specifications for their products and to make these available to potential users prior to any project. These specifications should make use of tests which can be carried out in commercial chemical laboratories and which would enable clients to have independent testing carried out should they so desire. In this way each supplier will necessarily supply a consistent product with a relatively well specified composition and properties and will need to conform with these. This will permit independent arbitration of contractual claims resulting from alleged poor performance of the chemicals.

Attempts to monitor roads constructed with SPPs which have suitable control sections met with little success as the records available were very poor .

It is recommended that the current materials specifications be modified for SPP-treated materials for lightly trafficked roads and that end-product type specifications be developed. Instead of specification of the properties of the borrow or construction material, a final requirement in terms of in-situ density, moisture and strength should be specified, based on the strengths (or preferably E moduli) required for the design traffic of that road.

6.3 RECOMMENDED TEST PROCEDURE FOR SULPHONATED PETROLEUM PRODUCTS

Based on extensive testing, the following test procedure is proposed:

1) Determine the indicator and classification properties of the natural material to be treated, i.e. Atterberg limits, grading, compaction characteristics, soaked CBR strengths;

2) Determine the reason for treating the product with an SPP; whether it is to increase the density in order to improve the stiffness or to "stabilise" the material in order to improve the strength and waterproof it. This is generally a function of the indicator and classification test results[b]

3) Carry out an X-ray diffraction analysis and cation exchange capacity determination to identify the type and activity of the clay minerals.

4) Evaluate the results as follows:

   a) If the material has a low plasticity, low fines content and/or little active clay components (vermiculite, montmorillonite, chlorite or interlayers of these minerals) the "clay stabilisation" reaction will not occur and a less concentrated solution of the product (0,01 ℓ/m^2) could be used *purely as a compaction aid*. However, if there is a high concentration of iron oxides, calcium carbonates or other amorphous material (all identifiable by X-ray diffraction) stabilisation reactions may be possible and the suppliers of the products should be asked to modify the formulation for these materials and to recommend an appropriate dosage rate.

   b) If the material has significant quantities of the active clays described above and a cation exchange capacity of more than 15 meq/100g, the material is suitable for treatment .

   c) Materials with properties lying between these two can be successfully treated with many of these products at a concentration of 0,02 ℓ/m^2.

5) Carry out a CBR test at the specified concentration with a selected SPP or preferably with all possible candidate SPPs. This is usually a function of economics. If the stabilisation reaction is expected to occur (method b), allow the CBR specimen to cure for 7 days prior to soaking and testing to establish a conservative strength for the pavement analysis.

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[b]   When the plasticity index results are analysed, the percentage of the total material passing the 0,425 mm sieve should be considered as well. A number of materials with high PIs have been tested but the very small weighted PIs indicate that the bulk material will probably not react adequately.

A number of specifications have been proposed for SPPs in various areas. Based on the evaluation of these, together with field observations, the following specifications have been proposed and found to be effective when used in conjunction with the testing procedures outlined above:

Plasticity Index	8 - 35 %
Bar Linear Shrinkage	> 4 %
Percentage passing 0,075 mm	15 - 55 %
Minimum density	98 % Mod AASHTO
Minimum in-situ CBR at OMC	35 for < 50 vpd
	45 for 50 - 250 vpd
	55 for > 250 vpd

In addition, the following can be used as a rough guide to the application rates of the chemicals, based on the AASHTO soil classification and assuming a treated compacted thickness of 150 mm:

A1, A3	0,01 ℓ/m^2
A2-4, A2-5, A4, A5	0,02 ℓ/m^2
A2-6, A2-7, A6, A7	0,03 ℓ/m^2

7 CONSTRUCTION AND QUALITY CONTROL

Investigation and observation of numerous SPP-treated roads during construction and with time after construction have shown that the construction procedure and quality control during construction are critical for the successful performance of the road. Many of the problems on roads showing failures and poor performance can be attributed, firstly, to poor construction procedures and secondly to inadequate quality control during construction. Much of the reported poor performance of SPP-treated materials is the result of poor construction and, in fact, recent work has shown that even materials marginal in relation to the specifications listed above can perform well if proper construction techniques are used.

