

Article

Basic Chemistry Explaining Engineering Properties of New-age (Nano) Modified Emulsion (NME) Stabilised Naturally Available Road Pavement Materials

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Featured Application: The stabilisation of road pavement materials has traditionally been based on a trial-and-error approach with little scientific input. This traditionally entrenched approach has its origin in the use of empirically derived material characterisation indicator tests some dating back more than a century. The reliance on archaic material characterisation tests, makes it basically impossible to predict long-term material interaction with reactive stabilisation agents. In order to effectively utilise available material nanotechnologies in pavement engineering, material characterisation need to incorporate scientific analysis procedures, identifying the mineralogy comprising the materials. An understanding of some of the basic chemistry defining available stabilising agents and the interaction with minerals will enable pavement engineers to assess potential engineering outputs. The key to the successful implementation of disruptive new concepts is not to get entrapped in complex fundamental chemistry. This article provides and put into context some basic chemistry which influences the characteristics and expected outputs applicable to the use of New-age (Nano) Modified Emulsion (NME) stabilising agents. The understanding of these basic concepts will increase confidence in the use of material compatible reactive stabilising agents and reduce risks towards the cost-effective use of naturally available materials.

Abstract: Nano-scale organofunctional silanes have been developed, tested and successfully applied to protect stone buildings in Europe against climatic effects since the 1860s. The same nanotechnologies can also be used in pavement engineering to create strong chemical bonds between a stabilising agent and the material substrata. The attachment of the organofunctional silane to a material also makes the surface of the material hydrophobic, reducing future chemical weathering. These properties allow naturally available materials to be used in any pavement layer at a low risk. In the built environment, scientists soon determined that the successful use of an organo-silane depends on the type and condition of the stone to be treated. The same principles apply to the implementation of applicable nanotechnologies in pavement engineering. Understanding the basic chemistry determining the properties of the stabilising agent and the organofunctional modifying agent and the chemical interaction with the primary and secondary minerals of the material are essential for the successful application of these technologies in pavement engineering. This paper explains some basic chemistry which fundamentally influences engineering outputs that can be achieved using New-age (Nano) Modified Emulsions (NME) stabilising agents with naturally available material in all road pavement

Keywords: nanotechnology in pavement engineering, stabilisations of naturally available materials, road pavement engineering, mineralogy, chemistry in emulsions, organofunctional silanes, anionic emulsion, cationic emulsion, New-age (Nano) Modified Emulsions (NME)

1. Introduction

The use of nano-scale products for the stabilization of granular materials in the construction of the pavement layers is nothing new. Per definition, products like cement, lime as well as bitumen emulsion all incorporate nano-scale particles and can be considered as nanotechnology products, i.e., containing particles of which at least one dimension is between 1 and 100 nm in size [1]. The use of the term “nanotechnology” only came to the fore after the development of equipment enabling scientist (including chemists, physicians and engineers) to see and manipulate nano-scale particles at a molecular level in the 1980s/90s [2,3]. This ability to manipulate nano-scale products has had an impact on all industries, including the built environment where silicon-based nanotechnology products are being used to improve building materials across basically all spheres of activity. Before the 1980s, through trial and error, silicon-based products have been developed, tested and used in the built environment to protect stone buildings in Europe since the 1860s [4]. The more than 150 years of “lessons learnt” from the built environment can assist pavement engineers to fast track the implementation of these proven technologies to also protect and improve naturally available materials for use in road construction.

Materials used in road pavements are traditionally classified using empirically derived criteria using material indicator testing dating back some more than a century [5]. These material classification systems most often classify naturally available materials in climatic regions of the world associated with a high potential for chemical decomposition (high temperatures in combination with seasonal rainfall [6]) as “non-standard”, “marginal” or even “sub-standard” [7]. Available and applicable nanotechnologies that could enable the use of these materials could substantially reduce the unit costs of road infrastructure.

Bitumen emulsion technology dates back to the early 1900s [8], when a nano-scale particle was discovered to enable an oil substance (bitumen) to be mixed this water. This nano-scale particle is commonly referred to as an emulsifying agent (also known as a surfactant and in the engineering industry commonly referred to as a “soap”). This technology enabled a relatively low bitumen content to be mixed with materials at ambient temperatures to construct road pavement layers incorporating several advantages, which include an ability to accommodate much higher tensile strains in comparison to cementitious bound materials [5, 9]. However, similarly to the manufacturing of asphalt, it is still a requirement to use aggregate/stone/gravel materials of a relatively high quality with the bitumen emulsion in the mix to construct a pavement layer, meeting the required engineering properties [10].

Similar to the manufacturing of asphalt for surfacings, the unmodified bitumen forms no chemical bonds with the aggregate/stone materials in the mix. Strength is only achieved through covalent bonds (relatively weak) and mechanical forces created through granular interlock and absorption of the bitumen into a porous surface of the aggregate. For this reason, some aggregates containing a high silicon content which usually result in relatively “clean breaks” during crushing, are notoriously difficult to use for the manufacturing of asphalt or bitumen emulsion stabilised layers, meeting the engineering requirements. In these mixes, the use of materials conforming to specific grading envelopes are of major importance in creating a firm granular matrix which results in high interlocking mechanical forces to be formed. The ability to create chemical bonds between the stabilising agent (e.g. bitumen or equivalent polymer) and the material to be stabilised (aggregate/stone/soil) is available through the introduction of and use of proven material compatible organofunctional nano-silanes. These nano-silane products attach to the material substrata creating relatively strong ionic-chemical bonds, with the organofunctional part of the molecule also rendering the surface of each particle of the material to become hydrophobic, preventing water access to primary and secondarily minerals within any mix. The high chemical bond strengths and the enacted hydrophobicity enable materials classified as “non-standard”, “marginal” or “sub-standard” to be

utilised successfully within any pavement structure at a low risk. The introduction of material compatible organofunctional nano-silanes in the field of pavement engineering is an example of a disruptive technology [11], requiring traditional approaches to the use of materials in pavement engineering to become irrelevant in the face of scientifically proven results. The general acceptance of disruptive technologies requires improved knowledge of the basic supportive science to become generally available and accepted. The key is not to get entrapped in complex fundamental chemistry, but to simplify facts to be easily understood in support of practical implementation.

Many products have been introduced throughout the last few decades claiming to be able to provide the ability to improve material characteristics to enable the use thereof in road pavement structures. These so called “snake oils” have usually failed to achieve the required results. In the absence of a scientifically based approach to material investigations and tests indicative of engineering principles (e.g. stresses, strains and durability), the same could happen to the introduction on applicable/proven nano-silane technologies in the pavement engineering field [12]. The lessons learnt from the built environment in essence emphasised that the successful use of a organofunctional silane technologies to improve material characteristics are fundamentally based on the compatibility with the type of stone (primary minerals) and condition of the stone (secondary minerals developing during chemical weathering).

It follows that material classification should be based on the scientific testing of the primary and secondary minerals of the available materials [12]. Knowledge about the mineralogy of the materials will enable engineers to select a material compatible technology to enhance marginal materials for use in the upper pavement layers.

A basic understanding of the chemical interaction between the minerals in the material and the potential available nanotechnology solutions is also for pavement engineers to understand and ensure that any potential risk associated with the use of silicon-based technologies is minimised, if not eliminated. The same principles apply to the nanotechnology chemistry influencing the characteristics of the stabilising agent (e.g. bitumen emulsions or equivalent) to be used in combination of the organofunctional silane modifying agent. This paper aims to give a basic description of some basic pre-dominant chemical characteristics of an emulsion stabilising agent, the nano-silane modification thereof and the chemical interaction with the mineralogy of the material substrata in the context of road pavement materials.

The informed selection of applicable material compatible technologies that are stable for practical application under often challenging practical field conditions, will often prove to be the difference between success and failure. It is not the intention to make pavement engineers chemists, but only to provide them with the necessary tools to make informed decisions in practice. The key is not to confuse through fundamental detailed chemistry, but to provide practical clarifications, explaining results and showing consequences of insufficient specifications. Knowledge about these basic chemical concepts controlling material behaviour in the field, will assist greatly in the informed application of materials and the use of material compatible technologies by engineers specialising in road pavement engineering. The successful introduction of new-age nanotechnologies is disruptive to traditional pavement engineering practices. Hence, the understanding of the basic chemistry controlling nanotechnology characteristics in combination with the mineralogy of naturally available materials can facilitate the acceptance of the engineering benefits in road construction, leading to a substantial reduction in transportation infrastructure costs.

2. Background

Silicon-based or organofunctional nano-silane products have been the main ingredient of stone protection technologies used in Europe for the protection of buildings against the negative impact of the environment and pollution since the early 1800s [4]. Initially, many of the scientists developing the products for the built environment rec-

ordered different results and a large variation in the successful treatment of buildings. These conflicting results led to the identification of the importance of the understanding of the role that the type and condition of the stone to be treated plays in the successful use of a specific product. Knowledge about the minerals comprising the different types of stone and the understanding of the chemical reaction during consolidation of the nano-silane product onto the material substrata is essential to ensure that the application of a specific product is successful. The successful consolidation of a specific nano-silane depends on the availability of primary minerals within the stone to form high-strength chemical bonds and penetration into the stone providing long-term protective layers.

The presence of secondary minerals in the stone caused by chemical weathering due to environmental exposure, also needs to be addressed during the application of a nano-silane products. Secondary minerals present in stone are normally highly sensitive to the influence of water (e.g. different clays) resulting in high volume changes, enhancing deterioration of the stone. Hence, the nano-silane application needs to be sufficient to neutralise these detrimental characteristics of the secondary minerals, rendering them hydrophobic and preventing water to access these minerals. The same basic principles will also apply to the use of nano-silane technologies in pavement engineering. Knowledge about the basic mineral composition of the materials to be treated/stabilised is essential to identify the best silane-based nano-technology to apply. Understanding these material characteristics in combination with the basic chemical characteristics of the nano-silane modified stabilising agent will minimise any future risks and will be fundamental to confidently select and optimise the application of organofunctional nano-silane products on a macro level [5,9].

Although mineralogy tests have been available for almost a century, empirically derived material indicator and bearing capacity tests (some dating back more than a century [5] have become imbedded in standard pavement engineering practice. Little development with regard to improved use of scientific information for the classification of granular materials has occurred over a number of decades, a contentious issue between pavement engineers and geologist for at least since the 1950s [6].

