A STUDY OF THE EFFECTS OF ADDING ICE RETARDANT ADDITIVES TO PAVEMENT SURFACE COURSE MATERIALS

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DECLARATION

The worked described in this thesis was conducted at the Nottingham Transportation Engineering Centre, Faculty of Engineering, University of Nottingham between November 2007 and April 2013. I hereby declare that the work is my own and has not been submitted for a degree at another University.

Michael Wright
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ABSTRACT

The formation of ice and snow on pavement surfaces is a recurring problem, creating hazardous driving conditions, restricting public mobility as well as having adverse economic effects. Current winter operations primarily consist of the correctly timed application of de-icing chemicals to the pavement surface to prevent hazardous conditions occurring.

It would be desirable to develop new and improved ways of modifying the pavement surface, to prevent or at least delay the buildup of ice and to weaken the pavement-ice bond; making the ice which forms easier to remove. This development could lead to economic, environmental and safety benefits for winter service providers and road users.

Recent research has identified "promising" chemical additives, which appear to have the potential to provide suitable anti-icing performance, as well as meeting requirements relating to the pavement surface life, economic and environmental factors. However, research relating to performance and durability of chemically modified asphalt for anti-icing purposes and the mechanisms by which the chemicals are transferred to the pavement surface is severely limited.

The research described in this thesis attempts to contribute to the field by assessing the impact that the "promising" chemical modifications of sodium formate and sodium silicate have on the anti-icing performance and durability of asphalt.

The research provides extensive data on how the chemically modified asphalt behaves in terms of the compactability, stiffness, fatigue, permanent deformation and skid resistance, relative to standard asphalt surface courses, under standard testing conditions and after high moisture absorption.

The research provides a better understanding of how the chemical additive can be transferred from bitumen mastics and bituminous materials to the pavement surface. The study also assesses the potential reductions in freezing point and ice adhesion that can be produced by the specific chemical concentrations. The study evaluates laboratory test results in conjunction with three full scale site trials in the UK designed to better replicate the variability in winter weather conditions and trafficking.

The study concludes that the addition of de-icing chemical formulations consisting of sodium formate and sodium silicate do not significantly reduce the asphalt performance when subjected to a number of standard asphalt test methods, including compactability, stiffness, permanent deformation and skid resistance.

The inclusion of de-icing chemical formulations can however, lead to an increased susceptibility to deterioration in the presence of water, combined with an ability to absorb moisture from the atmosphere. Site trials have demonstrated that this can lead to an increased risk of early life failure and reduce service life of the pavement surface course. The thesis recommends that revised screening tests and bituminous mix design procedure is developed for assessing potential de-icing chemical formulations, which places particular emphasis on the performance of asphalt in the presence of moisture/water.

The study concludes that de-icing chemical formulations can be transferred from within the bitumen mastic to the pavement surface. The chemical transfer to the pavement surface is heavily dependent on the relative humidity and the number and arrangement of surface voids. The transfer of de-icing chemical formulations to the pavement surface can reduce the freezing point of the pavement surface and/or reduce the ice adhesion.

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1.0 INTRODUCTION

1.1 BACKGROUND

The formation of ice and snow on the road creates hazardous driving conditions, restricts public mobility and has adverse economic effects. Hazardous driving conditions are caused by a reduction in the coefficient of friction between the tyres and pavement surface, and the presence of ice is not always apparent to the road user. In order to ensure, as far as possible, that road users can travel safely and with minimum disruption in cold and severe climatic conditions, highway authorities have a responsibility to provide adequate levels of winter service. Winter service is `*the collective term for all specialist winter operations*` (Road Liaison Group 2005). It is estimated by Thornes (2003a) that the cost of keeping UK local authority highways free of frost, ice and snow was in the region of £168 million for the year 2001 to 2002.

Current winter operations primarily consist of the application of de-icing chemicals to the pavement surface. A chemical de-icing material is defined by COST (2002) as a `*substance which modifies the properties of snow and ice by physical or chemical means*`. Chemical de-icers can be applied as proactive (anti-icing) or reactive (de-icing) winter road treatments. The key function of a chemical de-icer applied reactively is to break the bond between the road surface and the overlying ice. This enables passing traffic to mechanically break up the loosened ice or snow and disperse it from the trafficked area of the road. An even more efficient use of de-icers is to apply it preventively, termed anti-icing. `*Anti-icing is the snow and ice control practice of preventing the formation or development of bonded snow and ice by timely applications of chemical freeze point depressants*` (Ketchman et al 1996).

A number of different de-icing chemicals are used throughout Europe. These include sodium chloride, magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, urea, alcohols and glycol. The most popular de-icing chemical used throughout Europe is sodium chloride, commonly known as road salt. Sodium chloride was first used in the 1930s for snow and ice control to ensure public mobility and less hazardous road conditions and since 1970 `*U.S. highway agencies have applied approximately 10million tons of road salt each year*` (TRB 1991). It is by far the most popular chemical de-icer `*because it is reliable, inexpensive and easy to handle, store and apply*` (TRB 1991). It is estimated by Kuemmel and Hanbali (1992) that the direct user benefits by $6.50 for every $1 spent on maintenance during the first four hours after spreading on a two-lane highway.

However, it has been widely acknowledged that improvements to current practice can be made in order to make winter service operations more cost-effective and reduce the well publicised adverse environmental effects (Schraunfnagel 1965, Avery 1973, Backman et al. 1986 and D'Itri 1992). These include degradation of the environment along the roadside (wildlife/vegetation), vehicle and infrastructure corrosion and sodium infiltration of drinking water. In recent years improvements have been made to best practice by chemical advancements, pre-wetting techniques and improved spreading techniques to reduce such impacts. However, to date the alternative methods have been inferior to the application of salt when considering the highway networks as a whole. This is due to reasons which have previously been summarised by the 1978 report on the technical, environmental and economic aspects of highway de-icing salts by the National Conference of State Legislatures which states `*Several alternatives to de-icing salts have been investigated or tried, but they tend to be too expensive, damaging to highway structures, more toxic than de-icing salts or not as effective*`.

The buildup of ice and hard-packed snow on asphalt and Portland cement concrete highway surfaces is a recurring problem and current ways of coping are far from satisfactory. This is because of the need for continued application of de-icing chemicals throughout the winter months. This application needs to be correctly timed to prevent un-safe conditions developing and has significant economic impacts related to labour, plant and materials. It would therefore be `*desirable to develop new and improved ways of modifying the highway surface, to prevent or at least delay the buildup of ice, and to weaken the pavement-ice bond so that the ice which forms is easier to remove*` (Baum et al 1992).

One area that has previously been considered in order to improve current practice is the modification of the pavement surface course`. *Both physical and chemical modifications of the pavement surface are candidates for preventing the formation of ice or for reducing the strength of adhesion to a level that permits fast, complete, and low-force removal of ice or compacted snow*` (Baum et al 1992)**.** The concept of modified anti-icing pavement surfaces is to act as a preliminary de-icer by reducing the temperature at which ice forms. Such products are not intended to eliminate winter maintenance, but delay the formation of ice and reduce the need for winter maintenance.

A number of proprietary anti-icing surfaces have been tried in recent years. The first anti-icing surface developed in the 1970s was a product called Verglimit. Verglimit is a patented bituminous concrete pavement that contains calcium chloride pellets encapsulated in linseed oil and caustic soda. The proprietary additive generated significant interest with trials undertaken throughout Europe, Japan, Canada, and the United States.

During the Verglimit trials, unsubstantiated reports were made of low skid resistance during dry weather, with such problems being specifically blamed for a fatal crash, by a number of consultants at the time. These problems were combined with a reduced service life due to the cracking and spalling of the pavement surface, with some studies suggesting the pavement service life may be reduced by up to 50% (Stuart and Mogawer 1988). Following studies suggested stricter recommendations such as by Turgeon (1989) `*no future Verglimit sections should be constructed unless compaction problems are solved, crack opening and spalling can be decreased and cold-dry winter de-icing characteristics are displayed*`.

At the same time as the development of the Verglimit product, the Strategic Highway Research Programme (Baum et al. 1992) undertook a study to identify chemicals which could be placed in the wearing course of asphalt to reduce the freezing point of surface accumulations of ice and to weaken the ice-pavement bond. This study identified several promising compounds, which included water-soluble organic and inorganic compounds and oils. The study used the Verglimit product as a control for comparing other potential additives.

Literature investigations into de-icing additives has indicated that research into the area of de-icing pavement additives beyond the Baum et al. (1992) study has been severely limited and the recommended additives do not appear to have been tried. This may be due to concerns relating to skid resistance and service life. For example Wuori (1993), when referring to the skid resistance and service life drawbacks of the Verglimit product, states that `*because of these drawbacks and the general concern about chemical additives …………no work was done with chemical additives*`. It would therefore appear that research over the last century has been focused on improving the tried and tested method of salting roads, rather than a more revolutionary solution to the reoccurring problems caused by ice on the roads.

In recent years a limited number of anti-icing surface course products have emerged on the market, namely the Safelane product. Safelane is an overlay patented system developed by Michigan Tech University, comprising of absorptive aggregate that have the ability to store pre-applied de-icing liquids. The performances of these U.S. trials lead to the first UK trial in 2007 on the Southbound A46 approach to the A428 as part of the Highways Agency operating MAC area 11.

This may indicate a change in attitude towards pavement modifications for anti-icing purposes. Despite these changing attitudes, a lack of fundamental understanding of how a surface can be physically and chemically modified to promote anti-icing, the benefits of such applications and the implications of the modification on the mechanical properties of asphalt still exists.

1.2 PROBLEM STATEMENT

The development of an anti-icing pavement additive has the potential to reduce the temperature at which ice forms. A reduction by only a few degrees Celsius could significantly reduce the amount of precautionary works currently undertaken in the UK, with the potential of improved safety, a reduction in the use of sodium chloride and the associated environmental impacts and economic benefits.

Initial investigations by Baum et al. (1992) and background research indicates that individual chemical additives have the potential to provide suitable anti-icing performance, as well as meeting the criteria relating to the pavement surface life, economic and environmental factors. Despite the identification of the need to develop a modified pavement surface to reduce the buildup of ice, research relating to performance and durability of anti-icing chemical modifications and the mechanisms by which the chemicals are transferred is severely limited.

The only significant study on modified asphalt for anti-icing purposes conducted by Baum et al. (1992) has provided an initial ranking of potential additives based on preliminary testing. The study recognised the potential of a number of water soluble salts and hydrophobic liquids. The study by Baum et al. (1992) successfully reaches its objectives by providing preliminary testing to determine promising additives.

However, current knowledge and the research projects such as the study by Baum et al. (1992) do not provide a detailed understanding of the anti-icing performance and mechanical performance of asphalt.

Previous studies have not considered the anti-icing performance achieved when de-icing chemicals are blended into the pavement surface course and/or the mechanism by which the chemical is transferred. This is because the majority of the chemical testing has been undertaken on solutions of the chemical and not on a modified pavement surface course. Therefore allowances for a change in the behaviour of the chemical when blended with bitumen and mixed into asphalt surface courses have not been made.

The initial study by Baum et al. (1992) was required to screen a high number of chemicals in order to highlight the most promising chemicals. This screening process was primarily based on the ability of single chemicals to depress the freezing point of water. The study therefore did not reflect the benefits of low surface energy materials to reduce ice adhesion, which has been shown to be successful in many alternative applications (e.g. leading edges of airplane wings and overhead telephone wires).

Historical site trial data from previous products (e.g. Verglimit) has equal limitations. Anti-icing performance has been based on visual observation of the freezing point. For this reason the exact performance has not been substantiated and claims of the service life of such systems vary significantly. No detailed studies of the anti-icing life for chemically modified surface courses have been documented.

Mechanical Performance of chemically modified asphalt is of equal importance to anti-icing performance. The importance of this has been highlighted by previous products with issues relating to skid resistance, cracking and early decomposition reported.

The screening study by Baum et al. (1992) provided simplistic measurement of mechanical performance in terms of Marshall Stability and Flow for ranking purposes. However, the study of individual asphalt performance parameters was outside the scope of the project.

The study also acknowledges that the recommended chemical substances have a tendency to absorb significant quantities of moisture and this effect has been observed throughout site trials. Baum et al. (1992) suggest `high moisture absorption by a deliquescent salt could lead to problems of caking in the shipping bag if there were pinholes, expansion and cracking of the pavement, and too high a rate of humidity causing exudation of the additive, leading to slippery road conditions`. Despite these concerns no investigation of the implications of this moisture absorption have been undertaken, and the role this property would play with regard to the failing of previous products, related to durability and skid resistance, is unknown.

A further study into the anti-icing and mechanical performance of the recommended additives by Baum et al. (1992) does not appear to have been undertaken. This may be due to concerns raised by the Verglimit product. Recent developments of alternative pavement additive products do not appear to have provided a solution, due to the fact that they are not currently economical for application on UK roads or due to environmental implications.

This thesis aims to improve the understanding of the physical anti-icing performance and mechanical effects on asphalt surface courses when incorporating a select range of anti-icing formulations.

1.3 RESEARCH SCOPE AND OBJECTIVE

The use of freeze depressant additives has previously been tried with limited success, with studies into the use of chemical anti-icing pavement additives being very limited. Considering current practice and the climatic conditions of the UK, it is clear that such products may be beneficial for use in the UK.

This research aims to assess the impact that the ice retardant additives have on the mechanical properties of surface courses over the life cycle of the product and to provide a new understanding of the mechanisms by which previous products have failed/deteriorated and the role that moisture absorption plays in generating or accelerating such mechanisms.

The thesis also aims to provide new understanding of the chemical transfer mechanisms when a select range of ice retardant additives are added to pavement surface courses. It then aims to assess the associated anti-icing performance in terms of freezing point depressant and ice adhesion and the durability of the performance.

The objectives of the study are:

- To assess the impact that the ice retardant additive has on the mechanical properties of asphalt surface courses.
- To assess the levels of moisture absorbed by de-icing chemical pavement surface course and the associated impact upon the mechanical properties of asphalt.
- To determine the anti-icing performance and contributing physical mechanisms that occur when a select range of anti-icing additives are added to the pavement surface course.

The first objective is achieved by undertaking a range of standard European bitumen and asphalt performance tests to assess the service life of such products, with appropriate comparisons being made between ice retardant samples and control specimens. This range of testing is designed to assess standard pavement surface course failures and de-icing mechanisms of previous products. The objective will be supported by conducting site trials of promising chemical formulations and conducting detailed visual assessments and routine surface course testing.

The second objective will be met by conducting accelerated moisture conditioning of chemical and asphalt samples, to determine the potential level of moisture absorption of the ice retardant additives. Standard performance testing relating to the previous failure mechanisms of skid resistance, cracking and decomposition will be conducted on accelerated moisture conditioned specimens. The results obtained from laboratory testing will be supported by observations relating to moisture absorption of the site trials.

The final objective will be achieved based on a laboratory testing programme utilising specifically devised methods for measuring anti-icing performance of surface courses. Firstly, the method of chemical transfer will be assessed using Scanning Electron Microscopy. Secondly, freeze point depression will be assessed for the range of ice retardant additive formulations. Measurements of freezing point are conducted initially on chemical solutions. Freezing point measurements are also conducted on asphalt specimens at various soaking periods to determine the influence of asphalt properties and environmental exposure on the freezing point. Finally, the potential of reducing ice adhesion will be evaluated and assessed by determining the surface energy components of the chemicals and chemically modified mastics. Physical measurements of the adhesion between chemical solutions and bituminous surfaces are made.

Instrumented site trials of selected chemical formulations aim to provide an accurate measure of anti-icing performance over a prolonged period of varying conditions and enable anti-icing laboratory investigations to be related to real highway conditions.

1.4 ORGANISATION OF REPORT

This dissertation is organised into eight chapters. Chapter 1 has provided background to the problem of winter weather driving conditions. The chapter introduces current winter service techniques and previous attempts to modify the pavement surface course for de-icing purposes. The chapter presents the aims and objectives of the thesis.

Chapter 2 reviews the available literature relating to current winter service practices and provides details of how winter service is provided, the benefits of current practices, the negative impacts in relation to the environmental and economic factors and site specific locations.

Chapter 3 introduces the concept of anti-icing modification of pavement surface courses and provides a review of literature concerning the ice pavement bond. The chapter then reviews modified pavement surface courses to achieve anti-icing performance and details the mechanisms by which they work, the performance achieved and any negative aspects of the product.

Chapter 4 introduces the experimental programme and details the most promising chemical modifications. The chapter critically reviews knowledge of anti-icing pavement surface course and selects the chemicals for further study.

Chapter 5 characterises the physical and surface properties of the chemicals and fillers that form part of the experimental programme.

Chapter 6 provides an overview of the testing programme and the experimental findings for the select range of chemical additives. This is considered in terms of:

- Influence of the chemical additive on the mechanical properties of asphalt.
- Determination and influence of moisture absorption on the mechanical properties of asphalt.
- Influence of chemical additives on the physical properties of ice and the ice pavement bond.

Chapter 7 specifies the design and construction of site trials conducted using a select anti-icing surface course and analyses the performance of these materials against a control surface with regard to the three objectives highlighted above.

Chapter 8 provides a summary of the research project, the key conclusions drawn and the recommendations for future work.

2.0 LITERATURE REVIEW

2.1.0 WINTER WEATHER CONDITIONS – THE PROBLEMS AND NEED FOR WINTER SERVICE

2.1.1 WINTER WEATHER CONDITIONS

Hazardous winter driving conditions are caused by three principal factors. The first and most common factor is the formation of ice caused by the freezing of already wet sections of road due to decreasing temperatures. Secondly, slippery conditions can be created when ice is formed due to small amounts of moisture from sources such as condensation and freezing fog. Finally, hazardous driving conditions can also be formed directly from precipitation, in terms of freezing rain or snow. Freezing rain is `*A dangerous condition where raindrops fall on to surfaces below 0 °C, thus freezing instantly and causing widespread glaze ice*` (COST 2002).

The intensity, frequency and duration of winter weather conditions are very dependent on the climatic conditions. Climatic conditions strongly influence the strategy of winter maintenance of a particular country. The climatic conditions observed for a country or region is dependent upon altitude, latitude and geographical locations. A review of the climatic conditions experienced by European countries (COST 2002) defined seven different climate classifications. These include Maritime, Cold Maritime, Northern, Central-European, Continental, Mediterranean, and Mountain climate, see Figure 2.1.

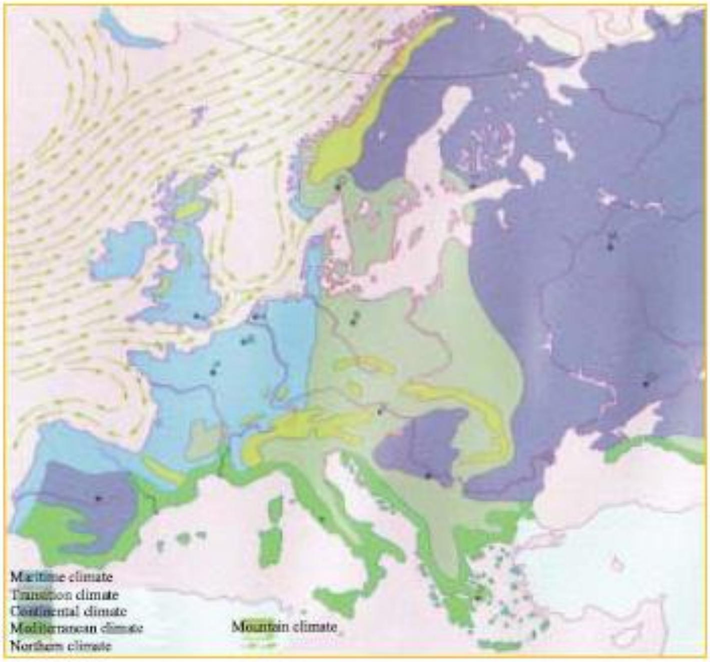


Figure 2.1 – Climatic areas of Europe (COST 2002)

2.1.2 CLIMATE OF THE UNITED KINGDOM

This study of physical or chemical modified pavement surface courses for de-icing purposes is principally based on the use of such products in the United Kingdom. It is therefore essential to fully understand the climate of the UK. The principal factors influencing the UK's climate are `*its northerly latitude (which ranges from 50° to 60° N), its close proximity to the Atlantic Ocean and, especially, the warming of the waters around the British Isles by the Gulf Stream*` (PIARC 2006). The COST report `344 - Improvement to Snow and Ice Control on European Roads and Bridges` (2002) specifies that the climatic classification for the UK is predominantly a maritime climate.

A maritime climate has a minimum average winter temperature around $0^{o}C$ with limited temperature fluctuations. COST (2002) identifies that this is problematic because of daily melting and freezing combined with high relative humidity and precipitation rates. Such conditions result in frequent icy pavement conditions and black ice events. For example, Figure 2.2 (Thrones 2003b) demonstrates that for the period 1961-90 in England the number of road frosts varied from approximately 25 in parts of West Cornwall to about 75 in the Pennines and Cumbria.

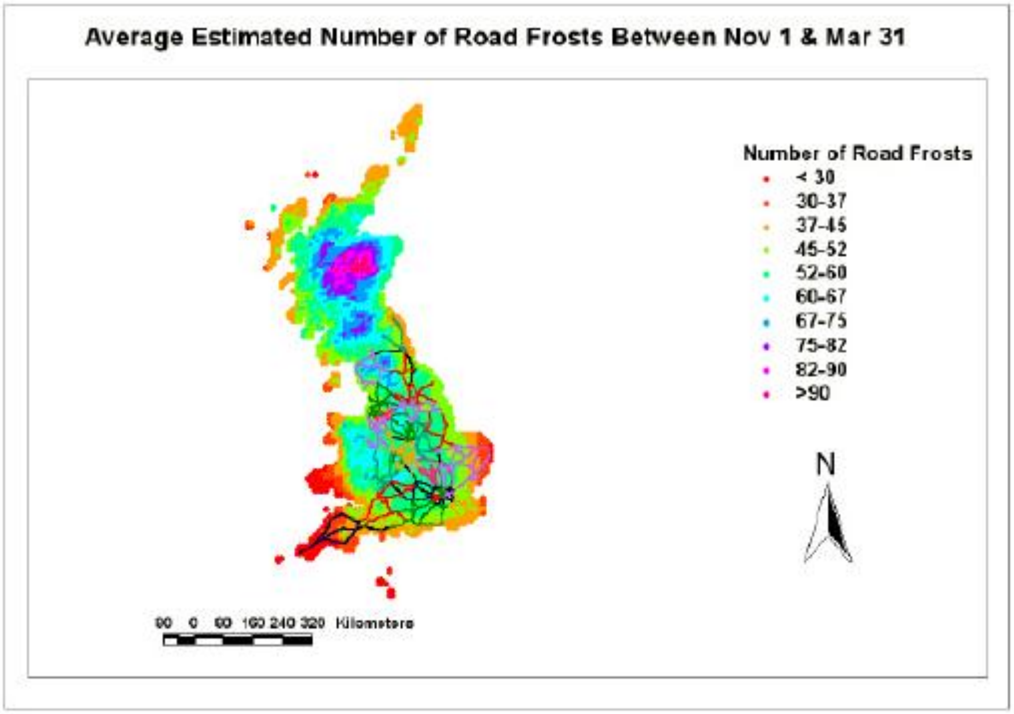


Figure 2.2 - Average estimated number of road frosts and area networks (Thornes 2003b)

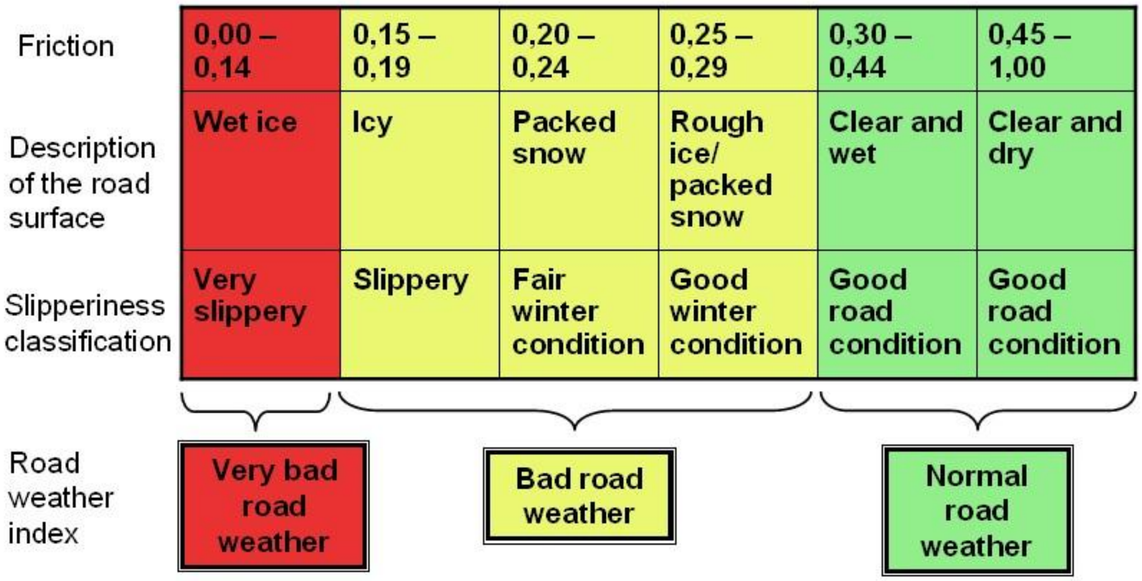
The marginal climate of the UK presents specific hazards. For example, icy roads in the UK are intermittent and road surface temperatures may fall below zero for just a short period of time. `*Hence drivers are not always expecting slippery road surface conditions as they are in colder climates*` (Thornes 2000).

Snowfall events in the UK are also variable. Since 1961, the number of days of lying snow has has varied from a few days of snowfall per year to a maximum of 24 days (Quarmby et al. 2010).

2.1.3 THE PROBLEM OF ICY CONDITIONS AND THE NEED FOR WINTER SERVICE

The formation of ice on the pavement surface creates hazardous driving conditions because of a reduction in the coefficient of friction between the tyres and pavement surface. The presence of ice creates further increases in accident risk because `*ice is not always apparent to the motorist and is not uniform, so that the driver is not always prepared when he/she encounters an icy section*` (Kuemmel 2007).

The effects of snow and ice conditions on the coefficient of friction are demonstrated in Figure 2.3 (Keskinen 2009). This demonstrates the severe reductions in friction (Gripnumber) caused by the presence of ice on the road surface.



Friction	0,00 – 0,14	0,15 – 0,19	0,20 – 0,24	0,25 – 0,29	0,30 – 0,44	0,45 – 1,00
Description of the road surface	Wet ice	Icy	Packed snow	Rough ice/ packed snow	Clear and wet	Clear and dry
Slipperiness classification	Very slippery	Slippery	Fair winter condition	Good winter condition	Good road condition	Good road condition
Road weather index	Very bad road weather	Bad road weather			Normal road weather	

Figure 2.3 – Correlation between friction in terms of the Gripnumber (Gn), description of the road surface, slipperiness classification and road weather index (Keskinen 2009)

To put the severity of this hazard into perspective, in 2010 there were 6,313 reported accidents during snow or icy road surface conditions in the UK, of which 628 were serious or fatal accidents (DfT 2010). Such accidents occurred despite extensive winter service programmes throughout the UK.

Snow and ice on roads also impacts upon public mobility. Such delays generate significant adverse economic impacts. Thornes (2000) estimates that the cost of winter weather conditions in terms of traffic delays would be £1,500m per year if salting did not occur. This figure takes into account wage loss for lateness to work, absenteeism, production losses and delayed deliveries.

2.2.0 CURRENT WINTER SERVICE PRACTICE

Winter weather conditions create hazardous driving conditions for road users. In order to ensure as far as possible, that road users can travel safely and with minimum disruption in cold and severe climatic conditions, the current practice is to undertake winter service.

Winter service is `*the collective term for all specialist winter operations*` (Road Liaison Group 2005). Winter operations include the application of de-icing chemicals to the pavement surface to mitigate the effects of ice and snow by physical and/or chemical modification. De-icing chemicals can be applied as a pre-treatment or as a post-treatment. These can be used in conjunction with weather forecasting systems, which may include thermal mapping, ice detection stations and weather radars to act as a decision support system.

Effective snow and ice control is an important service for national governments. It is required to ensure as far as possible, that road users can travel safely and with minimal disruption in cold and severe climatic conditions. In the UK, Highways authorities have a legal duty to provide winter service. `*In particular, a highway authority is under a duty to ensure, so far as is reasonably practicable, that safe passage along a highway is not endangered by snow and ice*` (Highways Act 2003). However, the Road Liaison Group (2005) states that `*This is not an absolute duty*` and `*it is not always practically possible either to provide the service on all parts of the network and ensure running surfaces are kept free of ice or snow at all times, even on the treated parts of the network*`.