The following construction process, using conventional earthmoving and regravelling plant, is recommended for optimum performance:

a) By means of a grader, remove vegetation and root systems where necessary by blading off a thin surface layer incorporating all this material. Should any other material (top soil) contain excessive organic matter, this should also be removed.

b) The in-situ material or existing road which is to be used should be scarified to the required depth. The final road shall be raised above the natural ground level. This obviously does not apply to cuttings or low water crossing areas. Where gravelly (often bouldery) windrows have developed on existing roads it is preferable to blade these to waste rather than to try to incorporate them into the newly treated layer.

c) Cut side-drains adjacent to the proposed shoulders in the required positions. Use the material from these to augment the scarified in-situ material in order to make up the required thickness. Shape the road to the approximate line and levels required. It may be necessary to import additional material to ensure that an adequate thickness is achieved. Additional imported material may also be necessary if the in-situ or existing material requires improvement of its properties to ensure successful use of SPP (i.e. not enough suitable fines). This material should be tested and should comply with the requirements. Imported material should be dumped at the required spacing and spread evenly over the full width and length of the road surface prior to mixing in order to get a good intimate mix of the different materials. To achieve a compacted thickness of 150 mm it is necessary to start compaction with a loose (bulked) thickness of at least 200 mm. A simple graduated probe can be used to measure the thickness.

d)   Check the in-situ moisture content of the material to be compacted. This may vary considerably if a combination of in-situ, side drain and imported materials is used and should be taken into account during the determination of the hygroscopic moisture content.

e)   From the Optimum Moisture Content (OMC) determined in the laboratory and the in-situ moisture content, determine the quantity of water required to bring the moisture content up to at least OMC.

f)   From the area to be prepared for the job-lot (usually one day's work) calculate the quantity of chemical required to provide the correct application rate as determined from the laboratory testing. Experienced teams can generally build about 700 metres of a 7 metre wide road in a typical one day (8 to 10 hour) shift.

g)   Divide the total quantity of water required for the job lot by the capacity of the water bowser, to give the total number of bowser applications required. Calculate the quantity of SPP necessary per bowser load. Although it is recommended that the chemical be distributed in as many tankers as possible, circumstances (e.g. high in-situ moisture contents, short production runs) may dictate that the chemical be added to fewer tankers, with a resultant increase in the possibility of poor or uneven distribution. Should fewer tanker loads be used, it is recommended that the chemical be added to the first tankers in order to facilitate penetration and mixing.

h)   Add the required quantity of SPP to the full water bowsers.

i)   Mixing of the chemical is done in the water bowser by driving the bowser alternately forwards and backwards over a short distance (about 10 metres), by circulation of the water through a pump (if fitted) or by the water cart travelling to site, if the chemical is added some distance from the site to be treated.

j)   Spray the solution onto the layer of material, which now consists of the scarified in-situ material, the material removed from the side-drains, imported material or a combination of these. Apply the water/chemical solution continuously whilst processing with a grader to break down large lumps of material and to obtain an even moisture content through the material. All stones and other solid material larger than the specified nominal size (usually 100 but preferably 50 to 75 mm) should be removed from the surface layer. This is best done manually for 100 mm maximum size or using portable sieves (grizzlies) for finer material.

k) It is important that, during the application of the solution, it is only applied within the limits of the surface to be treated. Subsequent applications of solution should not overlap and the solution should be mixed thoroughly into the surface layer with a grader, disc-plough or Rotovator. Care should be taken that the solution is not sprayed directly onto the underlying layer as this effectively results in less chemical for the treated layer.

l) When all the water/chemical solution has been applied, the soil should be close to OMC. The soil should be mixed until it is homogenous, care being taken not to incorporate any dry untreated material from the lower layers into the treated layer.

m) Compaction should commence at OMC or slightly above using conventional compaction equipment. Water can be added from time to time to supplement any losses through evaporation. Compaction should be carried out until the specified density is obtained, i.e. a minimum of 98 per cent Mod AASHTO, but the crown and appropriate cambers should be retained. Care should be taken that any depressions are filled with moist, treated material in order to ensure that adequate compaction is achieved over the full area of the road. Depressions which are not filled would not be compacted properly and will usually become loose and disintegrate under traffic.

