 doi:10.20944/preprints202101.0574.v1

Article

Fundamental principles ensuring successful implementation of New-age (Nano) Modified Emulsions (NME) for the stabilisation of naturally available materials in pavement engineering.

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Featured Application: Providing road transportation infrastructure using traditional design methods and materials comes at a considerable cost. The use of naturally available materials using New-age Modified Emulsions (NME) has been successfully implemented and tested. Proven material compatible nanotechnologies enhancement of materials, incorporating modern material sciences can considerably reduce the unit costs of road infrastructure and improve basic service delivery. However, the successful implementation of these new nanotechnology solutions depends on the assessment and scientific evaluation of various factors that will ensure success of implementation as addressed in this paper.

Abstract: Good transportation systems are pre-requisites to economic development. Materials used for road construction are traditionally classified based of empirically developed archaic tests, often classifying naturally available materials as unsuitable for use in the load-bearing road pavement layers. Consequently, design standards usually require the use of imported materials at considerable costs, severely restricting road network development under scenarios of limited funding. New technologies and test methods based on sound engineering criteria, incorporating basic material sciences can substantially change this scenario. Nano-silane technologies can be utilised to improve naturally available materials to meet the engineering requirements of all layers in road structures. Material test and design methods have been developed and successfully tested in South Africa to build New-age Modified Emulsion (NME) stabilised layers in roads, meeting all engineering requirements. Accelerated Pavement Tests (APT) done on actual roads, proved the concept. This work is based on a scientific approach and identification of various factors that will impact on the successful application of applicable nanotechnology solutions. This paper aims to identify these fundamental factors that are a pre-requisite for the evaluation of nanotechnology solutions to ensure that new technologies are introduced into pavement engineering designs at a low risk to any implementing.

Keywords: nanotechnologies; pavement engineering; scientific principles; material compatible design; mineralogy; safety, applicability and compatibility of new technologies; engineering principles

1. Introduction

Silicon-based new-age nanotechnology products have been used in the built-environment since the early 1800s. At the time, scientists were tasked in Europe with the challenge to develop products to protect stone buildings, monuments and statues from deterioration due to the observed detrimental effect of water and pollution [1]. Conflicting results by various scientist soon led to the conclusion that the type of stone

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and the condition of the stone play an important part in the successful use of a specific silicon-based product to be effective and achieve the required results. These conclusions were derived after decades of testing using a trial-and-error approach. The development of advanced investigation and observation equipment (such as the Atomic Force Microscope (AFM)) in the 1980/90s enabled scientists to observe and manipulate the behaviour of nano-size particles which led to the science of nanotechnology, influencing basically all major industries [2, 3].

It follows that since the 1980s, the science of new-age nanotechnology products for use in the built-environment have developed exponentially. These products are used throughout the industry to, inter alia, enhance and protect of all types of building products, including wood, gypsum-board, etc. as well as the relatively softer and vulnerable type of building blocks such as sand-stone, lime-stone and marble. These products that are widely used in the built environment, mostly incorporate silicon as a basic element that exhibits "excellent mechanical, optical, thermal and electrical properties" [4].

Most of the naturally available materials found in global climatic zones that are subjected to weathering due to chemical decomposition (high temperatures associated with seasonal rainfall [5]) are classified by road pavement engineers as marginal or unsuitable for use in the load bearing layers (upper layers) of a road structure. This "unsuitable" classification is mainly due to the risk associated with the secondary minerals (e.g. clays, etc.) that are present due to chemical decomposition of the primary minerals. The same nanotechnology silicon-based products used in the built environment can also be utilised to change this scenario. These naturally available materials can be treated, enhanced, and stabilised and the secondary minerals neutralised to enable these materials to be used in the load bearing layers of a pavement structure [6]. Testing has shown the potential of such stabilisation of materials on unsuitable quality can be used on roads carrying low to relatively high traffic loadings (in excess of 30 million dual wheel standard 80 kN axle loads (E80s)) [7, 8].

Many alternative "wonder" products have been introduced into the market to improve naturally available materials for use in roads over many a decade. These products were mostly based on a limited number of empirically based tests on a few selected materials. Invariably, these products did not meet expectations. As a result of these experiences, the engineering fraternity developed a scepticism and resistance towards the introduction of new technologies. It follows that any new-age nanotechnology needs to be based on a sound scientific basis to limit the risks associated with new products. A scientific approach also requires that material testing be extended to include the scientific analysis of the mineralogy of the materials in order to determine the primary and secondary minerals that need to be accounted for [6, 9].

New-age nanotechnology products offer significant advantages to the roads industry when introduced based on scientific analysis. This paper identifies the fundamental principles required for the evaluation, application and successful use of new-age nanotechnologies in pavement engineering, enabling the cost-effective use of naturally available materials in all the pavement layers of the road structure. A design process based on sound scientific principles also need to ensure that basic principles in terms of safety and responsible engineering in terms of environmental impact be met. The paper aims to identify all of these factors associated with the introduction of nanotechnology solutions in pavement engineering that will ensure that design approaches are developed that, as far as possible, ensures that pavement engineers adhere to the core of their profession, i.e. to optimise the use of available resources (including available funds) with a minimum associated risk. Considerable benefits can be realised when these new technologies (e.g. nanotechnologies) are used in a responsible scientifically based approach to deliver macro infrastructure projects (e.g. surfaced road infrastructure) through the enhancement of naturally available materials with less associated environmental damage, low required maintenance and hence, a considerable reduction in life-cycle costs [10].

2. Basic principles for a design approach to successfully incorporate new-age nanotechnologies in pavement engineering and reduce design associated risks

The understanding of the benefits to be gained and the principles associated with the use of new-age nanotechnologies are crucial to the successful introduction thereof in the roads industry. General concerns in terms of issues such as health and safety need to be addressed. The need for a scientific basis to ensure the successful use of materials traditionally considered to be sub-standard for use in the load bearing upper layers of a pavement structure need to be understood as crucial in an industry known for a conservative approach to change. Hence, the benefits and the positive effect thereof in terms of cost-effective service delivery, incorporating scientific principles in design are identified and explained while, important aspects are highlighted. The general adoption of new technologies is closely linked to the ease of application, not requiring complicated procedures (e.g. the introduction of new telecom (cellular phones) and IT devices (laptops)).