Currently, the Highways Agency Network Management Manual - Part 5 specifies that a decision to treat will depend upon many factors, but if road surface temperatures are predicted below plus 1°C, a precautionary treatment should normally take place. This is unless:

- No moisture is on or is expected to be on the road; or
- There is sufficient residual salt on the road to deal with the expected conditions.

The cost of managing the risks caused by icy road conditions through winter service is costly for local authorities and the Highways Agency in the UK. It is estimated by Thornes (2003a) that the cost of keeping UK local authority highways frost, ice and snow free was in the region of £168 million for the year 2001 to 2002. In addition to this approximately £51 million was spent on the winter service of motorways and UK trunk roads for this period.

In order to understand the potential benefits of modifying the pavement surface course to promote anti-icing; it is important to consider the current practice and application of de-icing chemicals. It is also important to understand the benefits and drawbacks of such techniques.

2.2.1 CHEMICAL DE-ICING/ANTI-ICING

A chemical de-icing material is defined by COST (2002) as a `*substance which modifies the properties of snow and ice by physical or chemical means*`. A number of different de-icing chemicals are used throughout Europe. These include sodium chloride, magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, urea, alcohols and glycol.

Chemical de-icers can be applied as proactive (anti-icing) or reactive (de-icing) winter road treatments. The key function of a chemical de-icer applied reactively is to break the bond between the road surface and the overlying ice. This is to enable passing traffic to mechanically break up the loosened ice or snow and disperses it from the trafficked area of the road, see Figure 2.4.

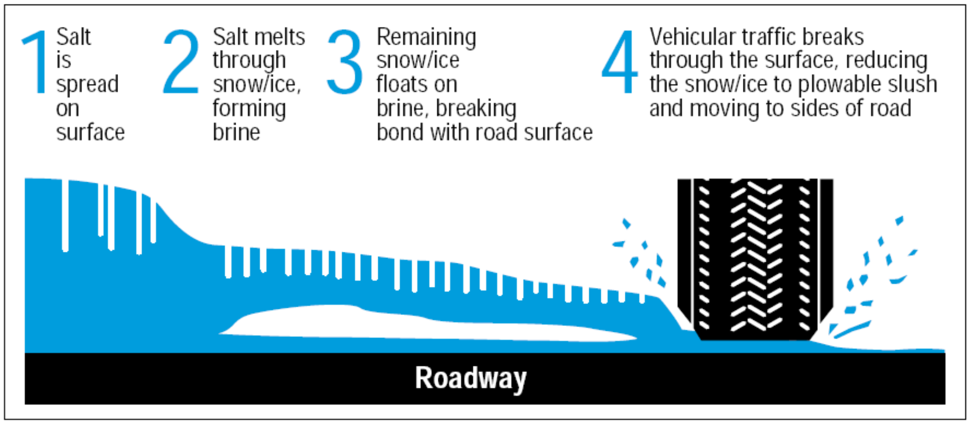


Figure 2.4 - Salt/Brine action on the road surface (Salt Institute 2004)

An even more efficient use of de-icers is to apply chemicals preventively, termed anti-icing. `*Anti-icing is the snow and ice control practise of preventing the formation or development of bonded snow and ice by timely applications of chemical freeze point depressants*` (Ketchman et al. 1996).

This is when a de-icing chemical is applied before the onset of the winter weather storm or before precipitation begins. This preventative application inhibits the formation and development of ice bonding to the pavement surface. This precautionary work can significantly reduce the amount of de-icer needed to keep roads free of ice and snow.

It is important to recognise that a number of factors affect de-icing performance. These include the timing of application, chemical concentration, pavement temperatures, weather conditions, pavement surface type, topography and traffic volume.

The Highways Agency Network Management Manual – Part 5 states `*Precise reasons for the formation of ice on a road surface despite the presence of an anti-icing treatment are not necessarily clear, but there are general factors that may often contribute to the situation. These include:*

- *Dry Road Surface*
- *No precipitation*
- *Road Surface Temperatures below 0^oC*
- *Road Surface Temperatures below Dew point temperature*
- *Relative humidity less than 80 per cent*
- *Closeness to winter solstice (21st December) [Shortest Day]*
- *Low traffic flows*
- *High winds*`

Factors such as dry road surface, no precipitation, low humidity and low traffic flow can combine resulting in an inadequate formation of a brine solution, see section 3.3 Freeze Point Depressants.

High winds can increase the probability of the chemical de-icer being transported away from the carriageway before brine can be formed.

Severe winter temperatures increase the speed and bond strength of ice or snow formations.

2.2.2 CURRENT PRACTICE

The current practice in the UK and throughout Europe is to apply de-icing/anti-icing chemicals directly to the pavement surface. The most popular de-icing chemical used throughout Europe is sodium chloride commonly known as road salt. Sodium chloride was first used in the 1930s for snow and ice control to ensure public mobility and less hazardous road conditions. Since 1970 `*highway U.S. agencies have applied approximately 10million tons of road salt each year*` (TRB 1991).

It is by far the most popular chemical de-icer `*because it is reliable, inexpensive and easy to handle, store and apply*` (TRB 1991). It works by creating a brine that has a lower freezing temperature than the surrounding ice with the ability to melt snow and ice at temperatures as low as -21.1^{o}C, (Section 3.3.1 Freeze depressants). In practice, sodium chloride works efficiently down to around –5 ^{o}C. However, `*below -10 $^{o}$C the amount needed increases to become environmentally and economically undesirable*` (Road Liaison Group 2005).

Alternative chemicals to sodium chloride have previously been researched (Mangold 2000, TRB 1991), these include:

- Calcium magnesium acetate ($CaJMgOOCCH_3$; more simply CMA)
- Magnesium chloride ($MgCl_2$)
- Calcium chloride ($CaC1_2$)
- Potassium acetate ($KOOCCH_3$; more simply KAc)
- Urea etc.

To date, the alternatives have been inferior to the application of salt when considering highway networks as a whole and have been restricted to specialist locations such as structures subject to corrosion.

The reasons for products being inferior have been summarised by the 1978 report on the technical, environmental and economic aspects of highway de-icing salts by the National Conference of State Legislatures `*Several alternatives to de-icing salts have been investigated or tried, but they tend to be too expensive, damaging to highway structures, more toxic than de-icing salts or not as effective*`.

Current winter service plans rely on the application of de-icing/anti-icing chemicals onto the road surface. The chemicals can be applied by dry salting or pre-wetting techniques.

Dry salting is when the chemical is spread as a granular rock salt. For precautionary treatments a spread rate of between 5-30 g/m^2 (COST 2002) is typically used. In mild climates, salt is spread in concentrations near the lower limit of the range indicated. For example, a target spread rate for a carriageway in the UK is typically 10g/m^2 for salt that is stored under cover (Highways Agency Network Management Manual Part 5). However, if dry salting is to be used as a reactive treatment on settled snow and ice, it should be spread at a rate up to 40g/m^2.

In recent years research has been focused on improving the tried and tested methods of applying de-icing chemicals to the road surface. The most significant area of this research has been in the area of pre-wetting, for example Burtwell (2004a). The principle of pre-wetting salt is that it enters into a solution much more effectively than dry granular salt. This enables anti-icing performance to be observed more quickly and eliminates the time lag for dry salt to form a brine.

The pre-wetting fluids that can be used include water, sodium chloride, calcium chloride or magnesium chloride brines. The proportion of the pre-wetting agent to dry salt is typically `*70% dry salt to 30% saturated brine by weight*` (Burtwell 2004a). Similar to the application of dry salting, the quantities applied to the pavement surface are dependent on the conditions at application. COST (2002) states that between 4 - 25g/m^2 should be applied as a preventive use. This depends `*on the condition of the road surface (dry, moist, wet road), on weather conditions (stable or changing), on the thickness of ice layer etc*`.

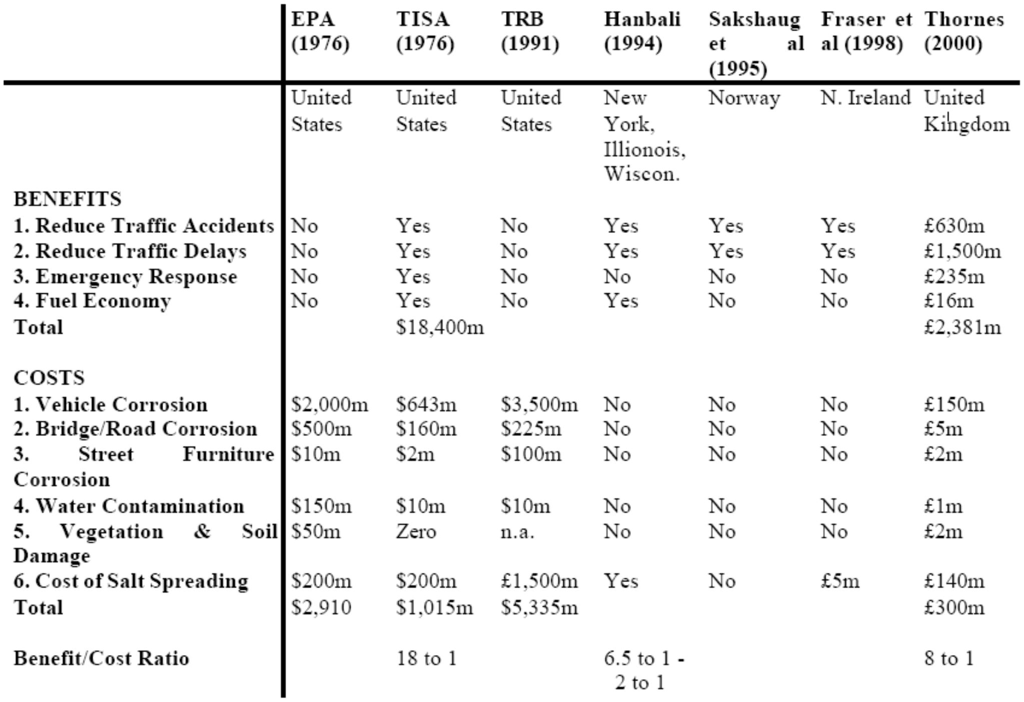
2.2.3 THE BENEFITS OF CURRENT PRACTICE

The effectiveness of applying de-icing chemicals such as sodium chloride to the road surface is evident by the fact that in general road user mobility is maintained and road traffic accidents and delays are minimised. A number of economic assessments have tried to place monetary values on the benefits of winter service. These have been demonstrated by Keummel and Hanbali (2007), Hanke and Levin (1998), Thornes (2000) and Quamby et al. (2010).

A number of cost benefit studies for winter maintenance operations have been undertaken worldwide and highlighted varying degrees of benefit to cost, these are summarised in Figure 2.5 (Thornes 2003b). The first estimation of the benefits of winter maintenance operations was a report published in 1976, Benefits and Costs in the Use of Salt to Deice Highways, by The Institute for Safety Analysis (TISA) which concluded that the use of de-icing salt has a higher benefit to cost ratio of 18:1.

More recently, Keummel and Hanabali (2007) estimated that the direct user benefits were $6.50 for every $1 spent on maintenance during the first four hours after spreading on a two-lane highway. Thornes (2000) predicted a slightly higher cost to benefit ratio of 8:1 in the UK.

Despite the variations in these estimates it is clear that current practice is a cost-effective way of reducing traffic accidents and delay caused by winter weather conditions.



	EPA (1976)	**TISA (1976)**	**TRB (1991)**	**Hanbali (1994)**	**Sakshaug et al (1995)**	**Fraser et al (1998)**	**Thornes (2000)**
	United States	United States	United States	New York, Illionois, Wiscon.	Norway	N. Ireland	United Kingdom
BENEFITS							
1. Reduce Traffic Accidents	No	Yes	No	Yes	Yes	Yes	£630m
2. Reduce Traffic Delays	No	Yes	No	Yes	Yes	Yes	£1,500m
3. Emergency Response	No	Yes	No	No	No	No	£235m
4. Fuel Economy	No	Yes	No	Yes	No	No	£16m
Total		$18,400m					£2,381m
COSTS							
1. Vehicle Corrosion	$2,000m	$643m	$3,500m	No	No	No	£150m
2. Bridge/Road Corrosion	$500m	$160m	$225m	No	No	No	£5m
3. Street Furniture Corrosion	$10m	$2m	$100m	No	No	No	£2m
4. Water Contamination	$150m	$10m	$10m	No	No	No	£1m
5. Vegetation & Soil Damage	$50m	Zero	n.a.	No	No	No	£2m
6. Cost of Salt Spreading	$200m	$200m	£1,500m	Yes	No	£5m	£140m
Total	$2,910	$1,015m	$5,335m				£300m
Benefit/Cost Ratio		18 to 1		6.5 to 1 - 2 to 1			8 to 1

Figure 2.5 - A comparison of international winter maintenance benefit/cost studies (Thornes 2003b)

The most significant benefits of applying winter service are contributed from a reduction in traffic accidents and traffic delays. Considering the fundamental issue of road traffic accidents alone, it has been demonstrated by Keummel and Hanabali (2007) that the application of salt (sodium chloride) or the combination of salt and calcium chloride resulted in an accident reduction of 88.3% on a two lane roadway. This was in comparison to the accident rate 4 hours prior to the application. The severity of accidents was reduced by 30% after application.

Similar benefits were demonstrated by Hanke and Levin (1998), Figure 2.6 shows typical accident rates before and after salting.

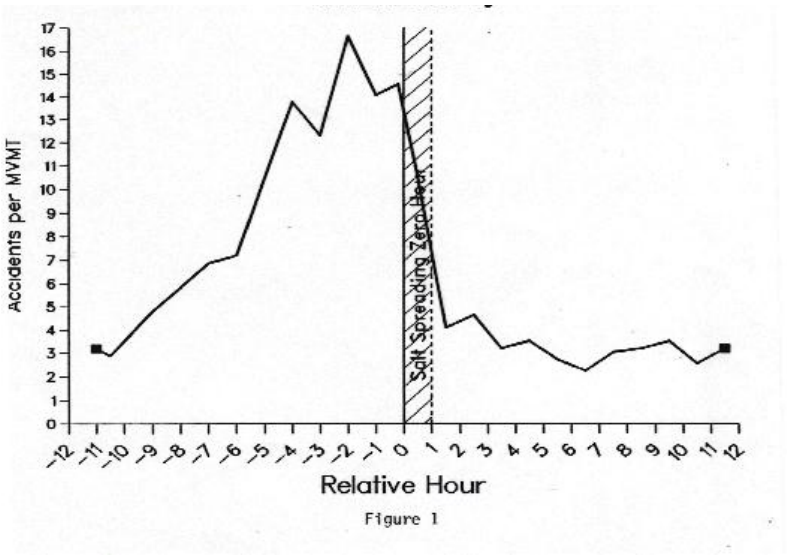


Figure 2.6 - Traffic accident rates in Million Vehicle Miles of Travel (MVMT) before and after salt spreading
(Hanke and Levin 1998)

It is estimated by Thornes (2000) that the economic benefit of salt spreading in the UK in terms of accident reduction is £630m per annum. Further accident analysis by Fraser and Drew (1998) highlights that `*70% of the accidents reported on icy roads were on roads that would normally have been salted*`.

Economic benefits in terms of traffic delays have also been estimated by Thornes (2000). The conservative estimate of £1,500m, as discussed previously, is based on wage loss for lateness to work, absenteeism and production losses and delivery delays.

2.2.4 PROBLEMS OF CURRENT PRACTICE

Current practice of applying the de-icing/anti-icing chemicals directly to the pavement surface is proven and cost effective. However, it is important to consider the negative effects of this practice and why it may not provide the optimum solution to the challenges faced during winter weather events.

2.2.4.1 PROBLEMS OF CURRENT PRACTICE – THE ENVIRONMENT

The negative impacts that chloride based de-icers can have on areas immediately adjacent to roads has been widely reported over the last three decades by Schraunfnagel (1965), Avery (1973), Backman et al. (1986) and D'Itri (1992). These include degradation of vegetation along the roadside environment, sodium infiltration of drinking water and corrosion to vehicles and infrastructure.

Such effects are observed because salt does not remain solely on the carriageway. It is transported onto highway verges either directly from salt spreaders or with the assistance of wind and bounce from the pavement surface. According to Burtwell (2004b) the `*salt mist has an impact on the local soil and vegetation, with the greatest concentration of salt found within 3m of the pavement edge and within the top 1m or so of soil*`. Surface runoff from stockpiles and the carriageway can also transport salt into the natural environment.

The most frequently reported negative impact of sodium chloride is the influence its use has on roadside vegetation and soil. Incidents of vegetation injury were first reported in Minnesota, USA during the 1950s. Further incidents were quickly reported, for example in 1957 New Hampshire, USA reported 13,997 dead trees along a 3,700 mile long highway (Avery 1973). Further investigations by Backman et al. (1996) concluded that `*The damage was by far the most pronounced in the immediate vicinity of the roads*`.

Vegetation damage occurs due to the intake of salt ions from contaminated soil or water, but it can also occur via salt spray from vehicles. This damage is primarily caused by excessive exposure to chloride ions rather than sodium ions. Vegetation damage can be observed by browning and falling leaves, stem dieback, stunted or abnormal growth, or premature death.

The impact that road salting has on vegetation is complex and highly site-specific. The severity of the impact can depend on the amount of salt, type of soil, distance from the roadway, slope of the road, total precipitation, wind direction, temperature, soil texture and drainage and the plant species. This was highlighted during Saskatchewan's 15 year study of the environmental impacts generated by de-icing salt (Y.C.Jin et al. 2004) `*A different set of geological characteristics could have led to an entirely different outcome*`.

The rate of salt application is also positively correlated with salt concentrations in roadside soil, as reported by D'Itri (1992). Although damage to vegetation is mainly from chloride ions, salt damage on soil is primarily due to the accumulation of sodium ions. According to TRB (1991), long-term salt accumulation can cause high soil density and lower permeability. These factors adversely affect plant growth and erosion control.

The impact of salt on vegetation and soil are interconnected with impacts on surface and groundwater. The effects of salt on surface water are confined mainly to small streams running adjacent to heavily salted highways. However for larger water systems the effect, in general, is significantly reduced. This is because the higher concentrations are quickly diluted. For example, Schraunfnagel (1965) found chloride concentrations greater than 10,000mg/L in highway spring runoff in Wisconsin, however adjacent surface waters only demonstrated a maximum concentration of 45mg/L.

Salt has a corrosive influence on infrastructure such as bridges, parking structures and most costly, to motor vehicles. The chloride ions in the sodium chloride disrupt the natural protective films of the metal surfaces and increase the conductivity of water. This induces and accelerates corrosion, see Figure 2.7 (TRB 2007). For example, when considering bridge decks, `*the chloride ions in salt penetrate concrete and cause reinforcing steel bars to rust, resulting in cracking and fragmenting of the surrounding concrete*` (TRB 1991). According to TRB (1991), `*During the past 30 years in the Northeast and Midwest (U.S), road salt has caused more premature bridge deck deterioration than any other factor*`.

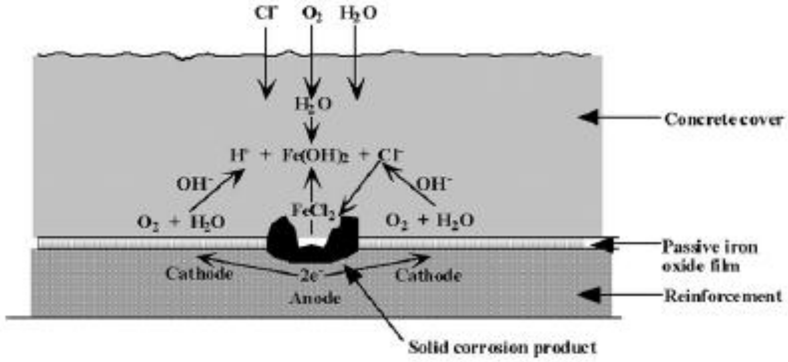
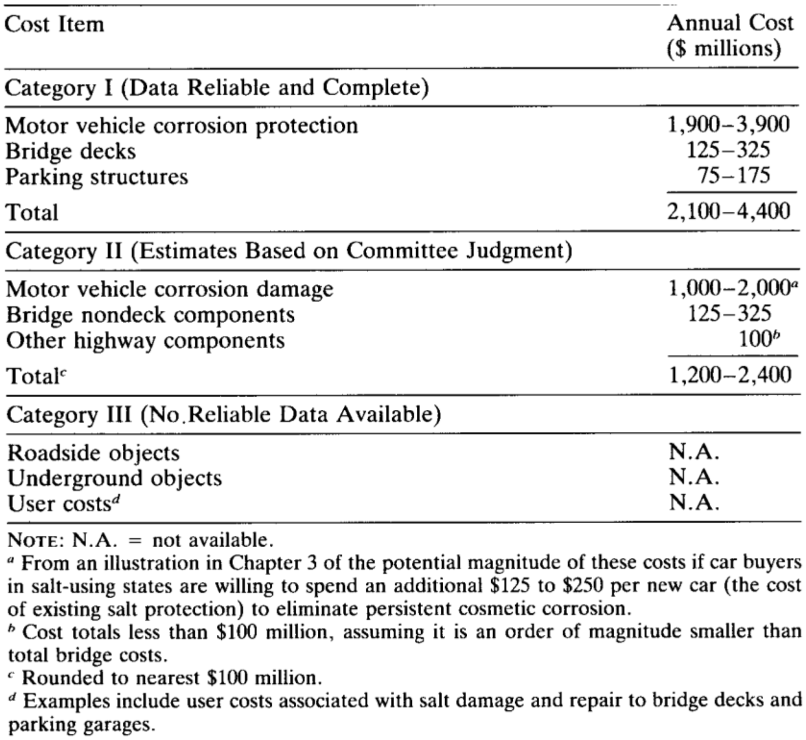


Figure 2.7 – Localised corrosion of steel reinforcements within concrete (TRB 2007)

The significance of the problem of corrosion is clear when further considering the summary of TRB (1991), which states that the overall cost estimate of corrosion in the U.S is between $3.5 billion to $7 billion per year.

A summary of the estimated cost of continued salt exposure on motor vehicles and infrastructure are detailed below in Figure 2.8 (TRB 1991). UK estimates by Thornes (2000) reported that the total cost of corrosion in the United Kingdom was £150 million.



Cost Item	Annual Cost ($ millions)
Category I (Data Reliable and Complete)	
Motor vehicle corrosion protection	1,900–3,900
Bridge decks	125–325
Parking structures	75–175
Total	2,100–4,400
Category II (Estimates Based on Committee Judgment)	
Motor vehicle corrosion damage	1,000–2,000[a]
Bridge nondeck components	125–325
Other highway components	100[b]
Total[c]	1,200–2,400
Category III (No Reliable Data Available)	
Roadside objects	N.A.
Underground objects	N.A.
User costs[d]	N.A.

NOTE: N.A. = not available.

[a] From an illustration in Chapter 3 of the potential magnitude of these costs if car buyers in salt-using states are willing to spend an additional $125 to $250 per new car (the cost of existing salt protection) to eliminate persistent cosmetic corrosion.

[b] Cost totals less than $100 million, assuming it is an order of magnitude smaller than total bridge costs.

[c] Rounded to nearest $100 million.

[d] Examples include user costs associated with salt damage and repair to bridge decks and parking garages.

Figure 2.8 – Economic impacts of salting on infrastructure (TRB 1991)

Similarly to economic assessment of the overall benefits of current practice, monetary value has been placed on the environmental impact. The overall environmental impact as a consequence of using dry salt as a precautionary treatment in the United Kingdom has been estimated to be £160 million per winter (Thornes 2000). Vitaliano (1992) reported that the true cost of salt used for de-icing roads in the United States is estimated at more than US$800 per ton (approximately £511 per ton at 2003 exchange rate).

Whilst it can be concluded that current practice provides an overall economic solution, if the content of chloride ions reaching the environment were to be reduced, significant environmental and associated economic benefits would be gained. Burtwell (2004b) summarised the benefits `*not least a reduction in the cost of structural repairs, a reduction in the contamination of highway runoff, reduced concentrations in watercourses, and reduced effects on flora and fauna*`.

The use of best practice guidelines can significantly limit the associated environmental impacts of current practice, as documented by the Highways Agency Network Management Manual Part 5 and Road Liaison Group (2005). These guidance documents are produced to ensure that the service provider considers all relevant materials available and selects the most appropriate treatment for each part of the network on each occasion, whilst also taking into account the cost of storing and spreading and the environmental impacts of the material. For example `*To be most effective, salt should be spread before ice forms or snow settles on the road*` (Highways Agency Management Manual – Part 5).

The manual also recommends that the service provider makes full use of specialised road weather forecasting services and the Road Weather Information System. Best practice guidance supports the Salt Institute (2004) philosophy for sensible salting which is based on the principle `*just enough and no more*`.

2.2.4.2 PROBLEMS OF CURRENT PRACTICE – CHEMICAL APPLICATION

Even with chemical advancements, current practice would not provide the optimum solution. This is because the buildup of ice on the road surface is a recurring problem and current practice does not eliminate or reduce the need for winter service but rather mitigates the effects of individual winter events. Every time a winter weather event occurs an appropriate response must be undertaken in-line with the winter service plan. This is significant considering the marginal climate of the UK, as discussed in Section 2.1.2, which identified minimum winter temperatures around 0 ^{o}C, creating frequent icy pavement conditions and incidents of black ice, if only for short periods.

Current winter service relies on accurate road weather information and forecasting predictions to ensure that a winter weather treatment is correctly timed. The timing of this response is of significant importance. For example:

- If a de-icing chemical is applied too early there is a higher chance of salt being mobilised and transported to the roadside environment.
- If the de-icing chemical is applied too late based on inaccurate road weather forecasting then a period of hazardous road conditions may exist leading to a higher risk of accidents occurring.

The Highways Agency Network Management Manual – Part 5 specifies that a decision to treat will depend upon many factors, but if road surface temperatures are predicted to be below plus 1^{o}C, a precautionary treatment should normally take place. This precautionary treatment is undertaken in anticipation of hazardous driving conditions and is therefore highly dependent on the accuracy of weather forecast.

Weather is a dynamic system with constantly changing conditions and the validity of the assumptions made in forecasting naturally lead to inaccuracies in the forecast. Analysis of road weather forecasts indicates that a significant level of inaccuracy is present in road weather forecasting. Met Office (2007) UK open road accuracy data (see Figure 2.9), demonstrates a relatively high false alarm rate of approximately 25%, indicating that a precautionary winter maintenance treatment was applied one in four times when frost or ice would not have formed.

Season (Nov-Apr)	**False alarm rate**	**Frost detection rate**	**Overall accuracy**
2001/2	28.6%	87.1%	89.1%
2002/3	23.7%	90.3%	89.9%
2003/4	24.8%	91.5%	90.1%
2004/5	25.2%	89.7%	90.2%
2005/6	25.5%	90.0%	86.9%
Target	**<=30.0%**	**>=87.0%**	**N/A**

Figure 2.9 - Accuracy of UK winter maintenance forecasts (Met Office 2007)

Precautionary salting contributes significantly to the cost of keeping UK local authority highways frost, ice and snow free. Thornes (2000) states `*Up to 80% of the winter maintenance budget is spent on the pre-salting of roads to prevent the formation of black ice*`.

A reduction in the temperature at which ice forms on the road by only a few degrees Celsius could significantly reduce the amount of precautionary work required. This could be achieved by delaying the point in time at which a precautionary intervention is required and/or allowing greater road weather station information to be gathered to allow more accurate forecasting.

Reducing the precautionary work could have significant economic benefits by reducing the need for labour, plant and de-icing chemicals used and limiting disruption to road users, whilst the chemical is being applied.

The benefits of this are significant when the costs of applying winter maintenance in the UK vary from £200/km to £800/km (Cornford and Thornes 1996). A reduction in this anti-icing work would also reduce the environmental impacts, with an estimation of this cost currently in the region of £100 million per winter (Thornes 1998), as highlighted previously.

Inaccurate forecasts can lead to significant precautionary treatments when frost or ice would not have formed. Analysis of frost detection rates and overall accuracy see Figure 2.9 (Met Office 2007), suggests that only 85 - 90% of frost is accurately detected. This indicates a more serious issue when frost or ice is not detected and a winter maintenance treatment is not applied leading to hazardous driving conditions. Reducing the temperature at which ice forms may eliminate a number of these events occurring. This is especially important for the UK, considering the frequent ice pavement conditions with limited temperature fluctuations around 0^{o}C identified in Section 2.1.2 Climate of the United Kingdom.

In recent years the accuracy of short-term weather predictions has significantly improved by the use of complex road weather information systems. This is an area that will see continued development in the future.

Considering a more holistic view of winter service, current practice also relies on the long term weather forecasts and appropriate planning to determine salt stock levels and re-stocking arrangements. If inappropriate forecasts and assumptions are made, the level of winter services that can be provided is vulnerable.