The lack of scientific knowledge of the mineralogy of materials and the chemical interaction thereof with any re-active stabilising agent (including traditionally used stabilising agents such as cement, lime, etc.) incorporates a relatively high risk of pre-mature (costly) failures [13]. The development and availability of improved stabilising agents and modifications to traditionally used stabilising agents have progressed remarkably since the 1980s with the development of scientific equipment that enabled scientists to observe and manipulate materials at a nano-scale at a molecular level [12]. Similarity, equipment for the testing of the mineralogy of materials are now producing six generation equipment with associated software that is the size of a desktop computer (X-Ray Diffraction equipment)[5]. These developments are key to the successful evaluation and use of naturally available materials and the selection of material compatible stabilising agents (or modified stabilising agents) to successfully enable these materials to meet engineering requirements in road pavement structures.

However, similar to the built environment, the successful implementation of such nano-technology solutions will rely on the understanding of the chemical interaction of available, proven, safe and applicable products in combination with the mineralogy of the materials [5]. In hot and wet climatic conditions (normally found between the Tropics of Cancer and Capricorn) the mineralogy could vary considerably as influenced by the geology and numerous climatic related aspects that influence the chemical weathering of the original materials over the past millennia [6]. The important differences of materials in these regions compared to the rest of the world is summarised in Figure 1.

Climatic conditions	Cold regions (little decomposition)	Warm/humid regions (considerable decomposition)
Property	Materials: Conventional (Crushed rock base, river gravels, glacier outwash)	Materials: Pedogenic (laterites, calcretes, ferricretes, silcretes, etc.)
Climate	Temperate to cold	Arid, tropical, warm temperate
Material Composition	Natural or crushed	Varies from rock to clay
Material Chemical reactivity	Inert	Reactive
Material Variability	Homogeneous	Extremely variable

Figure 1. Differences between Basic Rock and Weathered decomposed Materials (Adapted from [7,14])

A need exists to create awareness within the field of pavement engineering that optimal material usage require scientifically based information in terms of the basic material mineralogy. This information can relatively easily and cost-effectively be obtained using available equipment. Scientific knowledge about the material mineralogy and the basic chemistry involved with the application of re-active agents will largely eliminate the risks associated by trial-and-error approaches and ensure that applicable solutions are not disregarded due to the many uncertainties associated with empirically derived tests.

The purpose is not to provide a detailed micro-level scientific chemical and physics analyses of the available and proven nanotechnologies that are currently used in the built environment. However, a simplified explanation of the impact of some micro-level chemical compositions and the major macro-level implications on the material engineering characteristics applicable to the field of pavement engineering (material science) is needed. The field of pavement engineering is traditionally conservative. The understanding of some basic scientific concepts as applicable to the materials used in roads is considered instrumental to the general acceptance of disruptive nanotechnologies. A much-needed change in the mind-set of pavement engineers is required to accept the use of naturally available materials currently considered as being “non-standard”, “marginal”, “low-cost”, or even “sub-standard” [7] not only for the construction of Low-Volume Roads (LVR), but more specifically, also for use in the upper layers of major freeways, designed to carry relatively high traffic loadings.

3. Traditional use of nanotechnology products in road pavement engineering

The use of nano-scale material in the road industry (over and above the use of lime and cement) as stabilisation agents, dates back more than a century with the development of bitumen emulsions in the early 1900s [8]. As per definition [15], bitumen emulsion consists of bitumen, water and an “emulsifying agent” (also commonly referred to in industry as “soap” or as a surfactant). The emulsifying agent is in fact a nano-scale particle commonly referred to as a “Janus” particle [16] (from the Greek mythology meaning “two-faced”) due to the dual nature of the emulsifying agent particle, attracting oil on the one side and water on the other side.

It is not the intention to discuss in detail the technology involved in the production of bitumen emulsions [8,17,18,19]. It is generally known that numerous production factors etc. could influence the characteristics of bitumen emulsion which are discussed in detail in numerous publications. The objective of this paper is to concentrate on the effects of the chemistry involved in the additives and modifications used in the manufacturing of bitumen emulsion as a stabilising agent. Understanding the role of the emulsi-

fying agent is comparable to that of organofunctional nano-silane products used in the built environment. Hence, the discussion in this paper is limited to the role of the emulsifying agent that enables water to be mixed with an oil (organic substance – in this case bitumen) – substances which, under normal conditions, do not mix.

The mixing of the two mediums is achieved through the addition of a chemical nano-particle (the emulsifying agent, soap or surfactant) at high shear (e.g. high mix revolutions) which forces the oil and water together with the emulsifying agent through small openings or between plates which enables the bitumen (oil) particles to separate and mix and attached to the emulsifying agent already mixed and attached to water molecules. The emulsifying agent typically has a hydrophilic (water loving) head and a lipophilic (oil loving) (hydrophobic) tail consisting of between 12 and 18 carbon atoms [8]. The chemical composition of typical emulsifying agents is shown in Figure 2 (anionic) and Figure 3 (cationic). The Hydro-carbon tail of the emulsifying agents is often replaced in chemical formulas by the letter "R".

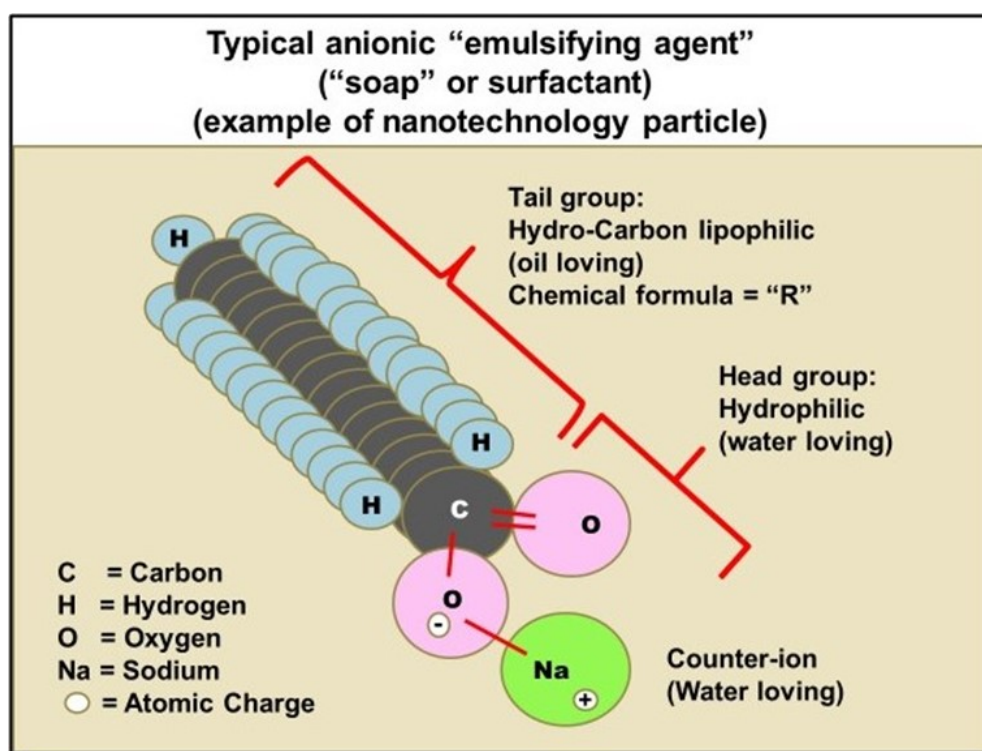


Figure 2: Typical composition of an Anionic emulsifying agent

The higher the number of carbon atoms in the hydro-carbon tail the more firmly the emulsifying agent will attach to the organic stabilising agent (bitumen molecule). The hydro-carbon tail embeds itself in the bitumen molecule. In comparison, if the earth resembles the size of a bitumen molecule the hydro-carbon tail of a good emulsifying agent (high number of carbon atoms) will typically penetrate the crust of the earth to a depth of approximately 8 km and covers an area of approximately 10 km² [18].

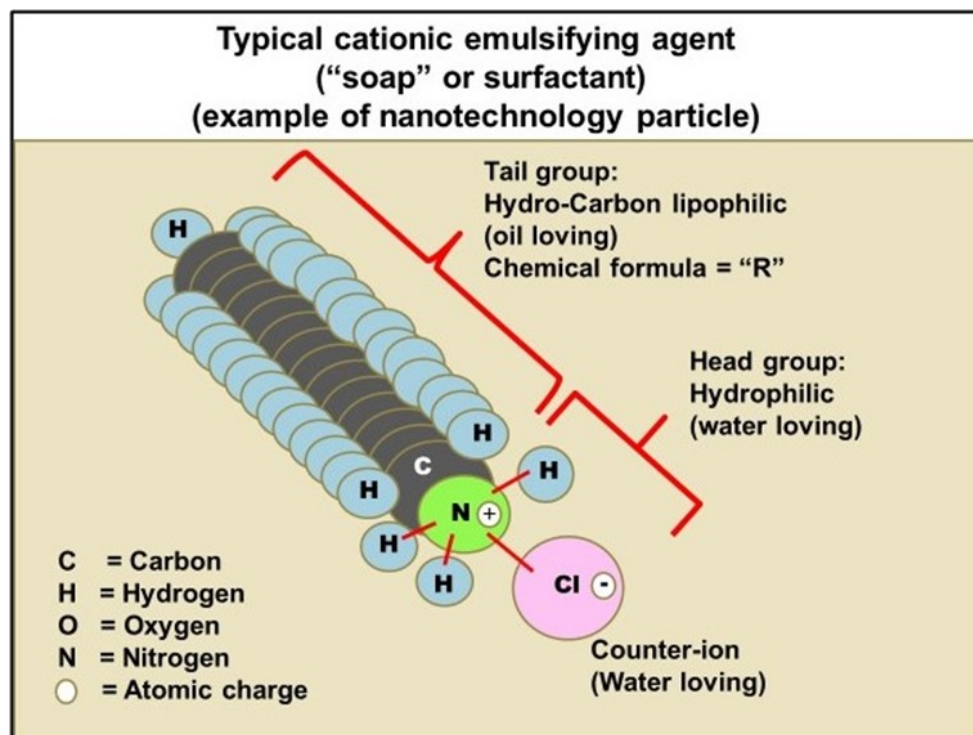
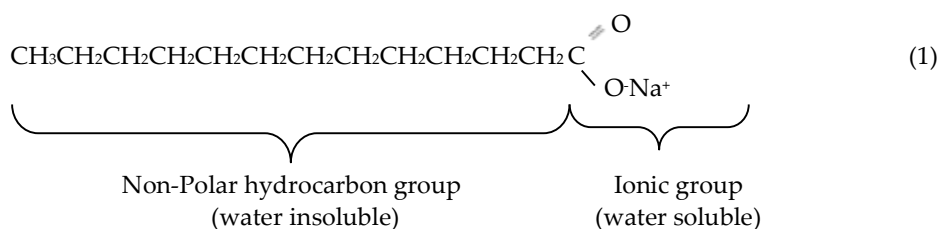
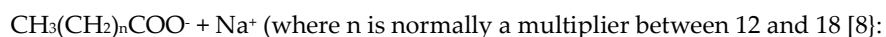


Figure 3: Typical composition of a Cationic emulsifying agent

The visual representation of the anionic emulsifying agent shown in Figure 2 is expressed in chemical formulation as follows [17,18]:



Equation (1) is simplified to:



with n typically varying between 12 and 18 [8].