The same principles will apply to the introduction of new technologies in the roads industry. Design methods must ensure that the risk associated to construction processes are reduced (this is ensured by following a scientifically based design process). In addition, any materials used in the construction process must be conducive to construction procedures applicable in a sophisticated as well as a developing environment with severe challenges with regard to material stability and handling of any materials requiring special equipment and / or complicated processing procedures. Ultimately, all of these aspects will have to be separately addressed in special construction specifications aimed at specific end-product specifications, allowing competition on an equal basis while eliminating products not meeting the basic requirements.

The following fundamental basic characteristics associated with available, proven and /or new nanotechnologies in association with suitable stabilising agents in a scientifically based design approach in pavement engineering will ensure that risks are minimised through the introduction of these technologies in the roads environment [6]:

- toxicology, health and safety of the use of various nano-scale products;
- environmental aspects, leaching and affecting ground water;
- surface area or coverage and volume;
- stability in a carrier fluid, e.g. water;
- nano-technology as a binder;
- hydrophobic characteristics;
- compatibility aspects of nano-silicon modifications to binders that will influence the successful application and use thereof, including;
    - compatibility with the mineralogy of the materials, and
    - compatibility with the stabilising agent to be modified;
- engineering evaluation of the effect of nano-silicon modifications in terms of required scientific properties (compressive strengths, tensile strengths and durability), and
- cost–aspects associated with the use of nano-technology based products.

3. Factors affecting the successful introduction of new technologies in pavement engineering

3.1. Toxicology, health and safety

The introduction of relatively new technologies needs to address from the onset any possible concerns about toxicology, dangers to health and safety and environmental influences (e.g. leaching into the sub-strata and affecting the quality of ground water). Two chemical processes are usually applicable with the addition and use of nano-scale products during mixing with a carrying fluid and construction, i.e. a process of hydrolysis when mixed with the carrying fluid (e.g. mixing with water) and condensation (when the product attaches to the material during treatment or

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stabilisation). During any of these processes by-products can be formed. It must be ensured that the nano-scale product used does not generate any gases that may be toxic in any way. It is a fact that the majority of organo-functional silanes are not suitable for general application and can be harmful to life-forms and to the environment. Silanes such as SiH_4 and silicon-hydrides ($R\text{-}SiH_3$) and silicon-halides are "toxic, volatile and generate hydrogen gas during hydrolysis" [1], the effect of which is shown in Equation (1).

$$\text{Hydrolysis: } SiH_4 + 4H_2O = Si(OH)_4 + 4H_2 \quad \ldots.(1)$$

Other reactive groups involving fluorine (F) and chlorine (Cl) also form volatile and dangerous acids under hydrolysis, such as hydrofluoric and hydrochloric acids that are also detrimental to the various mineral groups and hence, are not suitable to be used as stone consolidants [1]. Similarly, in combination with carbon (C), reactive groups containing chlorine (Cl) can produce chloroform ($CHCl_3$) as a by-product during the hydrolysis (during mixing with water) or consolidation process (when attaching to the material) which is generally difficult to detect, but dangerous and even fatal when applied in confined areas or under conditions with low or no wind-speeds.

In comparison, alkoxy-silanes (also referred to as organo-functional silanes) have low vapour pressures and do not form toxic gasses or acids during hydrolysis. It follows that the requirement of a health and safety toxicology report (Safety Data Sheet) should be a pre-requisite when considering the use of an appropriate nano-silane product for general application

The by-product formed during the hydrolysis process of the nano-silane when in contact with water is of fundamental importance in the selection of an appropriate and applicable nano-silane to be used in general engineering projects [6]. The most appropriate and designed alkoxy-silanes will form water as a by-product or at worst a non-corrosive alcohol [1].

It follows, that many silane couplings which are freely available commercially will form siloxane bonds. However, of these, only a few known nano-silanes will have the "correct balance of volatility and reactivity without being harmful to society" or the materials being treated [1].

3.2. Environmental aspects – leaching and ground water

During the consolidation process in contact with the stone / gravel / soil, the alkoxy-silane is bound to the sub-strata through a Si-O-Si bond (in the case of silicon rich materials), one of the strongest in nature. Hence, designed nano-silanes based on the mineralogy of the sub-strata will attach to the naturally available materials through "permanent" bonds [6] with no risk of leaching and / or contamination. In fact, the alkoxy-silane modification of traditionally used binders, such as bitumen (as contained in e.g. bitumen emulsions), will firmly attach the bitumen to the stone / aggregate / soil, preventing any bitumen from detaching from the soil and cause any contamination. It follows that the modification of bitumen and emulsions using an applicable alkoxy-silane will help in the least assist in containing if not preventing contamination.

3.3. Surface area or coverage and volume of alkoxy-silane modifications

Nanotrchnology considers the use of very small particles or functional molecules measured in nano-metres. The resultant effect is a high ratio achieved in terms of area covered by a relatively small volume of the nano-product. The surface-area to dimension thus increases dramatically with a decrease in dimension. This aspect is visually demonstrated in Figure 1 [11] where it is shown that the surface area of 1 kg of particles of a size 1 mm x 1 mm x 1 mm is equal to 1 mg of the same particles of dimensions of 1 nm x 1 nm x 1 nm.

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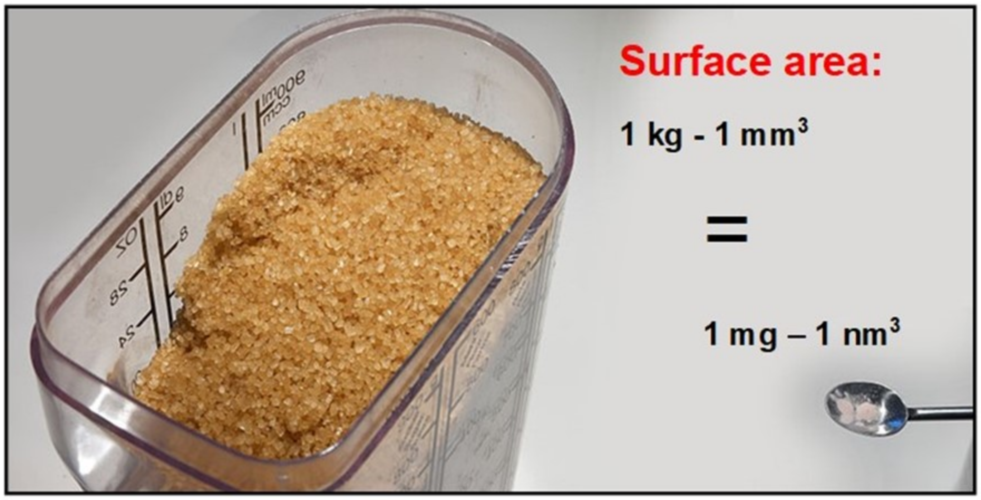

Figure 1. Comparative surface area versus reduction in dimensions [11]

A comparative equivalent measurement in terms of pavement engineering is that the coverage of about 1 000 l of bitumen with a particle size of about 4 µm, will be equivalent to 1 l of nano-particles of a size of 4 nm. The considerable differences in area versus dimension will naturally have a meaningful influence on the affordability of a modification using a nano-scale particle. A relatively expensive modification using an effective alkoxy-silane could have a relatively small influence on the cost of the modified binder.