If the material contains large particles of soft aggregate, initial rolling should be carried out with a grid roller in order to break these down. Once adequately disintegrated, the material should be re-mixed with a grader before being compacted with a vibrating flat roller of at least 12 tonnes mass. For very clayey material a tamping or sheep's-foot roller is most effective.

It is recommended that proof rolling be carried out at each site where obvious changes in the material occur. During this process a short section of road (about 20 metres) is rolled for a number of passes and a DCP test is done after each pass until no significant increase in strength is obtained after additional passes. This defines the number of roller passes necessary to achieve the desired density.

n) After compaction the surface of the road can be lightly skimmed with the grader. Care should be taken to ensure that any large stones which are dragged and cause furrows are removed, that the furrows are properly filled and compacted and that the shape of the road is maintained. It is recommended that materials with a PI less than 18 and percentage passing the 0.075 mm sieve less than 20 are then heavily sprayed with water and that a pneumatic tyred roller (PTR) be used to produce a tightly bound surface (slushing).

o) Curing should be carried out over at least a 4 day period using a light spray of pure water on the road surface.

p) Once the road has dried back so that there is no slippery material on the surface, it may be opened to traffic. Any deformation should be corrected by grading before the material dries out fully.

q) The road should be carefully finished off in terms of cosmetics to present an aesthetically pleasing product. Where the slushing process has left obvious signs of the PTR on the finished surface, these should be removed using careful grader blading or a weighted hessian or canvas drag. Areas in which ponding has occurred (e.g. at the bottoms of corners with steep crossfalls) may need mechanical or manual brooming after drying to remove excessive clay, which is likely to crack and flake.

As with any road construction project, the assurance of an acceptable quality of construction is essential. The following properties require careful control during the construction process:

a) **Material quality**

It is essential that the quality of the material is monitored on an ongoing basis in advance of the progress, so that areas with unsuitable material can be identified and action taken to ensure that the material on the sections is suitable (or that suitable material has been located and stockpiled) before that part of the road is ready for construction. The quality of the material should be based on the plasticity index , linear shrinkage or on some other indicator of suitably active fines. Experience has shown that, once it has been determined, the clay mineralogy is mostly consistent in any area unless significant changes in the geology occur. It is imperative, however, that adequate fines are always present and excessive oversize material is removed.

b) **Thickness of the material**

The thickness of the material should be controlled prior to compaction by ensuring that the bulked layer thickness after watering and mixing is at least equivalent to the required thickness plus a bulking factor (typically about 30 to 35 per cent). This can usually be controlled by inserting a scaled probe into the layer until the unworked lower layer is reached and by reading the depth of material off the scale.

c) **Amount of chemical added**

This can only be controlled by balancing the volume of chemical used during a shift with the area of road constructed. This has to be corrected for roads with varying widths so as to

prevent under- or over application. Daily records of chemical usage should be kept in case of dispute.

d) Density

The density should be controlled using sand-replacement or nuclear density measurements. This is not always possible in remote areas where the nuclear device is not available or a laboratory with ovens and weighing facilities is not on site. In this case the following testing is suggested:

During laboratory testing to determine the maximum dry density and optimum moisture content, the prepared samples are penetrated to determine the unsoaked CBR at the respective moisture contents and densities.

Immediately afterwards, the strength is also determined adjacent to the CBR test penetration scar using a DCP. From this a record of the DCP penetration rate at various moisture and density determinations is compiled. The penetration rate at the relevant density is then used to ensure that the density is achieved during construction.

Proof rolling is recommended for natural materials as the maximum density at the field moisture content for any compaction equipment is thus obtained and the effect of natural variability is minimised.

e) Moisture

Monitoring of the moisture content prior to compaction is necessary to ensure that the moisture content is within the required limit, i.e. OMC ± 1,5 per cent. It is not always possible to control this because of the difficulty of drying soil materials rapidly. Equipment such as the "Speedy" moisture meter can, however, be used for this. Recent research[33] has, however, shown that, if the material is at OMC, only two or three passes of appropriate rollers are necessary to achieve 100 per cent Mod AASHTO density. The traditional "squeeze" test can be used, but if any doubt exists, it is preferable to err slightly on the wet side and to add more water.

f) Strength

The in-situ strength of chemically treated materials is considered as the main criterion of their success and should be used as an end-product specification for SPP work. The in-situ strength immediately after compaction, as determined by a Dynamic Cone Penetrometer (DCP), is compared with the results obtained from tests on the material being utilised, carried out in the laboratory during initial investigations, or the values suggested in Section 6.3.