This was clearly evident when `*February 2009 saw a sustained period of cold weather and snowfall that resulted in significant disruption to travel, to a range of public services and to business across the country. Whilst some highway authorities managed well, many came close to running out of salt for treating highways and there was a real danger that some would have run out had milder weather not arrived*` (Road Liaison Group 2009). The causative factors of the event above can be considered to be as a result of a combination of `*A long period of severe conditions across the country and a trend towards lower stocks of salt held by highway authorities*` (Road Liaison Group 2009).

Following the second severe winter in 2009/2010, an independent review of the resilience of England's transport systems to severe winter weather was commissioned by the then Secretary of State in March 2010. This review was conducted by Quarmby et al. (2011) and highlighted the vulnerabilities of salt stocking and supply in the UK.

The review highlighted that despite the lessons from the 2008/2009 winter, "*pre-season stockholdings were again going to be insufficient to meet the need*" for the 2009/2010 winter (Quarmby et al. 2010). Analysis by Quarmby et al. (2010) highlighted a shortfall in salt stocks. A summary of the analysis of salt stocks during 2009/2010 presented Table 2.1. The demand during this winter was only fulfilled by drawing on stocks (held by highway authorities and suppliers), intervention by the government in the form of the Salt-Cell, importing salt and drastic reductions in salt use to conserve supplies.

Stock Flow	**Quantity**
Total salt stocks at highway authorities and suppliers – March 2009	0.5m tonnes
Production by UK suppliers for England	1.35m tonnes
Salt imported in the year	0.15m tonnes
Salt use by highway authorities during the year	-1.8m tonnes
Total salt stocks remaining – March 2010	0.2m tonnes

Table 2.1 – Annual analysis of stock flows for England 2009/2010 (Quarmby et al. 2010)

Concerns were also raised regarding future salt production and supplies in the UK. (Quarmby et al. 2010) concluded "*UK supply is insufficient to meet the needs of Britain's – and England's – highway authorities in a severe winter*".

Analysis of salt demand and production capacity in the UK highlighted a shortfall in the UK production capacity for a severe winter, as shown in Table 2.2. This would lead to the need to import salt, which typically costs 50–100% more per tonne than UK production delivered to the highway authority's barn.

For Britain	**Average winter**	**Moderately severe winter**	**Nationally severe winter**
Unconstrained demand	1.5m tonnes	2.8m tonnes	3.3m tonnes
Constrained demand	n/a	2.2m tonnes	2.7m tonnes
UK production capacity	2.0m tonnes	Up to 2.4m tonnes	Up to 2.4m tonnes

Table 2.2 – Salt demand and production capacity in Britain (Quarmby et al. 2010)

A number of important lessons have been learnt over these winters and a series of recommendations to increase the resilience of England to severe weather have been reported by Quarmby et al. (2010). The need for stocking capacity, coordination and collaboration of supplies and contingency planning to increase the resilience of winter service is highlighted.

The vulnerability of the UK to severe weather over the 2008/2009 and 2009/2010 has highlighted that any reduction in precautionary salting will inevitably reduce the vulnerability of winter service.

Overall, reducing the temperature at which ice or frost forms on a road surface could significantly reduce the amount of precautionary winter service treatments. This would allow more time for data collection to enable more accurate forecasting, reduce salt demand, increase the resilience of winter service and provide financial savings.

2.2.4.3 PROBLEMS OF CURRENT PRACTICE – SITE SPECIFIC LOCATIONS

When applying current de-icing techniques, site specific locations require specific attention. These locations include porous pavement surfaces, bridges, environmentally sensitive areas and entry/exit slip roads.

It is widely acknowledged that porous asphalt surfaces experience different freezing characteristics to that of dense asphaltic concrete surfaces and therefore require greater attention when managing highway networks. The Highways Agency Network Management Manual – Part 5 states that ` *This is due to different characteristics in respect of surface temperature, humidity and the ability to retain salt on the surface*`. According to Noort (1996b)`*The porous asphalt drops below freezing sooner and as the air temperature rises, the temperature of the porous asphalt stays below freezing for longer than that of comparable road section of dense asphalt*`. To put this effect into context, the temperature of porous asphalt road surfaces falls below freezing point at an average of half an hour earlier than that of dense road surfaces, whilst temperature rising above freezing point take an average of an hour longer (Highways Agency Network Management Manual – Part 5). It is also estimated that in extreme weather conditions (little wind, clear sky), the surface temperature of roads surfaced with porous asphalt is about 1°C lower than that of comparable roads with dense road surfacing materials.

The behaviour of porous asphalt as temperature changes can be explained by the relatively high insulation value of the road surface due to the high proportion of voids. Heat is less easily transported from the warmer sub-grade to the surface. The voids also provide a greater surface contact area with the cold air allowing greater temperature interchange. In general, more anti-icer/de-icer material is required for treatment of a porous asphalt road surface than for a dense surfacing material. The Highways Agency Network Management Manual – Part 5 states that an extra 25% of the selected treatment should be used for precautionary work. This is because much of the de-icing agent spread on roads made of porous asphalt disappears into the voids, and only a small proportion remains on the surface. Due to the 'air pumping action' effect of vehicle tyres, traffic will ensure that the thawing agent in the pores is brought back to the surface of the road. If the traffic intensity is low a greater loss of de-icing chemical into the voids will be observed as it is not brought back to the surface. The pores of porous asphalt surfaces absorb extra moisture, resulting in a reduced de-icing concentration.

As a result, this surface therefore creates challenges for winter service providers. A number of factors need to be considered when making decisions on treatment, such as precipitation and traffic intensity. The service provider also needs to consider the amount and impact that any retained de-icer will have.

Bridges also provide challenges for winter service providers. Not only are there significant corrosion issues as highlighted previously, they also demonstrate different freezing characteristics. Observations made by Noort (1996a) in the Netherlands found that `*Especially during clear and windless nights the temperature of the road surface of these steel bridges often drops below freezing, whereas the temperatures of adjacent road sections may stay well above freezing*`. Such characteristics are related to the exposure of the bridge as heat loss can occur from above and below the pavement surface. `*The humid maritime climate often causes condensation on these bridges*` (Noort 1996a). This scenario presents a problem for current practises as the high cost of mobilising winter service teams to treat only small bridge section(s) does not provide an economical solution.

Entry and exit slip roads can also create specific operational challenges due to dead running. Highways Agency (2008) `*Dead running refers to the travel associated with accessing entry and exit slip roads at junctions, and includes the turning and returning movements required to completely treat the slip roads during winter service. The distance between junctions can result in excessive dead running, where a spreader has to travel on carriageways previously treated to access the slip roads, or turn around. In some instances, distances can be equal to or greater than some treatment distances and a second spreader is required to carry out precautionary treatment to slip roads at the junctions to meet response times*`. This lead to the Highways Agency reviewing alternatives including automated spray technologies, thermal methods and surface material enhancements.

2.2.5 CONCLUSION

The application of de-icing chemicals to winter weather conditions, preventively and reactively, is tried, tested and proven to be effective and economic.

It does not however, provide the complete solution. The formation of ice is a recurring problem and an application is required at each winter weather event. This involves significant precautionary work, where the effectiveness is based on the accuracy of weather forecasts and road weather information systems. The supply and stocking of site has also been proven to be vulnerable in severe winter weather. Chloride based chemicals used generate significant environmental impacts to the roadside environment. Finally, specific sites such as bridges, porous asphalt surfaces and slip roads require special attention and often require greater levels of treatments.

The ability to reduce the freezing point of water, by modifying the road surface may therefore, offer significant cost savings, reduce environmental damage and increase the resilience of winter service in the UK.

3.0 PAVEMENT SURFACE COURSE AND ICE PAVEMENT BOND PREVENTION

Road pavements consist of a series of layers, each layer having its own unique structural properties and engineering characteristics. The pavement surface course (or wearing course) is arguably the most important layer in any pavement because it is the layer that the road user interacts with. It is therefore designed to provide good ride quality, resistance to deformation under vehicle loadings and to provide adequate levels of skid resistance.

The pavement surface is also fundamental to the ice pavement bond. A number of methods for achieving bond reduction between the ice and the pavement surface have been considered throughout history. These include chemical and physical modifications to the surface course, infra-red radiation systems, electro-magnetic radiation systems and ultra-violet light based systems (Wuori 1993). This paper will focus solely on the effects the physical and chemical surface course modifications can have on the ice-pavement interface.

This chapter will firstly provide background information on the types of pavement surface courses and the key properties of this pavement layer.

The chapter will then discuss the factors that influence the bond between ice and the pavement surface. It is important to understand this interaction prior to considering methods of preventing/reducing this bond.

Finally, the chapter will discuss in detail, chemical methods of modifying pavement surface courses and discuss how these mechanisms have been used previously by a number of different proprietary pavement surface course modifications, which claim to chemically and/or physically prohibit/reduce the adhesion of snow and ice to the pavement surface.

3.1 PAVEMENT SURFACE COURSES

The pavement surface is designed to have the following properties:

- Resistance to deformation by traffic
- Durable and resist the effects of weather
- Have acceptable ride quality
- Generate acceptable levels of spray and noise
- Provide a skid-resistant surface

3.1.1 SURFACE COURSE TYPES

There are many types of surfacing used worldwide on highway networks. These include but are not limited to:

- Bituminous surfaces
- Concrete surfaces
- Surface Dressings
- Micro-Asphalts
- High Friction Surfaces

The main types of bituminous surfacing used on the UK network include (but are not limited to) Hot Rolled Asphalt, Thin Surfacing and Stone Mastic Asphalt surfaces.

Hot Rolled Asphalt

“Hot Rolled Asphalt” (HRA) was used extensively in the UK for several decades. The mixture predominately has a high percentage of bitumen/sand and filler mortar which provides a very smooth surface finish. To provide skid resistance, pre-coated chippings can be added to impart texture to the running surface. These are placed by a chipping machine that follows immediately behind the paver.

The usage of Hot Rolled Asphalt has reduced since the emergence of Thin surfacing systems and Stone Mastic Asphalt, due to resistance to permanent deformation and lower noise under traffic. In recent years a number of local authorities have moved back to HRA surfaces due to perceived durability benefits.

Thin Surfacing Systems

Thin surfacings are the standard material of choice by the Highways Agency in the UK for both new construction and maintenance. They were introduced to the UK in the early 1990’s by adapting French technologies to the UK requirements of skid resistance and texture depth. In the UK Thin Surfacings are proprietary products which are monitored and certified through the British Board of Agreement (BBA) Highway Authority Product Approval Scheme (HAPAS).

Thin Surfacings are specified in accordance with Clause 942 of the Manual of Contract Documents for Highway Works (2008). The key benefits of thin surfacing systems are the relatively low levels of noise and spray, superb surface regularity and high level of skid resistance generated by the negative texture of the pavement surface.

Stone Mastic Asphalt (SMA)

Stone Mastic Asphalt was developed from Gussasphalt in Germany in the 1970's for use on trunk roads and autobahns. These were introduced and trialled in the UK in 1994. As a result a variety of thin stone mastic products were developed.

SMA has a stone skeleton of interlocking crushed rock, comprising of single sized aggregate to make up the matrix. This aggregate skeleton provides high levels of deformation resistance under loading.

The aggregate matrix leaves a relatively high void content (typically of 3-5% air voids) between the aggregate particles in comparison to Hot Rolled Asphalt. These air voids are partly filled with a rich binder mastic which binds the skeleton together making the surface course impervious.

Surface Treatments

Surface treatments are also extensively used on the UK network to restore the surface characteristics of pavement and to extend the pavement life by sealing the surface and preventing deterioration from water ingress.

Two of the most widely used types of surface treatments for highway maintenance are:-

- Surface Dressing. A long established and proven highway maintenance technique. "*In simple terms it involves the even spray application of an emulsion bituminous binder through a purpose built spray tanker onto the existing road surface followed immediately by the even application of aggregate chippings to 'dress' the binder"* (Adept/RSTA 2011.

- Micro-surfacings and Slurry surfacing. These are cold applied, thin bituminous surface courses incorporating bitumen emulsion and fine graded aggregate with fillers.

3.1.2 STANDARD TEST METHODS FOR BITUMINOUS PAVEMENT SURFACE COURSE MATERIALS

A range of standard British and European test methods have been develop for assessing bituminous pavement surface course materials. Testing requirements for the UK are set out in PD 6691:2010 and/or BBA HAPAS: `*Guidelines Document for the Assessment and Certification of Thin Surfacing Systems for Highways.*`

General testing requirements for surfacing products typically include, but are not limited to:

- Gyratory Compaction
- Air Void Content and Hydraulic Conductivity
- Stiffness
- Water Sensitivity
- Resistance to Fatigue
- Resistance to Permanent Deformation
- Resistance to Fuel and De-icing Fluids

3.2 ICE PAVEMENT BOND

3.2.1 ICE FORMATION

Computer modelling of the formation of ice on the pavement surface by Penn and Meyerson (1992) identified that a cold pavement initially froze a thin layer of ice. After this, the conditions in the bulk water predominated and, in turn, were determined by atmospheric conditions. This means that despite ice initially forming on the pavement, this ice does not grow upwards. It forms another layer of ice at the water-air interface which proceeds downwards. `*The result is a junction of two freezing fronts a few millimeters from the pavement surface*` (Penn and Meyerson, 1992). This process is explained by Penn and Meyerson (1992) below:

- Nucleation is more likely to occur at the solid surface because of its roughness.
- The heat released by crystallization at the pavement surface layer is conducted away slowly because of the low thermal conductivity of the pavement, thus preventing the newly formed ice layer from cooling to temperatures below 0 ^{o}C. This is turn slows further crystal growth near the pavement surface.
- During this period nucleation and growth at the air-water interface begins and is rapid.

Computer simulations by Penn and Meyerson (1992) indicate that `*ice nucleation occurred below but very close to 0$^{o}$C under a wide variety of atmospheric conditions, the nucleation temperatures being between 0$^{o}$C and -1$^{o}$C. Also, nucleation occurred within 1 to 4 minutes after water temperature fell below zero*`. Further laboratory experiments indicated nucleation and crystal growth may occur at a faster rate and within a minute of the start of cooling.

3.2.2 ICE BOND STRENGTH AND INFLUENCING FACTORS

The bond established between ice and pavement surfaces is a complex function comprising of many parameters including temperature, rate and direction of freezing, and the physical and chemical conditions of the substrate surface.

Penn and Meyerson (1992) found that `*several fundamental features of both the pavement and the ice lead to excellent bonding between the two, with the result that bond prevention is difficult*`.

The enhanced bond strength is caused by the small scale roughness and the high surface energy of the pavement surface. Considering further the influence that the pavement surface characteristics have on the ice bond strength, it is generally accepted that when exposed to the environment, the bitumen comprising the asphalt pavement surfaces ages by oxidising. Infra-red spectrometry data by Penn and Meyerson (1992) has revealed that `*The significance of these oxidising products is that they have the potential for strong polar interactions and hydrogen bonding with water or ice, thereby increasing the magnitude of interaction across the ice-pavement interface and enhancing adhesive bonding*`.

Surface energy estimations suggest that the adhesion strength of ice on aged bitumen could be twice as great as the adhesion strength on un-aged bitumen, due to an increase in polarity (Penn and Meyerson 1992).

High bond strengths are also formed due to the properties of water. The low viscosity of water allows good contact and relatively large energy of interaction with the pavement. Penn and Meyerson (1992) identified that `*the pavement nucleates small, bubble-free ice crystals that are strong and difficult to remove mechanically*`.

Finite element analysis undertaken by Wuori (1993) confirmed the high bond strength on conventional pavement surface course. The study indicated that resultant stress concentrations at the ice pavement interface from conventional tyre passages are not of sufficient magnitude to promote favourable ice debonding from Portland cement concrete or asphalt concrete even when exaggerated pavement surface profiles are considered. This led to the conclusion by Wuori (1993) that `*Laboratory results show it is not possible to debond ice from conventional Portland cement concrete and asphalt concrete surfaces with passages of wheeled vehicles*`.

Considering the research highlighted above it can be concluded that features of both the pavement surface and ice lead to excellent bonding between the two. A number of studies have looked at ways to prevent this ice-pavement bond. Blackburn et al. (1993) provided a fundamental study on debonding. Baum et al. (1992) focused on chemical surface course modifications and Wuori (1993) focused on physical surface modification, as well as passive and active modifications. This Chapter will specifically focus on physical and chemical modifications of the pavement surface course itself by the inclusion of additives.

3.3 PAVEMENT MODIFICATIONS

A limited number of physically and chemically modified pavement surface courses have been tried in the past. The concept of these products is to act as a preliminary anti-icer by reducing the temperature at which ice forms and/or preventing ice adhering to the pavement surface. This resultant reduction in ice formation delays and possibly eliminates the point at which maintenance crews are required to apply a traditional de-icing chemical, resulting in a reduction in the de-icing chemical applied at each instance. Current limitations of anti-icing performance and knowledge of surface course modifications would indicate that these products are not intended to be a substitute for winter maintenance. If successful, they could however, significantly reduce precautionary salting. The potential benefits of a system can be summarised by:

- A reduction in the use of chemical de-icers for precautionary salting, leading to a reduction in the number of emergency call-outs, environmental impacts and the associated economic benefits.
- An increased skid resistance due to the slower formation of ice, leading to road safety benefits.
- The reduction of the corrosion on bridge decking, reinforcement bars and infrastructure.
- A reduction in the environmental degradation of the roadside environment.
- Additional physical attributes/characteristics of the pavement surface relating to material laying and durability.

The potential benefits are of greater significance when considering the marginal climate of the UK as discussed in Section 2.1.2. This identified minimum winter temperatures around 0^{o}C, creating frequent icy pavement conditions and incidents of black ice for only short periods.

The concept of modifying the surface courses to prevent a bond between the ice and pavement surface was studied in detail by Baum et al (1992). This will be discussed in Chapter 4.0 of this thesis. The objective of the study was to develop chemical and physical pavement modifications to reduce the bond strength of ice or compacted snow on the pavement surface. It involved investigating a range of water-soluble organic, inorganic compounds and oils.

The study recognised three principle mechanisms that can act independently or collectively to debond ice from the pavement surface. These are:

1). Freeze point depressants
2). Deformability - such as using rubber dispersed in the wearing course to lower the modulus of stiffness of the surface and promote the cracking of the ice under traffic.
3). Low energy surface - to reduce the strong bonds between the ice and the pavement surface.

In order to understand the potential methods of reducing the bond between ice and the pavement surface it is important to consider each of the above points in turn.

3.3.1 FREEZE POINT DEPRESSANTS

Penn and Meyerson (1992) concluded that the most effective way of preventing the formation of a strong layer of small ice crystals directly on the pavement surface is by the use of nucleation preventing chemicals. `*Obviously if early nucleation at the pavement surface could be prevented, the ice directly contacting the pavement would probably be weaker and less well-adhered due to entrapped bubbles of larger crystallite size as found in the bulk ice*` (Penn and Meyerson 1992).

This is the principle mechanism by which chemical de-icers are used in current practice. This is because they act as freezing-point depressants by interfering with hydrogen bonds and changing the inherent structure of water. This principle is explained in relation to current practice below. The mechanism by which the freezing point is depressed remains the same for de-icing chemicals incorporated directly into the asphalt surfacing.

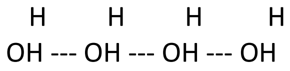
Considering current practice, for a chemical de-icer to prevent ice forming or to melt snow it must form a brine solution. This solution can be formed prior to application, by the moisture from snow/ice on the road surface or from the air humidity. A brine solution is required because when the de-icing chemical dissolves freely into water the de-icer dissociates (i.e. it ionizes and yields charged ions). For example:

Sodium Chloride: $NaCl + \text{water} \xrightarrow{\text{ionization}} Na^{+} + Cl^{-}$

Calcium Chloride: $CaCl_2 + \text{water} \xrightarrow{\text{ionization}} Ca^{++} + Cl^{-} + Cl^{-}$

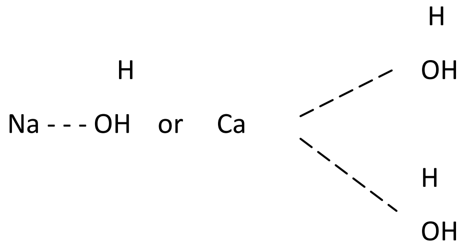
According to Adams (1973) `*The charges between salt ions and water ions are essentially equivalent and are, for all practical considerations non-reactive. This means that salt ions are free to react with water molecules rather than water ions (HOH rather than* H^+ *or* OH^-*), which provides the key to salt's profound ability to lower freezing points and thereby assist in melting ice and snow*.`

This is because pure water interacts with itself, with hydrogen bonds forming between water molecules as indicated below:



$$\overset{\mathrm{H}}{\mathrm{OH}}\ ---\ \overset{\mathrm{H}}{\mathrm{OH}}\ ---\ \overset{\mathrm{H}}{\mathrm{OH}}\ ---\ \overset{\mathrm{H}}{\mathrm{OH}}$$

These hydrogen bonds give water its characteristic density and specific gravity. However the hydrogen bonds are relatively weak and are easily influenced by the presence of competing substances. The addition of a de-icing chemical causes the de-icing (salt) ion to react with the water molecules disrupting the existing hydrogen bond. Adams (1973) reported that salt ions interfere with hydrogen bonds because the bonding potential of salt ions exceeds the strength of the hydrogen bonds and salt ions are favoured preferentially. As the number of broken hydrogen bonds increases, the characteristics of density and specific gravity change proportionality and water becomes less dense. This is demonstrated below with sodium chloride and calcium chloride:



It is important to note that in the above diagram, one calcium ion (Ca^{++}) can interfere with two hydrogen bonds simultaneously, compared to sodium ion (Na^+) which can only associate with one molecule at a time.

As the quantity of de-icing chemical (the solute) is increased, the concentration of water molecules in the solution reduces. This results in a reduction of the freezing point of a solution, to a point which is well below that of water at 0°C. The continued addition of the de-icing chemical reduces the freezing point of the solution to a finite point, known as the Eutectic point. This point is the lowest temperature to which freezing can be lowered. Any further addition of solute at this point will only result in precipitation, as the solution is saturated. Sodium chloride and calcium chloride have eutectic points of -21°C and -52°C, respectively (COST 2002). The effect of saturation can be observed by considering sodium chloride, see Figure 3.1 (Dickerson 1969).

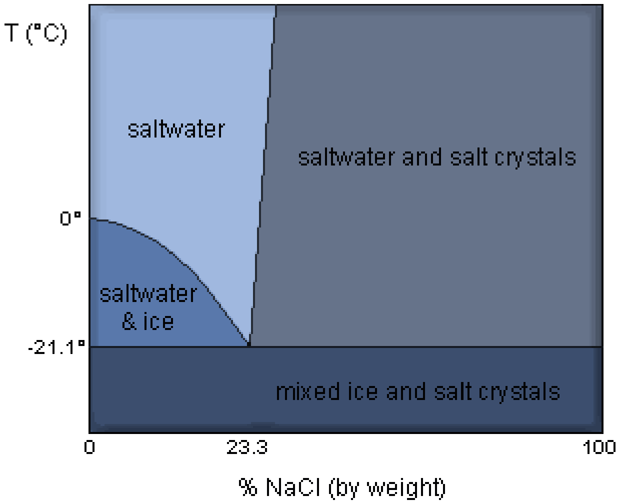


Figure 3.1 - Phase map for salt water. Drawn from a diagram by R. E. Dickerson (1969)

As the percentage of sodium chloride is increased to 23.3%, the freezing point is reduced from 0 to -21.1°C. After this point, no matter how much sodium chloride is added the effective freeze point of the solution cannot be reduced below -21.1°C. Any further addition of sodium chloride results in the solution becoming saturated.

3.3.2 DEFORMABILITY

Research by Wuori (1993) identified that a possible solution to the ice-pavement bond debonding problem is to produce desirable fractures in the ice/snow layer. The \`desirable\` fracture referred to by Wuori (1993) relates to fractures at the ice-pavement interface or in the ice very close to the interface, leaving bare pavement conditions. In addition to this it would be desirable to minimise the energy required to break and dislodge the ice by increasing the number of fractures or fracture surfaces.

One method considered to achieve such \`desirable\` fractures is the use of a deformable pavement surface. The development of deformable pavement surfaces has focused on the inclusion of rubber additives to create a more flexible pavement surface to facilitate debonding under traffic loads. Two different methods of incorporating rubber into paving mixes have been developed. The first type of rubber modification uses finely ground rubber tyre buffings that are mixed into the hot asphalt cement to create a rubberised asphalt binder (termed asphalt rubber concrete). The second method focused on blending rubber particles as a substitution for a specific amount of stone aggregate, see Section 3.4.4.

The mechanism by which a deformable pavement works to achieve debonding is to increase the elasticity of the surface. As the elasticity of the surface is increased, the amount of support provided to the ice decreases, due to the increased presence of elastic rubber particles. This results in a decreased ability of the ice formed on the surface to support the wheel loads. The increased elasticity of the surface also means that the ability of the pavement surface to support the wheel loading diminishes, and the wheel load must increasingly be supported by the ice layer. Consequently, thin ice layers begin to crack and fatigue after repeated loading and are eventually debonded and separated from the asphalt surface. It was concluded by Wuori (1993) that \`*The extent of the ice cracking on the specimens varied with rubber content and number of wheel passages from no cracking to total debondment. The results clearly indicate that increased rubber content (i.e., an increased presence of larger rubber particles on the pavement surface) increased the incidence of cracking.*\`

3.3.3 LOW ENERGY SURFACE

Surface free energy is defined as `*the magnitude of work required to create a unit area of a new surface of the material in a vacuum*` (Adams 1940). Surface energy is important because liquid and solid surfaces have varying energies due to structural differences, resulting in varying degrees of intermolecular attraction. Surface energy is therefore commonly used to predict adhesion between two materials and is dependent upon the surface energies of the two substances which meet to form an interface. Surfaces with the least affinity for other substances are typically very low in surface energy.

Creation of a low energy surface is an approach widely investigated for de-icing purposes of ships, leading edges of airplane wings and overhead telephone wires. It is therefore logical to consider the potential of lower energy surface for pavement de-icing. This is a view supported by Baum et al. (1992). In order to lower the ice adhesion as much as possible, surface energy components must be made as small as possible. The lower the values of these components, the lower the overall forces that hold the ice to the surface will be, and the easier it is to remove.

The principle that a low-energy pavement coating material could be used to minimise the ice-substrate intermolecular interactions and reduce the energy required to separate ice from the pavement was studied by Penn and Meyerson (1992). The study found that ice is strongly dependant on molecular interactions resulting from surface free energy. However, Penn and Meyerson (1992) discovered that the work of adhesion between water and substrate, a quantity related to substrate surface energy, is not linearly related to the fracture energy of the ice-substrate bond. The fracture energy (i.e., the work to separate the ice substrate interface) follows a power law. This means that for all but the lowest energy surfaces, the adhesion is inherently very high, and separation of ice from the substrate requires increasingly more energy. Unfortunately Portland Cement Concrete and aged asphalt concrete are relatively high energy materials, making ice removal an inherently energy consuming process. Blackburn et al. (1993) measured a work of adhesion between water and Portland Cement Concrete and asphalt as 134mN/m and 63.2mN/m, respectively as displayed in Table 3.1.

Substrate	**Contact Angle (degrees)**	**Work of adhesion (mN/m)**
Teflon	120	34
Mylar	71	74
PCC Mortar	22	134
Limestone	28	130
Bitumen	95	63.2

Table 3.1 – Work of adhesion of water from contract angle measurements, reproduced from (Blackburn et al. 1993)

Work of adhesion measurements by Penn and Meyerson (1992) indicated that coating the pavement surface with low surface energy materials such as Teflon, Silicon and Frekote 33 would promote easier ice removal, as displayed in Table 3.2.

Substrate	**Water (mJ/m^2)**
Teflon	45.2
Silicon/ Frekote	52.4
Polypropylene	54.9
Unaged asphalt	(54.9)
Polystyrene	70.6
Polycarbonate	103
Aged asphalt	(103)
E-glass	133
Portland cement concrete	(133)
Stainless steel	144

Table 3.2 - Work of adhesion of water and metylene iodide on model and reference substrates (Penn and Meyerson 1992)

Note - All values in parenthesis are by analogy to values directly above (Penn and Meyerson 1992).

Despite the conclusions that low surface energy material would promote easier ice removal, questions regarding practicality of such coatings have been raised. Penn and Meyerson (1992) concluded that despite `*The obvious recommendation to coat the pavement surface with a fluorocarbon or with a completely unoxidised hydrocarbon, is not a practical one for existing pavement. However, low energy materials could be incorporated into novel highway surface designs in the far future*`.