3.4. Stability of the nano-scale modification stabilising agents

The stability of any stabilising agent to road building materials is of fundamental importance when dealing with projects influenced by variations in conditions beyond the control of the contractor, such as weather, political influences (e.g. labour unrest) and projects in remote areas with access limitations. It is essential to clearly specify and have knowledge about any limitations with regard to the use and storage of any modified stabilising agent. The physics of the stability of nano-size particles are controlled by the physics of basic science. Particles in a carrier fluid are subjected to gravitational forces. When suspended in a carrier fluid, particles are continuously subjected to forces imposed on each particle due to the collisions caused by the fast-moving molecules of the carrier fluid called Brownian movements [12]. The true meaning of Brownian movements and the influence thereof on particle movement were only fully explained by Einstein in 1905 [13]. Physics dictate that particles of a nano-scale will stay in suspension due to the fact that the forces caused by the Brownian movements exceeding that of gravitational forces [13] (Figure 2).

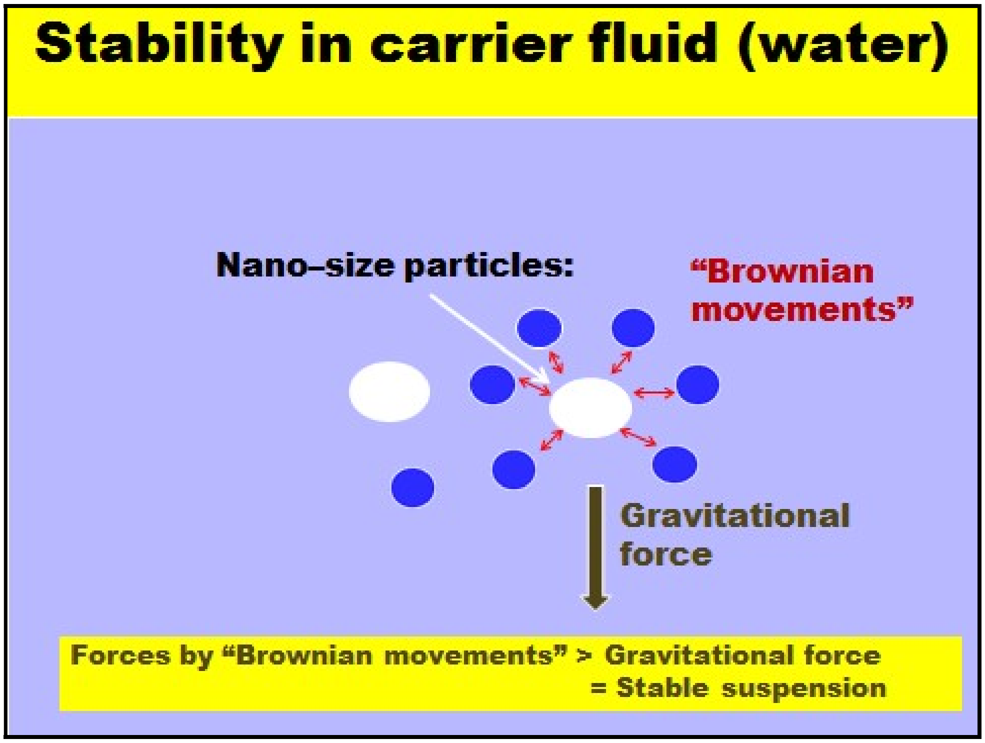

Figure .2 Demonstration of the stability of nano-scale technologies in a water carrier fluid

It follows that a nano-scale alkoxy-silane as manufactured and delivered in a container to site, will remain stable and effective as long as it is not placed in contact with an ingredient that will cause a reaction with the reactive compounds of the organo-functional silanes

3.5. Nano-silane technology as a binder

Alkoxy-silanes have been shown to be effective as stone preservatives following a process of hydrolysis and condensation [1], [6]. These functional molecules are typically as small as a few nano-metres in size. This logically limits its ability to effectively bridge gaps and bind together stone / aggregate / soil particles with gaps exceeding that of a three-dimensional gel formed during the consolidation phase of the alkoxy-silane treatment. This bridging distance is usually limited to a maximum distance of between 10 µm and 60 µm [1].

In terms of practical road pavement engineering, granular materials are graded in terms of aggregate sizes varying from 63 mm to less than 0.075 mm fractions. It follows that applicable nano-silane technologies have considerable limitations in being used as a soil / material stabilising agent on its own. However, at these fractions the non-reactive Si-CX or Si-(R) bond (similar to that of an emulsifying agent) of the alkoxy-silane (which is added to the stabilising agent such as bitumen emulsion or equivalent) embeds itself firmly into the bitumen molecule [6]). When the modified bitumen emulsion is added to the aggregate the reactive bonds of the silicon molecule attaches the bitumen firmly to the minerals in the aggregate (Figure 3). In practice, the alkoxy-silane modification to traditional stabilising agents such as bitumen emulsions, acts as an effective aggregate adhesive. In addition, it also changes the surface of the stone / aggregate / soil to be hydrophobic. Water is actively being pushed out of the layer and the minerals in the layer are denied access to the water molecule with significant benefits in terms the future prevention of weathering due to chemical decomposition (with water being a pre-requisite for weathering to occur*).*