Where a DCP reading does not meet the criteria, the area should be investigated and additional rolling, or even remixing and rolling where necessary, should be done. If the weakness of the area is due to excessive moisture (frequently the case), additional rolling should be applied later (the next day) until the DCP results are satisfactory. An indication of the value required is obtained from the proof rolling.

g) **Width**

The width of the section being chemically treated should be constantly monitored as this is usually the basis for determining both the quantity of chemical to be added and the payment. Frequently, the mixing and windrowing operation results in windrows at the edge of the road encroaching onto the layer being treated, thus reducing the layer width.

h) **Drainage**

It is important that the road be well shaped and that it has a centre-line crown and cambers at 2 to 4 per cent in each direction in order to remove water from the road surface. Where the existence of windrows could result in ponding of water on the road surface, openings should be made to allow the water to escape. Application of water during the slushing process will generally enable the problem areas which need attention to drainage, to be identified.

i) **Visual inspection**

This is the most important part of construction and quality control. Site supervisors and foreman are required to "patrol" the road during the mixing and compaction processes and to look for depressions, dry spots, wet spots, poor mixing, stone furrows, untreated material bladed in from windrows, large stones, etc. which should be rectified. On all projects enough labourers with suitable tools should be available to rectify these problems.

Any deficiencies recorded during visual inspections should be remedied before compaction is completed and definitely before the equipment required for the remedial action is employed on the next job-lot. If necessary, additional chemical can be added manually over small areas which have not been treated adequately or at all. Care should be taken not to add excessive chemical to the material.

j) **Slushing and curing**

Once the road has been compacted and is of acceptable quality, slushing should be properly done and curing of the compacted layer with a light water spray should continue over a period of at least 4 days. The road should be kept closed to traffic during this period to avoid the

material drying out with significant tyre marks and ruts. Proper curing is essential for successful performance of SPP-treated roads.

k)   General

The quality control procedure for final DCP testing should follow a prescribed statistical quality control program such as that described in TRH5[31]. In this way, random selection of sampling sites ensures minimum bias and a selected confidence limit for the acceptance of various parameters is used to ensure that the natural variability of the materials is taken into account.

Should any lot be rejected, corrective measures should be taken immediately in order to avoid the difficulties often associated with ripping treated material which has dried out. No additional chemical should be added to reworked material as, once the chemical has been added, it is not lost by evaporation or leaching.

Quality control testing should be carried out immediately after the vibratory rolling has been completed and prior to the application of the water at the start of slushing.

8   RECOMMENDATIONS

The use of sulphonated petroleum products as stabilisers for in-situ or local materials has a number of advantages:

- Application is simple; the product can either be sprayed-on or mixed-in during wetting for compaction (the latter is recommended);
- The material can be trafficked soon after compaction if necessary, although it is recommended that it is not trafficked until after curing;
- Very small amounts of chemical are needed;
- The chemical treatment is theoretically permanent;
- The treatment is cost-effective.

Provided the material is shown to react with the proposed product, SPPs can be considered for many uses in roads, both for the provision of structural layers in lightly trafficked roads and for the improvement of otherwise poor materials deeper in the pavement or even of subgrade for both lightly and heavily trafficked roads. In this way scarce resources can be conserved and the amount of material spoiled is minimised.

It is recommended that all materials be tested prior to treatment with SPPs to ensure that an appropriate electro-chemical reaction will take place and the product is not wasted. As a first indication, a minimum PI of about 8 is necessary to ensure the presence of some clay minerals, although SPPs can be effectively used in lower concentrations for less plastic materials.

The recommended construction procedure should be closely followed and effective quality control should be carried out.

9   CONCLUSIONS

Although ionic soil stabilisers have been in use for many years, they have not been marketed to their fullest potential. Recent work has shown that, provided they are used in the right context with suitable natural soils, significant savings can be achieved, particularly in low volume roads. This could be particularly beneficial in view of the increasing need for improvement of the road network in rural areas and in areas undergoing rapid urbanisation.

The ongoing research is providing a better understanding of the processes and mechanisms involved in the use of sulphonated petroleum products. This is providing means of establishing for which materials and under what conditions the appropriate ionic soil stabiliser can be economically used.