It is important to consider the influence of low surface energy materials on the performance of asphalt. Little and Bhasin (2006) state that the `*Principles of thermodynamics can be used to quantify the propensity of asphalt binders to debond from aggregate surfaces in the presence of water based on their surface energy components. This probably is directly related to the moisture sensitivity of asphalt mixes*`.

Based on available literature, it would appear that the use of low surface energy materials has the potential to promote easier ice removal; however the application method and affects on the performance of asphalt are likely to present specific challenges.

3.4 HISTORY OF ANTI-ICING SURFACE COURSE

A number of proprietary pavement surface course modifications claim to chemically and/or physically prohibit/reduce the adhesion of snow and ice to the pavement surface. Analysis of these previous studies has provided some evidence in the following areas:

- Anti-icing mechanisms and potential effectiveness
- Problems experienced with anti-icing surface course
- Causative factors that have lead to unsatisfactory performance

3.4.1 VERGLIMIT

One of the first proprietary anti-icing modified pavement surface courses marketed was a product called Verglimit.

Verglimit is a patented bituminous concrete pavement that contains calcium chloride pellets encapsulated in linseed oil and caustic soda (MDOT 2007). It was developed in Switzerland in the 1970's and has been trialed in America, Canada, Switzerland, France, Japan and the UK.

The calcium chloride is situated in the pavement surface pores and is not in direct contact with the traffic. At high humidities the exposed calcium chloride will attract moisture into the pores of the pavement surface. As the pores become full, the solution spills over and prohibits adhesion of snow and ice to the pavement. `*As the humidity decreases after a winter storm, water in the solution evaporates, leaving the liquid calcium chloride in the pore for the next storm*` (MDOT 2007).

Similar to all additive products, the concept of Verglimit is to act as a preliminary de-icing agent. Verglimit is described as being designed to be an effective de-icing surface to temperatures of -3^{o}C, below this point the surface becomes less effective due to the absorption of water. However, tests in New Jersey have found the material to be effective at -4^{o}C (MDOT 2007).

De-icing performance of Verglimit has been assessed on a number of road trials. These include sites at Ontario, Quebec, New Jersey and two sites at New York. The report from these trials concludes that the de-icing ability of Verglimit is satisfactory and that the material does prevent the snow and ice from binding to the road surface, enabling traffic to break up the ice. This performance was demonstrated by an 86% reduction in the rate of snow and ice-related accidents over a two year period on New York state roads, Tanski (1986). However, studies at New Jersey demonstrated that to initiate the full de-icing potential of Verglimit, heavy traffic of at least of 5,000 ADT is required in order to expose a suitable amount of the product.

Concerns relating to the performance of Verglimit surface have been published with respect to anti-icing ability, safety and service life. Studies by Turgeon (1989) concluded that `*significant de-icing benefits were not observed*` and` *the moisture created by the Verglimit captured blown snow creating a more snow covered appearance on the control section*`. It is postulated that these differences in performance may relate directly to the winter conditions. Areas with relatively warm, wet winter demonstrated positive results e.g. Europe, New York and Pennsylvania, in contrast to colder drier winters such as those of Illinois.

More concerning is the potential for the road to become slippery when the Verglimit additive is introduced. `*The roads became supper-slippery resulting in accidents, including one in which eight people were hurt and one person killed*` (Michigan Roads and Construction 1998). In this case it is postulated by a number of consultants that `*contractors failed to adequately compress the mixture, leaving gaps in the Verglimit pellets which let moisture in and prevent the compound's ability to prevent ice from bonding to the road surface*`.

A number of reports support the concept that the road was slippery particularly in the early life and/or under light trafficking (MDOT 2007, Stuart and Mogawer 1988, Lohrey 1992). For example, `*the road surface appears to be more slippery when traffic is lighter*` (MDOT 2007). To overcome such concerns strict mixing and laying specifications exist, which include the rinsing of exposed calcium chloride and linseed oil from the pavement surface for several days post application.

Additional reports of a reduction in service life of the Verglimit product have been recorded, relating to the cracking and spalling of the pavement surface. Some studies suggest that the pavement service life may be reduced by up to 50% (Stuart and Mogawer 1988). Studies by Turgeon (1989) also concluded that `*The cracks in the test section are more open and ravelled than those found in the control section*` and recommended that `*no future Verglimit sections should be constructed unless compaction problems are solved, crack opening and spalling can be decreased and cold-dry winter de-icing characteristics are displayed*`.

The cost of Verglimit is `*three times the cost of standard asphalt concrete*` (Morian and Arellano 1987). The high cost of Verglimit has reportedly limited its use to hazardous areas prone to icing such as `*bridge decks, ramps, shaded areas and steep grades*` (Turgeon 1989).

3.4.2 GRIKOL

Grikol is an anti-icing filler additive for asphalt concrete mixes developed in the 1980s by the Institute of NPO ROSDORNII in Russia. It comprises of 80% NaCl, 10% $CaCl_2$ and 10% Siakor. Siakor is a silicon-organic compound which has a water rejecting and freezing-point lowering effect.

It is claimed the Siakor is a non-toxic non-flammable silicon compound available in powder form with a freezing point at -50^{o}C. It is an inhibitor against corrosion and can also be used as a water rejecting substance. Siakor gives the chlorides an extra de–icing effect and reduces the corrosion because it binds the redundant chlorides from the Grikol and produces an indissoluble compound.

It is claimed that Grikol has a anti-icing effect in temperatures between 0 to -6 degrees Celsius and that a Grikol pavement is about 25% more expensive than a regular pavement. It is recommended that the percentage of Grikol used in a product is between 3 - 5% by weight (Grikol 2009)

According to Grinevitch (1998) `*the anti-icing filler is introduced into the asphalt concrete mix substituting part of the mineral powder*`. The filler is 80% passing 0.071mm and for this reason `*The anti-icing filler comprise with the binder a bitumen – mineral mixture. Therefore, everywhere, where the upper layer is bitumen "black", the anti-icing filler is present*.`

The anti-icing effect of the additive is achieved by the migration of the hydrochloric solution through the pores and capillaries of the asphaltic concrete pavement to the pavement surface. The anti-icing properties being present in filler results in the anti-icing effects being observed throughout the pavement service life. This, according to Grinevitch (1998), is because 1mm of asphalt concrete is worn out each year due to action of studded tyres. This wearing out of the pavement by wheel passage `*is the reason of the constant presence of salt on the anti-icing pavement*`.

It is also claimed that the pavement surface containing Grikol reduces the adhesion of ice to the pavement surface, see Figure 3.2 (Grikol 2009). According to Grinevitch (1998) the high dispersability of the pavement surface provides for 10-15 particles of the anti-icing filler to be present on each $1mm^2$. This creates a reduction in ice adhesion because the silicon based component (Siakor) of the filler is a water repellant and reduces the surface tension. This factor combined with the chloride solution prevents re-freezing to the surface.

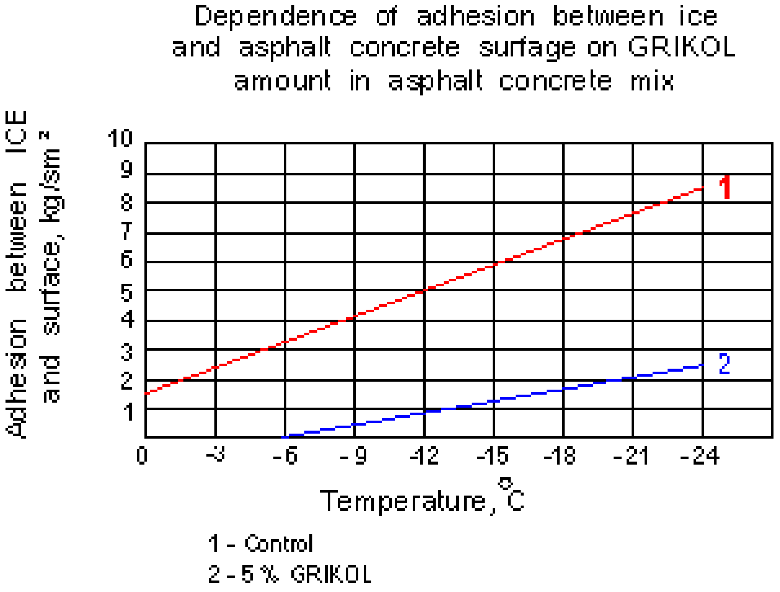


Figure 3.2 – Comparison of ice adhesion between Grikol and control surface (Grikol 2009)

One of the negative aspects of this additive is that the filler is chlorine based, which could lead to the potential negative impacts highlighted previously for Sodium Chloride. Laboratory studies by Grinevitch (1998) indicate that such effects are significantly less than that of road salt, with claims of a reduction of 2.8 – 3 times in metal corrosion. Grinevitch (1998) indicates that 5 - 7 times less salt is washed out from the pavement surface compared to the quantity of salt present for traditional methods. However it is important to recognise that such results for trials do not appear to be available.

According to the Grikol website, over 2 million square metres of Grikol pavements comprising of Stone Mastic Asphalt and Slurry Seal type materials have been laid in Russia. A typical anti-icing service life is 3-4 years for Stone Mastic Asphalt applications under the action of studded tyres.

The Grikol systems underwent trials on nine test roads as part of the development process, eight of which werein Stockholm, Sweden. Grikol claims the product to have demonstrated successful de-icing ability. It is claimed that on the Vagverkets road station in Taby, Sweden, a need for winter maintenance was reduced by 70% (Grikol 2009). However, reports from two Swedish test sites express concerns that the pavement may experience abnormal erosion or decomposition.

3.4.3 SAFELANE

Safelane is an overlay patented system developed by Michigan Tech University and licensed by Cargrill. The anti-icing overlay consists of a thin layer of epoxy spread over a bridge deck or pavement surface and a layer of an absorptive aggregate spread over the surface of the wet epoxy (Thomas and Martinelli 2007). This absorbent aggregate has the ability to store de-icing liquids that have been pre-applied prior to hazardous winter weather conditions. The de-icing liquid typically applied is a salt brine or magnesium chloride. This de-icing liquid is then slowly released from the aggregate to the surface over a period of time to prevent ice and frost from forming. A single application of the Safelane technology is claimed to prevent multiple ice events.

The total thickness of a single lift of the overlay systems is approximately 3/8” inches (9.5 mm) and according to Thomas and Martinelli (2007) `*The overlay system is estimated to have a 10 to 15 year wear life*`. The residual effect from the aggregate/anti-icing liquid interaction allows for a minimum (one to five) number of liquid applications during the winter season.

Safelane was trialed in 2003 in Wisconsin in the U.S. A further six trials were carried out between 2003 to 2006. The performances of these U.S. trials lead to the first UK trial in 2007. The trial for the Safelane product was undertaken on the Southbound A46 approach to the A428 near Coventry, as part of the Highways Agency operating MAC for Area 11. In total, the overlay was applied to 952 square metres of carriageway. To date (2012) no information regarding the performance of this surface in the UK has been released.

Initial trials from the U.S. suggest Safelane gives a good de-icing performance, with test sections remaining clear of snow and ice under weather conditions when snow and ice were accumulating on control sections. In some cases when snow was falling and snow accumulation was inevitable, it was observed that test sections could be kept clear with lower applications of chemicals. A 50% reduction in the use of solid chemical de-icer was achieved on the Ironwood Bridge (Nixon 2006).

The Blatnick Bridge, Wisconsin reported no accidents in the first year of the installation of Safelane. This is in contrast to 20 accidents occurring in the four years prior to the installation (Nixon 2006). For this section, the Safelane system was charged with approximately 15 gallons per lane mile of magnesium chloride brine (35 litres/km) and up to 400 lbs per lane mile (112 kg/km) of solid granular salt when the conditions required.

The McLean Bridge, Texas was trialed in November 2005. This section was treated with 30 gallons of magnesium chloride brine per lane mile (21 litres/km) (Nixon 2006). During this trial, the test section never iced over and no accidents occurred. This was in contrast to control sections where a number of accidents occurred.

Despite the generally positive response from the trials, Nixon (2007) reports instances when the Safelane test sections performed less well. On December 7th 2006, the Mitchell Bridge in Minnesota reported that the `*test section is 50% frost covered while the control section is clear*` (Nixon 2007). On other occasions the test section was reported to perform no better than the control section. The cause for this is reported to be that `*in the presence of heavy moisture it will dilute (the ice control chemical) and eventually perform no differently than other pavement types*` (Nixon 2007).

As part of a study by Thomas and Martinelli (2007), surface friction was measured using a WisDOT ATSM Friction Trailer at U.S.H 8 Forest County Bridge Deck (Wolf River); the I.H 535 Douglas County (Blatnik Bridge); U.S.H 53 at U.S.H. 2 Bridge and Ramp Douglas Country. At the U.S.H. 8 Wolf River installation, average friction values appear relatively constant with values between 45.4 and 56.8 recorded over a 3 year period. At the U.S.H 53 at U.S.H 2 locations, higher average values between 55.3 and 60.8 were recorded. According to Thomas and Martinelli (2007) values greater than 40 are considered acceptable surface friction. At the I.H 535 Blatnik Bridge location, comparison between the overlay frictional values and the adjacent Portland Cement Concrete (PCC) pavement surface recorded values of 55.0-55.7 for the Safelane overlay and 40.4 and 44.2 for the PCC pavement. This lead to the conclusion that `*Friction values obtained on the anti-icing overlay were equivalent to numbers obtained on dry pavements*`. Whilst this may be true, it is important to recognise that the age of the adjacent PCC may mean it is not an exact control surface suitable for direct comparison.

Similarly roughness measurements were undertaken on the same sites using a road profiler between 2005 and 2006. On the Internation Roughness Index (IRI) scale, a value of 0.00 relates to a new pavement in perfect condition and 12.00 relates to a severely damaged pavement. IRI values of 4.32 were recorded for the anti-icing overlay and 3.06 for the adjacent PCC pavement This would indicate that the overlay system has a poorer performance than the adjacent PCC surface. However, lower values between 1.56 and 2.21 were reported by Thomas and Martinelli (2007) on the U.S.H 53 site.

Concerns exist that if the ice-control liquid is applied at relatively high surface temperatures (above 40^{o}F or 4.4^{o}C), there is a possibility that as the liquid penetrates the road surface, it may pass through a state which can be very slippery. Slickness could possibly occur if `*way too much liquid is applied*`, however one of the test sections in Nixon (2006) and Nixon (2007) reported no problems of slickness. Neither were such concerns demonstrated at the Harrisonburg trial in Virgina, when temperatures between 39 and 51^{o}F (3.9 and 10.6^{o}C) were experienced. (Nixon 2006) `*To date there is no reason to believe that the Safelane overlay is any more susceptible to chemical slipperiness than any other pavement*` (Nixon 2007).

A negative aspect of the Safelane system is the need for the continued application of sodium chloride or magnesium chloride brine to `charge` the pavement aggregate. Evidence gathered in Nixon (2006) suggests that this may be required every two to three weeks, creating cost and operational implications. This estimation coincides with observations discussed in Thomas and Martinelli (2007) which stated `*The anti-icing overlay surface required only one liquid* $MgCl_2$ *application per month unless a rain or freezing rain event flushed the liquid from the surface. Then a reapplication would have to be made*`. It could therefore be suggested that the Safelane product does not solve the reoccurring problems of the formation of ice and snow on the road. It does, however, have the potential to reduce winter service operations. It is also important to recognise that the conclusions from the eight trials to date have all been based on observational informational with no instrumented site trials undertaken.

3.4.4 PLUSRIDE

In the late 1960s a rubber modified product named `Rubit` was developed by two Swedish companies Skega AB and AB Vaegfoerbaettringar. This product generated significant interest due to the perceived skid resistance, noise reduction and anti-icing benefits. This product underwent a significant number of trials across the United States (Mogawer et al. 1991, Allison 1990, Peters and Schutlz 1987) where it was known by the trademark `PlusRide`.

PlusRide is a patented bituminous mixture which contains granulated tyre rubber, of particle size 0.16 to 0.64cm (Mogawer et al. 1991). These larger rubber particles were blended into the mix as a substitution for some stone aggregate to form a gap graded aggregate mix. The product developers claimed that the elastic nature of the aggregate results in it flexing on the pavement surface leading to ice debondment under the action of trafficking, in a similar way as described in Section 3.3.2.

The performance of PlusRide has been observed over a 5 year evaluation (Allison 1990). During this trial it was concluded that the PlusRide material did not give better frictional properties, noise reduction or increased service life. There results were confirmed by Peters and Schultz (1987) (compared to Class D, which is a conventional asphaltic concrete pavement surface to Washington State Department of Transportation specification) `*The PlusRide cost 50 percent more than the Class D and the friction resistance, noise levels and fatigue properties were the same for the PlusRide and Class D. The de-icing characteristics could not be confirmed due to the absence of surface icing on highways in the Yakima area*`.

Studies by Mogawer et al. (1991) also indicated an increase in susceptibility to moisture damage and rutting, whilst also showing reduced Marshall stability and retained tensile strength. The study did demonstrate an increased resistance to low temperature cracking. Reports in Mogawer et al. (1991) suggests the additive doubled the cost of the mixture.

Simulated traffic (wheel passage) tests of ice grown on the PlusRide rubber-aggregate asphalt *s*amples were described by Wuori (1993) as `*somewhat encouraging*`. `*The test results did not show significant ice debonding but did suggest a way the mix design could be altered to improve the ice debonding performance under traffic conditions. It was decided to increase the size of rubber aggregate to increase the potential for ice debonding under wheel loadings. Consequently, further testing of the PlusRide mix concept was halted in favor of testing larger rubber aggregate mix designs*` (Wuori 1993).

3.5 CONCLUSIONS

Pavement surfaces can be modified by physical or chemical means to produce a pavement surface course with anti-icing properties. Such anti-icing properties can be attributed to the use of freeze point depressant, low energy surface and/or deformable particles.

These modified pavement surface courses are intended to act as a preliminary de-icer by reducing the temperature at which ice forms. This delays the point at which maintenance crews are required to apply a traditional de-icing chemical, resulting in a reduction in the amount of de-icing chemical applied at each instance. Such products are not intended to be a substitute for winter maintenance, but can delay the formation of ice.

The concept of developing an anti-icing modified pavement surface course has been investigated since the 1970's, with a range of processes tried from chemically modified pavements to deformable rubber particles. Early experience with chemically modified pavement surface have demonstrated a degree of anti-icing performance, however problems of low skid resistance and poor service life have generated significant concerns.

In recent years a limited number of anti-icing surface course products have emerged on the market, specifically the Safelane product. This may indicate a change in attitudes towards pavement modifications for anti-icing purposes. Despite these changing attitudes, a lack of fundamental understanding of how a surface can be chemically modified to promote anti-icing, the benefits of such application in comparison with traditional methods and the implications on the mechanical properties of asphalt still exists.

4.0 EXPERIMENTAL PROGRAMME - CHEMICAL MODIFICATIONS

The previous chapter highlighted the interest in modified pavement surfaces to promote anti-icing. To date, the use of proprietary products would indicate that a complete solution to the problem has not yet been realised. This may be because of the de-icing ability of the pavement surface course has not consistently materialized. Safety concerns regarding a slippery surface and/or concerns regarding the asphalt's durability.

4.1 STUDY OF CHEMICAL ADDITIVES TO DATE

The only significant study of chemical additives, undertaken by Baum et al. (1992), identified that the criteria for any pavement modification or treatment is that it should be ` *economical to manufacture, install and maintain, not affect the structural integrity, have a long service life, be non-toxic and non-corrosive, be effective over a wide range of climatic and traffic conditions, and not have adverse effects on the coefficient of friction between rubber tyres and pavement*`. These criteria are still applicable to date and any surface course modifications should be considered against each aspect.

Baum et al. (1992) considered two hypotheses that had previously been postulated for choosing additives to be blended internally in asphalt. Firstly, water soluble salts and organic liquids to lower the freezing point. It was proposed that these water soluble additives would then become available at the pavement surface by rain extraction and road wear. Secondly, the use of hydrophobic organic liquids which would become available at the pavement surface by exudation because of the difference in compatibility with the asphalt and road wear which could weaken the ice bond.

The project considered a significant range of potential additives and initial screening tests were undertaken to eliminate additives deemed to have lower potential. The primary screening test was a `slush test`. The slush test is a semi-quantitative test in which the additive was cooled to -20°C for 16 hours and judged against a devised scale of the consistency of frozen salt solution. The assessment scale to determine the consistency of the frozen solution ranged from 0 indicating `*solid cake*` to 10 indicating `*Slush, ½ liquid and Fine Crystals*`.

Following preliminary testing, the anti-icing performance was judged on freezing point, moisture pick up and ice adhesion tests. Baum et al. (1992) characterised ice adhesion on asphalt specimens coated with the de-icing solution.

Freezing point measurements were assessed by cooling solutions at concentrations of 5%, 10% and 20%, by weight, in a test tube and detecting the change in state through continuously measuring the temperature.

Moisture pick up was measured by Baum et al. (1992). High moisture absorption could lead to caking in shipment, expansion and cracking of the pavement. Too high a rate of humidity could cause exudation of the additive leading to slippery road conditions. The moisture pick up test involved measuring the hydrated weight after set time periods against the initial dried sample weights.

Preliminary measures of the impact that the additive had on the mechanical properties of the asphalt were based on friction measurements, Marshall stability and flow tests.

Baum et al. (1992) identified a number of promising chemical additives. The study concluded that the additives which lower adhesion to the greatest extent are sodium formate, sodium acetate, sodium chloride, triethylene glycol and ICE-B-Gon (CMA). Baum et al. (1992) identified that ` *The final choices (referring to the best additive) would depend on other future results, e.g. resistance to repeated washing, friction versus time etc.* `.

Considering the potential benefits of such systems it seems logical to undertake detailed literature investigations into the recommended water–soluble chemical additives identified by Baum et al. (1992) for modifying asphalt surface courses for anti-icing purposes. Due to concerns expressed by Wuori (1993) and research of previous products relating to slickness in summer months, hydrophobic organic liquids were not considered in this study.

This Chapter will provide background details on the recommended chemicals by Baum et al. (1992) in terms of anti-icing performance and their implications on asphalt service life. It will also consider other applications of these chemicals and provide background information relating to economic, health and safety and environmental factors. The available information has then been critically assessed in conjunction with the previous literature review on methods of ice debonding to select the most promising chemicals formulations for further study.

4.1.1 SODIUM FORMATE

Sodium formate ($HCOONa$) is the sodium salt of formic acid. It is produced commercially by absorbing carbon monoxide under pressure in solid sodium hydroxide at 160^{o}C and usually comes in the form of a white deliquescent powder.

$$CO + NaOH \longrightarrow HCOONa$$

Screening tests conducted by Baum et al. (1992) indicated that sodium formate at 10% and 20% concentration to water by weight had a slush rating of between 9 and 10, indicating that ice is likely to be easily removed. At 5% concentration, values between 4 and 7 were observed indicating moderate ease of ice removal. Freezing point measurements indicated that water freezes at -3^{o}C, -5^{o}C and -13^{o}C for 5%, 10% and 20% concentrations respectively. These values are comparative with that of sodium chloride and indicate the potential use of sodium formate for anti-icing purposes.

Further test results demonstrated that sodium formate exhibited high moisture pick up reaching a value of 126% moisture pickup after 2 weeks, however this effect leveled off after approximately 5 weeks.

Sodium formate demonstrated low ice adhesion with the shear strength to remove a disc of ice measured at 172.4KPa (25 psi), 20.6KPa (3 psi) and 6.9KPa (1 psi) for 5%, 10% and 20% concentration by weight, respectively. The results were more promising when asphalt concrete briquettes were modified by blending the asphalt with sodium formate powder. For these modified specimens, a value of 117.2KPa (17 psi) was observed at -5^{o}C for a 6.4% addition to the aggregate. However a simple washing experiment to determine such effects over a long in-service period showed ice adhesion increased from 117.2KPa (17psi) to 275.8KPa (40psi) after 4 washes compared to a control specimen exhibiting shear strength values of 441.3KPa (64 psi).

Preliminary studies on the effect of the sodium formate on the in-service performance of the asphalt pavement surface course would appear to indicate that there are no apparent negative effects. Friction measurements highlighted negligible differences with a control surface. This was demonstrated with a British pendulum number of 50BPN in the dry and 35BPN in the wet compared to the control (with no additive) of 49BPN in the dry and 35BPN in the wet. Marshall testing to determine the mechanical influence on asphalt indicated a Marshal Flow of 3.8mm (0.15) Inches and Marshall Stability of 11.1kN (2500lb). These values comply with the Conneticut material specifications.

Considering the Baum et al. (1992) study as a whole, it would appear the sodium formate has the potential to promote anti-icing with indications that sodium formate does not have adverse impacts on the pavement surface life. Background research on sodium formate indicates it is suitable for such an application based on economic, toxicity and corrosivity factors. Sodium formate is not listed as part of the EU classification of hazards and has a low toxicology meaning low concentrations are compatible with sewage systems. The high melting point of 253^{o}C makes sodium formate suitable for asphalt production. These factors, combined highlight the potential for sodium formate to be used as an anti-icing pavement additive relative to other chemical additives.

Sodium formate is significantly less corrosive than sodium chloride. Studies by Hassan et al. (2002) focusing on the effects of runway de-icers on pavement materials when applied to the pavement surface course showed some positive results. The study presented a comparative indicator between the effects for sodium formate, sodium chloride and distilled water and highlights the effects of the pavement composition on degradation.

The first test measured the effect de-icing solutions have on the durability of aggregates during freeze-thaw cycles. The test involved saturated aggregates in de-icing solutions, and subjecting the aggregates to 30 freeze-thaw cycles. The amount of damage experienced by each sample was quantified in terms of weight loss. This showed that sodium formate was initially more damaging to limestone aggregates than sodium chloride, however similar results were experienced for the two de-icers when a quartzite was used.

The effects of de-icers when applied to asphaltic concrete specimens were also considered. Indirect Tensile Strength was carried out on samples after 25 and 50 cycles freeze-thaw cycles. After 25 cycles `*the average ITS was almost constant for all four deicers and slightly higher than that corresponding to distilled water only*` (Hassan et al 2002). This was demonstrated for distilled water, sodium chloride and sodium formate by ITS values of 0.588, 0.657, and 0.675MPa respectively. This would indicate that, initially distilled water would appear more damaging to the strength of the mix than the de-icing chemicals. However, results for distilled water at 50 cycles showed almost no additional damage with a value of 0.572 units, unlike sodium chloride and sodium formate with values of 0.620 and 0.547 respectively.

The penetration of recovered bitumen from the asphalt cores was also considered after 25 and 50 freeze-thaw cycles. This showed significant hardening for road salt and urea, whilst values for sodium formate remained relatively unchanged. Gradation of the aggregate indicated moderate damage for sodium formate and road salt.

The important conclusion to be taken from this study is that `*no significant increase in deterioration to the mechanical properties was reported due to the exposure to potassium acetate, sodium formate, or road salt relative to distilled water*` (Hassan et al. 2002). While this study did not focus on blending sodium formate into the asphalt it provides further indication that sodium formate is not detrimental to the service life of asphalt.

The initial cost estimates of sodium formate is between £250 and £350 per tonne. This is significant cost and at a 3% addition by weight could increase the cost of the asphalt surface course by over 20%.

4.1.2 SODIUM ACETATE

Sodium acetate (NaAC) is the sodium salt of acetic acid. Sodium acetate has commonly been applied as a runway de-icer, as the de-icer is classified as non-corrosive.

Research from Baum et al. (1992) demonstrated the potential anti-icing performance of sodium acetate. Slush ratings of 4-7, 8 and 9 were observed for 5, 10 and 20% concentrations respectively. These results are comparable with sodium formate and sodium chloride, discussed previously. Freeze point measurements of -2, -3 and -10°C for the same concentrations of 5, 10 and 20% concentrations indicate lower freezing points than that of sodium formate. The freezing point measurements would also indicate that to see the greatest anti-icing benefit from sodium acetate, a high concentration of additive would be required.

Sodium acetate moisture pick up is also high, therefore there is the potential for similar problems described for sodium formate relating to moisture absorption.

Ice adhesion measurements on de-icing solutions placed on asphalt briquettes demonstrated low ice adhesion with the shear strength to remove a disc of ice measured of 441.2KPa+ (64+ psi), 117.2KPa (17 psi) and 4.8KPa (0.7 psi), obtained for 5%, 10% and 20% concentration, by weight respectively. Whilst these values indicate lower ice adhesion, comparisons with sodium formate indicate significantly higher ice adhesion for sodium acetate. Similarly with the freezing point, to see maximum performance in terms of ice adhesion, high concentrations of sodium acetate are required.

When asphalt concrete briquettes were modified by blending the asphalt with sodium acetate powder more promising results were observed. These contradicted results observed for ice adhesion on de-icing solutions. A value of 34.4KPa (5 psi) was observed at the temperature of -5°C for a 6.4% addition to the aggregate, rising to 179.3KPa (26 psi) after 4 washes. These results indicate significantly lower ice adhesion for sodium acetate modified briquettes relative to sodium formate modifications.