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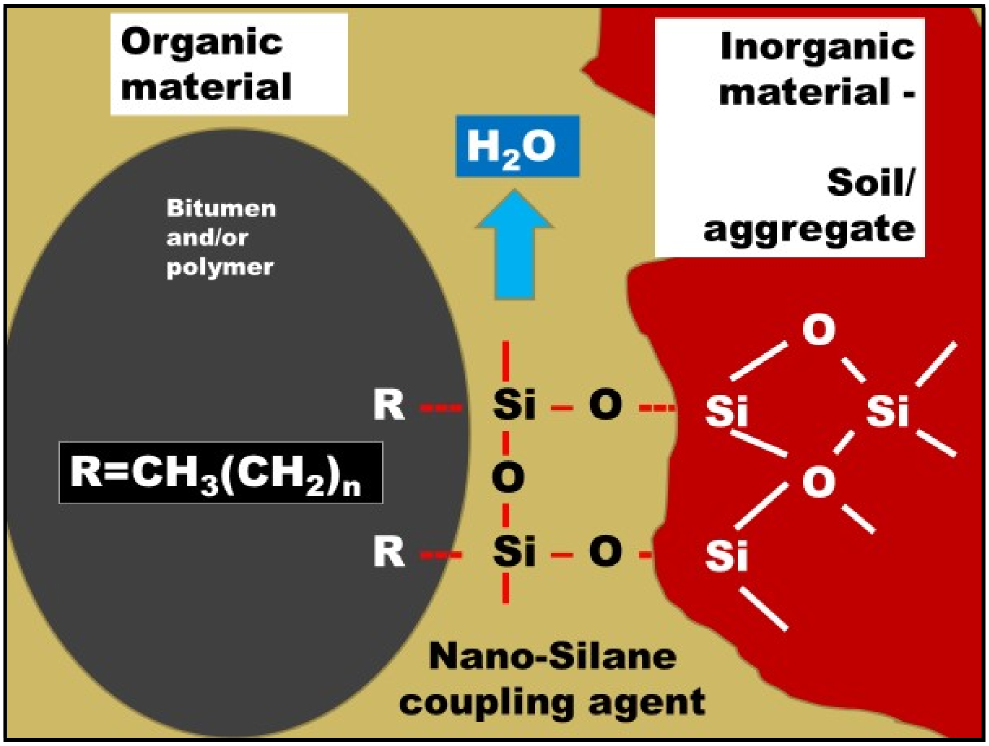

Figure. 3 Nano-silane modification to an organic material (bitumen in bitumen emulsion or equivalent) acting as an aggregate adhesive and water repellent

3.6..Hydrophobic characteristics of an alkoxy-silane modification and / or treatment

The treatment of stone / aggregate / soil using an alkoxy-silane or alkoxy-silane modified binder changes the surfaces of the material to become hydrophobic as shown in Fig. 3. The effective nature of the power of the water repellence created is directly related to the size of the alkyl group attached to the silicon atom [1]. The water repellent nature of material is usually observed through a beading effect [14] which is measured by the contact angle of the water with the material (Figure 4).

When the contact angle is less than 90° the material will be subject to water ingress and a positive absorption will be observed with time, resulting in capillary rise. Material samples placed in water will show a wetness of the material appearing above the water-line showing a positive water absorption rate (Cos of the angle (θ) is positive between 1 and 0). When the contact angle is between 90° and 180° the material is hydrophobic, not allowing water to penetrate the material. Samples of the material placed in water will show no wetness above the water line, indicating a negative capillary rise (Cos of the angle (θ) is negative between 0 and -1). The practical pavement engineering effects of the hydrophilic and hydrophobic effects and capillary rise caused by the nano-silane modification of bitumen emulsion stabilisation of materials are shown in Figure 5(a) and Figure 5(b).

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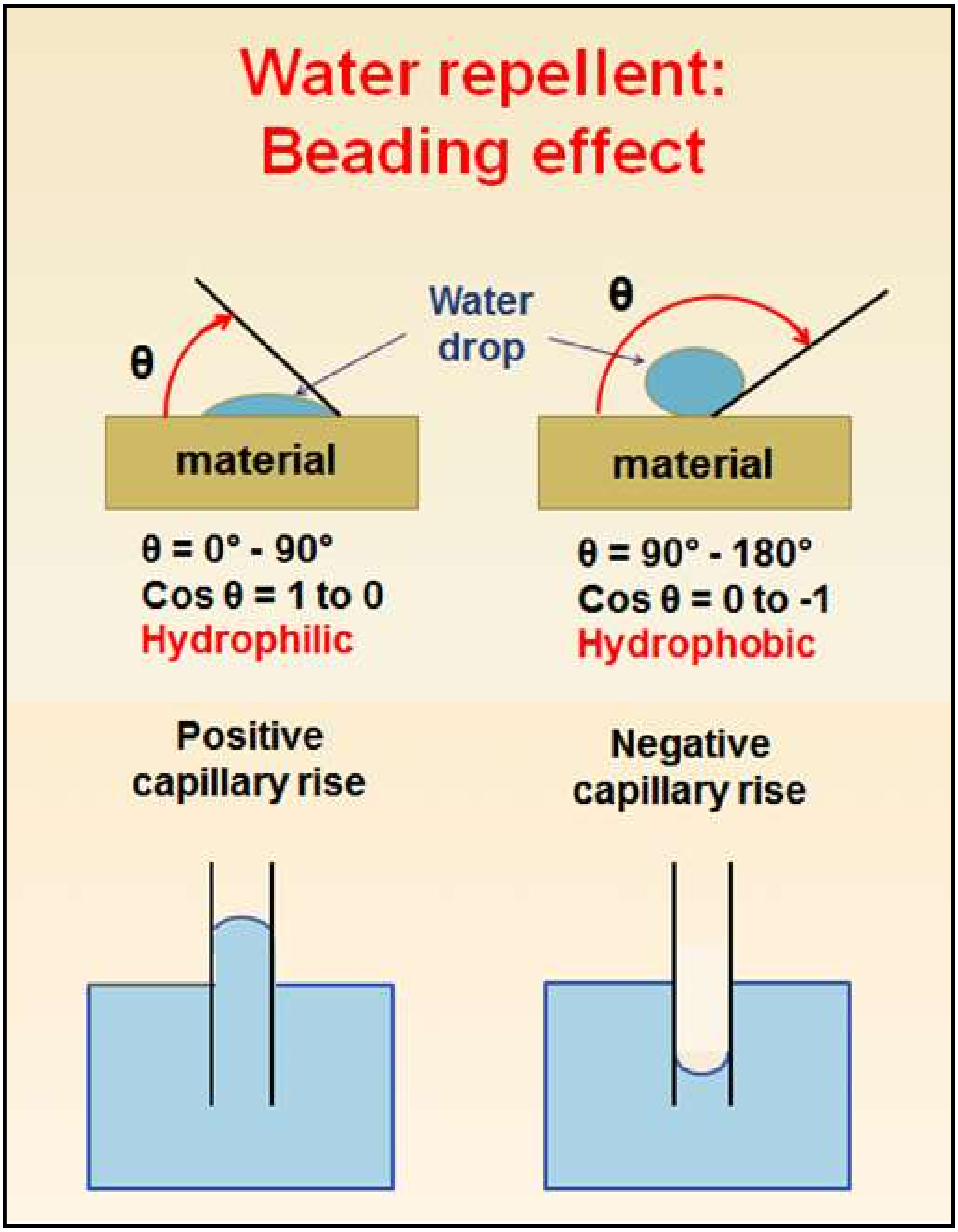