Formula (2) is further simplified to:



Similarly, a typical cationic emulsifying agent shown in Figure 3, would be depicted as:



The properties and stability of the emulsion is a function of numerous factors, including the properties of the emulsifying agent (e.g. the length of the carbon-tail shown as "n"), the percentage of the emulsifying agent, the manufacturing process and the properties of the bitumen. In terms of the chemical stability, it is worth noting that the bond strengths between the various atoms in the emulsifying agent differs substantially. These bond strengths could also play a major role in the stability of the emulsion, especially in combination with a second nano-particle and/or when a modification to the emulsification agent is introduced. The bond strengths between some of the major atoms comprising the emulsifying agent is summarised in Figure 4 (compiled from information published in [20]).

Emulsifying agent – “soap”	
Anionic vs Cationic	
Bond between well-known elements (Diatomic molecules)	Bond strength in kcal mol ⁻¹ (kilocalories per molecule) at 25°C
C = O	298.4
C - O	256.7
HC = HC	230.0
Si - O	188.0
C - N	184.0
H ₂ C = CH ₂	173.0
C = C	166.0
N - O	149.7
N - Si	105.0
H - O	102.4
H - N	75.0
H - Si	71.4

Figure 4: Comparison of the bond strengths between the various elements comprising the different emulsifying agents (anionic in pink and cationic in green) (compiled from [20])

From Figure 4 it is seen that the bond strengths between the elements comprising an anionic emulsifying agent (pink arrow combinations) is considerably stronger than the bond strengths comprising the typical cationic emulsifying agent (green arrow combinations). This simplified chemistry explains the general trends found in the stability normally associated with anionic versus cationic bitumen emulsions in practice, assuming all manufacturing processes are optimised in line with good practices. The implication in practice is that an anionic emulsion would normally have a longer shelf life than a cationic emulsion – an important practical factor especially considering remote areas of implementation, uncertain climatic conditions and a construction industry often faced with unplanned delays due to political and managerial factors not within the control of the contractor.

4. Influence of the chemical characteristics of the emulsifying agent on the potential engineering properties achievable

A good emulsifying agent (i.e., an emulsifying agent with a relatively long carbon tail also contributes significantly towards engineering properties to be achieved when used for the stabilisation of materials for use in roads. These characteristics are normally not addressed in specifications (e.g. [15]). It follows that bitumen emulsions manufactured according to such specifications could result in substantial differences in the engineering properties when used to stabilise the same materials. Under conditions where procurement procedures are based on the award of tenders based mainly on the lowest tender, bitumen emulsion manufacturers would need to produce bitumen emulsions within specification using the lowest possible input costs. The lowest cost emulsifying agents are normally also associated with carbon tails (as demonstrated above) of limited length.

The influence of the chemical characteristics of the emulsifying agent is demonstrated by testing the engineering properties of stabilised materials, sourcing eight different bitumen emulsions from five different suppliers (some using more than one different emulsifying agent). Variations in bitumen characteristics are limited by ensuring that all suppliers use bitumen produced by the same refinery. External factors other than the type of emulsifying agent is further reduced to stabilised materials of the same quality from the same quarry, mixed together to ensure material variations will have a limited impacts on results. All samples are mixed, cured and tested in the same laboratory using the same technicians in a blind testing regime. The Unconfined Compressive Strengths (UCS) tests (dry and wet [9]) and the Indirect Tensile Strengths (ITS) tests (dry and wet [9]) were measured and compared using the eight different bitumen emulsions all manufactured meeting the specifications [15].

The results using the eight different bitumen emulsion stabilising agents relative to the maximum results are shown in Figure 5 (UCS dry and wet), Figure 6 (ITS dry and wet) and Figure 7 (Retained Compressive Strength (RCS) (UCS_{wet}/UCS_{dry} as a percentage) and Retained Tensile Strength (RTS) (ITS_{wet}/ITS_{dry} as a percentage). The different suppliers are identified by the letters A to E. The number of different emulsions received from each supplier is shown by the number following the alphabet letter, e.g. A1, A2. Where the emulsifying agent is known and to compare the same emulsifying agents from different suppliers, these emulsifying agents are identified by a further number, e.g. A1-1 and D1-1. The average values of three samples each of the UCS dry and wet tests and ITS dry and wet tests and the RCT (% (UCS_{wet}/UCS_{dry}) and RTS (% ITS_{wet}/ITS_{dry}) are shown in the comparative results.

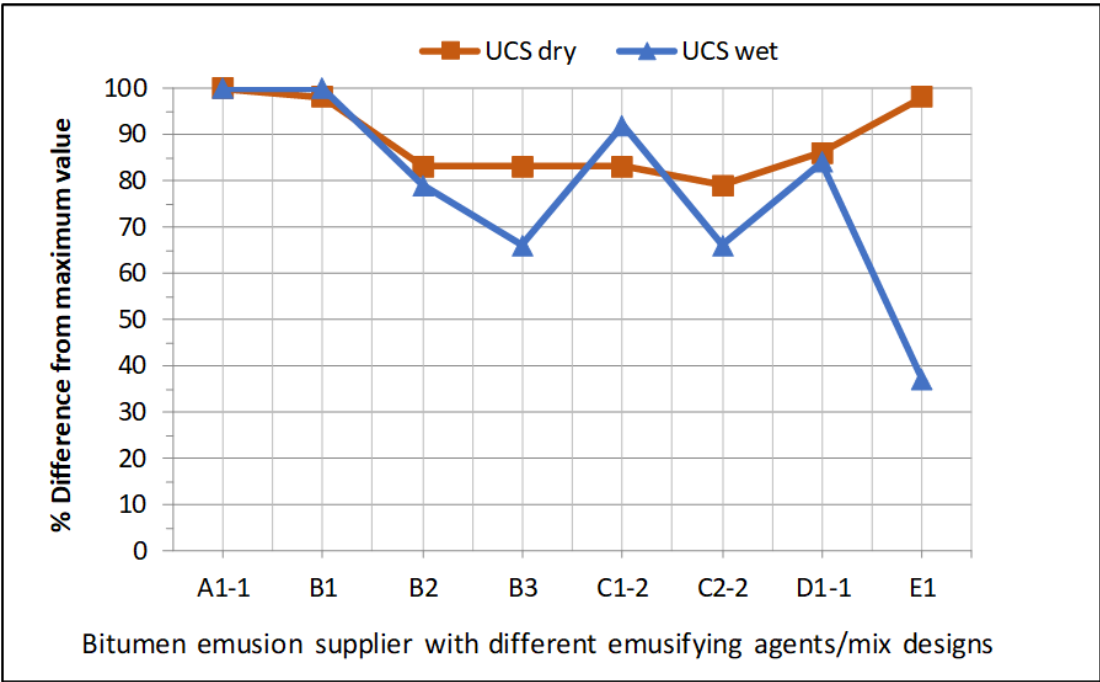


Figure 5: Comparison of the UCS results (dry and wet) using 8 different bitumen emulsions from 5 different suppliers, with variations in the emulsifying agent used in the manufacturing of the bitumen emulsion – all manufactured products was meeting the national specifications [15]

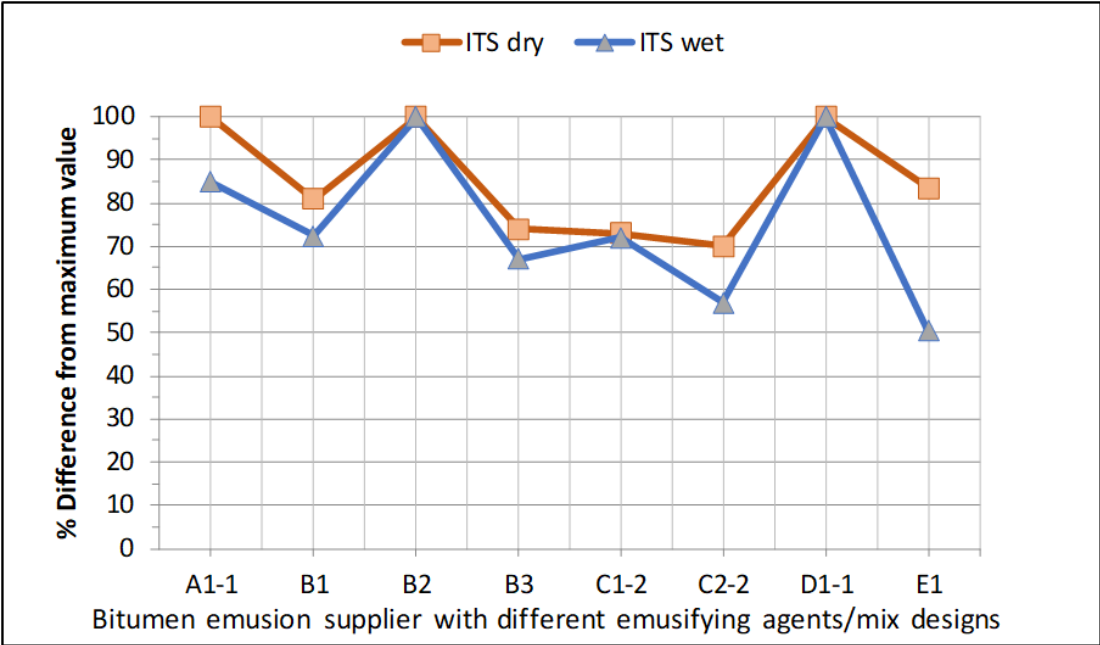


Figure 6: Comparison of the ITS results (dry and wet) using 8 different bitumen emulsions from 5 different suppliers, with variations in the emulsifying agent used in the manufacturing of the bitumen emulsion – all manufactured products were meeting the national specifications [15]