Preliminary studies on the effect of the sodium acetate on the in-service performance of the asphalt pavement surface course would appear to indicate that there are no apparent negative effects. This was demonstrated by dry frictional values of 39 BPN and comparable wet friction values of 34 BPN relative to that of the control and sodium formate. Marshall testing to determine the mechanical influence on asphalt indicated a Marshal Flow of 3.7mm (0.145 Inches) and Marshall Stability of 11.5kN (2576 lb). These values met the local “Connecticut Specification” and are similar to that produced for sodium formate.

Sodium acetate also has very low toxicity; this is demonstrated by its use in low concentrations as a food additive.

The initial indicative cost of Sodium Acetate based on Baum et al. (1992) is in the region of £800 per Tonne. This is considerably higher than the estimated cost of Sodium Formate and could increase the cost of the asphalt surface course by over 40% per Tonne based on a 3% addition by weight.

4.1.3 CALCIUM MAGNESIUM ACETATE (CMA)

CMA was recognised in the 1980s by the Federal Highway Administration as a possible replacement for salt. It is manufactured by reacting dolomitic lime with acetic acid. The performances of this as a de-icing chemical are described as promising. Better Roads (1986) `*It has been called the most promising non-salt chemical de-icing agent which is both effective and environmentally accepted*`. However `*the most significant impediment to its use has been its price, which is more than 20 times that of salt*` (TRB 1991).

Research from Baum et al. (1992) considering the suitability of the use of CMA as an anti-icing pavement additive was based on the proprietary CMA product of `*Ice B Gon*`. This study indicated a slush rating of 4-7, 7 and 9 for 5, 10 and 20% concentrations and freezing points of -2 and -11 for 5% and 20% concentrations indicating comparative performance to the additives discussed previously. The Ice B Gon product also indicated a relatively low moisture pick up indicating a low risk of caking, expansion and cracking of the pavement and exudation leading to slippery conditions. No leveling off of moisture pick up was observed after 8 weeks indicating high levels could be reached over a period of time.

Ice adhesion measurements based on de-icing demonstrated low ice adhesion with the shear strength to remove a disc of ice measured at 337.8KPa (49 psi), 62.1KPa (9 psi) and 6.9KPa (1 psi) for 5%, 10% and 20% concentration by weight respectively. Ice adhesion for modified asphalt briquettes containing 6.4% chemical additive by weight indicated ice shear strength values of 55.2KPa (8 psi), initially, rising to 248.2KPa (36 psi) after 4 washes. Examining ice adhesion relative to the other additives of sodium formate and sodium acetate would indicate moderate ice adhesion.

The influence that Calcium Magnesium Acetate (CMA) has on pavement surface course service life is inconclusive. This is because Marshall testing to determine the mechanical influence on asphalt on CMA was not undertaken as part of the preliminary study by Baum et al. (1992), with no explanation provided. The addition of CMA to the asphalt surface course did not have any adverse effects on surface friction values. Dry friction values of 48 BPN in the dry and 37 BPN in the wet were comparable to the control and sodium formate.

Comparisons with sodium chloride indicate an acceptable de-icing ability. `*In selective and experimental situations in which it has been used, it has often performed acceptably, although generally not in the same manner and not quite as effectively or consistently as salt*` (TRB 1991). `*Compared with salt, it is slower acting and less effective at lower temperatures below -5$^o$C and in freezing rain, drier snowstorms and light traffic*` (TRB 1991). As CMA is slower acting when applied during or after the snowstorm, application prior to the snowstorm is desired. Considering the point of view of blending CMA into the asphalt surface course these aspects will not necessarily detract from the performance of the product. This is because the chemical will be in place prior to the snowstorm and temperatures below -5^{o}C are less frequent in the UK.

CMA is usually applied in greater quantities as a reactive treatment relative to sodium chloride at approximately 20% increase by weight. More recent experience with improved physical properties, the product on the Zilwaukee Bridge showed a 1:1 CMA:salt ratio to be satisfactory (MDOT 2007). Such observations coincide with the study by Baum et al. (1992) which demonstrated significantly lower freezing points at higher concentrations.

An important performance advantage of applying CMA to the road surface is that the residual CMA on the road can last up to two weeks creating further de-icing for subsequent weather storms. Therefore fewer subsequent applications are required which offset the potentially higher initial applications. In terms of blending CMA into the asphalt surface course, this may indicate a long lasting anti-icing performance of the surface course.

The main advantages for the use of CMA over sodium chloride are over environmental concerns and corrosion factors. CMA has very few negative environmental effects and does not significantly impact roadside vegetation. `*It is also biodegradable and exhibits poor mobility in soils, it is less likely to reach groundwater*` (TRB 1991). CMA is much less corrosive than salt and therefore the influence of steel bridge decks, rebar and motor vehicles is reduced. Studies into the corrosiveness of CMA in Michigan indicated that metals exposed to CMA experience between one-third to one-ninth the corrosion of those exposed to road salt (Kinney et al. 1986).

CMA has significant potential as an anti-icing pavement additive based on previous studies, the low toxicity and corrosivity and the promising results measured by Baum et al. (1992).

The initial indicative cost of CMA based on Baum et al. (1992) is in the region of £500 per Tonne. This is considerably higher than the estimated cost of Sodium Formate and could increase the cost of the asphalt surface course by over 30% per Tonne based on a 3% addition by weight.

4.1.4 SODIUM SILICATE

Sodium Silicate (also known as water glass) is the generic name for a series of compounds derived from soluble sodium silicate glasses. They are water soluble solutions of sodium oxide (Na_2O) and silicon dioxides (SiO_2) combined in various ratios. Commercial grades of liquid sodium silicates range in weight ratio of SiO_2 to Na_2O from 1.6 to 3.3. Sodium silicate is widely used throughout industry; however it has not been used significantly in the asphalt industry to date. Its current applications include adhesives, detergents, soil stabilisers and concrete treatment.

Sodium Silicate was considered as part of the Baum et al. (1992) study. Due to the large number of chemicals preliminary screened by means of the slush test, it meant that sodium silicate was discounted as a suitable surface modification.

Despite being discounted from the Baum et al. (1992) experiment, sodium silicate is of interest to this study because of the relatively high silicone content. Previous research by Penn and Meyerson (1992) displayed in Section 3.3.3 Table 3.2 showed the significant reduction in the work of adhesion between water and sodium silicate relative to aged asphalt. As this chemical additive is added as filler, it is postulated that the chemical addition will reduce the surface energy over the surface of the pavement and therefore reduce the strength of the bond between the pavement surface and the ice.

Sodium silicate was selected as the silicone component because it is a significant component of zeolites. Zeolites have been introduced to create warm asphalt technologies since 1997 with Eurovia's asphamin product. Zeolites have a high moisture content of approximately 20% and the release of this fine water vapor creates `*a volume expansion of the binder that results in the formation of asphalt foam, allowing increased workability and aggregate coating at lower temperatures*` (Harrison and Christoduakie 2000). The addition of zeolites allows aggregate to be fully coated at lower mixing temperatures by reducing the viscosity of the binder at a given temperature.

Zeolities create the benefits of reduced fuel costs, reduced emissions, reduced mixing and compaction temperatures, early site opening and less binder ageing. It is postulated that the high moisture content of sodium silicate (between 14 and 22%) will produce similar effects to that of zeolites and the associated economic and environmental benefits. Sodium silicates also meet the basic criteria by Baum et al. (1992) as it is non-flammable, non-explosive and non-toxic.

The negative aspect of sodium silicate is that it is an alkaline material with a pH typically between 11 and 12.5, which poses hazards to the skin and eyes. Sodium silicate is also required to be stored in dry conditions because in humid conditions the product will absorb moisture and may cause caking or loss of free flowing properties. This results in a limited product shelf life, approximately 6 months.

4.1.5 SUMMARY OF ADDITIVE KNOWLEDGE

The only significant study into modified asphalt for anti-icing purposes by Baum et al. (1992) has provided an initial ranking of potential additives based on preliminary testing. The study recognised the potential of a number of water soluble salts and hydrophobic liquids. The results are summarised below in Table 4.1.

Additive	Ice Adhesion KPa (psi)	British Pendulum Friction Dry/Wet	Average Marshall Stability kN (lb)	Average Flow mm (Inches)	Price £/Kg ($/lb)	Slush Test Rating	Corrosivity
Control (Water)	>441.3 (>64)	49/35	15.3 (3433)	3.0 (0.120)	-	-	-
Verglimit	0.7 (0.1)	32/33	-	-	1.2 (0.82)	-	Y
Sodium Formate	0.7 (0.1)	46/34	14.2 (3195)	3.4 (0.135)	0.3 (0.20)	9	N
Sodium Acetate	1.4 (0.2)	38/32	5.6 (1251)	3.4 (0.132)	0.8 (0.58)	8	N
Sodium Chloride	0.7 (0.1)	45/34	-	-	0.1 (0.03)	10	Y
Ice-B-Gon (CMA)	9.0 (1.3)	45/34	-	-	0.5 (0.34)	-	N
Propylene Glycol	82.7 (12)	47/32	8.0 (1806)	3.9 (0.154)	0.8 (0.56)	9	N
Dipropylene Glycol	41.4 (6)	46/32	-	-	0.8 (0.57)	8	N
Tetraethylene Glycol	27.6 (4)	34/35	4.2 (945)	3.8 (0.148)	1.3 (0.88)	8	N
Triethylene Glycol	5.5 (0.8)	36/35	6.0 (1344)	3.4 (0.135)	0.8 (0.54)	8	N
Carbowax 300	55.2 (8)	33/32	-	-	1.1 (0.73)	7	N
Poly G 71-530	82.7 (12)	45/33	4.8 (1071)	3.4 (0.133)	1.2 (0.85)	-	N
Connecticut Class I Specification	-	-	>5.3 (>1200)	2.0-3.8 (0.08-0.15)	-	-	N

Table 4.1 - Summary of best additive systems, reproduced from (Baum et al. 1992)

Note:- Conversion from US dollar to British pound based on an exchange rate of $1=£0.66

4.2 CRITICAL REVIEW OF CHEMICAL ADDITIVE KNOWLEDGE

The study by Baum et al. (1992) successfully reaches its objectives by providing preliminary testing to determine promising additives for asphalt. From the extensive literature review undertaken as part of this project, it would appear that the recommended additives have not been considered in detail.

This could be due to concerns raised about previous products. Wuori (1993), referring to the skid resistance and service life drawbacks of the Verglimit product, states that `*because of these drawbacks and the general concern about chemical additives …………no work was done with chemical additives*`.

Research over the last century has therefore been focused on improving the tried and tested method of salting roads and specifically pre-wetting, rather than a more innovative solution to the reoccurring problems caused by ice on the roads.

There are a number of limitations in the knowledge of the recommended anti-icing chemical modifications. These relate to:

- Impact of the chemical modification on the mechanical performance of asphalt
- Anti-icing performance
- Screening process

This next section highlights the limitations in the current knowledge of the proposed chemical additives in the context of lessons learnt from previous products.

4.2.1 IMPACT UPON MECHANICAL PERFORMANCE OF ASPHALT

Mechanical performance of chemically modified asphalt is of equal importance to anti-icing performance. The importance of this has been highlighted by previous products with concerns relating to skid resistance, cracking and early decomposition reported.

The study by Baum et al. (1992), made the judgments on the impact that the additives have on the mechanical properties of asphalt, based on a very limited number of tests. Baum et al. (1992) provided simplistic measurement of mechanical performance in terms of Marshall Stability and Flow for ranking purposes. The study of individual asphalt performance parameters were outside the scope of the project and the study did not consider the failure methods of previous products. A detailed study of this area is therefore required.

The study also acknowledges that the recommended chemical substances have a tendency to absorb significant quantities of moisture; this effect has been observed on site trials. No investigation on the implications of this moisture absorption have been undertaken and experience of previous products suggests the implications of this need to be determined in terms of pavement service life and safety.

4.2.2 ANTI-ICING PERFORMANCE

The study by Baum et al. (1992) primarily ranks the chemicals based on the freezing point of aqueous solutions at selected concentrations.

The study does not provide a complete understanding of the anti-icing performance when the chemical is blended into the pavement surface course. This is because the majority of the chemical testing has been undertaken on solutions of the chemical and not on modified pavement surface course. Considering the chemical is encased by bitumen to form part of the asphalt mastic when the pavement surface course is constructed, it is logical that there is the potential for a significant variation in performance when the chemical is added to the pavement surface.

The durability of the anti-icing performance is of equal importance. In order to be economically viable any additive system would be expected to last more than one winter season. The study by Baum et al. (1992) has only evaluated the effects of ice adhesion in relation to continual washing. This testing has provided an initial assessment of the durability of such chemicals. However knowledge of the service life is limited as the washing experiments conducted were for relatively short periods of time and do not directly represent the highway network conditions such as trafficking. Considering the variations in the reported anti-icing service life of previous products and based on current knowledge, it is not possible to realistically determine the service life of such products.

The method of activation is equally only postulated from observations of previous products becoming available at the pavement surface by rain extraction and road wear. A more detailed understanding of the mechanisms by which the chemical is transferred to the pavement surface and the effects of environmental conditions and pavement characteristics on the anti-icing performance would be a significant step forward.

4.2.3 LIMITATIONS OF SCREENING PROCESS

The study by Baum et al. (1992) is based on one chemical system. Research into ice debonding by Wuori (1993), Penn and Meyerson (1992) and previous products discussed in Chapter 3, has identified previously that low surface energy can reduce ice adhesion. For example, Penn and Meyerson (1992) identified that `*low energy materials could be incorporated into novel highway surface designs in the far future*`.

Baum et al. (1992) presents an initial study in anti-icing modifications and therefore a large number of chemicals were screened to evaluate promising additives. Preliminary screening was conducted by means of the slush test at -20 ^{o}C to discount chemical additives.

This screening process reflects more severe conditions than experienced in the UK and therefore additives which could have potential benefits for less severe climates such as maritime climates may have been discarded. The slush test is predominantly based on freeze point depressant effects and additional benefits such as the ability to reduce ice adhesion by lowering surface energy were not fully considered.

4.3 CHEMICAL ADDITIVE SELECTION FOR EXPERIMENTAL STUDY

The literature review and specifically research by Baum et al. (1992), has identified three additives of initial interest to this study, these are sodium formate, sodium acetate and Calcium Magnesium Acetate (CMA).

Time constraints and the wide scope of the project has meant that the investigation into only one of the chemical additives recommended by Baum et al. (1992) could be assessed as part of this study into the effects of modifying pavement surface course materials.

Following further investigations and reviews of available literature, Sodium Formate is arguably the most promising chemical for anti-icing modification purposes and has been prioritised over sodium acetate and Calcium Magnesium Acetate (CMA).

The reasons for perceiving sodium formate as the `most promising` chemical are based on anti-icing performance and mechanical asphalt performance measurements conducted by Baum et al. (1992), the use of the chemical as a specialist de-icer, cost of the chemical relatively to alternative chemicals recommended by Baum et al. (1992) and the availability of the chemical in the UK.

The use of low surface energy materials for ice debonding has been used extensively in other industrial applications. As described in the previous section the slush test screening process conducted by Baum et al. (1992) favoured freeze point depressant and a number of low surface energy materials were eliminated.

An `optimum system` might be produced by combining freeze depressant additives with low surface energy components. Formulations of freeze point depressants in conjunction with the low surface energy materials would combine two ice debonding mechanisms and therefore eliminate ice formation or enable easier removal of ice from the pavement surface.

It is for this reason that the perceived `*most promising*` chemical of Sodium Formate identified by Baum et al. (1992) will be combined with the low surface energy component of Sodium Silicate.

After an extensive review of chemicals, this component was selected as sodium silicate, a silica based additive. This is because of indirect uses of the product in asphalt and the inclusion of Sodium Silicate in the Baum et al. (1992) study.

The author acknowledges that a number of silica based products exist which may be suitable alternatives to sodium silicate for this performance. However due to project constraints and lack of available information Sodium Silicate has been prioritised.

4.4 CONCLUSIONS

Investigations by Baum et al. (1992) and background research have identified that individual chemical additives have the potential to provide suitable anti-icing performance, as well as meeting the criteria relating to the pavement surface life, economic and environmental factors. Historically the use of these anti-icing chemicals in combination with low surface energy materials has not been considered in detail for highway applications.

The creation of freeze depressant and low surface energy formulations could provide a unique solution preventing ice formation and the bond between the ice and the pavement surface.

This study will consider the anti-icing performance of the following chemical and combined chemical modifications:

- Sodium Formate - The perceived `most promising` anti-icing modification from Baum et al. (1992) due to the positive anti-icing (freezing point depressant and reduced ice adhesion) and limited impact upon on the mechanical performance of asphalt.

- Sodium Silicate – A low surface energy material with the potential to reduce ice adhesion.

- Limestone filler - One of the most common filler used in asphalt production. Limestone filler is used for control purposes for physical and mechanical testing.

4.5 KEY POINTS FROM LITERATURE REVIEW

The following points summarise Chapters 2, 3 and 4:-

- The formation of ice and snow on the road creates hazardous driving conditions, restricts public mobility and has adverse economic effects.
- The intensity, frequency and duration of winter weather conditions are very dependent on the climatic conditions of that region.
- The climate of the UK is predominantly a maritime climate. A maritime climate has a minimum average winter temperature around 0^{o}C with limited temperature fluctuations. Such conditions result in frequent icy pavement conditions and black ice events.
- The formation of ice on the pavement surface creates hazardous driving conditions because of a reduction in the coefficient of friction between the tyres and pavement surface.
- Effective snow and ice control is an important service for national governments. It is required to ensure as far as possible, that road users can travel safely and with minimal disruption in cold and severe climatic conditions.
- The current practice in the UK and throughout Europe is to apply de-icing/anti-icing chemicals directly to the pavement surface.
- It is estimated by Thornes (2003a) that the cost of keeping UK local authority highways frost, ice and snow free was in the region of £168 million for the year 2001 to 2002.
- The most popular winter maintenance treatment is the application of sodium chloride commonly known as road salt to the pavement surface. It is by far the most popular chemical de-icer `*because it is reliable, inexpensive and easy to handle, store and apply*` (TRB 1991).
- The effectiveness of applying de-icing chemicals is evident by the fact that generally; road user mobility is maintained and road traffic accidents and delays are minimized. Economic assessments of winter services in the UK indicate a benefit to cost ratio of 8 to 1 for current practice.

- Despite the high benefit to cost ratio, current practice does not provide the optimum solution due to environmental, logistical and site specific factors.
- The build up of ice on the road surface is a recurring problem. Current practice does not eliminate/reduce the need for winter service but mitigates the effects of specific winter events. Every time a winter weather event occurs an appropriate response must be undertaken in line with the winter service plan for that local authority.
- It would be desirable to develop new and improved ways of modifying the highway surface, to prevent or at least delay the buildup of ice, and to weaken the pavement-ice bond so that the ice which forms is easier to remove.
- Several fundamental features of both the pavement and the ice results in excellent bonding between the two, meaning that bond prevention is difficult.
- A number of methods for achieving bond reduction between the ice and the pavement surface have been considered previously.
- Three principle mechanisms have been considered to debond ice from the pavement surface. These are freeze point depressants, deformability and low surface energy.
- Freezing point depressants work by interfering with hydrogen bonds and changing the inherent structure of water so that the solution freezes at a lower temperature.
- A deformable surface is created by increasing the elasticity of the surface. As the elasticity of the surface is increased, the amount of support provided to the ice decreases, allowing traffic to break up the ice.
- Low surface energy materials minimise the ice-substrate intermolecular interactions and reduce the energy required to separate ice from the pavement.
- A limited number of proprietary anti-icing pavement surface courses have been tried throughout history. The concept of these products is to act as a preliminary anti-icer by reducing the temperature at which ice forms.
- This resultant reduction in the ice-forming temperature delays and possibly eliminates the point at which maintenance crews are required to apply a de-icing chemical, resulting in a reduction in the amount of de-icing chemical applied.
- Early experience with chemically modified pavement surface has demonstrated a degree of anti-icing performance. However, problems of low skid resistance and reduced service life have generated significant concerns.

- The only significant study of chemical additives by Baum et al. (1992) identified a number of promising chemical additives. These are sodium formate, sodium acetate, sodium chloride, triethylene glycol and ICE-B-Gon (Calcium Magnesium Acetate).
- The extensive literature review undertaken as part of this project has identified that the recommended additives have not been considered in further detail.
- It is postulated that this is because of concerns over previously tested products resulting in research over the last century being focused on improving the tried and tested method of salting roads and specifically pre-wetting, rather than a more innovative solution to the reoccurring problems caused by ice forming on the roads.
- The study by Baum et al. (1992) successfully reaches its objectives by providing preliminary testing to determine promising additives. The study does not provide a complete understanding of the anti-icing performance when the chemical is blended into the pavement surface course.
- The study by Baum et al. (1992) is also based on a one chemical system. Research into ice debonding and previous products has indicated that an `optimum system` may be produced by combining freeze depressant additives with low surface energy materials.
- The creation of anti-icing chemicals and low surface energy formulations could provide a unique solution preventing ice formation and the bond between the ice and the pavement surface.

5.0 CHARACTERISATION OF REFERENCE MATERIAL

5.1 INTRODUCTON

Chemicals and fillers have different physical and surface characteristics which may influence the mechanical properties of asphalt and the associated anti-icing performance.

Such physical characteristics include:

- Particle size distribution
- Particle density
- Particle shape
- Particle packing
- Chemical solubility

Surface characterisation also includes the measurement of:

- Specific surface area
- Surface energy

In order to make direct comparisons and conclusions it is necessary to measure and characterise these properties. The reference materials considered as part of this experiment are Sodium Formate, Sodium Silicate and Limestone Filler. All reference materials were sourced from high quality industrial suppliers.

This chapter discusses the key properties, characterisation methods and the results and implications of the physical and surface characteristics of the reference materials.

5.2 PHYSICAL PROPERTIES

5.2.1 PARTICLE SIZE DISTRIBUTION

Introduction

Particle size distribution (PSD) describes the range of particle sizes found within a substance. Particle Size Distribution of filler is an important measure because it can strongly influence the behaviour of bitumen and asphalt in terms of the flow of the mastic and compactability and stiffness of the asphalt.

Particle size distribution is typically expressed as the percentage of particles passing a particular size. To be classified as a filler, there is a particle size requirement of a minimum of 70% passing 63 micron (*BS EN 13043:2002).* Test results can also be shown graphically, either by percentage mass or volume of particles within a particular range.

For many materials, sieving is a simple technique for producing PSD data. For very fine materials, such as fillers and chemical powders, this method has limitations due to electrostatic interactions between particles and blinding of the sieve apertures.

Laser diffraction is a technique commonly used to overcome the limitations of sieving and to measure the particle size distribution of fine materials. This technique represents a fast, accurate means of obtaining a particle size distribution. Laser diffraction instruments consist of a light (typically a laser), a particulate dispersing device and a detector for measuring the scattering pattern, see Figure 5.1.

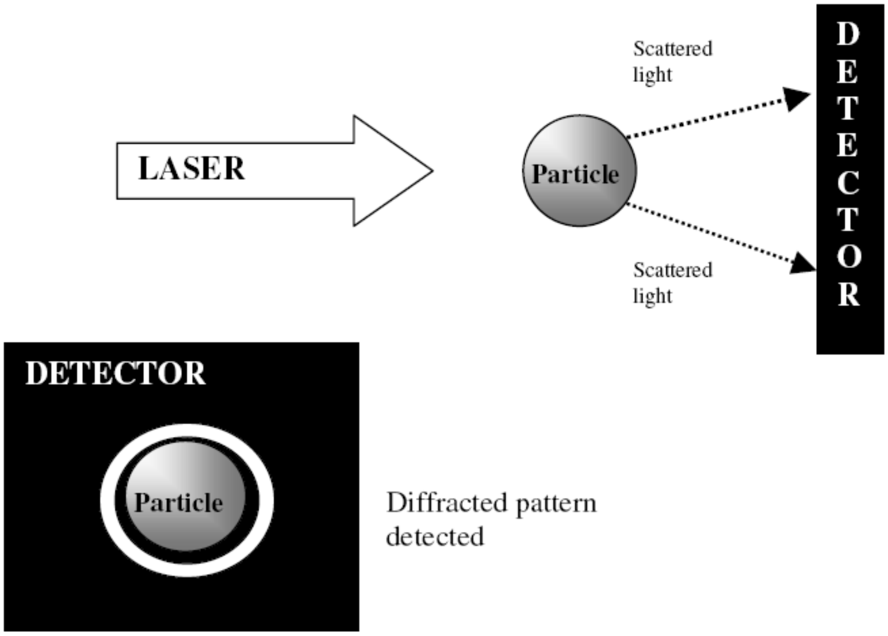


Figure 5.1 – Principles of particle size measurement and detection

Test Procedure

The laser diffraction technique is based on the phenomenon that particles scatter light in all directions with an intensity pattern that is dependent on particle size. The technique assumes that each particle is of spherical shape. The diffracted patterns are detected and analysed to produce a particle size distribution. The principles of laser diffraction are set out in BS ISO13320-1:1999.

Testing of the Particle Size Distributions was carried out using the `Malvern Mastersizer S` Particle Size Analyser, see Figure 5.2. This device is capable of measuring particle sizes from 0.5µm to 900 µm.

Figure 5.2 – Malvern Master sizer S

To undertake testing, an optical transparent liquid of known refractive index was used. The selected test liquid was water as it was compatible with the material and has a refractive index which differs significantly from that of the particulate material. The chemical concentration was selected to allow a sufficient number of large particles to be present.

Prior to testing the instrument was allowed a period of 1 hour to stabilise. The instrument was then calibrated to ensure proper alignment of the optical part of the instrument and the background of the scattering pattern measured. Particle size measurements were then undertaken in accordance with BS ISO13320-1:1999.

Test Results

Firstly, the volumetric particle size distribution of the investigated chemicals and filler were considered, as displayed in Figure 5.3.

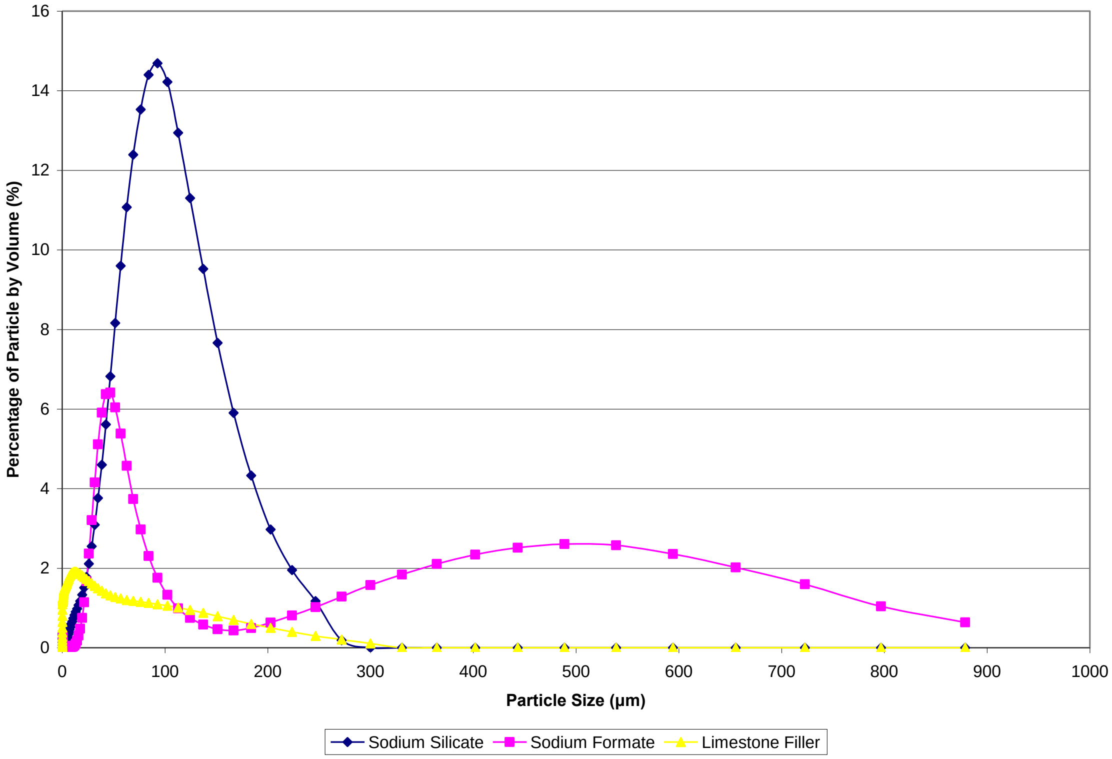


Figure 5.3 – Volumetric particle size distribution of chemicals and fillers

Figure 5.3 shows that the limestone filler and sodium silicate are typically normally distributed around a relatively low particle size. In contrast, the sodium formate sample tested has two distinctive regions, a relatively normally distributed section with a peak at 46.8µm and a larger continuous distribution between 200µm and 900µm.