Figure 4. Beading effect: illustrating the water repellent nature of a material indicating the water repellent nature of the material

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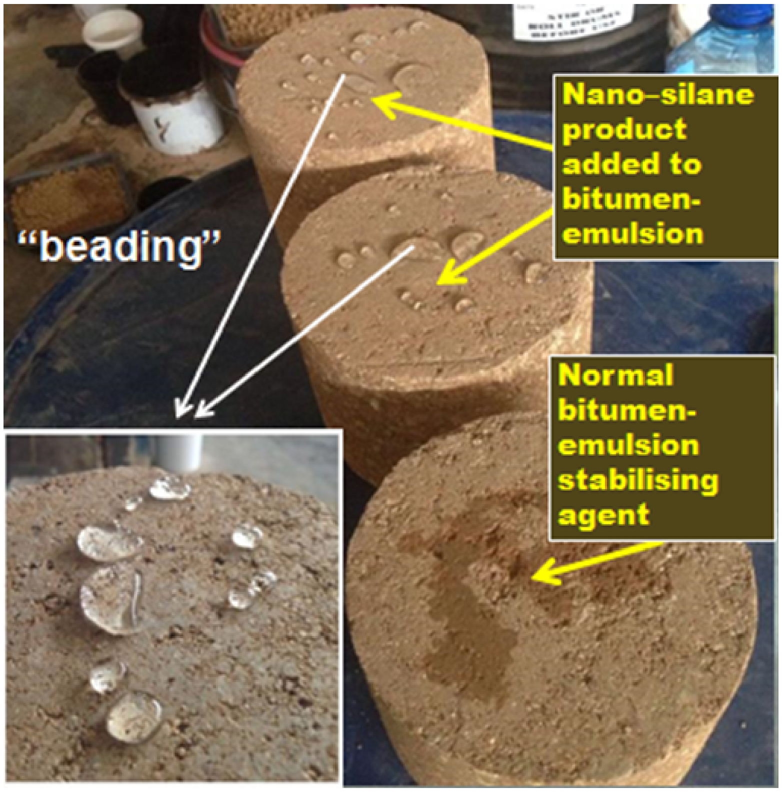
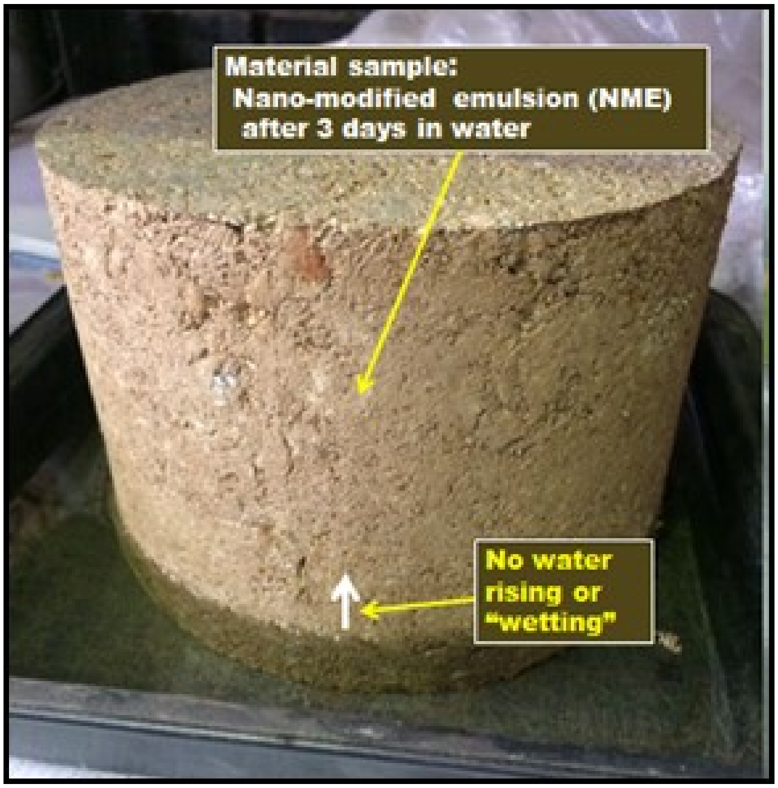


(a)



(b)

Figure 5. Beading effect (hydrophobic) in Fig. 5(a) indicating the water repellent nature of nano-silane modification of bitumen emulsion and the negative capillary rise shown in Fig. 5(b) resulting from the nano-silane modification

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3.7. Compatibility aspects of alkoxy-silane modifications to binders that will influence the successful application and use thereof

3.7.1. General

As mentioned previously, alkoxy-silane modifications are designed to attach firmly to the minerals present in the stone / aggregate / soil to form (for example), strong Si-O-Si bonds. This example logically assumes that silicon atoms are present in large quantities is the stone / aggregate / soil that is being treated. Although this assumption applies to a large percentage of the crust of the earth, this assumption is not always true and the principle inherent in this assumption cannot be uniformly applied. The applicability of the alkoxy-silane modification not only depends on the primary minerals comprising the stone / aggregate / soil, but also to the condition of the stone / aggregate / soil (weathering due to chemical decomposition) indicated by the presence of secondary minerals [9]). It follows that the applicability and hence, expected behaviour of any nano-modification of a stabilising agent will depend on a detailed analysis of the mineralogy of the material. Enough detail must also be obtained to enable the identification of the chemical decomposition that is already present in the material under the specific climatic conditions [9]).