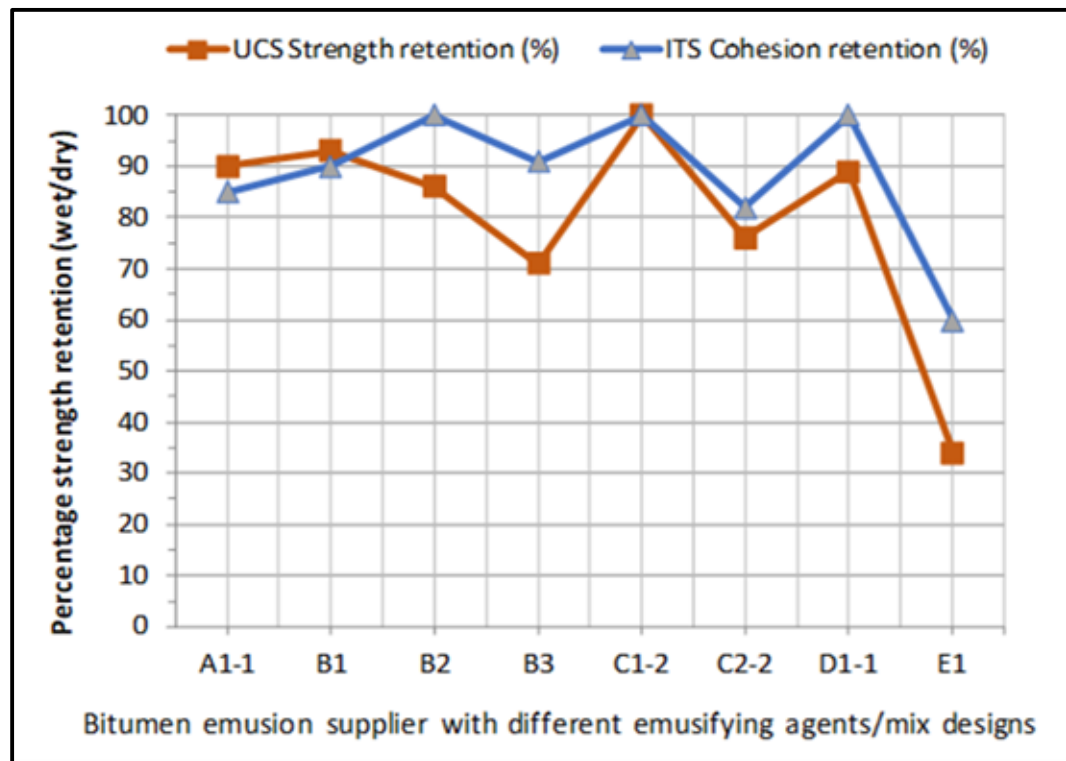


Figure 7: Comparison of the relative retained UCS strengths (UCS_{wet}/UCS_{dry} as a percentage) and ITS cohesion retention (ITS_{wet}/ITS_{dry} as a percentage) using 8 different bitumen emulsions from 5 different suppliers, with variations in the emulsifying agent used in the manufacturing of the bitumen emulsion – all manufactured products were meeting the national specifications [15]

Although all the emulsions used conformed to the National standards [15] currently used in practice in South Africa, some alarming variations in the measured UCS, ITS, RCS and RTS engineering properties are shown. Depending on the property tested a variation of 30 to more than 50 per cent in the average measurements between the eight different products were recorded. Given the relatively good material (CBR >45 @ 95% mod AASHTO [21,22]) used to compare the engineering properties, these results are alarming and could result in end products not meeting the requirements, especially when used in combination with naturally available materials of poorer quality. It follows that the manufacturing of bitumen emulsion not specifying the characteristics of the emulsifying agent can be problematic in practice and can lead to unforeseen construction problems. In an open procurement process the achieving of the engineering properties is the prime objective. Hence, the use of inferior products can be limited through end product specification. In such cases the contractor and supplier must guarantee that the product to be used will meet the minimum engineering properties to be achieved. Such an approach will ensure that the end product will meet the engineering requirements of the design and limit any risk associated with chemical variations.

5. Basic chemistry influencing the successful application of New-age (Nano) Modified Emulsions (NME)

5.1. Silicon characteristics in the material sub-strata and applications within the built environment

Silicon (Si) is the second most abundant element (after oxygen) comprising more than 26 per cent of the crust of the earth (by weight). In comparison, Oxygen makes up more than 49 per cent by weight of the crust of the earth. The rest of the elements con-

tained in the crust of the earth in combination makes approximately 25 per cent by weight of the crust of the earth. Silicon is found in nature as oxides (SiO_2) or silicates (SiO_4) forming the basis of most rock-forming minerals [6]. Commonly known naturally available materials such as granite, feldspar, hornblende, asbestos, clay and mica are a few examples of materials normally containing high percentages of silicon [19].

Silicon is also one of the most useful elements to mankind. In the form of sand and clay it is commercially used as a cost-effective product to produce building components such as pottery, bricks, cement, glass, etc. Silicon also plays an important role in plant as well as animal life, forming part of cell-structures and found in plant remains as well as skeleton structures. It is considerably versatile in application, inherent to most of the nanotechnology-based products currently in common use in the built-environment, with “excellent mechanical, optical, thermal and electrical properties” [20].

The silicon present in nature as silicates can form 4 bonds with oxygen atoms which may be orientated in various geometric structures forming a three-dimensional infinite structure [23,24] to form minerals and the surface of the sub-strata or rock surface as commonly referred to. Figure 8 shows a very simplified illustration of the composition of naturally available materials (rocks), as numerous elements are found in nature that combine with the basic silicon lattice to form a large variety of minerals commonly found in all rock formations. Of importance is the illustrated attraction of siliceous materials to water molecules freely available in the atmosphere.

Rock surfacings contain “broken chains” of chemical bonds that form a layer of free energy [6] on the surface of rock/gravel or soil. The surfaces of these naturally available materials (with a few exceptions) are hydrophilic (water-loving) and attract water molecules freely available in the atmosphere. Hence, freshly crushed stone is instantaneously covered by numerous layers of water molecules that (a water molecule is 0.1 nm in size or 1 Angstrom ($^{\circ}\text{A}$)). These layers of water molecules covering the area of the stone is invisible to the eye and other senses (touch/smell). Water molecules (H_2O) are always accompanied by its natural derivatives of negatively charged oxygen (O^{2-}) and positively charged hydrogen (H^{+1}) in the atmosphere that surround the surface of rock/gravel/soil and is attached to the surface as shown in Figure 8.

The freely available hydrogen (H^{+1}) combines with the negatively broken oxygen chains of the minerals to form $(\text{OH})^{-1}$ bonds on the surface. The siliceous surfacings containing O^{2-} and $(\text{OH})^{-1}$ bonds are hydrophilic in nature and hence, attracts water. The simplified lattice shown in Figure 8 forms the basic understanding of the application of various nanotechnologies developed using the properties of the silicon element which have been used in the built environment for more than a 150 years [4]. The same basic technologies can also find wide application in pavement engineering enhancing the characteristics of road building materials.

5.2. Chemistry of organofunctional nano-silanes for application in pavement engineering

Most of the nanotechnology products currently used in the built environment to protect, preserve and/or strengthen building materials are based on the silane (SiH_4) derivative of silicon which has found application as the basis for the development of stone consolidants for more than a century and a half [4]. Each hydrogen (H) atom in the silane (SiH_4) can be replaced by any other element or group(s) to form a large variety of nano-products with numerous fields of application.

The most common reactive groups are hydrogen (H), chloride (Cl), fluorine (F) and RO where R is the general symbol for the alkyl group also known as the organo-functional group in silane-chemistry (also referred to as the hydrocarbon group discussed and explained in the composition of the emulsifying agents demonstrated in Figures 2 and 3) which may, inter alia, include chemical compounds such as CH_3 (methyl) or CH_3CH_2 (ethyl).