Volumetric particle size distribution and particle size distribution by mass can be inter-converted by making assumptions of the density and shape of the particles. Typically in such calculations the particles are taken to be spherical.

Analysing the data in this manner enables direct comparison between the components to be easier. These are demonstrated in Figure 5.4.

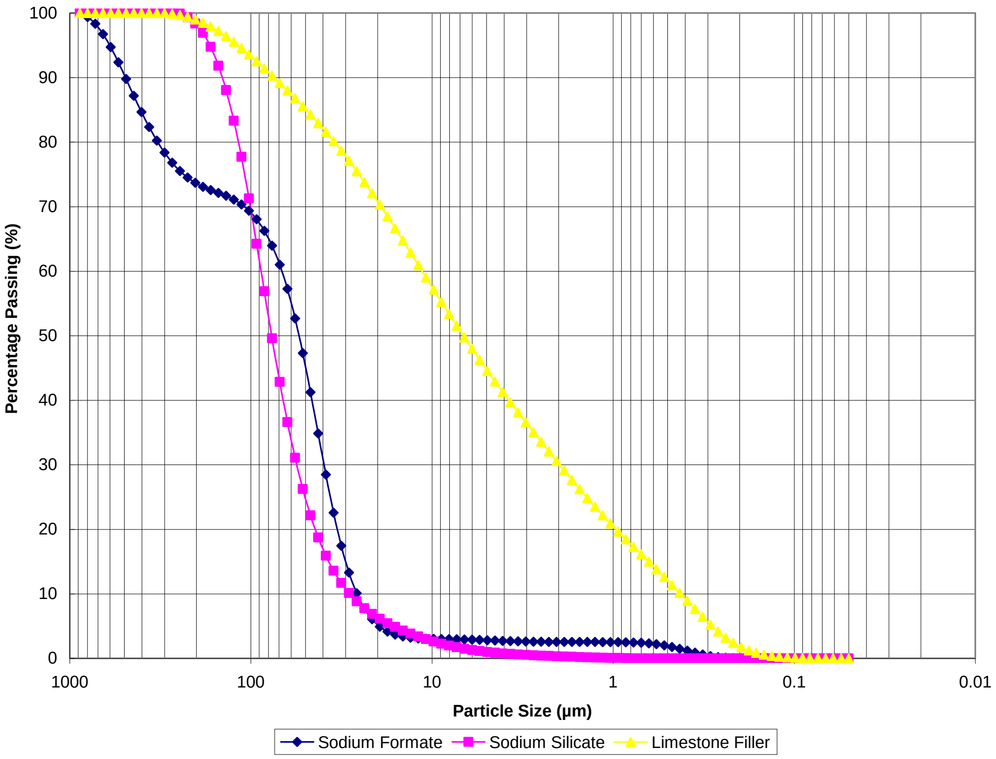


Figure 5.4 - Particle size distribution, represented as percentage by mass passing a particular particle size

Discussion of Test Results

The data demonstrates that the limestone filler typically used in asphalt production is significantly finer than the anti-icing chemicals being investigated as part of this project. Considering the chemicals in conjunction with the filler requirement of a minimum of 70% passing 63 micron, it is clear that the chemicals cannot be categorised as fillers in accordance with `*BS EN 13043:2002 - Aggregate for Bituminous Mixtures and Surface Treatments for roads, airfields and other trafficked areas*`. This could cause future challenges when specifying an anti-icing surface course in the future.

In order to allow more convenient comparisons between two or more sets of particle size distribution data, mathematical descriptors of PSD curves such as Fineness Modulus and Coefficients of Uniformity are sometimes used for fillers. The Coefficient of Uniformity gives an indication of the range of sizes within a particle size distribution. A low coefficient of uniformity indicates a PSD with a small range of particles. It is typically calculated as follows:

$$Uc = \frac{D60}{D10}$$

(Eq. 5.1)

Where:
Uc = Coefficient of uniformity
D60 = the size (µm) at which 60% of particles are smaller than (by mass)
D10 = the size (µm) at which 10% of particles are smaller than (by mass)

Fineness modulus is an empirical mathematical description of the fineness of a material and is typically derived by taking the sum of the percentage of material passing different sizes. The higher the value of fineness modulus, the finer the material.

This approach has been adopted for asphalt fillers (Kandhal et al., 1998; Harris and Stuart 1998) and the Fineness Modulus of asphalt fillers has been calculated using the following formula:

$$Fm = \frac{P75 + P50 + P30 + P10 + P3 + P1}{100}$$

(Eq. 5.2)

Where:

FM = Fineness Modulus

Px = the percentage passing diameter size x by mass, where x = µm

For each chemical and filler, Uniformity Coefficient and Fineness Modulus were calculated and results are presented in Table 5.1.

	Sodium Silicate	Sodium Formate	Limestone Filler
Uniformity Coefficient (D60/D10)	3.08	2.59	26.44
Fineness Modulus	0.97	1.42	4.42

Table 5.1 - Uniformity coefficient and fineness modulus of chemicals and fillers

The Uniformity Coefficient demonstrates that sodium silicate and sodium formate are very uniform with limited particle size variation between 60 and 10 µm. The fineness modulus indicates that the sodium silicate and sodium formate are significantly coarser than the limestone filler.

The higher uniformity coefficient for the limestone filler indicates a wider range of particle sizes and the fineness modulus is typical for filler used in asphalt production. Such conclusions are consistent with the analysis in Figure 5.3, showing the percentage passing by volume. These parameters will strongly influence the behavior of the bituminous mastic and, consequently, the performance of the asphalt.

5.2.2. PARTICLE DENSITY

Introduction

Density is defined as the mass of an object per unit space and is an important characteristic as it determines the space an object will occupy. The density measured for powders is the skeletal density. The skeletal density is the sum of the volumes of the solid material and the closed pores within the material.

Test Procedure

The skeletal density was calculated using the gas pycnometry technique. This technique determines the density and volume by measuring the pressure change of helium in a calibrated volume.

Prior to commencing the test, the samples were dried to constant mass at a temperature of 105^{o}C. This was to ensure that all water was evaporated from the sample so that water is not taken into account in the density of the sample.

Testing was carried out using a Micrometrics AccuPyc 1330 pycnometer, which is a type of gas displacement pycnometer, see Figure 5.5. The pycnometer essentially consists of two chambers, one with a removable gas-tight lid to hold the sample, and a second chamber of known calibrated volume. The device additionally comprises of a valve which admits a gas under pressure to the first chamber and a valve connecting the first chamber to the second chamber. A pressure measuring device is then used to the measure the pressure of the two chambers, see Figure 5.6.

Figure 5.5 – Photographs of gas displacement pycnometer

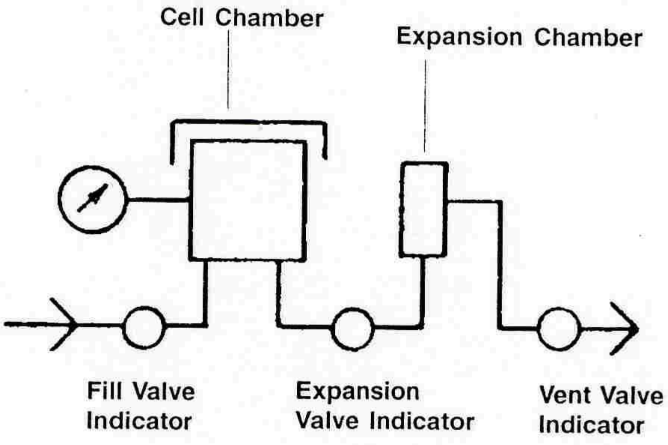


Figure 5.6 - Schematic of the gas displacement pycnometer

The procedure calculates the volume by employing the method of gas displacement. The volume to pressure relationship is known as Boyle's Law. The working equation of a gas pycnometer wherein the sample chamber is pressurised first is as follows:

$$Vs = Vc + \frac{Vr}{1 - \frac{P1}{P2}}$$

(Eq. 5.3)

Where:

Vs = Sample volume

Vc = Volume of the empty sample chamber (known from a prior calibration step)

Vr = Volume of the reference volume (again known from a prior calibration step)

P1 = The first pressure (i.e. in the sample chamber only)

P2 = The second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber.

The density can then be determined by dividing the pre-weighed sample specimen by the calculated volume. Measurement of the volume was carried out three times for each sample. The sample weight was measured to four decimal places with weights ranging between 3-5g.

Test Results

Skeletal density is the sum of the volumes of the solid material and the closed pores within the material. The results for the average density of the five tests and the standard deviation of these measurements are displayed in Table 5.2.

Material	Average Density (g/cm^3)	Standard Deviation
Limestone Filler	2.797	0.0072
Sodium Formate	1.938	0.0003
Sodium Silicate	1.751	0.0019

Table 5.2 - Average skeletal density and standard deviation of the chemicals and filler under consideration.

Discussion of Test Results

The results in Table 5.2 demonstrate significant differences between the average density for each material. Limestone filler is the denser material and is approximately 42% and 60% denser than the chemicals of sodium formate and sodium silicate respectively. The relative density of sodium formate and sodium silicate is of a much smaller magnitude.

The difference between the density of the limestone filler and the two chemicals will have to be considered in detail for each test individually. Asphalt production is typically based on formulating mixtures by mass.

A number of tests are highly dependent on the volumetric proportions of each component, for example the stiffening behavior of bitumen.

The low standard deviations demonstrate the high accuracy of repeatability of testing by this method on the chemicals and fillers and the uniformity of the particle density.

5.2.3. PARTICLE SHAPE

Introduction

Particle shape of fillers and chemicals is typically examined using microscopy, due to the very small particle sizes. Particle shape is important as the shape of the filler particles directly affects the maximum packing fraction (see section 5.2.4).

Aspect ratio describes the relationship between the longest and the shortest dimensions of a particle. The aspect ratio of solid particles in suspension has a significant effect on the rheology of suspensions (Barnes, 2000). For asphalt fillers derived from natural aggregates, aspect ratios fall in a relatively small range, typically 1.3-2.3 representing regular shapes.

Particle shape has a significant effect on the packing characteristics of filler and the value of maximum packing fraction. As the effects that filler have on viscosity of a suspension are scaled by the maximum packing fraction, particle shape is clearly an important factor.

Test Procedure

A simple characterisation of the shape of the filler particles was carried out using optical microscopy. Several digital photographs of the control filler and two chemicals were taken under normal light. The average aspect ratio was calculated as the ratio of the longest dimension of the filler particle to the shortest dimension, using 100 particles of each filler type and image recognition software.

Test Results

The mean values of aspect ratio determined by optical microscopy are displayed in Table 5.3, below:

	Average Aspect Ratio
Limestone Filler	1.681
Sodium Formate	1.904
Sodium Silicate	1.615

Table 5.3 – Average aspect ratio measured by optical microscopy

Discussion of Test Results

The results demonstrate that the aspect ratio for the limestone filler and sodium silicate are consistent. The particle shape of sodium formate is more elongated relative to the limestone filler and sodium silicate. The particle shapes of the three chemical fillers are consistent with those traditionally used in asphalt product.

The images taken from the optical microscopy found in Figures 5.7 to 5.9 of this report provide a qualitative assessment of surface roughness. It can be seen in the images that the particles of the limestone filler and sodium formate have significant small scale roughness. In contrast, sodium silicate particles are relatively smooth.

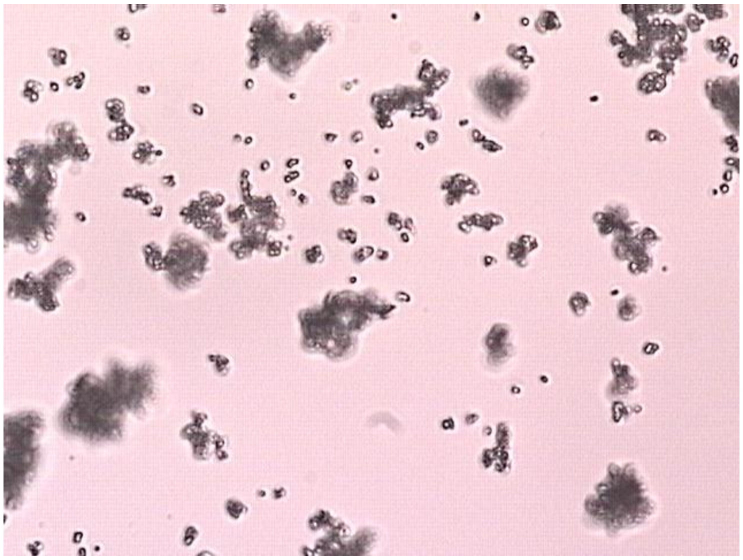


Figure 5.7 - Limestone filler at x10 magnification

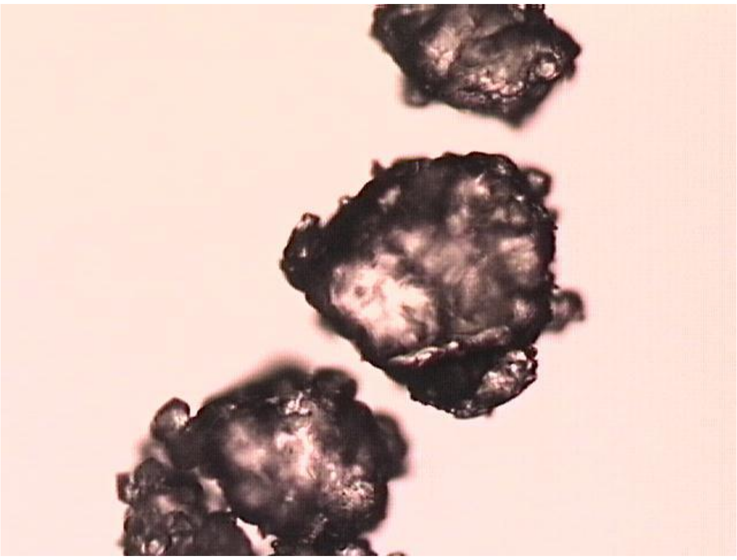


Figure 5.8 - Sodium formate at x20 magnification

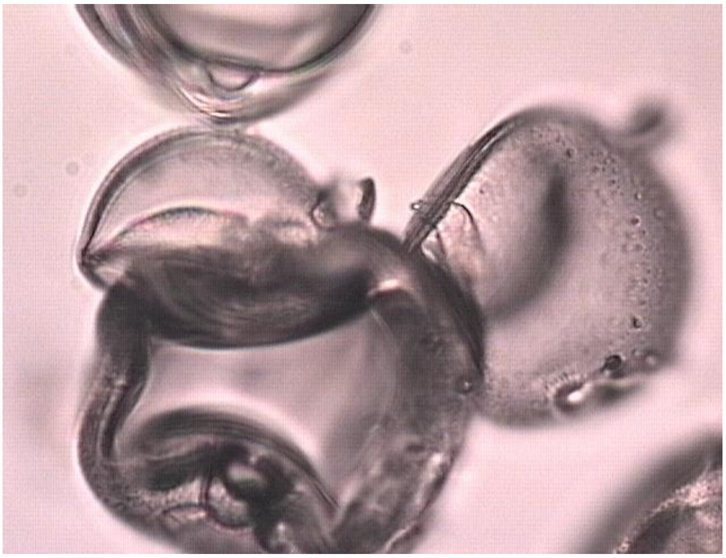


Figure 5.9 - Sodium Silicate at x20 magnification

5.2.4. COMPACTED TAP DENSITY AND ESTIMATION OF MAXIMUM PACKING FRACTION

Introduction

“Rigden Voids” is the air void content of the filler obtained under standard test conditions and relates approximately to the maximum packing fraction. “Rigden Voids” have consistently been found to be the best single property of the filler which relates to the increase in stiffness, or reduction in flow, of the mastic when filler is added. “Rigden Voids Content” of filler is termed a “tap density”.

“Tap density” is the maximum density a filler can attain through repeated tapping, tamping, vibration or other means of compaction. Filler is added to a container of known volume and tapped a prescribed number of times, or alternatively, vibrated for a set time. The filled container is weighed and the bulk density calculated by dividing the mass of filler by the volume of the container. The tap density is the bulk volume of filler and includes the air voids between the particles, see Figure 5.10.

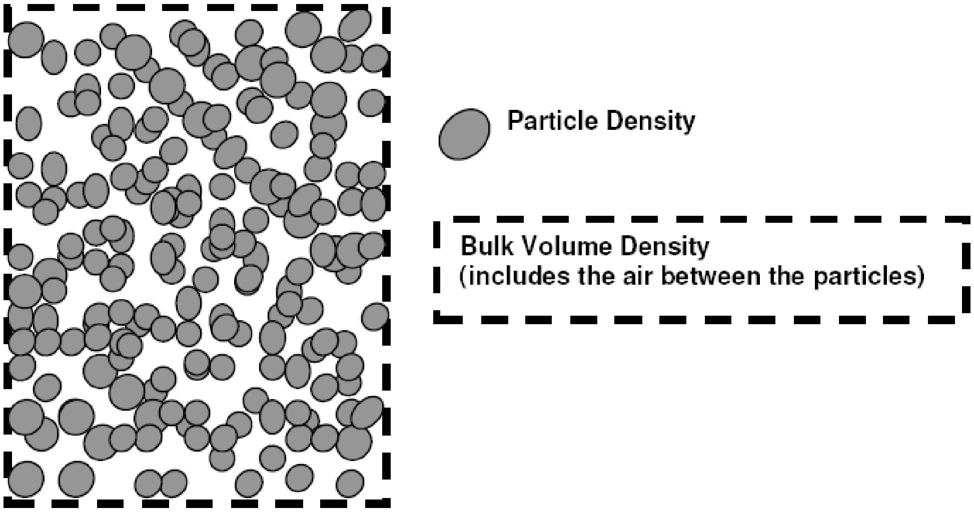


Figure 5.10 – Bulk volume density and particle density

From the tap density the maximum packing fraction can be calculated. The maximum packing fraction is defined as ‘the solid volume content of a suspension at which the viscosity of the suspension becomes infinite’ (Taylor 2007).

Test Procedure

Testing was carried out using Rigden apparatus in accordance with BS EN 1097-4:1999. This test method is applicable to natural and artificial fillers. Prior to testing, the samples were prepared by drying to a constant mass at 110°C and dry sieved using a 0.125mm sieve. A sample of 10±1g of filler was then placed in a dropping block of known weight. The plunger was inserted and compacted by means of raising and dropping the dropping block 100 times at 1 second intervals. The height of the compacted filler was measured and the dropping block weighed to determine the mass of the compacted filler.

The volume of percentage voids in the filler (% V Filler) can be calculated by:

$$\%\, V\ Filler = 100 \times \frac{(1-\ \rho\, Tap)}{\rho\, Particle}$$

(Eq.5.4)

Where:

% V Filler = Volume of percentage air voids in the filler

ρTap = Measured density of the filler/chemical after compaction

ρParticle = Measured particle density of the filler/chemical

Compacted tap density was measured on the reference chemicals and combinations of sodium formate and sodium silicate. These combinations were conducted to ensure consistency with the experimental programme for the three phases of testing, see Section 6.2. Experimental Programme – Chemical Formulations.

Test Results

Testing was repeated three times for each specimen. The mean voids after tapping and the resultant tap density were calculated. These results are given in Table 5.4 below.

Material	Voids after Tapping (%)	Standard Deviation	Tap Density (g/cm^3)	Standard Deviation	Estimated Maximum Packing Fraction
Limestone Filler	39.53	3.764	1.691	0.113	0.604
100% - Sodium Formate	35.38	2.130	1.252	0.041	0.646
70% - Sodium Formate 30% - Sodium Silicate	42.79	2.175	1.073	0.041	0.570
50% - Sodium Formate 50% - Sodium Silicate	50.49	0.800	0.913	0.015	0.495
30% - Sodium Formate 70% - Sodium Silicate	54.37	0.849	0.825	0.015	0.456
100% - Sodium Silicate	59.11	2.432	0.716	0.043	0.409

Table 5.4 - Results of Rigden voids testing and an estimation of the maximum packing fraction.

Discussion of Test Results

The Rigden Voids of 39% and maximum packing fraction of 0.604 for the limestone filler, is typical of fillers employed in asphalts. Harris and Stuart (1998) suggested that Rigden Voids in excess of 39% could stiffen the bitumen too much and cause compaction problems/cracking of the asphalt, whilst Rigden Voids less than 34% could lead to binder drain down.

The Rigden Voids of 35% and higher maximum packing fraction of 0.646 for sodium formate is still within the range suggested by Harris and Stuary (1988). The Rigden voids is lower relative to limestone filler and indicates that sodium formate compacts easier relative to the limestone filler.

It is difficult to relate the differences observed to a single parameter, however the difference between sodium formate and limestone filler can be attributed to the particle size distribution, particle size and particle shape.

In contrast, sodium silicate reduces the ability to compact the chemical. This is demonstrated by the significant increase in Rigden Voids of 59% and decreasing maximum pack fraction for sodium silicate to 0.409 relative to limestone filler.

Chemical blends of sodium formate and sodium silicate demonstrate values ranging between the individual chemicals, with the reduction in maximum packing fraction proportional to the sodium silicate content.

5.2.5. CHEMICAL SOLUBILITY

Introduction

Chemical solubility is the property of a solid, liquid or gaseous substance to dissolve in a liquid to form a homogenous solution. The ability to form a solution is dependant on the chemical properties of the solute, temperature and pressure. The extent of the solubility of a substance in a specific solvent is measured as the saturation concentration when adding more solute does not increase the concentration of the solution.

Chemical solubility is a fundamental property which is required to be characterised, as the rate at which the chemical enters a solution will strongly influence:

- The freezing point
- Ice pavement bond
- Durability of the anti-icing performance

Chemical additives are required to have solubility parameters that mean the chemical will enter solution and provide the required level of anti-icing performance. However, if the solubility is too great there is an increased potential for the chemical to leech out of asphalt over a short period reducing the anti-icing service life.

Test Procedure

The objective of the test procedure was to measure the solubility of sodium formate and sodium silicate at various temperatures ranging from 0°C to + 40°C. These temperatures were selected to assess the solubility of the chemicals at the full range of temperatures typically experienced by a pavement surface. Measurement of chemical solubility was subcontracted to the external chemistry laboratory LPD Laboratory Services.

The basis for measuring the solubility at different temperatures was to make solutions that were just saturated at a given temperature. A sample of the supernatant 'solution' with dissolved salt(s) would be taken and evaporated to dryness, the weight loss recorded and the solids content (solubility) calculated.

The calculation of the total solids content enables the solubility in terms of the percentage weight by volume to be calculated, as summarised in Table 5.5.

Test Results

Temperature (°C)	Solubility (weight/volume)	
	Sodium Formate	Sodium Silicate
0	52.0%	-
10	51.0%	-
20	50.2%	70.0%
30	48.0%	-
40	22.5%	-

Table 5.5 – Chemical solubility results for sodium formate and sodium silicate over a range of temperatures

Discussion of Test Results

The testing demonstrates that sodium formate is very soluble in water and dissolves to give 50% weight/volume at room temperature. During the testing it was observed that sodium formate dissolves rapidly.

Sodium silicate is also very soluble in water and dissolves to give 70% weight/volume at room temperature. Sodium silicate forms viscous clear 'water glass solutions' at high solids concentrations that are super saturated. This makes it difficult to specify solubility figures with any accuracy for sodium silicate at the temperatures noted previously and therefore only one measurement solubility measurement was taken at 20^{o}C. Whilst, there is some uncertainty regarding the precise solubility figures, the test results confirm that sodium silicate is very soluble in water.

Observations of sodium silicate indicate a relatively slower dissolution rate in water compared to sodium formate.

5.3 SURFACE PROPERTIES

5.3.1 SPECIFIC SURFACE AREA

Introduction

Specific surface area represents the ratio of a particle's surface area to its mass. Specific surface area measurements combine the effects of particle size, shape and texture. Surface area can be derived from particle size distribution curves, related to air permeability, or be derived from gas adsorption experiments.

Test Procedure

The simplest procedure for calculating surface area is using data from particle size distribution tests. Assuming a particle shape it is possible to calculate the surface area of a substance. Calculating surface area from particle size distribution data does present several difficulties due to the number of assumptions made in the calculation, see Figure 5.11. The typical assumption of a spherical particle shape does not allow for variations due to deviations in shape and surface texture. As the particles being measured become finer and more numerous for filler samples, the surface and any error becomes larger.

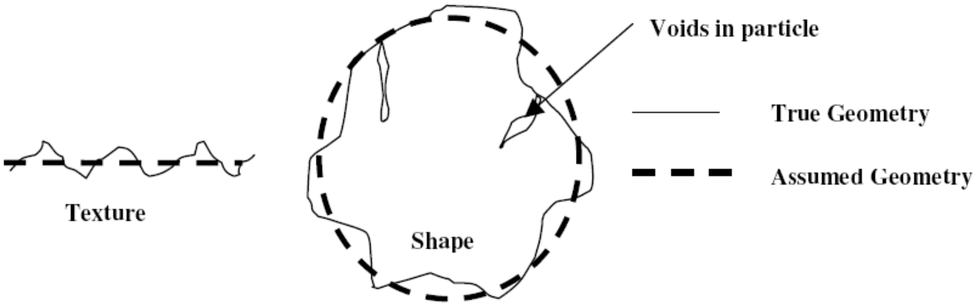


Figure 5.11 – Sources of error calculating surface area using assumed geometry

An alternative method of accurately measuring a specific surface area of fine particles, such as fillers is Dynamic Vapour Sorption. This method is considered more accurate because measurements take into account the surface texture and shape of the particles, by measuring both the external surface and the internal surface of the pores that are accessible to the gas.

Absorption of the gas occurs because of the presence of an intrinsic surface energy. When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. This process is considered non-selective because filling the surface step by step is dependant on the available solid surface and the relative pressure. Filling a complete layer enables the measurement of the surface area of the material to occur. This is because the amount of gas absorbed when the mono-layer is saturated is proportional to the entire surface area of the sample.

Any gas can be used for this experiment provided it is physically absorbed by weak bonds (van der Waals) at the surface, and can be desorbed by a decrease in pressure at the same temperature. The specific surface area can be measured by creating a sorption isotherm. This is calculated by plotting the weight increase of the specimen as the pressure of the sorptive gas is incrementally increased, to determine how much gas is absorbed.

The most common means of determining the surface area of a solid from a sorption isotherm is referred to as the “BET” method as standardised in Europe (BS EN 4359-1: 1996). The method assumes that the heat of absorption is constant throughout the formation of the first monolayer. It also assumes that the heat of absorption for subsequent monolayers is equal to the heat of condensation of the bulk liquid. Brunauer et al. (1938) were able to derive a relationship between the relative pressure of the gas and the volume absorbed per unit specimen mass.

Test Results

Specific surface area results were taken from the laser diffraction determinations of particle size distribution. This technique assumes that the particles are solid and spherical. The BET technique is based on the specific surface area by dynamic vapour sorption. The results for the specific surface area by laser diffraction and the BET technique are displayed below in Table 5.6.

Material	Specific Surface Area by Laser Diffraction (m^2/g)	Specific Surface Area by BET (m^2/g)
Limestone Filler	1.7148	4.7131 – 8.114
Sodium Formate	0.2023	-
Sodium Silicate	0.0546	-

Table 5.6 - Average specific surface area and standard deviation of the chemicals and filler under consideration.

The measurement of specific surface area using the BET was conducted using Octane, Chloroform and Ethyl Acetate gases. It was not possible to compute a result for sodium formate and sodium silicate using the probe liquids selected in the test procedure. This was because significant variations in the recorded mass indicated a possible chemical reaction or swelling which led to poor quality data and potential inaccuracies.

Discussion of Test Results

The specific surface area measured by laser diffraction for limestone filler of 1.7 m^2/g is typical for fillers used in asphalt applications. Values typically range from 0.6 to 1.9 m^2/g. The values of specific surface area measured by laser diffraction for the chemical additives are significantly lower than that of the limestone filler. This means that the surface area of the chemical particle is very low compared to the mass.

Specific surface area measurements using the BET technique includes pores accessible to the probe gas. Therefore results using this technique are typically higher than the values obtained by laser diffraction, which assumes the particles are solid. The significant differences between the results produced by laser diffraction and the BET technique for limestone filler indicates a high number of voids and deviation in the particle geometry.

5.3.2 SURFACE ENERGY

Introduction

Surface energy is a measure of the work required to increase the surface of a material by unit area. Surface energy is important because liquid and solid surfaces have varying energies due to their structural differences. These result in varying degrees of intermolecular attraction. Surface energy is commonly used to predict adhesion between two materials and is dependant upon the surface energies of the two substances which meet to form an interface, see Figure 5.12.