As discussed previously, alkoxy-silane treatments alone will not be effective to fulfil the normal role of a stabilising agent when treating stone / aggregate / soil. A larger molecule is required to act as a binder bridging the gaps between the stone / aggregate / soil particles. This aspect immediately points to another important aspect related to the applicability of the nano-technology product to be used, i.e. compatibility with the stabilising agent (such as bitumen emulsion or equivalent) to which the nano-particle (in this case alkoxy-silane as an aggregate adhesive) need to attach. It follows that the applicability or compatibility of an alkoxy-silane is affected by both the (Figure 3):

- mineralogy with which it is to be firmly bonded, and
- characteristics of the stabilising agent, the bitumen emulsion and /or compatible polymers(s) to which it is added as a modification.

3.7.2 Compatibility with the mineralogy of materials

Some available nano-silane products are indeed only effectively in the presence of large quantities of silica and have severe limitations in the presence of secondary minerals. It follows that any mineralogy investigations need to determine both the primary as well as the secondary minerals present in naturally available materials to ensure that the most applicable alkoxy-silane product is applied to the available materials. This requirement is a basic pre-requisite to the successful application of any applicable nano-scale product to be successfully applied as a modification to any stabilising agent used in material design in pavement engineering [16, 17]. The influence of minerals in the successful application of nano-silane consolidants as protective coatings of various stone types was already recognised in 1926 [18]. At that time, the application of silica-ester to acidic materials was observed to result in the successful formation of a protective gel while an alkaline sub-stratum will result in the formation of a "useless" gel when treated with silica-ester [18].

It is of importance to note that at the most basic of geology terms, materials can be classified as either acidic, i.e. silicon-based minerals or basic, i.e. calcite that forms the basis of carbonate ($CaCO_3$) (alkaline) based minerals. Acidic rocks are normally considered to contain in excess of 50 per cent of acid components, i.e. SiO_2 and CO_2 [5]. In the absence of silicon and the presence of calcite minerals, different nano-silicon technologies need to be applied.

` For example, calcite forms few if any hydroxyl (HO) groups with which alkoxy-silanes can react to form bonds (Figure 3). Hence, complementary nanotechnologies have to be added with stone / aggregate / soils exhibiting high

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percentages of calcite. The problem with a lack of HO groups on the surface particles of materials can be resolved by chemically altering the surfacing of the material using approaches such as a Hydroxy Conversion Treatment (HTC) [19]. The HTC will convert the surface of a crystal of calcite to produce hydroxyl (OH) groups (Figure 6) that facilitates alkoxy-silane bonds.

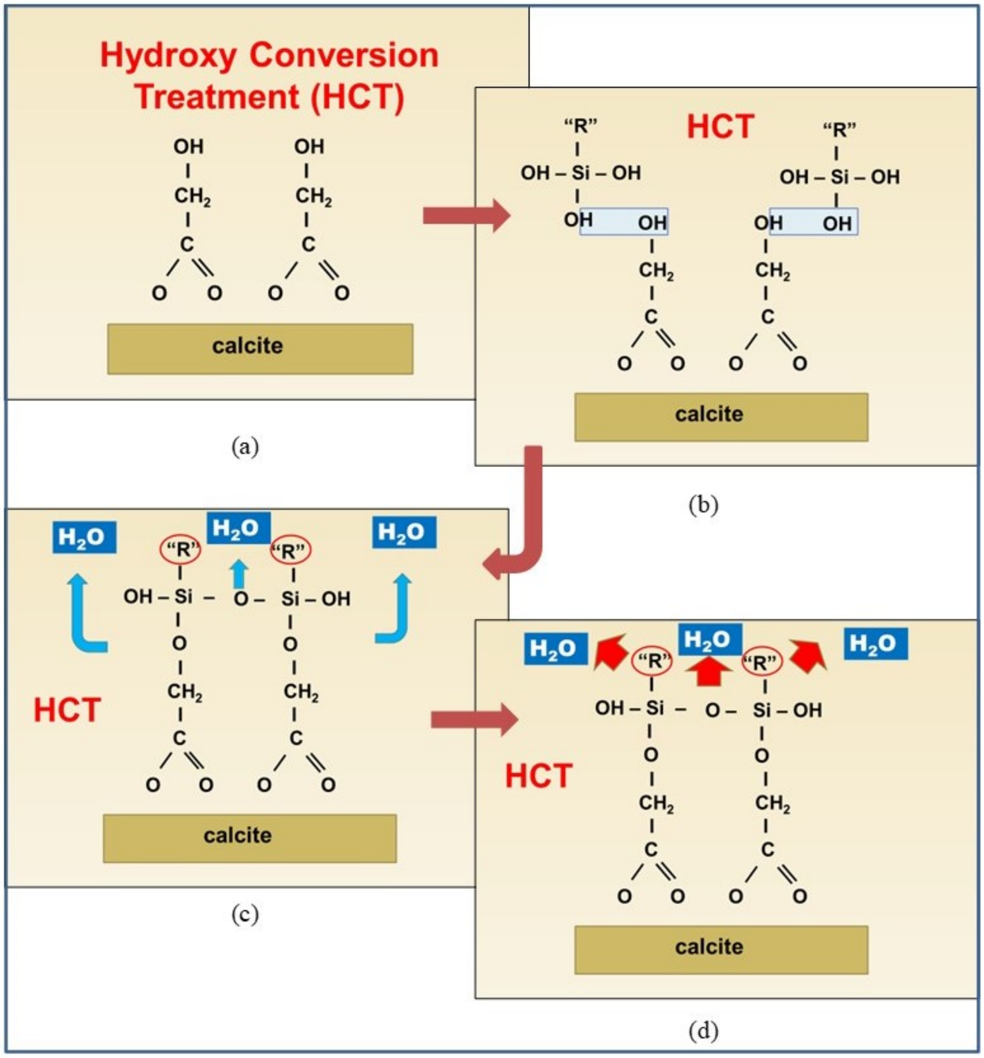

Figure 6. Treatment of calcite sub-strata with a Hydroxy Conversion Treatment (HCT) to create hydroxyl groups for nano-silane couplings

The development of coupling agents and the ability to attach to different sub-strata are continuously being improved to create new products that cater for a wide spectrum of different minerals. In practice, (not only in pavement engineering) it is important to be aware of limitations that do exist in the nano-silane technologies that are commercially available to be used. Both the designer and contractor must ensure that the nano-silane technology specified / used is effective and compatible with the naturally available materials to be treated and stabilised.