A recommendation on the selection of the type and quantity of possible SPPs for treatment of various materials is given in this report. It involves tests which can be carried out at most soils or agricultural laboratories, although X-ray diffraction techniques may require specialist input.

A properly controlled construction and quality control procedure should be employed on every project to ensure that the SPP is applied correctly and that the required end-product is achieved.

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Appendix A: The Determination of Cation Exchange Capacities Using Methylene Blue Adsorption

A.1 BACKGROUND

The method described here is based on a method described by Cokca and Birand[29]. The use of methylene blue in the determination of cation exchange capacities of clays was described as early as 1957 by Fairbairn and Robertson[32]. Certain changes have been made to the method described by Cokca and Birand, but the principle of the method is the same. The method was found to be easy to perform, it is a rapid procedure and the results from the test are comparable to those from conventional methods. This may be an advantage as the equipment required for the test procedure is available in most soil laboratories and, because of the speed of the test, it is possible to get results in a reasonable time.

The adsorption of methylene blue onto clays is attributed to two mechanisms. The first is that of cation exchange resulting from isomorphous substitution in the alumino-silicate lattice. The second is related to adsorption mechanism which might be either physical (Van der Waals) or chemisorption with the surface SiOH and AlOH of the alumino-silicate lattice[29]. Methylene blue hydrochloride consists of an organic base combined with an acid. When this is dissolved in water, methylene blue cations and chlorite anions are formed. The methylene blue can replace certain cations on the clay mineral surface and cover the clay surfaces. The exchange reaction is irreversible.

The test method works on the principle that, when methylene blue is added to a clay sample, it is adsorbed by the clay. At the cation exchange capacity (CEC) of the clay, the amount of methylene blue added to the sample equals the amount of methylene blue adsorbed onto the clay. Beyond the CEC, additional dye is not entirely adsorbed.

The method, like many other test procedures, has some limitations. The main disadvantage is the difficulty in establishing the purity of the dye. It is believed, however, that the chemical impurities in the highest grade of the dye are not large or variable enough to invalidate the method.

The method has been adopted by a wide range of disciplines because:[29]

- The necessary material is easy to obtain and is inexpensive;
- No special specimen preparation is necessary. The test permits activity of the clay fraction to be quantified without its being separated from the rest of the soil;
- The test can be performed in field laboratories;
- Test duration is usually between 10 and 40 minutes, depending on soil type, and
- The test results give a good indication of the mineralogy of the soil.

A.2 EQUIPMENT REQUIRED

- enough soil to provide at least 30 g of <0,425 mm material
- 0,425 mm soil sieve
- balance accurate to 0,01 g
- constant temperature oven capable of maintaining a temperature of 105 °C
- 500 mℓ or 1 ℓ glass beaker
- 50 mℓ or 100 mℓ burette
- glass rod or "dropper"
- variable speed electric mixer
- medium soft grade filter paper
- medical quality methylene blue
- distilled water

A.3 TEST PROCEDURE

The soil sample to be tested is sieved through the 0,425 mm sieve and testing is performed on the material passing this sieve. The material is oven-dried at 105 °C (overnight or until no further loss of weight is noticed).

A solution of methylene blue is prepared. The concentration of the solution is 10 g/ℓ. 10±0,1 g methylene blue dye powder ($C_{16}H_{18}N_3SCl$) is placed in a glass container, 1 ℓ distilled water is added and mixed thouroughly. A burette is filled with the solution and the volume of solution in the burette recorded.

A sample of 30 g of the oven-dried material is added to a suitable container (glass beaker) and mixed with 200 mℓ of distilled water until the mixture is homogeneous. Mixing should preferably be done using an electric mixer (700 rpm).

A small amount of methylene blue solution is added to the soil mixture, which is agitated continuously at about 400 rpm throughout the test. A drop of the slurry is placed on a filter paper with a glass rod and examined. More methylene blue solution is added if the examination indicates that the end point has not been reached and the process is repeated.

During the initial stages of the test, a blue spot will appear on the filter paper, surrounded by a transparent, clear ring of water which soon evaporates. The colour of the inner spot will become progressively darker with successive drops as more of the methylene blue dye is adsorbed onto the clay. The outer ring will remain transparent and clearly marked. Eventually the outer boundary of the blue spot on the filter paper breaks down into a light blue-green halo, radiating outwards.