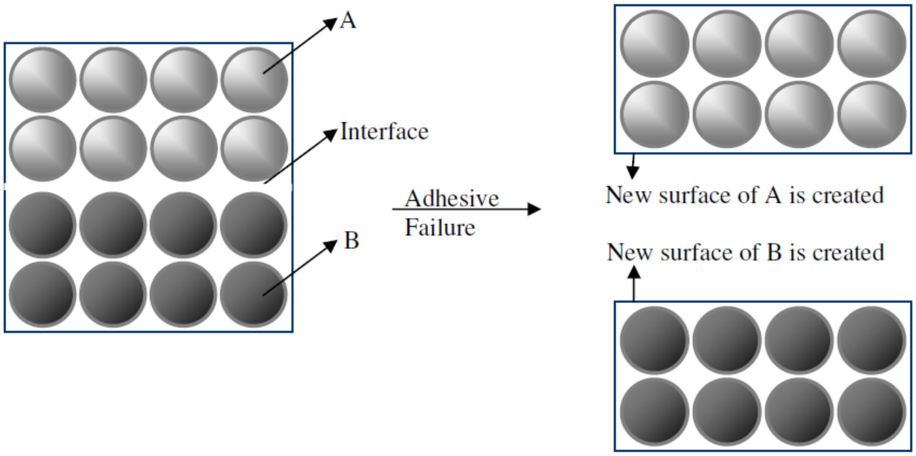


Figure 5.12 – Adhesive failure of two materials and creation of new surface area (Bhasin 2006)

Surfaces with the least affinity for another substance are typically very low in surface energy. These surfaces are often described as hydrophobic surfaces as they have poor affinity to water, see Figure 5.13. Creation of a low energy surface is an approach widely investigated for de-icing purposes on ships, leading edges of airplane wings and overhead telephone wires.

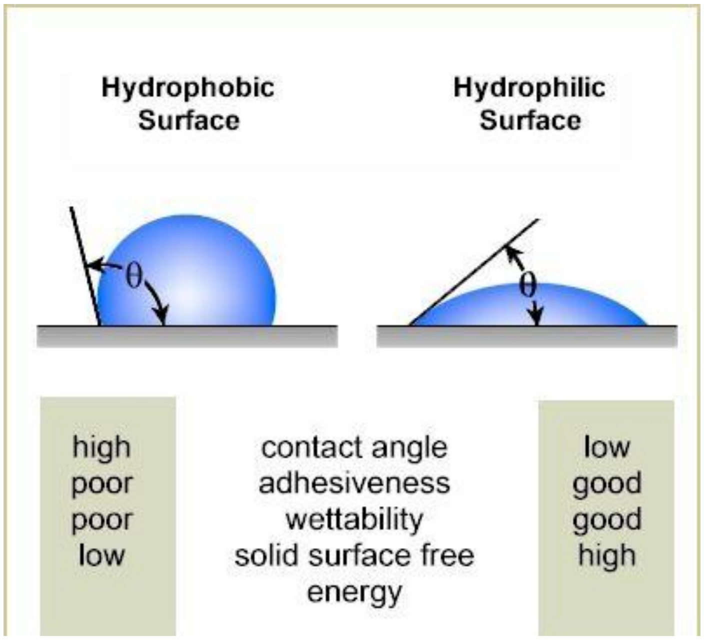


Figure 5.13. Influence of contact angle on surface energy, Rame Hart website (2009)

In contrast hydrophilic surfaces are attracted to water and the water will spread over large areas of the surface. A surface is typically described as hydrophilic if the contact angle is less than 90^o. Measuring the values of a solid is less straightforward because direct measurement of the solid surface energy is not possible. Surface energy measurements of solids are typically determined indirectly and reflect the thermodynamics of a fluid (liquid or gas) and solid interaction.

Test Procedure

The surface energy of the de-icing chemicals can be used to predict adhesion between the de-icing chemicals and a second material such as bitumen or ice.

Measurement of the surface energy of fine powders, like fillers and chemicals is relatively complex. Two methods were employed to characterise the powders included within this study. These included Dynamic Vapour Sorption and the Capillary Rise Technique.

Dynamic Vapour Sorption (DVS) is a technique developed to measure the surface energy of high surface area solids, such as fillers (Levoguer et al., 2003). In a vapour sorption measurement the surface tension of the liquid is considerably less than the energy of the solid surface and spreading occurs. The resulting contact angle is 0^{o} and the magnitude of the spreading pressure significant. This relationship forms the basis of the vapour sorption approach of measuring surface energy.

The equilibrium spreading pressure is defined as ‘the net change in surface energy of a surface resulting from the absorption of vapour onto the surface’. As the surface energy of the liquid is known from literature, the solid-liquid work of adhesion can be calculated if the spreading pressure is known. According to the approach developed by Van Oss and others (Good, 1992; Good and Van Oss, 1992), by using a polar gas for one experiment, the dispersive component can be determined directly. The use of two (or more) further gases of differing polarity allows the calculation of surface energy components of the solid.

Samples of the fillers were prepared and surface energy measurements determined using Dynamic Vapour Sorption. The test liquids used in the Dynamic Vapour Sorption experiment were Octane, Chloroform and Ethyl Acetate. The surface energy components of the test liquids used in the vapour sorption tests are presented in the Table 5.7.

Liquid	Total Surface Energy	Liftshitz Van der Waals	Lewis Acid	Lewis Base
	γTotal (mN m^2)	γ^{LW} (mN m^2)	γ^+ (mN m^2)	γ^- (mN m^2)
Chloroform	27.32	25.0	3.80	0.00
Octane	21.62	21.62	0.00	0.00
Ethyl Acetate	23.97	19.60	0.00	19.20

Table 5.7 – Test liquids used in Dynamic Vapour Soprtion test

The DVS technique provided a suitable measure for the limestone filler, however complications were experienced when using the probe liquids selected in the test procedure on sodium formate and sodium silicate. This was because of significant variations in the recorded mass. In particular a reduction in the mass of the test specimen indicating a possible chemical reaction or swelling resulting in potential inaccuracies.

An alternative sorption technique of conducting Surface Energy measurements of the chemical compounds was achieved by using the Washburn technique. Testing of this element was subcontracted to the specialist chemistry laboratory – Kruss GmBH, whom performed contact angle measurements using a K100 tensiometer and surface free energy calculations using Labdesk software.

Determination of the contact angles of the sodium formate and sodium silicate was achieved by the capillary rise of a pure liquid into a porous medium (which in this case was the powder). This implies the replacement of the solid-air interface by a solid liquid interface. The ‘capillary constant’ for each powder is determined first which characterises the structure of the powder bed using a totally wetting liquid such as siliconoil M3. This liquid perfectly wets out the surface of the powder without interacting by processes such as dissolution, swelling, or chemical interaction. This value can then be used to calibrate the subsequent test liquids assuming a contact angle of 0^o.

Surface free energy of the samples was determined using the Van Oss model, inputting the contact angle data from the liquids dimethylesulfoxide, ethylenglycol, diiodomethane, formamide and water. All measurements were performed at room temperature (T=23°C.)

The necessary physical properties (density, viscosity, total surface energy, dispersive component, polar component, the acid and base part) of these test liquids are summarised in table 5.8.

	Density (g/cm^3)	Viscosity (mPas)	SFT (mN/m)	SFT polar part (mN/m)	SFT polar disperse (mN/m)	Acid part (mN/m)	Base part (mN/m)
Siliconoil M3	0.910	3.000	18.50	0.0	18.5	-	-
Diiodomethane	3.325	2.762	50.80	0.0	50.8	0.00	0.00
Ethyleneglycole	1.1009	21.810	48.00	19.0	29.0	1.92	47.01
Dimethylesulfoxide	1.100	2.140	44.00	8.0	36.0	0.50	32.00
Formamide	1.133	3.607	58.00	19.0	39.0	2.28	39.60
Water	0.998	1.002	72.80	51.0	21.8	25.50	25.50

Table 5.8 – Test liquids used in capillary rise test

Where:

- SFT = Total Surface Energy - the amount of energy/work required to create a unit surface area of a material in vacuum.
- Dispersive Component = Acid-Base component
- Polar Component = Lifshitz-Van der Waals component
- Acid Part = Lewis acid component of surface interaction
- Base Part = Lewis base component of surface interaction

According to the Washburn theory there is a relationship between the wetting properties i.e. the contact angle and the mass increase during the sorption process which can be described by:

$$\cos \emptyset = \frac{m^2}{t} . \frac{\eta}{\rho^2 \ \sigma Liq. C \ Solid}$$

(Eq. 5.5)

Where *m* is the total mass, t the time, ρ the density, η the viscosity, σ the surface tension of the liquid and *C* the capillary constant of the powder sample in the sample holder. In order to determine the constant *C,* a measurement with a liquid which exhibits a contact angle of 0° when in contact with the solid, is performed i.e. Siliconoil M3.

As a result of the experiment and the physical data of the test liquid, the contact angle can be easily measured for other liquids. By determining the slope of the square of mass versus time it is possible to calculate the contact angle, see Figure 5.14.

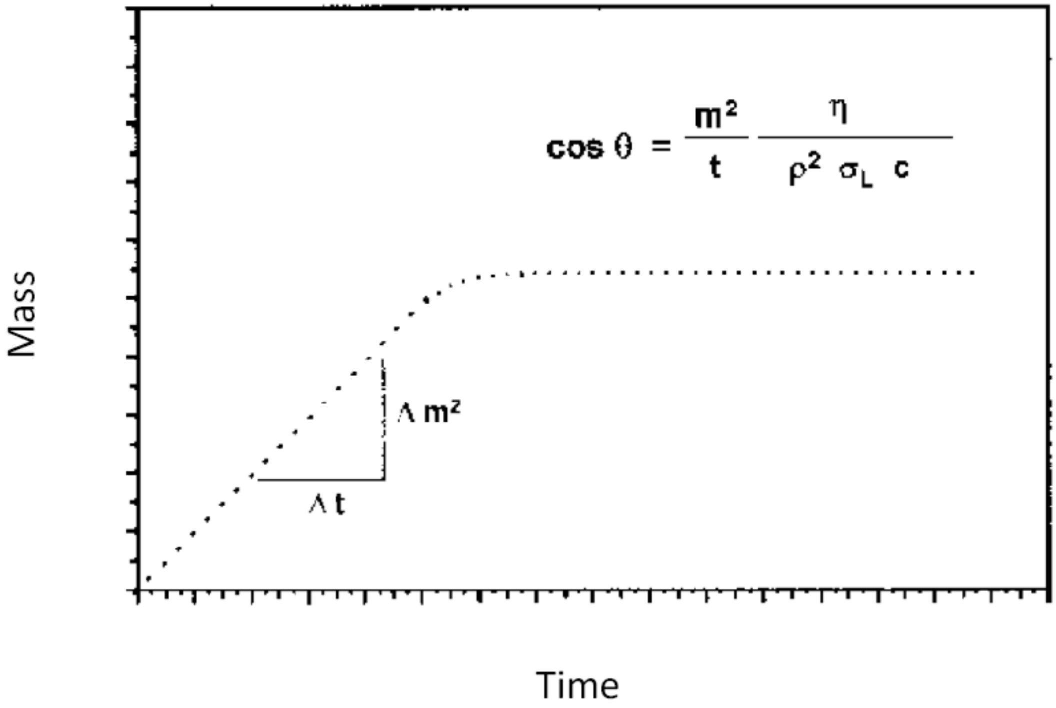


Figure 5.14 – Example plot of Washburn calculation

An attempt to compare the surface energy measured by both the DVS and Capillary Rise test (section 5.3.2) for limestone filler was not possible. This is because a zero contact angle was recorded for multiple probe liquids, these included water, ethylene glycol, diiodomethane, benzyl alcohol, isopropanol, ethanol, toluene and glycerol. This was due to the relatively high surface energy of the limestone filler because any probe liquid with a surface energy less than that of the material to be tested will readily spread on the surface of that material. This either give a zero contact angle or makes it very difficult to obtain a true contact angle value.

Test Results

Overall a number of techniques have been used to measure the surface energy of the different powders being investigated.

The mean spreading pressure for each of probe liquids on limestone filler using the DVS technique are reported in Table 5.9.

The mean contact of probe liquids for sodium formate and sodium silicate using the Washburn technique are presented in Table 5.10.

Surface energy components of the reference materials were computed by applying the Van Oss theory. The total surface energy and the surface energy components are presented in Table 5.11.

The results produced using the different techniques are not directly comparable, however they do provide an indication of the potential surface energy characteristics of the chemicals/filler and confirm whether the reference material is likely to have a high surface energy or a low surface energy.

	Mean Spreading Pressure (mJ/m^2) for each Probe Liquid		
	Octane	Ethyl Acetate	Chloroform
Limestone Filler	26.09	87.82	75.2

Table 5.9 – Mean spreading pressure of probe liquids for limestone filler using dynamic vapour sorption

	Mean Contact Angle (^{o}) for each Probe Liquid				
	Dimethylesulfoxide	Ethyleneglycol	Diiodomethane	Formamide	Water
Sodium Formate	53.3	71.1	83.8	70.1	86.3
Sodium Silicate	58.6	65.6	86.1	54.9	78.2

Table 5.10 – Mean contact of probe liquids for sodium formate and sodium silicate using the washburn technique

	γTotal	γ^{LW}	γ^{AB}	γ^{+}	γ^{--}
Limestone Filler	246.9	55.3	191.6	51.6	178.1
Sodium Formate	26.8	15.1	11.7	2.8	12.4
Sodium Silicate	23.2	16.3	6.9	1.8	6.7

Table 5.11 – Surface energy components of reference materials computed by applying the Van Oss theory

Discussion of Test Results

The chemicals sodium formate and sodium silicate have demonstrated very different physical and surface properties in comparison to limestone filler. These differences are likely to influence the mechanical properties and the anti-icing performance of asphalt.

In terms of the mechanical properties of asphalt:-

- Sodium formate is coarser, less dense and more elongated than standard limestone fillers with significant surface roughness. Sodium formate has a low Rigden Voids and higher maximum packing fraction.
- Sodium silicate is also coarser and less dense than standard limestone fillers, however the particles are spherical in nature and in a consistent manner to limestone filler. The particles are well rounded and smooth. Sodium silicate has a higher Rigden Voids and lower maximum packing fraction.
- The combined effect of these materials may provide similar compactabilty characteristics.

In terms of the anti-icing performance:

- Both sodium formate and sodium silicate have a much lower surface energy than limestone. This may reduce ice adhesion but may make the asphalt more sensitive to water.
- Sodium formate and sodium silicate are both highly soluble at room temperature. The chemicals are likely to be transferred from asphalt pavement surface to promote anti-icing.

6.0 TESTING PROGRAMME

6.1 INTRODUCTION

A number of tests were devised to assess the suitability of a select number of de-icing additives at different formulations for applications as potential anti-icing surface course.

These tests were designed to firstly assess the influence chemical additives have on the mechanical properties of the asphalt, thereby identifying if any reduction in the service life of the surface course is caused by de-icing chemical additives.

The second phase of testing is designed to assess the levels of moisture absorbed by de-icing chemical pavement surface course and the associated impact upon the mechanical properties of asphalt in response to concerns raised by previous products.

The final phase of laboratory testing is designed to determine the anti-icing performance and contributing physical mechanisms that occur when a select range of anti-icing additives are added to the pavement surface course.

The tests conducted in each phase of testing are consistent with the thesis objectives and are shown schematically overleaf in Figure 6.1.

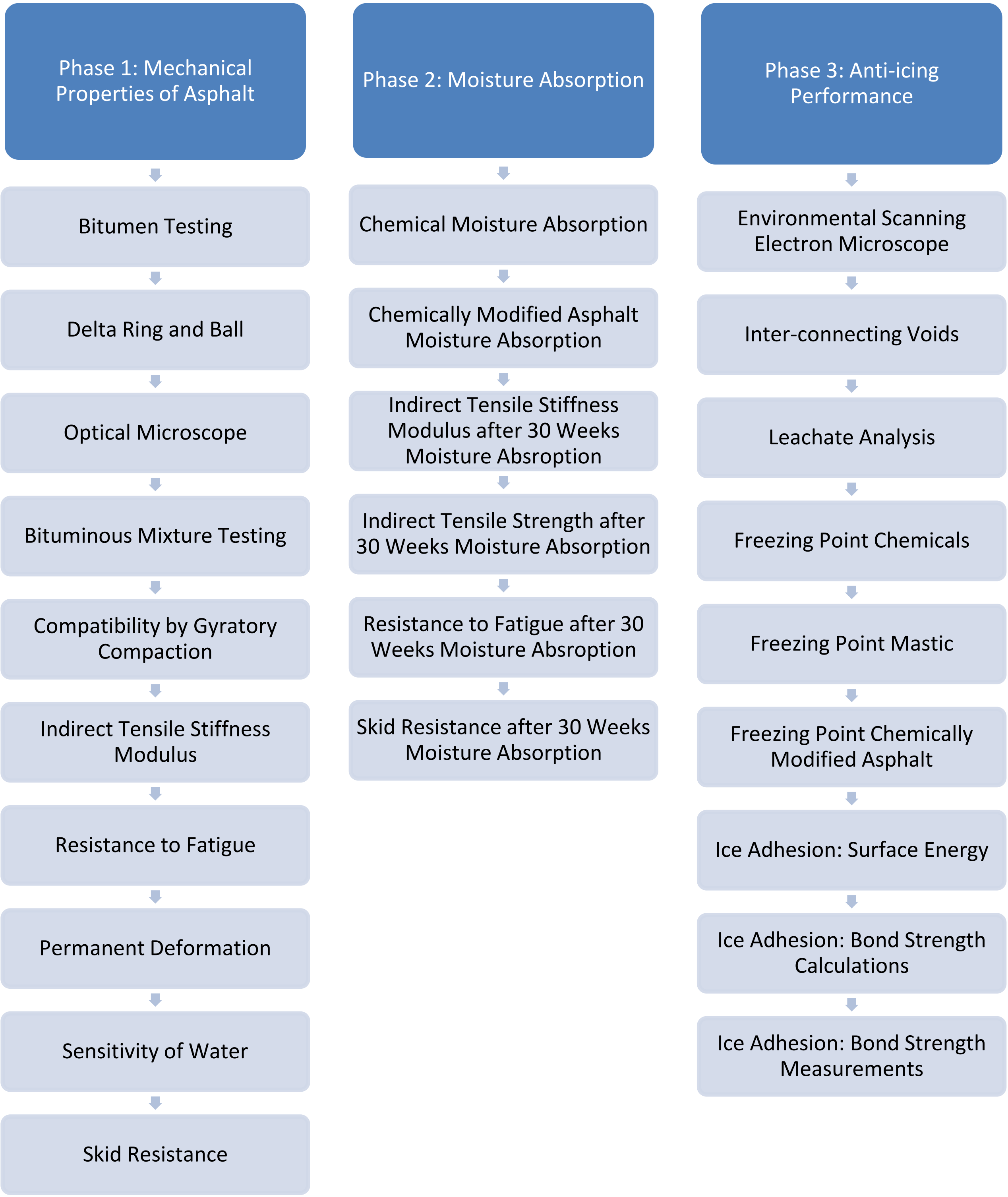


Figure 6.1: Overview of testing phases and test programme

6.2 EXPERIMENTAL PROGRAMME–CHEMICAL FORMULATIONS

The experiment programme is designed to assess the potential of modifying pavement surface courses with two pre-selected chemicals of sodium formate and sodium silicate for anti-icing purposes, see section 4.3 Chemical Additive Selection for Experimental Study.

In order to consider the combined effects and behaviour of these two different chemical modifications, a number of tests will be carried out on the formulations of the two chemicals (termed de-icing chemical formulation from this point). The de-icing chemical formulations considered as part of this study are as follows:

- 100% Sodium Formate (100SF)
- 70% Sodium Formate and 30% Sodium Silicate (70SF 30SS)
- 50% Sodium Formate and 50% Sodium Silicate (50SF 50SS)
- 30% Sodium Formate and 70% Sodium Silicate (30SF 70SS)
- 100% Sodium Silicate (100SS)

The ratios above were designed to cover the full spectrum of ratios between sodium formate and sodium silicate.

6.3 EXPERIMENTAL PROGRAMME - PAVEMENT SURFACE COURSE

The standard pavement surface investigated during this study is a 10mm Stone Mastic Asphalt surface. The surface was selected due to its open aggregate structure, the availability of aggregates and for economic reasons. Due to project constraints, the influences of de-icing chemical formulations on other surface courses were not considered as part of this study.

The Stone Mastic Asphalt surface was formulated to comply with current European specifications set out in "*BS EN 13108-5, Bituminous Mixtures – Material Specifications - Stone Mastic Asphalt*." (BSI 2008) The compliant bituminous mixture comprised of 62% 10mm high PSV aggregate, 32% crushed rock fines and 6% limestone filler which is modified with 0.3% fibres by weight. The properties for the aggregate types used are shown in Table 6.1.

The bitumen used was the preferred paving grade for Stone Mastic Asphalt, this is a 40/60 penetration grade bitumen.

The de-icing chemical formulations were added at 3% by weight and directly replaced 3% of the limestone filler specified in this asphalt mixture.

The results obtained for each of the de-icing chemical formulations are compared against a control specimen. This control specimen is the standard pavement surface with the full amount of filler comprising of limestone filler.

	10mm Coarse Aggregate	Crushed Rock Fines
Particle Size Distribution (Sieve Size)		
14mm	100%	100%
10mm	100%	100%
6.3mm	94%	100%
4.0mm	2%	90%
2.8mm	1%	83%
2.0mm	0%	75%
1.0mm		55%
0.500mm		40%
0.250mm		29%
0.063		14%
Particle Density – Apparent Density (EN 1097-6)	2.720 Mg/m^3	2.770 Mg/m^3
Aggregate Abrasion Value (EN 1097-8)	7.6	3.2 (10/14mm fraction)
Polished Stone Value (EN 1097-8)	70	58 (8/11mm fraction)
Flakiness Index (EN 933-3)	9	15
Water Absorption (EN 1097-6)	0.9%	0.3% (8/11mm fraction)

Table 6.1 – Aggregate properties provided by suppliers

Prior to mixing, the particle size distribution was determined using an excel spreadsheet. It was used to produce a grading curve to ensure the samples complied with the desired particle size distribution set out in BS EN 13108-5.

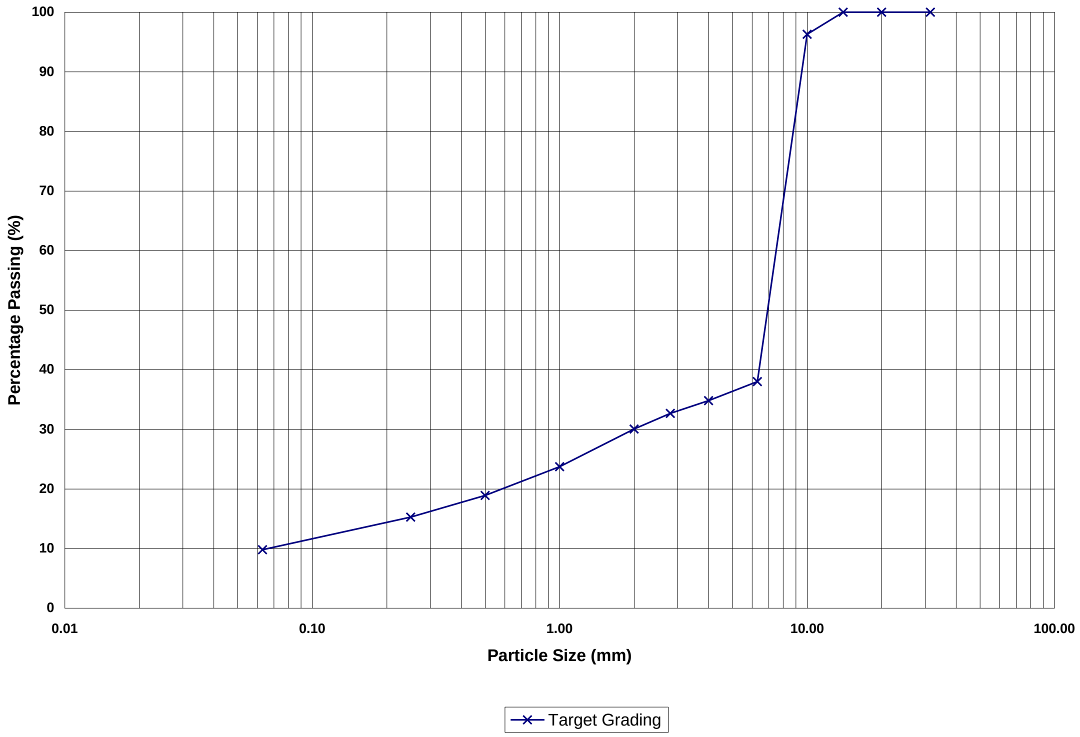


Figure 6.2 Particle size distribution of the control Stone Mastic Asphalt surface course

The grading curve was determined measuring particle size distribution of the aggregates and crushed dust in accordance with "*BS EN 933-1:1997: Tests for geometrical properties of aggregates – Determination of particle size – Sieving method*" (BSI 1997). The particle size distribution for the chemical additives has previously been characterised in Section 5.2.1.

The de-icing chemical formulations produced different grading characteristics, resulting in a slightly coarser mixture. The differences for the mixes were relatively small and the differences in the grading curve were not deemed detrimental to the overall results and would enable a more accurate comparison than changing the percentages of dust and filler to account for any particle size differences.

6.4.0 PHASE 1 – INFLUENCE OF THE CHEMICAL ADDITIVE ON THE MECHANICAL PROPERTIES OF ASPHALT

The influence that the chemical additive has on the mechanical properties of asphalt and the pavement service life is of equal importance to that of the anti-icing performance. This has been highlighted with previous products where despite demonstrating a degree of success at anti-icing, there are problems concerning slipperiness and reduced service life, which have restricted the use of these products.

This phase of testing aims to assess the influence that the select range of anti-icing formulations have on the mechanical properties of asphalt. The objective is considered in two parts, firstly the influence the chemical additives have on the properties of the bitumen and bitumen mastic. Secondly, the influence the chemical additives have on the mechanical properties of asphalt, with specific attention given to the failure mechanisms of previous products.

Testing of the bitumen and bitumen mastic includes:

- Stiffening effects of bitumen by delta ring and ball
- Optical microscopy

Testing of the Mechanical Properties of Asphalt includes the measurement of:

- Compatibility by gyratory compaction
- Indirect Tensile Stiffness Modulus
- Resistance to fatigue
- Permanent deformation using the large wheeltracker
- Sensitivity of water (Work of adhesion calculations, binder affinity, BS EN 12697-12, BBA HAPAS A1 and submerged wheeltracking)
- Skid resistance

6.4.1 INFLUENCE OF THE CHEMICAL ADDITIVE ON THE MECHANICAL PROPERTIES OF BITUMEN

When bitumen is combined with mineral filler, a mastic is formed. This mastic can be viewed as the component of the asphalt mixture that binds the aggregates together. It can also be viewed as the component of the asphalt that undergoes deformation when the pavement is stressed under traffic loading.

The characteristics of the filler sized particles can significantly influence the properties of the mastic, thus the filler properties can have significant effects on asphalt mixture performance. Investigating the influence the filler and/or de-icing chemical formulations have on the mastic is essential in determining the reasons for any variations in the asphalt mechanical performance.

The testing phase of this study will assess the influence of the chemical additives on the properties of bitumen by undertaking optical microscopy and stiffening testing on a range of mastics formulated using de-icing chemical formulations and the control limestone filler.

6.4.2 EXPERIMENTAL PROGRAMME – MASTIC SPECIMENS

Chemical blends of the filler, sodium formate and sodium silicate were manufactured to be volumetrically consistent with the control pavement surface course as highlighted in section 6.3.0. This comprised of 73.9% bitumen and 26.1% filler volumetrically, see Table 6.2. Volumetric proportions can have a significant influence of the behavior of bituminous mastics and in particular the viscosity, as shown by rheological models developed by Einstein (1906),Mooney (1957) and Krieger and Dougherty (1959). The relatively low density of sodium silicate and sodium formate significantly influence the volumetric proportions and physical characteristics of the mastic blend.

The test samples were produced by heating the bitumen at 180^{o}C for two hours. The bitumen was weighed to the nearest 0.1g and returned to the oven for 30 minutes to achieve target temperature. The chemicals and fillers were weighed to the nearest 0.1g and stirred to form a uniform blend.

The bitumen and filler component were mixed by hand. This process involved placing the bitumen on a hot plate and continuously stirring while adding small proportions of the filler component until the sample visually appeared to be uniform.