3.7.3 Compatibility of the nano-modifier and the stabilising agent

The compatibility of the stabilising agent (bitumen emulsion and / or polymer(s)) with the modifier (alkoxy-silane) is fundamental to the stability and successful application of any emulsion (substance mixed with a carrier fluid). For purposes of

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discussion, the basic properties of bitumen emulsion are used to discuss the influence thereof of on the selection of a successful application of an alkoxy-silane modifying agent. Even the most basic differences in bitumen emulsions, i.e. cationic versus anionic, will have an important influence on the stability and performance of any modifying agent added to the emulsion.

Anionic emulsions will only provide a low-risk stable product, ensuring a long shelf-life and performance characteristics in combination with an applicable anionic alkoxy-silane and vice versa with cationic emulsions. The combination of non-compatible nano-particles (the emulsifying agent and the nano-silane) will result in either short-term or medium-term problems in terms of stability, separation and / or neutralisation of the nano-particles within the carrier fluid and an ineffective product not useable in practice. Prevention of failures before stabilisation is a design approach based on the understanding of the chemistry of the various nano-particle combinations together with the mineralogy of the materials to be treated [6]. In the case of an anionic or cationic emulsion, the emulsifying agent determines the main characteristics of the mix at micro-level. In order to blend successfully during the modification of the emulsion, the nano-silane also needs to be compatible with the emulsifying agent in order for it to attach firmly to the bitumen molecule.

The modification of the bitumen emulsion through an emulsification process is required to ensure that the alkoxy-silane is thoroughly distributed throughout the bitumen emulsion. The emulsification process is done at high shear to ensure that the two emulsification agents are well distributed throughout the emulsion and that the bitumen molecules are separated effectively into the smallest possible particle sizes. The manufacturing process should optimise the production of the modified emulsion with a resultant emulsion with a low viscosity and high stability. Unique properties and advantages which will retain its stability and viscosity over periods of months without detrimental effects (as has been shown and proven under actual field conditions) are required [20].

3.8 Engineering evaluation of the effect of nano-silicon modifications

The engineering evaluation of the effect of the nano-modification of materials using alkoxy-silanes is determined with practical tests indicative of the required engineering properties. The effect of the treatment and stabilisation of the stone / gravel / soil using the NME is measured in terms of the compressive strength, tensile strength and durability using standard test procedures under dry and wet conditions [9]. These results are compared to minimum specified criteria [6] as an indication of the suitability of stabilised materials for use in the various road pavement layers [6, 17]. The effect of the nano-modification will naturally be the difference in test results without and with the modification [21].

It should be noted that in terms of other uses in the built environment, compressive strength measurements are considered the least useful due to the impact of the stone type on compressive strength. In most cases tensile or flexure tests (e.g. 3 point and 4-point bending tests) are considered of greater value and will be more representative of the actual influence the nano-modification to a stabilising agent [1]. In terms of the use in pavement engineering, the retained compressive strength (percentage of the wet test compared to the dry test results) has been observed to play a role in the resistance of the material to the formation of potholes when exposed and subjected to water [6]. The water repellent characteristics are of importance both for the evaluation of the durability of the materials during wet and dry cycles, as well as the ability to prevent or at least minimise future weathering due to chemical decomposition within the road pavement structure. It should be noted that the design measurements done under laboratory conditions should be verified during construction to ensure that minimum requirements are been met in the field [6, 20].

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3.9 Cost aspects associated with the use of nanotechnology-based products

The objective of the investigation of the use of new technologies for macro application in the field of road pavement engineering is to meaningfully lower the unit costs of road infrastructure delivery, improve the properties of materials and reduce the risk of premature failures with special reference to applications also in a developing environment where sever challenges with regard to funding and maintenance ability exist. By achieving improved resistance to future in-situ weathering and reduced maintenance costs, the reduction of life-cycle unit costs of the roads will be dependant mainly on the cost of the NME enabling the use of naturally available materials compared to the cost of using high quality materials as per current specifications. The cost of the NME is a function of the unit cost as well as the volume required in order to achieve the required objectives. Different volumes may be required using different products in order to meet the minimum engineering requirements (due to various factors including the particle size of the modifying agent).

One of the major advantages of nano-scale products is the area versus size benefit (as discussed previously). In practice it will be necessary to determine the quantity (volume) of the modifying agent that is required to effectively cover the material that is being treated. In terms of road pavement engineering, quantities are normally calculated in terms of volume (m^3) of material that will be processed to determine the qualities in terms of weight (kg) or volume (litres) that will be required to treat the material in order to meet the required specifications. However, due to the vast difference in volume that may be required to meet the required engineering properties, is is essential to specify the cost per cubic meter stabilised and not the cost per volume (litre) required to achieve the required end result. Per volume (litre) any nano-scale product may be relatively expensive, but due to the small volumes required, it could be factors less expensive compared to products consisting of micro-size particles to achieve the required results per cubic meter stabilised.

The density of the naturally available materials available to be used to construct road pavement layers varies considerably due to various factors including the type of material (mineralogy) and the various fractions (sizes) that constitute a specific volume of material. Hence, volume calculations are usually done based on the standard weight of the material (e.g. 1 kg), and the various fractions in terms of generally available sieve seizes to determine the grading of the materials (normally varying between 63 mm and 0.075 mm) that will be used to construct a certain layer in the road pavement structure. The material fractions will also impact dramatically on the volume of any material required to cover the surface area of the various fractions of the materials to be used. In theory, this can be calculated using Equation (2).