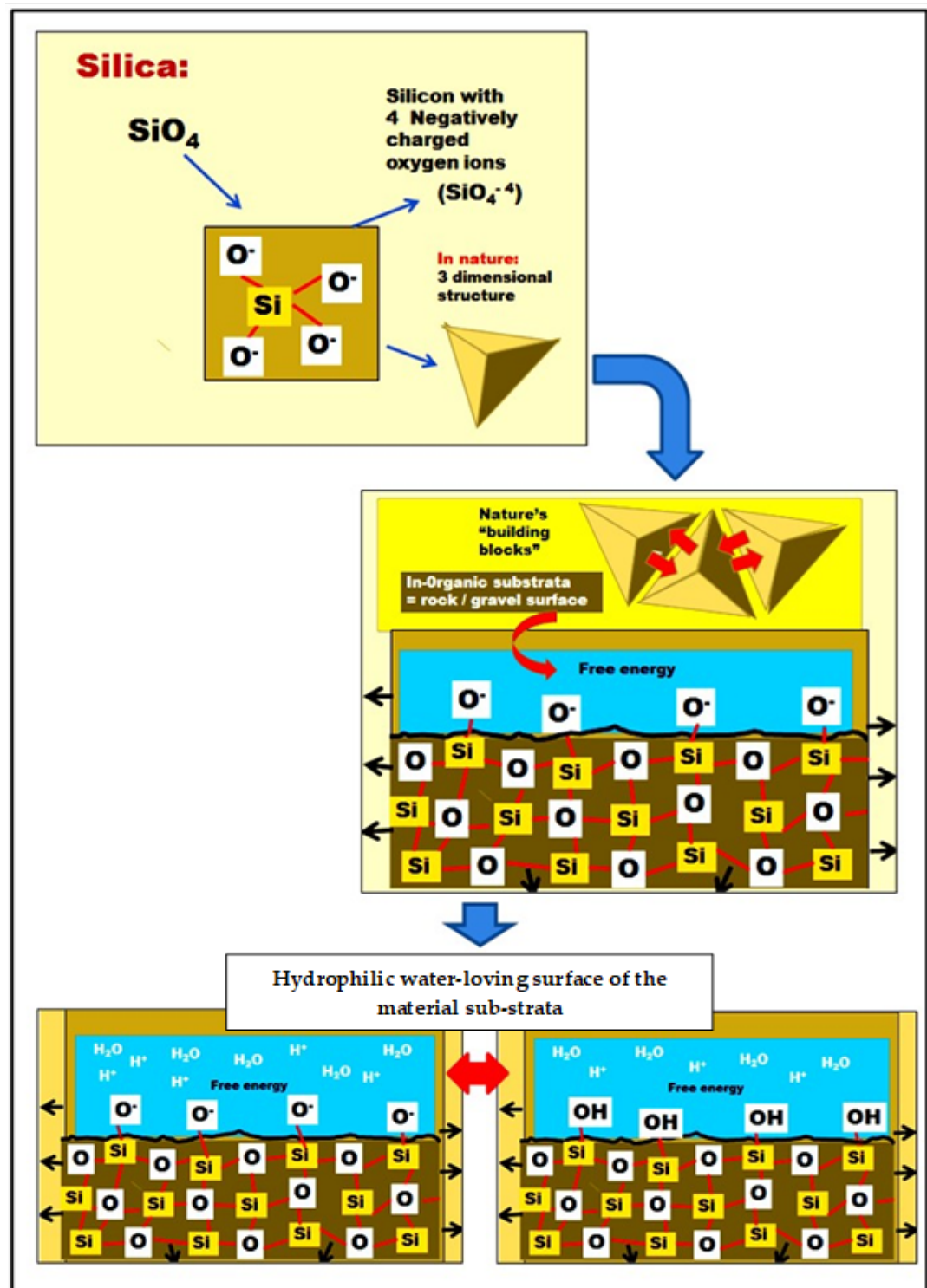


Figure 8: Simplified demonstration of the most common sub-strata or rock formations in nature

The $\text{CH}_3\text{-Si}$ bond is a very stable (non-reactive) bond (known as an organo-silane), with a low surface energy with hydrophobic (water-repellent) or oleophilic (oil-loving) characteristics. The reactive group RO is referred to as an alkoxy (alkyl + oxygen) group [4]. Silicon (Si) forms the centre of the RO group together with second functional group(s) (X) (e.g. methoxy, ethoxy, etc.) to form the chemical molecule RO-Si-X . These secondary

functional (pendant) groups may be highly reactive (in cases where the element of carbon (C) is excluded from the formulation) and defines the compound's functionality [4]. The functional group (R) will attach to organic material (such as bitumen or an alternative material compatible polymer), while the functional group(s) (X) will attach to inorganic material (such as rock/gravel/soil). Hence, an organo-functional nano-silane combines the functionality of a reactive group with a non-reactive group in a single molecule.

It should be noted that the organofunctional nano-silane is not replacing the stabilising agent in the stabilisation of road building materials. The molecule is too small to effectively bridge the gaps between the material fractions. However, in practice, the nano-silane can very effectively fulfil the role of a bonding agent (adhesive agent) which is designed to permanently bind the stabilising agent (the bitumen or equivalent organic substitute) to the stone/aggregate/soil material sub-strata. Si – O chemical bonds are some of the strongest found in nature (refer Figure 4). Due to the high surface ratio obtained by the nano-silane particle [25] (depending on the type of nano-silane and the quality of the product the size of nano-silanes may vary from about 5 nm to less than 1 nm) a relatively small amount of the nano-silane is required to totally encapsulate the stone/gravel/soil material particles (for example, 1 litre of nano-silane could easily have the same area coverage of about a 1000 litres of bitumen – the bitumen molecule being in the order of 1000 to 5000 nm in size) [8,25].

As mentioned, the organofunctional nano-silane particle will, in effect, have the properties of a "coupling agent" commonly referred to in pavement engineering as an aggregate adhesive. Aggregate adhesives or aggregate promoters are well known terminologies in pavement engineering and have been in use for at least two decades [26] as modifiers to bitumen emulsions. However, the use of silicon-based nanotechnology in pavement engineering is relatively new and has been developed mainly over the last two decades.

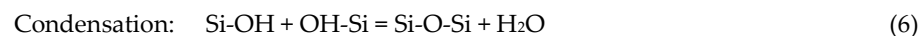
The functionality of the silane R-Si-X molecule in terms of an aggregate adhesive mainly refers to the ability of the (X) re-active group to be removed from the molecule when in contact with water (to effectively be removed by water) and replaced by a hydroxyl (OH) group, during a process referred to as hydrolysis [4]:

Where:



The one product of hydrolysis is the Si-OH binding referred to as silanol [4]. Silanols are now able to re-act with each other to form siloxane bonds in a condensation reaction when in contact with an inorganic substrata (e.g. rock/gravel/soil) [4], covering the total area of the material sub-strata. It should be noted that the by-product during condensation should preferably be water (H₂O), as shown in the example (not all available nano-silane products produce water as a by-product - at worst a non-toxic alcohol should be allowed to form as a by-product during condensation):

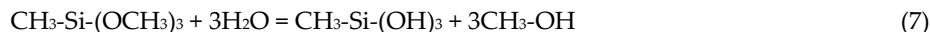
Where:



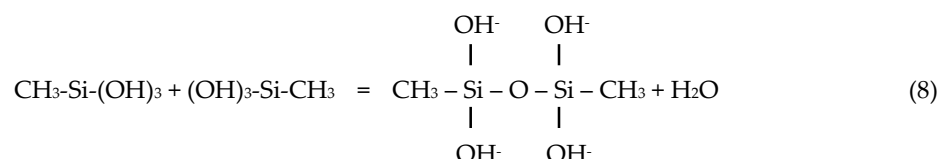
Of importance to the field of pavement engineering is that the organic (R) (organofunctional) group attached to the silicon by means of a direct Si-C bond is not affected by hydrolysis and will remain stable also during condensation. It follows that in the case of CH₃-Si-(OCH₃)₃ (methyl-trimethoxy-silane) the methyl group (CH₃) directly attached to the silicon atom will remain stable throughout the process of hydrolysis and condensation, while the hydrogens in the methoxy ((OCH₃)₃) groups will react with water. These effects of hydrolysis and condensation are demonstrated as follows [4]:

Where:

Hydrolysis:



Condensation:



In order to be effective as a consolidant, the silane-compounds must be able to form three-dimensional networks and hence, must have at least three reactive groups. The pavement engineering implications (macro-effect) of the above nano-silane formulations are demonstrated in Figure 9, which should be considered together with Figure 8 and the similarities with the emulsifying agent shown in Figures 2 and 3.

The effective result shown in Figure 9 is that the material sub-strata (rock/aggregate /soil) surface will change from a hydrophilic (water-loving) to a hydrophobic (water-repellent) state that attracts an organic material (such as oil/bitumen or an equivalent material compatible polymer) and actively repels the water molecules that are naturally attracted to aggregate or soil surfaces due to broken bonds as discussed and demonstrated in Figure 8, as well as the water that is the by-product formed during the condensation phase in the example shown.

Figure 9 represents a most basic schematic explanation of the practical use of nano-silane science in pavement engineering. The changing and matching of re-active and non-reactive bonds to the silicon element will result in literary numerous different nano-products with different characteristics which could match the numerous minerals available in naturally available materials such as gravel or soils.

At the same time, through creating the appropriate bonds the surface of these materials will become water repellent, negating the negative impact that water have on the durability of materials through the prevention of (or at least limiting) weathering due to chemical decomposition. A pre-requisite of the process of weathering of materials through chemical decomposition (chemical change) and the formation of resultant secondary minerals is the presence of and access to water [6]. In pavement engineering design analyses, it is usually assumed that material mineral properties will stay unchanged during the design period. This basic assumption is incorrect and even over a design period of 20 to 40 years, dramatic changes can occur (even in freshly crushed stone) which will influence the design assumptions considerably.

This aspect alone shows the potential benefit of the use of organofunctional nano-silane products in pavement engineering as a protective agent for high-value, freshly crushed stone against chemical decomposition and deterioration over its design life (e.g. a 20-year normal design period). Rehabilitation investigations done on major freeways in the Gauteng province of South Africa have shown that high quality newly constructed stone G1 (Figure 10) [27] base-course material can deteriorate over a period of 22 years to an equivalent G4 to G6. Similarly, secondary roads in the Gauteng region of South Africa have shown that a cement-treated base-course layer can deteriorate from a Cement treated layer (UCS 750 to 1500 kPa) quality layer to as equivalent G7/8 material [27] over a period of 20 years (rehabilitation investigations undertaken in the Gauteng Province of South Africa by main author).