At the first appearance of this halo, titration is stopped and five more drops of the solution are placed on the filter paper. If the halo does not persist, titration is continued. If the halo persists, the end point has been reached. At this point the reading on the burette is recorded.

A.4 CALCULATIONS

The volume of methylene blue solution added to the soil solution (V_{cc}) is calculated by subtracting the initial reading on the burette from the end point reading. The cation exchange capacity of the soil is determined by using the following formula:

$$CEC = \frac{100}{W_m} \ x \ V_{cc} \ x \ N_{mb}$$

where:

CEC = Cation Exchange Capacity (meq/100g clay)

W_m = weight of clay specimen (g)

V_{cc} = volume of methylene blue titrant (mℓ)

N_{mb} = normality of methylene blue (meq/mℓ)

The normality of the methylene blue is determined using the following formula:

$$N_{mb} = \left(\frac{weight \ of \ methylene \ blue \ (g)}{320} \right) \ x \ \left(\frac{100-X}{100} \right)$$

where:

N_{mb} = normality of methylene blue (meq/mℓ)

X = moisture content of methylene blue (%)

320 = molecular mass of anhydrous methylene blue (g)

The moisture content of the methylene blue dye (X) can, for most practical purposes, be determined sufficiently accurately by determining the quantity of water of hydration in the dye. This can be done by drying the dye at 105 °C to constant weight.

Appendix B: Long Term Changes in pH of Soils Treated with Anionic Stabilisers

B.1 BACKGROUND

The test procedure described here for the determination of changes in pH of soil samples treated with anionic stabilisers is based on the standard pH method as described in TMH1[7] (method A20). Certain changes have been made to the original procedure in order to ensure reliable and repeatable results over long periods. The procedure is recorded here for purposes of completeness and it is recommended that it be applied for research purposes only.

B.2 SAMPLE PREPARATION

- A sample of the soil for testing (< 0,425 mm fraction only) is weighed out and dried overnight in an oven at 105 °C.
- 30 g of the oven-dried material are weighed out and placed in a glass container. This material will be treated as the reference sample. The container is closed properly in order to prevent excessive changes in the moisture content of the sample.
- For each of the ionic stabilisers to be evaluated, at least one 30 g sample of the same material as the reference is weighed out and placed in separate containers.
- The required amount of ionic stabiliser is added to the samples and mixed properly. This amount is calculated as 1 mℓ per 5 g of soil, i.e. 6 mℓ for a 30 g soil sample.
- Distilled water is added to all the samples, including the reference, so that the amount of fluid in each sample equals 75 mℓ. Each sample is stirred for a few minutes.
- The sample containers are closed properly and left to stand undisturbed for at least two hours.

B.3 DETERMINATION OF pH

- The pH-meter is set up and calibrated according to its specifications and adjusted for temperature.
- The electrode should be kept in distilled water for at least an hour before testing. Between tests it should be cleaned and replaced in the distilled water.
- The sample material is stirred properly. The electrode of the pH meter is lowered into it, care being taken to ensure that it does not touch the container.
- It is left to stand for five minutes after which the pH is measured. The measurement is recorded accurate to two decimals.
- The electrode is removed from the sample. It is cleaned with distilled water and dried. The procedure is repeated three times on the same sample to give three measurements.
- The average of the three measurements is reported.
- The procedure is repeated for the other samples.

B.4 STORAGE OF SAMPLES

After determination of the initial series of pH values, the samples are properly sealed to prevent changes in the moisture content through evaporation. Sample containers should be clearly marked

with the sample number, date of preparation, type of ionic stabiliser used and other relevant information. These sample containers should then be stored in a safe place at room temperature.

Experimental testing is performed on day one (day of sample preparation), day 2, day 3, day 4, day 7 and thereafter at weekly intervals. Results of the reference sample may show slight variation, depending on the competence of the tester, quality control, etc. Results of the reference sample are adjusted to the same level as the initial measurement and the numeric values of adjustments recorded for each test number. Results of the other samples are subsequently adjusted by the recorded amounts. In this way, a clear indication of the variations in pH with time is given.