Per unit of the material to be stabilised (e.g. kg):

$$\text{Nano-silane (kg)} = \frac{\sum_{i=0}^{n} \text{surface area of material passing sieve } ((i)-(i+1))(m^2)}{\text{Nano-silane coating area } (m^2/kg)} \quad \ldots..(2)$$

Where:

i = Sieve seizes normally used to determine the grading of materials varying from 63 mm to 0.075 mm; when n = 0.075 mm sieve size, then n+1 = 0 mm (i.e. the surface area of the material passing the 0.075 mm sieve)

n = number of sieves used to determine the material grading, where the last sieve size, i.e. the n^{th} sieve size = 0.075 mm

In practice, these calculations may proof basically impossible to execute to any degree of accuracy. Although the size of the modifying agent (alkoxy-silane nano-particles) which are going to attach to the material to be stabilised may be known with a degree of certainty, the scale to which these calculations are done (nano-scale)

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make the calculations of the area to be covered very difficult even if the various particle fractions in terms of grading is known. The porosity and texture of the material (stone / aggregate / soil) alone could add a multiplying factor to the area to be covered in terms of nano-surface. In general pavement engineering practice, normally only the fraction passing the 0.075 mm sieve size using normal sieve sizes is measured. The minerals comprising the 0.075 mm fraction of material may vary from 0.075 mm (e.g. fine-grained quarzitic particles) to clay crystals (normally considered as less than 2 μm) that may be less than 1 nm in size.

However, the percentage passing the 0.075 mm sieve together the information obtained from the XRD tests of the fraction passing the 0.075 mm sieve [6] can be used to get an indication of the percentage and the type of the nano-size particles present in the material to be stabilised. This information can form the basis to adjust the amount of alkoxy-silane required to achieve the required hydrophobic action. The mineralogy of the material (from XRD scans) usually also gives an indication of the relative surface area. For the same particle size, the influences of the type of minerals could vary considerably. Table 1 [22] gives an indication of some of the relative surface areas of different materials.

Table 1. Differences in surface area of different materials per unit mass (m^2/g) [22]

Material	Surface area of material (m^2/g)
Glass	0.1 to 0.2
Quartz (SiO_2)	1 to 2
Calcium silicate (Ca_2O_4Si)	2.6
Calcium carbonate ($CaCO_3$)	5
Clay	7
Talc	7

Due to the considerable variation (also in the size of the nano-scale modifying agents) it is important to compare costs on the basis of the volume (m^3) of the material to be treated and stabilised in order to meet the minimum required engineering specifications. The considerable area to size advantage of the use of applicable nano-scale technologies should normally render the cost of alkoxy-silane modifications (which are relatively affordable in terms of available nanotechnologies) to have a minimal influence if the objectives in terms of the use of engineering requirements can be met using naturally available materials. Freshly crushed stone normally specified for use in the upper pavement layers (or alternative thick asphaltic layers) come at a considerable cost to provide surfaced road infrastructure using traditional material specifications. The use of NME stabilising products together with naturally available materials can considerably reduce the unit costs for the provision of surfaced roads [6, 7, 8].

4. Conclusions

Many of the characteristics used through the application of proven nanotechnologies in the built environment directly impacts of the use of naturally available materials in road design and construction. These proven nano-scale products are applied to improve products such as sealants, adhesives and a diverse group of building material varying from wood to concrete to gypsum and have been in everyday use for decades. The nanotechnology-based products are used to protect buildings from the effect of climate and pollution with a proven history dating back more than a century and a half.

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The lessons learnt from the built environment also applies to the use of materials in roads industry. During the early years scientists tasked to developed products to protect buildings discovered through trial and error that the type of stone (primary minerals) and the condition of the stone (secondary minerals) have a major impact on the successful application of a specific nano-silicon based products. Of all the products developed over many years, only a few have been proven to contain the properties to enhance material characteristics and neither be harmful to living creatures and the environment.

It follows that the successful introduction of applicable nanotechnologies in the field of pavement engineering need to take cognisance of the available experience from the built environment. Knowledge of primary minerals (type of stone) and the secondary minerals (condition of the stone) and the understanding of the various implications associated with the use of silicon-based nanotechnologies need to be understood and recognised. The development of scientifically based design approaches using the available knowledge was used to successfully test, implement and verify designs using Accelerated Pavement Tests (APT) in South Africa. Due to the use of basic scientific principles and fundamental science in the evaluation of results, the design approach is universally applicable.

The identification of the fundamental properties and scientific aspects evaluated and used to develop the design approach developed to reduce the risk of using new technologies and successfully introduce New-age (Nano) Modified Emulsions (NME), enabling naturally available materials to be used in all pavement layers below a relatively thin asphaltic surfacing (e.g. appropriate chip seal). The following fundamental aspects and the evaluation of scientific principles associated with these aspects are crucial to the reduction of risks associated with the introduction of new-age technologies into macro engineering projects, including the provision of road transport infrastructure:

- toxicology, health and safety issues;
- environmental aspects, leaching and affecting of ground water;
- surface area or coverage versus volume;
- stability of nano-particles in a carrier fluid, e.g. water;
- nanotechnology products as a binder;
- hydrophobic characteristics to be achieved using applicable products;
- compatibility aspects of nano-silicon modifications to binders that will influence the successful application and use thereof, including;
    - compatibility with the mineralogy of the materials, and
    - compatibility with the stabilising agent to be modified;
- engineering evaluation of the effect of nano-silicon modifications in terms of required scientific properties (compressive strengths, tensile strengths, durability and stability), and
- Cost–aspects associated with the use of nano-technology based products based on the volume of material to be treated.

The design approach developed on the basis of fundamental scientific principles are universally applicable. The successful introduction of new-age technologies in the provision of macro infrastructure projects, considerably reducing unit costs, is only possible through the following of sound scientific principles. Archaic material classification tests and systems need to be substituted through the identification of the minerology of material and the identification of material compatible stabilising agents. The developing world is in urgent need of climate resistant long-lasting affordable road infrastructure. These available nanotechnology solutions could assist to a large extent to address these urgent service delivery needs.

5. Acknowledgements

The support of GeoNANO Technologies (Pty) Ltd, Germiston, South Africa, www.geonano.co.za, info@geonano.co.za, in support of students in the Department of Civil Engineering, University of Pretoria, Pretoria, South Africa to test a wide variety of materials as part of final year projects and post-graduate theses, testing the various principles identified in this paper, is acknowledged.

Author Contributions: Professor Jordaan under the directive of the Head of Department of Civil Engineering, Professor Steyn, has been leading the research into the provision of affordable road infrastructure at the faculty of Engineering, University of Pretoria. Professor Steyn recognized the potential of nanotechnology solution in the field of pavement engineering more than a decade ago. Professor Jordaan, through is involvement in the private sector and the support of road authorities, have been instrumental in the development of scientific principle, ensuring that implementation can be achieved at a minimum risk.

Funding: This research received no external funding

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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