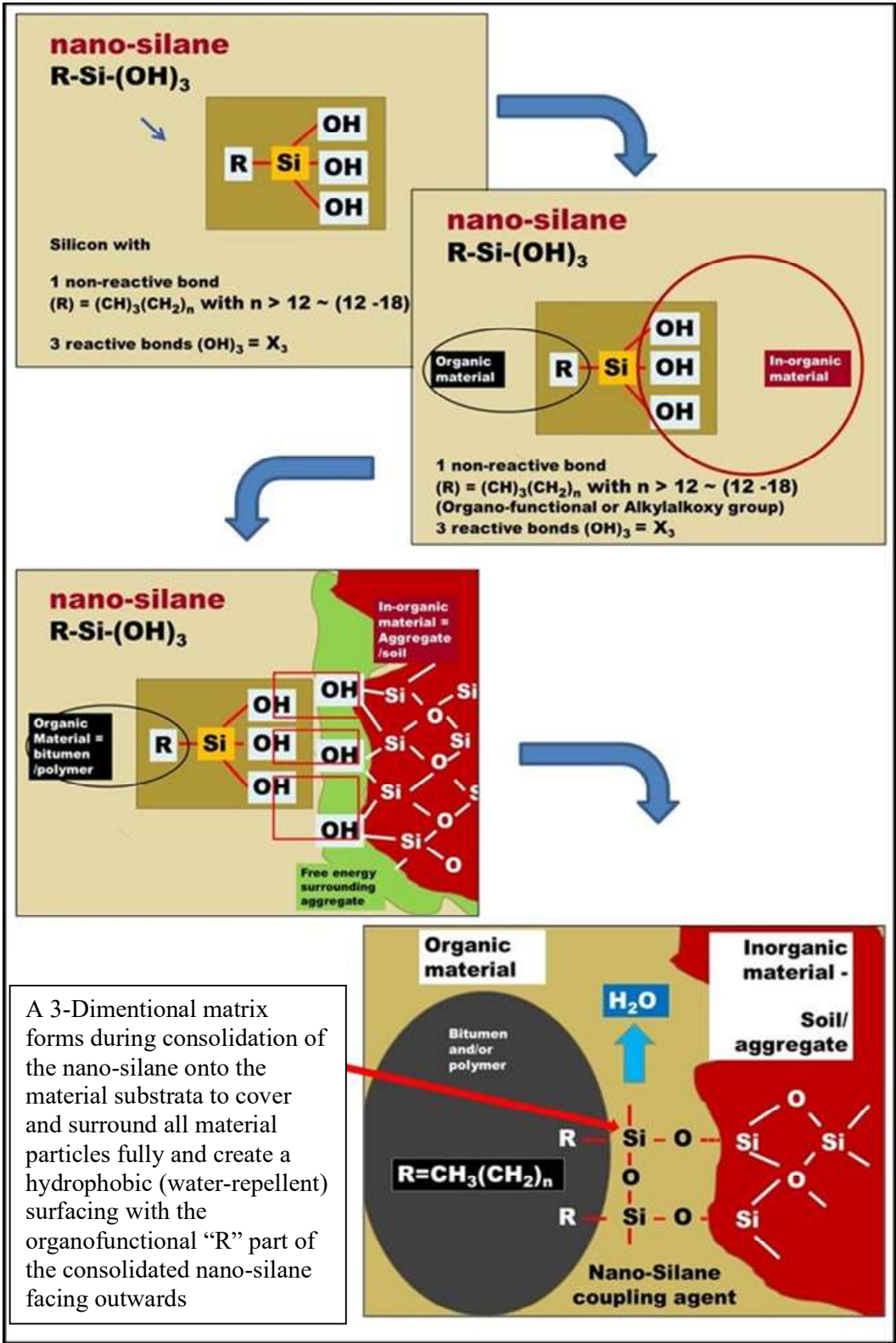


Figure 9: Simplified demonstration of the chemical interaction between a stabilising agent, organofunctional nano-silane modification and the mineralogy of the rock/stone/soil material sub-strata

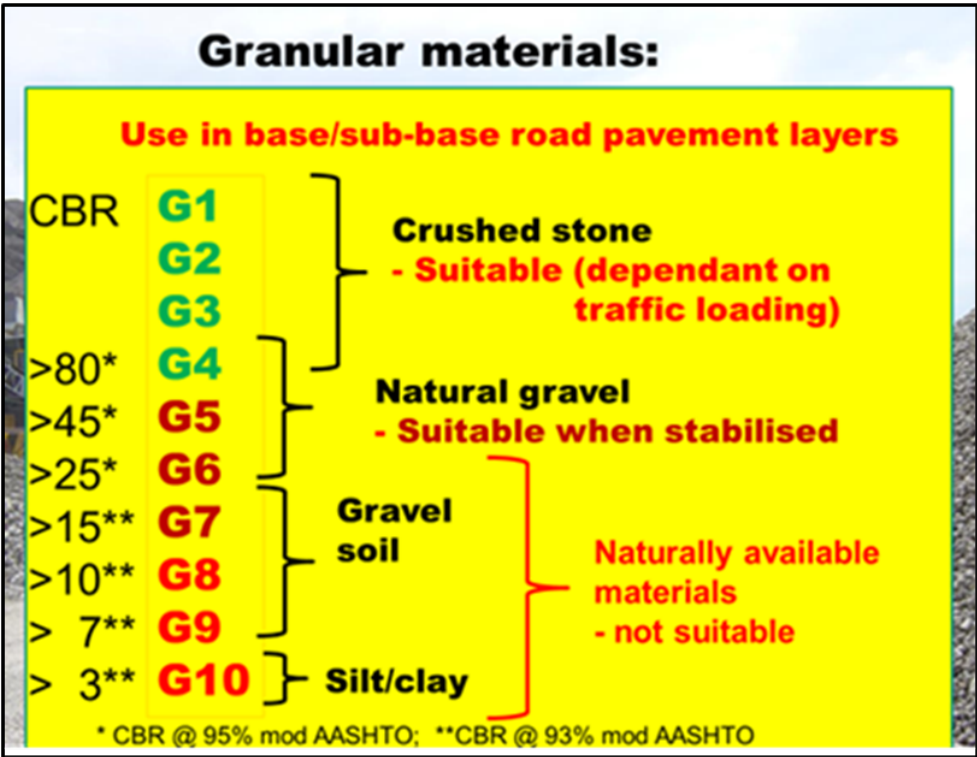


Figure 10: Classification of granular materials [27]

5.3. Modification of nano-silanes through Hydroxy Conversion Treatments (HCT) based on the mineralogy of the material sub-strata

Although approximately 60 per cent of the crust of the earth contains Si-O bonds, not all naturally available materials are silicon rich. Non-silicate materials include carbonate materials such as calcretes and dolerites that are predominant in certain areas of the world and laterites (abundant in warm/humid conditions conducive to chemical weathering and the leaching-out of silicate materials). In such cases (e.g. with calcretes, dolomites, etc.) very little or even no silicon may be available in the material to create the Si-O-Si bonds as explained in the example.

The part of the earth exposed to the environment is subjected to chemical weathering due to moisture and seasonal temperature variations. These environmental effects are especially pronounced between the Tropics of Capricorn and Cancer. The mineralogy of the naturally available materials (especially in areas close the Equator), may be deprived of readily available Silicon and may not be able to form Si-O bonds with the nano-silanes as shown in Figure 9. In these areas the nano-silanes need to be complemented with a material compatible nano-particle conversion to created strong chemical bonds with the minerals in the material sub-strata. This conversion of a nano-silane is generally referred to as a Hydroxy Conversion Treatment (HCT), which is best characterised by its ability to form bonds with the available minerals in the material sub-strata. For example, in the case of carbonate rich materials (e.g. dolomites and calcretes), the nano-particle added to the nano-silane in the form of a HCT must be able to form strong chemical bonds with the $\text{Ca}(\text{CO}_3)$ in the material. The example of an HCT treatment of a nano-silane for use with carbonate material is demonstrated in Figure 11, where the added HTC is designed to form strong chemical bonds with the carbon elements in the material sub-strata.

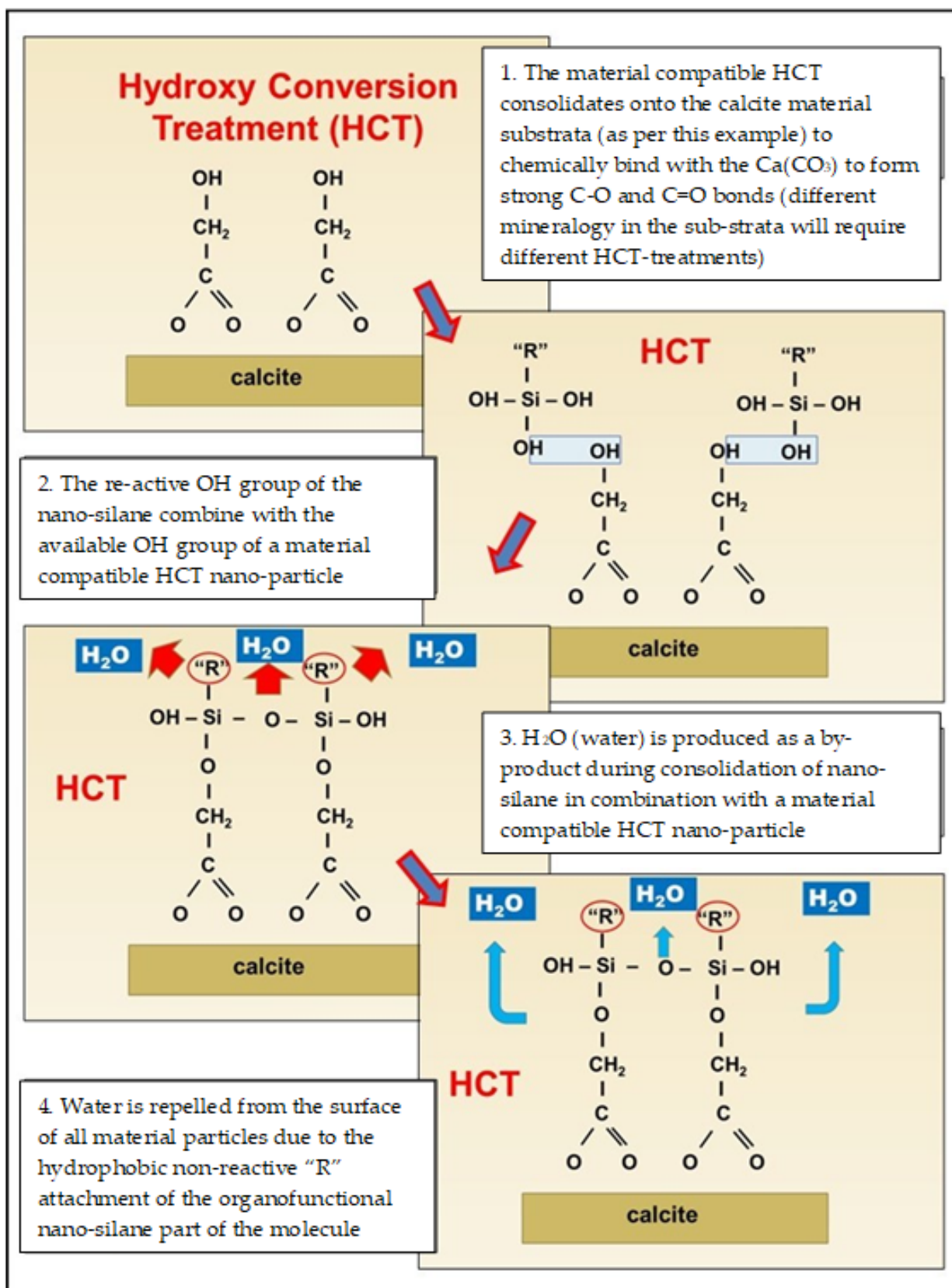


Figure 11: Hydroxy Conversion Treatment (HCT) of a nano-silane modification to a stabilising agent to enable a strong bond with carbonate materials

From the above example, it should be clear that the different nano-products applicable to various mineral compositions must accurately be identified in a scientific process [12] in order to have a successful application and to eliminate the risk of failure. Similar conversions will be required in other materials that may contain minerals with a relatively low silicon content. For example, laterite may contain anything from 90 per cent to 10 per cent silicon-based minerals [14] which may, inter alia, depend on the parent material (primary minerals), the climatic conditions and the extend of chemical weathering that has taken place [12].

The identification of a material compatible HCT treatment in the case of highly chemically weathered materials, may be more complex due to the high percentages of secondary minerals with little silicon present in the naturally available materials. The predominant minerals present in these materials are usually closely associated with a high percentage of clay within the materials. Such materials may present additional challenges in terms of practical constraints associated with workability. Due to the sub-nano size of some clay particles (Figure 12) and the formation of nano-sheets by high percentages of clays, the nano-silane particle size to be added need to be able to penetrate the clay matrix in order to achieve a hydrophobic stable state within the material. In the absence of such internal hydrophobicity, the clay sheets will shear under loading, breaking any protective stabilising agent and allow water to access the clay crystals within the clay matrix, rendering the hydrophobicity of the stabilised material to become ineffective. The stabilising agent also needs to be of nano-size in order to effectively bind the material together in combination with the applicable nano-silane.

A micro-size molecule in the stabilising agent will prove problematic with the nano-size material particles effectively “swimming” within the relatively large particles of the stabilising agent with no bonding between the material particles possible. This aspect is practically demonstrated by the results shown in Figure 13. The material stabilised with a material compatible NME stabilising agent as shown in Figure 13, contained between 20 and 25 per cent of fines passing through the 0.075 mm sieve of which more than 60 per cent was identified as mica, clay and talc minerals. The NME stabilising agent was a NME manufactured using a bitumen emulsion. It is seen that an increase in the stabilising agent from 1 per cent to 1.5 per cent led to a decrease in the UCS_{dry} from about 4800 kPa to 2600 kPa (highlighted in pink), while the ITS_{dry} decreased from 420 kPa to 230 kPa (highlighted in pink). Although these results are still very good considering the quality of the material that was stabilised (demonstrating the considerable advantages of the use of a material compatible NME stabilising agent), the decrease in the measured engineering properties are considerable. This decrease can directly be attributed to the relatively large particle size of the stabilising agent (1000 to 5000 nm) together with the relatively high percentage of the material passing the 0.075 mm sieve size of which a large percentage can be considered as problematic materials.

5.4. Material compatible NME nanotechnologies making the impossible possible in pavement engineering

The example shown in Figure 13 is a good indicator of the disruptive nature of the introduction of proven available technologies into the field of pavement engineering. Using traditional material classification systems, the material results shown in Figure 13 would have identified the material to be unsuitable for use in any load-bearing layers of a pavement structure. However, the stabilisation results gave confidence to the rehabilitation of the material in the sub-grade with 1 per cent NME stabilising agent (highest results in terms of tensile strength and with 1.5 per cent in the base layer (highest RCS). A high RCS can be related to a high resistance to possible damage due to water-ingress from the top in the case of a compromised surfacing layer. This pavement structure constructed with the NME stabilisation as indicated was evaluated using Accelerated

Pavement Tests (APT) [29,30]. The design traffic loading of 3 Million Standard 80 kN dual wheel axle loads (E80s) was surpassed with ease with an estimated load bearing capacity estimated to be at least 3 times that of the design traffic loading. The stabilised materials have also shown a remarkable resilience against overloading with a damage co-efficient of $n < 2$. (Normally assumed to be 4 to 4.2). NME stabilised road pavement structures containing NME stabilised layers will be ideally suited for the construction of roads where law enforcement in terms of vehicle over-loading is limited or even totally absent.

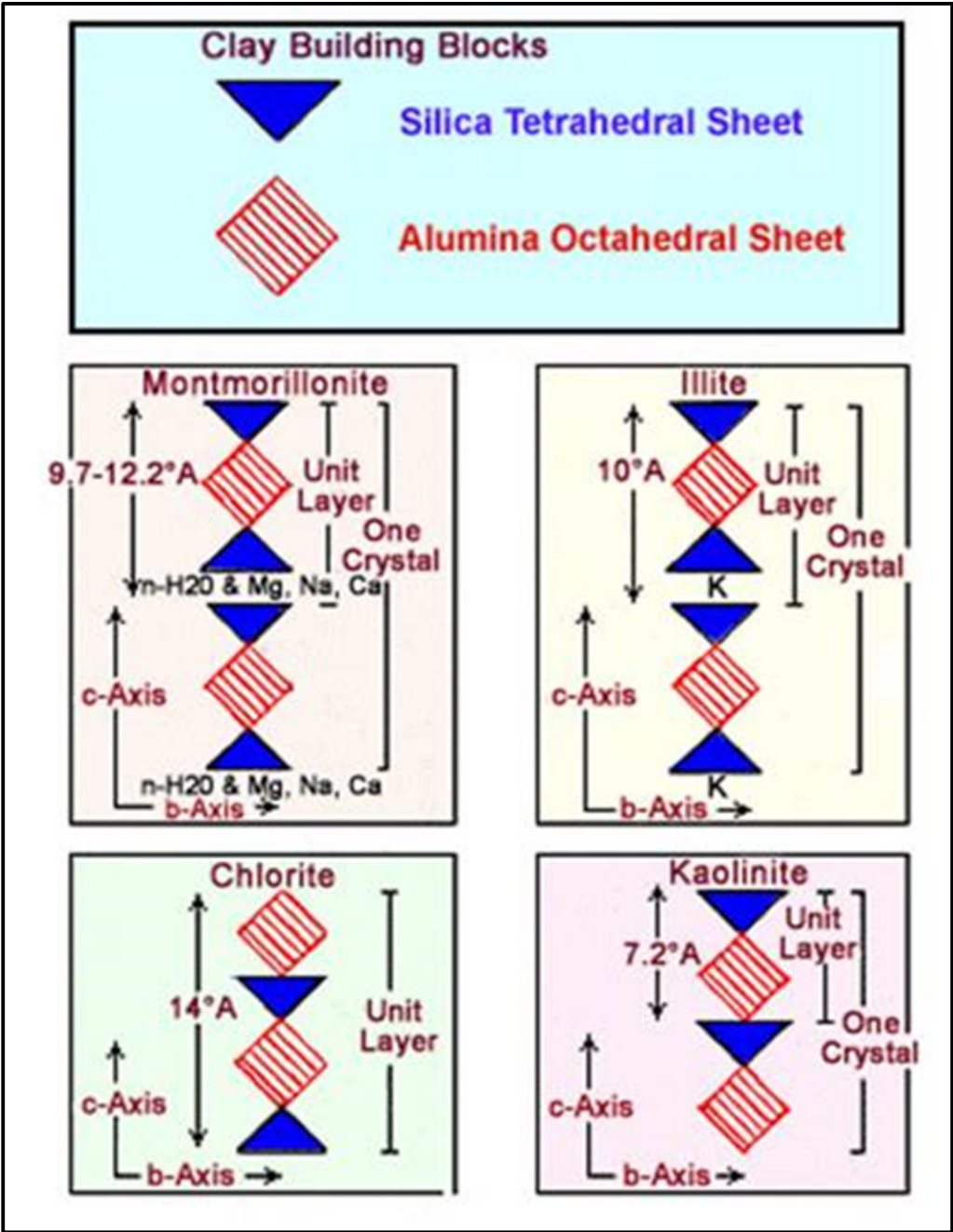


Figure 12: Typical dimensions in Angstrom of commonly available clay crystals that form during chemical decomposition within naturally available materials [28]

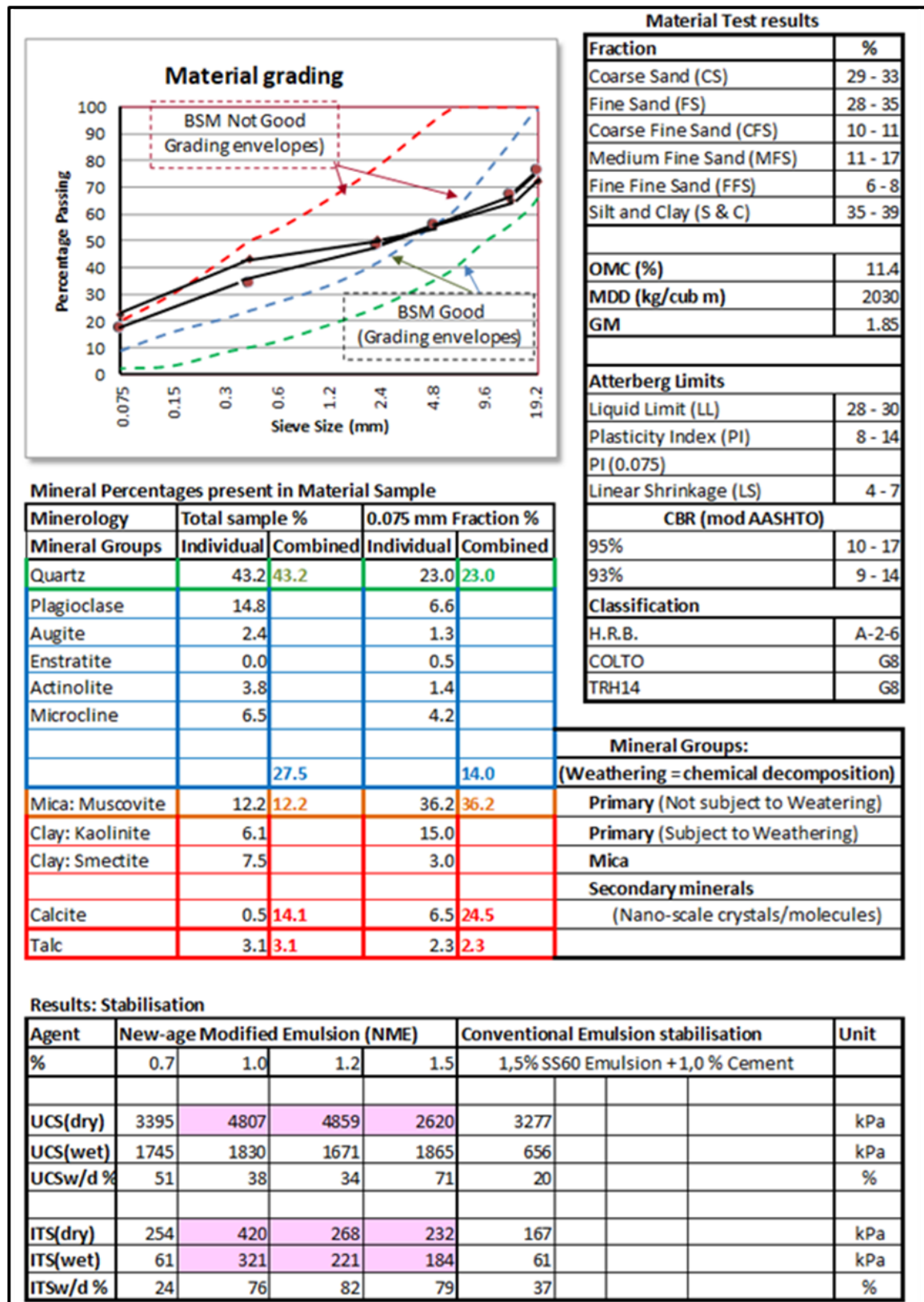


Figure 13: Results from the NME stabilisation using a bitumen emulsion of a material containing between 22 and 25 per cent of fines passing through the 0.075 mm sieve size of which more than 60 per cent consist of mica, clay and talk particles

The nanotechnology solutions in terms of material compatible NME stabilisation to change and stabilise unsuitable materials to acceptable (suitable) for use in the load bearing layers of road pavement structures has been proven. This ability is strongly reliant on the understanding of the basic chemistry involved in the selection of a material compatible stabilising agent as explained, as well as detailed knowledge about the mineralogy of the materials to be stabilised. Available nanotechnologies have been used under laboratory conditions to achieve engineering results on materials on considerably poorer quality than shown in Figure 13.

Figure 14 shows the exposed surface of a material sample crushed during an ITS_{wet} test of a relatively poor laterite. This material contained almost 50 per cent of fines passing through the 0.075 mm sieve size of which almost 70 per cent was identified through XRD scans as kaolinite clay particles. In this case a material compatible HCT modified high-quality sub-nano size silane was used with a nano-polymer to stabilise the material. The crushed sample shown in Figure 14 showed an ITS_{wet} of 80 kN [31] with clear hydrophobicity achieved throughout the sample as shown by the beading [25] of the water sprayed onto the broken surface. The sub-nano size silane and nano-polymer need to be carried into the material using water as a carrier and thoroughly mixed. As known, high percentages of clay in a wet condition present considerable challenges in terms of workability in the field. In practice, workability may need to be addressed by mixing a percentage of material such as sand or naturally available gravel into the material to practically enable the material to be workable when adding the modified stabilising agent into the material using water as a carrier.



Figure 14: Water beading on an exposed laterite material sample stabilised with a material compatible HCT modified sub-nano size silane and graded nano-polymer after crushing performing an ITS_{wet} test – almost 50 per cent of the material passed through the 0.075 mm sieve size of which almost 70 per cent is clay particles

Although this material may be considered to be an extreme material sub-strata considered for use in traditionally accepted pavement engineering, such materials are all too common in areas close to the equator, associated with high humidity and high temperature conditions. Such materials may be the only material available over considerable distances. Hence, any improved use of such very poor materials may have considerable cost benefits on any road project.

Although unthinkable in traditional pavement engineering terms, it has been proven that with knowledge about the mineralogy [12], material compatible nano-technologies can be cost-effectively [32] utilised to change the material characteristics to an extent where poor quality laterites can effectively be treated to become hydrophobic and stabilised (using sub-nano size silanes in combination with a material compatible HCT and a graded nano-polymer) to be used in a road pavement structure.

6. Conclusions

Nano-silicon based products have been in use in Europe for almost two centuries to protect stone buildings against the impact of climate and pollution. Early in the 1800s the development of these products was done on a trial-and-error basis with scientists often encountering conflicting results. These conflicting results soon led to the realisation that the “type of stone” (primary minerals) and the “condition of the stone” (secondary minerals) are important aspects that determine the successful outcome of the application of a specific nano-scale silicon-based product developed for use in the built environment. Over the last few decades numerous silicon-based nanotechnology products have been developed for use in the built environment, utilising the “excellent mechanical, optical, thermal and electrical properties” inherent in the silicon element. The same nanotechnologies, incorporating the “lessons learnt” from the built environment, can find direct application in road pavement engineering to enhance, protect and stabilise naturally available materials that are traditionally considered inadequate for use in the upper pavement layers of a road pavement structure.

In order to limit risks and eliminate the possibility of failure, engineers need to take cognisance of the lessons learnt in the built environment. It is essential to know the scientifically determined mineralogy of the material that is available for use. In addition, it is also of importance to understand the basic chemistry involved in the use of various nanotechnology products to understand the advantages and limitations of any one available material compatible product in combination with the naturally available materials for use in a pavement structure. An understanding of the basic chemical interactions between the nano-silicon based technologies and the mineral composition of naturally available materials are considered essential to ensure that applicable technologies are used and that the impact on engineering results is understood and any potential risk identified and timeously addressed.

Unmodified bitumen emulsions do not create chemical bonds with the material sub-strata that when used as a stabilising agent. Bond strengths are achieved through electrical and mechanical forces and absorption into the material surfacing services. However, strong chemical bonds can be achieved through the introduction of material compatible nanotechnology organofunctional nano-silane modifications to the bitumen emulsion (or any equivalent polymer stabilising agent). The chemical interaction of the nano-silane modifier can be compared to the use of an emulsifying agent (nano-particle) to create bitumen emulsion which enables water to be mixed with oil (bitumen). The characteristics and the bond-strengths of the elements comprising a specific emulsifying agent will also affect the stability of the emulsion and the properties of the end product. Changes in chemical composition of the emulsifying agent (also known as a surfactant or “soap”) can meaningfully influence the engineering properties that can be achieved using products all manufactured within National Specifications. Using 8 different products from 5 different suppliers with differences only in the emulsifying agent, it is shown that differences of up to 50 per cent is possible in the measured UCS and ITS results. It is

recommended that this aspect be addressed in practice by engineers through the introduction of end product specifications. The introduction of end product specifications will put the onus on the contractor and his supplier to ensure that quality products are used meeting the minimum engineering specifications.

The induction of organofunctional nano-silane modifications to emulsion stabilising agents for road pavement engineering materials adds another layer of re-active complexity to the successful implementation of nanotechnologies into the field of pavement engineering. The identification and understanding of the basic chemistry of the technology will ensure that risks are minimised. The testing of the basic bitumen stabilising agent and the influence of the nano-particle (the emulsifying agent or surfactant) on the engineering properties was performed with the specific objective to demonstrate the need for engineers to realise the importance of quality control during manufacturing, ensuring that material compatible materials are utilised with chemical properties that will guarantee that macro projects can successfully be implemented using new disruptive nanotechnologies by adhering to basic scientific principles.

The main objectives of the modification of an emulsifying stabilising agent are to:

- Ensure that a high strength chemical bond is established between the stabilising agent and the naturally available material sub-strata;
- Achieve a high level of hydrophobicity of each particle within the material sub-strata through a 3-dimensional consolidation of the nano-silane, covering the total the surface area of each particle, and
- Protect each particle within the material sub-strata against the effect of water and neutralise any secondary minerals within the sub-strata by ensuring that a material compatible nano-silane (modified where necessary with a HCT nano-particle).is utilised based of the mineralogy present in the material substrata.

The objectives can be met with the necessary scientific knowledge about the primary and secondary mineralogy present within the material sub-strata to be stabilised through use within the pavement sub-strata. A material-compatible organofunctional nano-silane with an applicable HCT where needed, is introduced into the stabilising agent that will ensure that the required chemical bonds are activated during the stabilising process. The quantity of the modifier to be added is a function of the surface area to be covered. It follows that the fine fractions (the percentage passing the 0.075 mm sieve size and the percentage of clay (less than 0.002 mm fraction) is of importance in the adjustment of the nano-silane percentage to be added to achieve the objectives successfully. It is obvious that the modification of the stabilising agent to optimally achieve the required engineering properties is not conducive to a "one solution fits all" product approach.

With the application of scientific knowledge and applying high quality nano-silane products with the required dimensions and chemical compositions through the introduction of material compatible HCT modifications, materials of a quality unthinkable using traditional pavement engineering approached to material utilisation, can be treated and stabilised to obtain the required engineering properties in terms of compressive strengths, tensile strengths and durability. Such disruptive nanotechnologies have been proven in the laboratory and can, with applicable engineering processes be utilised in the field where practical workability may present some challenges. However, engineers are trained to adequately address challenges and workability should not be the reasons for the non-introduction of New-age (Nano) Modified Emulsion technologies, which enables the use of naturally available materials traditionally considered to be "non-standard, marginal, low-cost, or even sub-standard" applying available, proven and safe material sciences.

Author Contributions: G.J.J. under the directive of the Head of Department of Civil Engineering, W.J.vdM.S., has been leading the research into the provision of affordable road infrastructure at the faculty of Engineering, University of Pretoria. W.J.vdM.S. recognized the potential of nanotechnology solution in the field of pavement engineering more than a decade ago. G.J.J., through in-

volvement in the private sector and the support of road authorities, has been instrumental in the development of scientific principles, ensuring that implementation can be achieved at a minimum risk.

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