During the mixing process it was observed that when filler formulations containing sodium silicate were added to the bitumen a significant proportion of bubbling and volumetric expansion occurred. This bubbling lasted for the process of mixing, however after the 30 minute reheating period the bubbling effect had disappeared. This phenomenon is likely to be due to the high moisture content (18.5%) of the sodium silicate, resulting in a foaming effect of the bitumen.

Foaming of bitumen has traditionally been used to allow easier coating of aggregate particles by increasing the volume of the binder in the mix, thereby improving the workability and compactability of the finish product.

	Control - Filler		100SF			70SF 30SS			
Component of Specimen	40/60 Pen Bitumen	Limestone Filler	40/60 Pen Bitumen	Sodium Formate	Limestone Filler	40/60 Pen Bitumen	Sodium Formate	Sodium Silicate	Limestone Filler
Gravimetric Proportion (%)	51.0	49.0	51.0	16.7	24.5	51.0	11.9	4.6	24.5
Density (Mg/m^3)	1.03	2.80	1.03	1.94	2.80	1.03	1.94	1.75	2.80
Volumetric Proportion (%)	73.90	26.10	73.90	13.05	13.05	73.90	9.17	3.93	13.05

	50SF 50SS				30SF 70SF				100SS		
Component of Specimen	40/60 Pen Bitumen	Sodium Formate	Sodium Silicate	Limestone Filler	40/60 Pen Bitumen	Sodium Formate	Sodium Silicate	Limestone Filler	40/60 Pen Bitumen	Sodium Silicate	Limestone Filler
Gravimetric Proportion (%)	51	8.5	7.7	24.5	51	5.1	10.5	24.5	51	15.4	24.5
Density (Mg/m^3)	1.03	1.94	1.75	2.80	1.03	1.94	1.75	2.80	1.03	1.75	2.80
Volumetric Proportion (%)	73.90	6.53	6.53	13.05	73.90	3.93	9.17	13.05	73.9	13.05	13.05

Table 6.2 – Volumetric proportions of mastics

6.4.3 OPTICAL MICROSCOPY

Introduction

Optical microscopy refers to the magnification of samples using a microscope reliant on a light source. Images from the microscope are viewed and qualitatively analysed to determine the dispersion and structure of the chemical within the bitumen.

Test Procedure

Slides were produced by manufacturing bituminous mastics in accordance with Section 6.4.1. A small sample of the bituminous mastic was then sampled using a heated metal rod and the sample deposited onto a preheated glass slide. The slide was viewed under a range of magnifications using an appropriate light source and images were taken from the microscope.

Test Results

A number of images were taken from the optical microscope for a range of de-icing formulations. The images were analysed to determine any differences in the particle arrangements and dispersion. A select range of the images from the optical microscopy can be found in Figures 6.3 to 6.5.

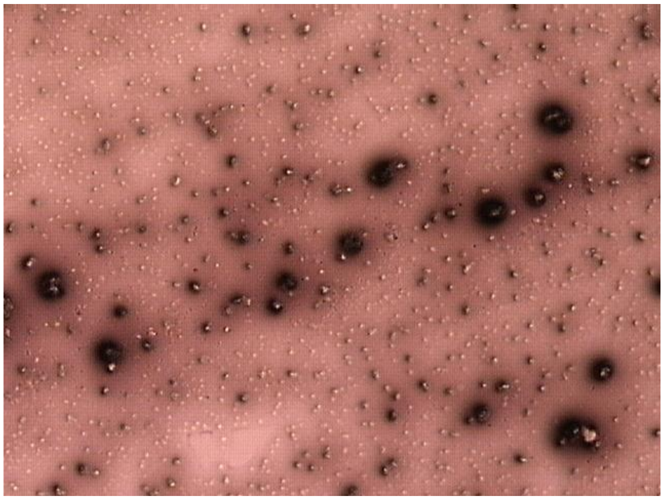


Figure 6.3 – Chemical formulation of 70% Sodium Formate 30% Sodium Silicate at a magnification of 10x.

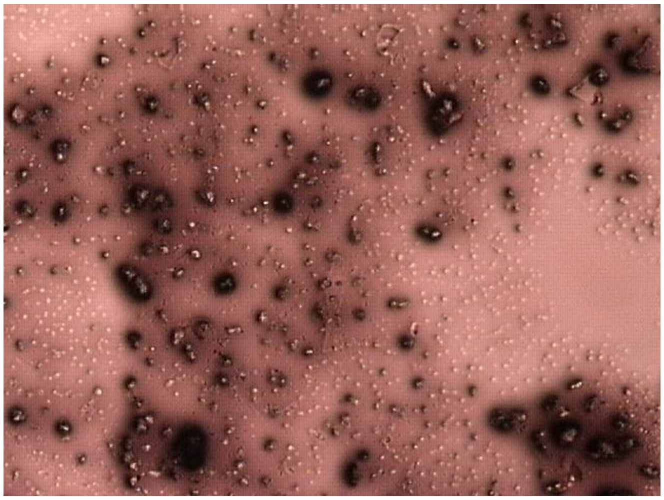


Figure 6.4 – Chemical formulation of 50% Sodium Formate 50% Sodium Silicate at a magnification of 10x.

Figure 6.5 – Chemical formulation of 30% Sodium Formate 70% Sodium Silicate at a magnification of 10x.

Discussion of Test Results

Optical microscopy slides identified that the chemicals were equally dispersed, with no significant structural differences. Identification of exact chemical locations was not detectable visually. The quality of images produced was highly dependable on the method of slide manufacturing.

6.4.4 INVESTIGATION OF ADDITIVE STIFFENING EFFECT ON BITUMEN

Introduction

Delta Ring and Ball is a standard test procedure for determining the stiffening effect of filler when mixed with bitumen.

It is based on the softening point test. The softening point test has been commonly used for many years to determine the consistency of bitumen. In the test, two brass rings filled with bitumen were prepared and placed in a beaker with liquid, usually water (although glycerol can be used for materials with softening points higher than 80^{o}C).

A steel ball was placed on each ring and the samples were heated at a rate of 5^{o}C per minute until the bitumen is soft enough to allow the ball to drop through the bitumen and touch a plate mounted 25mm below the rings. The softening point of the bitumen is defined as the temperature at which this occurs.

Test Procedure

Delta Ring and Ball tests are conducted in accordance with BS EN 13179:2000 (BSI 2000) and follow the standardised Softening Point Test procedure.

The Delta Ring and Ball test procedure is based on comparing the softening point of mastics prepared to a standard volume to the softening point of the penetration grade bitumen. The Delta Ring and Ball value is recorded and the difference in the softening point between the penetration grade bitumen and the mastic.

The standard Delta Ring and Ball test procedure presented in BS EN 13179:2000 is based on a composition of 0.375 filler to 0.625 bitumen and using a 100/170 pen bitumen. For consistency with asphalt mixture design these formulations have been modified and are based on the volumetric proportions presented in Table 6.1 using a 40/60 pen bitumen. Testing was conducted twice for each mastic and the mean of the results taken as the Delta Ring and Ball.

Test Results

The mean results for the measured softening point and computed Delta Ring and Ball are displayed below in Table 6.3.

De-Icing Chemical Formulation	Mean Softening Point (^{o}C)	Δ Delta Ring and Ball (^{o}C)
40/60 Bitumen	54.4	-
Control – Limestone Filler	60.9	6.5
3% 100SF	60.5	6.1
3% 70SF 30SS	62.4	8.0
3% 50SF 50SS	62.5	8.1
3% 30SF 70SS	63.0	8.6
3% 100SS	63.9	9.5

Table 6.3 – Mean Delta Ring and Ball results

Discussion of Test Results

The Delta Ring and Ball testing has demonstrated differences between the softening point of the control limestone filler mastic and the de-icing chemical formulations. The Delta Ring and Ball temperature significantly increases with sodium silicate content. The inclusion of sodium formate results in a slight lower Delta Ring and Ball temperature relative to the control mastic.

Combinations of the two chemicals are highly dependent on the sodium silicate content. The inclusions of sodium silicate is therefore likely to impact upon on the performance of bitumen mastic and also the mechanical properties of asphalt.

A number of rheological models to describe the increase in viscosity caused by increasing quantities of solid particles in suspension have been derived. The first model was developed by Einstein (1906) Several later models such as Mooney (1957) and Krieger and Dougherty (1959) developed the Einstein model by introducing the term maximum packing fraction. The equation for Mooney (1957) and Krieger and Dougherty (1959) are shown below, respectively.

Mooney (1957) equation:-

$$\eta = \eta_0 \exp\left(\frac{[\eta]\phi}{1 - \frac{\phi}{\phi_{\max}}} \right)$$

(Eq. 6.1)

Krieger and Dougherty (1959) equation:-

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_{\max}} \right)^{-[\eta]\phi_{\max}}$$

(Eq. 6.2)

Where:

η = the viscosity of the suspension,

η_0 = the viscosity of the liquid phase,

$[\eta]$ = the intrinsic viscosity of the solid phase and

ϕ = the solid phase volume

ϕmax= the maximum packing fraction

To understand the reasons behind the differences in Delta Ring and Ball results the rheological models have been considered. In particular the maximum packing fraction (ϕmax) has been considered based on Ridgen Voids, as shown previously in Table 5.4. The maximum packing fraction is defined as 'the solid volume content of a suspension at which the viscosity of the suspension becomes infinite' (Taylor 2007). It has been consistently found to be the best single property of the filler.

The maximum packing fraction relates the increase in stiffness or the reduction in flow of the mastic when filler is added. The combined effects of particle size distribution, particle size, shape and density are encompassed in this key property of fillers.

Considering the models above, the increase in stiffness can be attributed to the maximum packing fraction. As the mastic produced in Delta Ring and Ball tests was manufactured at a fixed volumetric ratio, the solid volume fraction (ϕ) is fixed. The Delta Ring and Ball value should therefore be related to the maximum packing fraction of the filler in the rheological model as the effects of solid volume are scaled by maximum packing fraction.

On this basis, the relatively high maximum packing fraction of sodium formate should result in the lowest Delta Ring and Ball value. In contrast the lower maximum packing fraction of sodium silicate should result in the highest Delta Ring and Ball value.

By plotting the maximum packing fraction against the Delta Ring and Ball value, the relationship between the two parameters can be determined. The relationship between maximum packing fraction and Delta Ring and Ball is displayed in Figure 6.6, below.

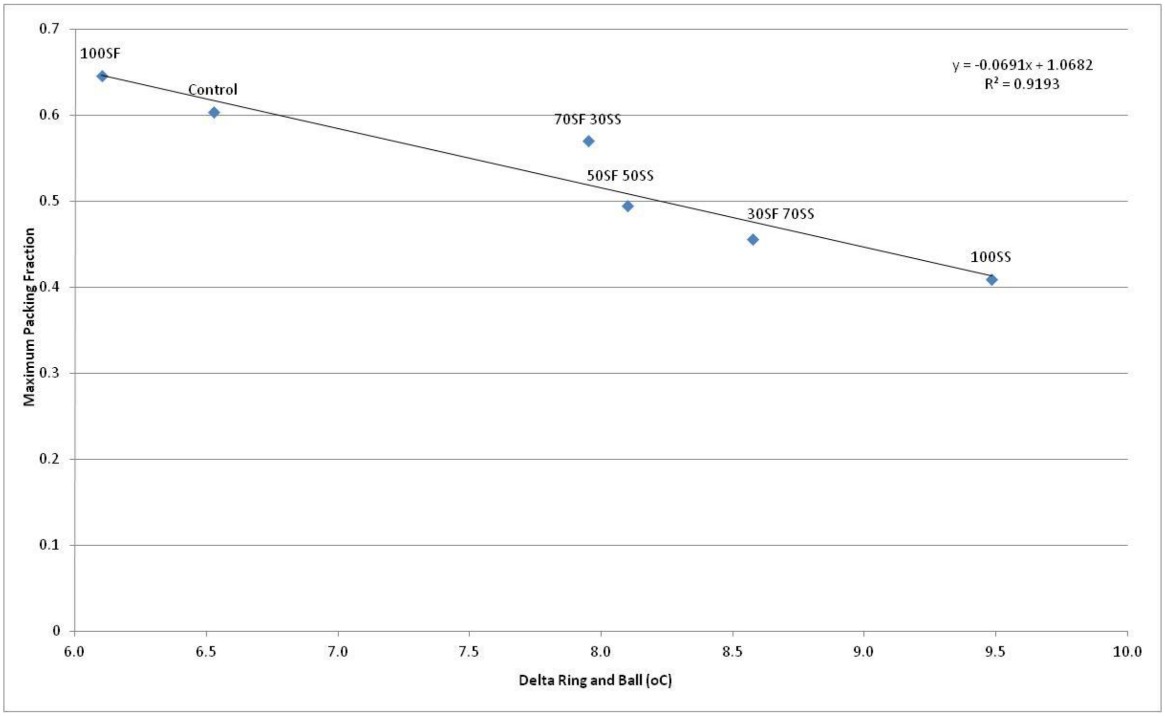


Figure 6.6 – Maximum Packing Fraction against Delta Ring and Ball for each mastic

This figure demonstrates that a relationship between Delta Ring and Ball and maximum packing fraction is consistent for these de-icing chemical formulations. Fillers with lower maximum packing fraction such as sodium silicate result in higher ratios of the solid phase volume relative to the maximum packing fraction (ϕ/ϕmax) and results in larger increases in softening point.

6.4.5 INFLUENCE OF THE CHEMICAL ADDITIVE ON THE MECHANICAL PROPERTIES OF ASPHALT

The influence that the chemical additive has on the mechanical properties of asphalt and the pavement service life is of equal importance to that of the anti-icing performance. The testing phase will address these issues by undertaking fundamental asphalt performance tests. These have been designed to cover the range of failure mechanisms or concerns related to previous products.

This testing will consist of gyratory compaction due to the concerns of inadequate compaction of previous products.

Indirect Tensile Stiffness Modulus, resistance to fatigue, water sensitivity and permanent deformation testing have been undertaken to assess the likely service life of such products.

Finally, skid resistance testing has been conducted due to previous concerns regarding slipperiness of such products.

6.4.6 MANUFACTURE OF ASPHALT SPECIMENS

The modified Stone Mastic Asphalt surface courses (as described in 6.3) were manufactured in accordance with "*BS EN12697-35:2004 Bituminous Mixtures – Test Methods for Hotmix Asphalt: Laboratory Mixing*" (BSI 2004) using a Freundl laboratory mixer. The bituminous mixture was manufactured at a target temperature of 155°C as specified for the selected grade of bitumen used.

Prior to mixing, the aggregates and filler were prepared by drying to constant mass and weighing the correct quantity required using a balance with an accuracy of 2g for the aggregate fractions and 0.1g for the limestone filler/de-icing chemical formulations.

The appropriate quantities of the aggregate and filler were then placed in a ventilated oven at target temperature for a minimum of 8 hours.

The binder was prepared in accordance to "BS *EN 58:2004 Bituminous and Bituminous Binders – Sampling Bituminous Binders*" (BSI 2004) and heated to target temperature for the duration of between 3.0 to 5.0 hours. The bitumen was then manually stirred and the temperature was verified.

The de-icing chemical formulations were prepared by passing the individual chemicals through a 4mm sieve to ensure that the chemical additive was broken down and to avoid caking of the chemical. The chemical additive formulation was weighed to the correct weight and bottle rolled for approximately 1 hour at a speed of 30RPM to ensure that the de-icing chemicals formed a uniform blend.

Before mixing commenced, the Freundl mixer bowl was pre-heated to the target temperature with an accuracy of 0.1^{o}C. The aggregate samples and filler were weighed into the mixing bowl and allowed to reheat to target test temperature.

The aggregate and filler were mixed for precisely 1 minute at a speed of 50RPM. The cold additive and fibres were added and mixed for a further minute. The bitumen was added and checked by weighing the container before and after to ±1% of the mass. This was mixed for a further 3 minutes until a homogenous mixture was obtained and the aggregate was entirely coated with the binder.

Throughout this phase of testing, quality was controlled by ensuring each component of bituminous mixture was from the same batch and each specimen was correctly sampled and stored in an appropriate manner, as specified by the manufacturer.

6.4.7 INVESTIGATION OF COMPACTIBILITY USING GYRATORY COMPACTION

Introduction

Compactability refers to the ease at which under a compactive effort the density of material can be increased and the air void content reduced. Compaction of asphalt is critical if the material is to perform to its full potential.

A well-compacted homogeneous asphalt layer will be more resistant to rutting, crack initiation and propagation relative to a poorly compacted material.

The addition of a de-icing chemical as a filler replacement to the bituminous mixture may influence the workability/compactibility of the material.

Poor compaction has previously been attributed to reduced service life (e.g. the Verglimit product), therefore compactability measurements form a key part of this study.

The compactibility of a material can be measured using a gyratory compactor to determine the air void content over a number of gyrations. The gyratory compaction involves compacting cylindrical specimens of bituminous mixtures by combining a rotary shearing action and a vertical resultant force applied by a mechanical head.

Test Procedure

Gyratory Compaction testing was conducted in accordance with "*BS EN 12697–31:2007 Bituminous mixtures – Test methods for hot mix asphalt – Specimen preparation by gyratory compactor*" (BSI 2007).

The test consists of applying a compaction pressure of 600kPa in a gyratory motion to 150mm diameter cylindrical specimens. The test is repeated three times for each formulation. Prior to testing, the mould was configured and placed in a ventilated oven at the test temperature of 155^{o}C for a minimum of 2 hours.

The mass of the mixture was calculated in accordance with BS EN 12697–31:2007 6.1.2 Equation 1. It is based on the internal diameter of 150mm, a minimum height of 150mm and the maximum density calculated from the particle density of each constituent.

The filled mould was placed in a ventilated oven at a temperature of 155^{o}C, for a minimum 30 minutes prior to testing. Following this, the specimen was placed in the gyratory compactor and the height and density of the specimen was measured over 200 gyrations. This process was repeated for three specimens and the results averaged to produce density vs. number of gyrations and air voids vs. number of gyrations curves.

Test Results

Gyratory compaction testing was carried out to determine if the addition of a de-icing chemical to the bituminous mixture may influence the compactibility of the material. The change in density was recorded for each specimen over a period of 200 gyrations, as displayed in Figure 6.7 for each de-icing chemical formulation.

The data presented in Figure 6.7 demonstrates that the differing de-icing chemical formulations reach different densities over the period of 200 gyrations. This observation can be expected due to different particle densities of the limestone filler, sodium formate and sodium silicate.

To allow for the different particle densities and understand the effect that de-icing chemical formulations have on compactability this data has to be translated into air voids.

The air void content can be calculated based on the maximum density of the bituminous mixture as defined in BS EN 12697-8:2003 "*Determination of void characteristics of bituminous specimens*". In this experiment the maximum density was determined based on the theoretical maximum density based on the measured particle density for the limestone filler and chemical components as shown in Table 6.4.

Bituminous Mixture Formulation	Theoretical Maximum Density (kg/m^3)
Control – No Additive	2471
3% 100SF	2444
3% 70SF 30SS	2441
3% 50SF 50SS	2439
3% 30SF 70SS	2438
3% 100SS	2435

Table 6.4 –Maximum density used in calculation

Alternative methods for calculating the maximum density of bituminous mixtures exist, for example the volumetric method. This method involves measuring the volume of the sample by the displacement of water in a pyknometer.

The volumetric method was not used because it is acknowledged that de-icing chemicals are water soluble and may not give a true reading.

The adjusted data showing air void content against number of gyrations for each de-icing formulation is demonstrated in Figure 6.8.

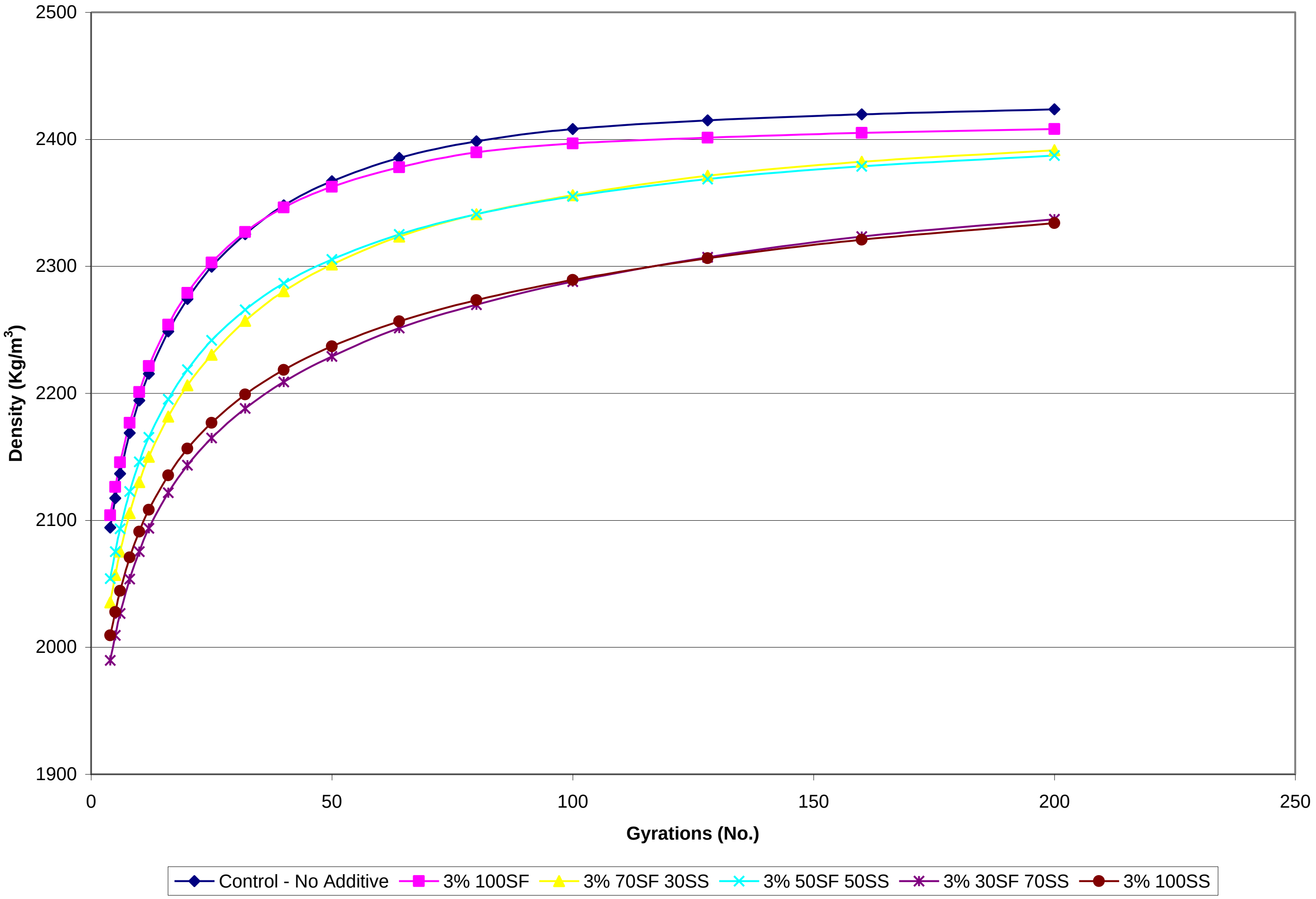


Figure 6.7 – Density against number of gyrations for each de-icing formulation

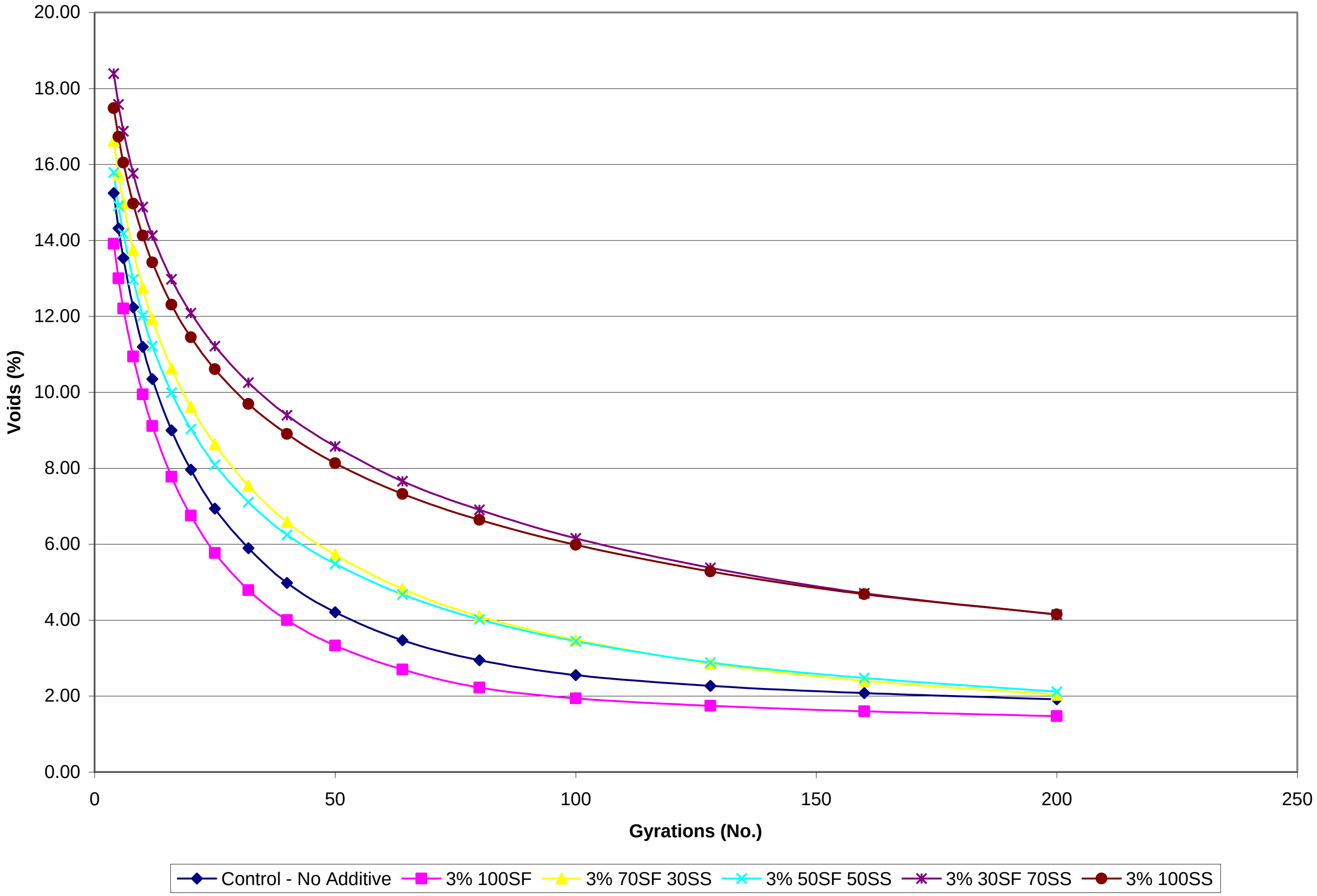


Figure 6.8 – Void Content against number of gyrations for each de-icing formulation

Discussion of Test Results

The measured air void content against the number of gyrations in Figure 6.8, demonstrates that the addition of 100% sodium formate marginally improves the compactability of the asphalt specimen by approximately 0.45% air voids after 200 gyrations.

There are negligible differences between the compactiblity of the control and additions of 50% sodium formate and 50% sodium silicate, 70% sodium formate and 30% sodium silicate after 200 gyrations.

Additions of sodium silicate reduce the compactability of the bituminous mixture and could affect the overall performance of the material. This is demonstrated with a 3% addition of 30% sodium formate and 70% sodium silicate blend and the 100% sodium silicate increasing, the compacted air void content at 200 gyrations by 2.23% and 2.24%, respectively. This relative increase in air void content is considered significant based on the repeatability limits of 0.95% air voids defined as part of the precision levels of the BS EN 12697-31 test method.

The variations in compaction correlate to the measured Delta Ring and Ball and the maximum packing fraction results in Section 6.4.4. This relationship between Delta Ring and Ball and air void content at 200 gyrations is shown in Figure 6.9. This confirms that the differences in compaction are directly correlated to the stiffening effects of the bitumen caused by the addition of the de-icing chemical formulations.

Sodium silicate provided the greatest increase in the softening point due to the lowest maximum packing fraction as demonstrated in Section 6.4.4. The increase stiffness of the sodium silicate mastic reduced the viscosity of the bitumen and resulted in the highest air void content for a given compaction. This stiffening affect was more prevalent than the foaming of the bitumen due the high moisture content of sodium silicate and the compatibility of the mixture was reduced.

In contrast, sodium formate provided the least increase in the softening point due to the highest maximum packing fraction as demonstrated in Section 6.4.4. Thereby, resulting in a higher viscosity relative to the other de-icing formulations and resulting in the lowest air void content for a given compaction.

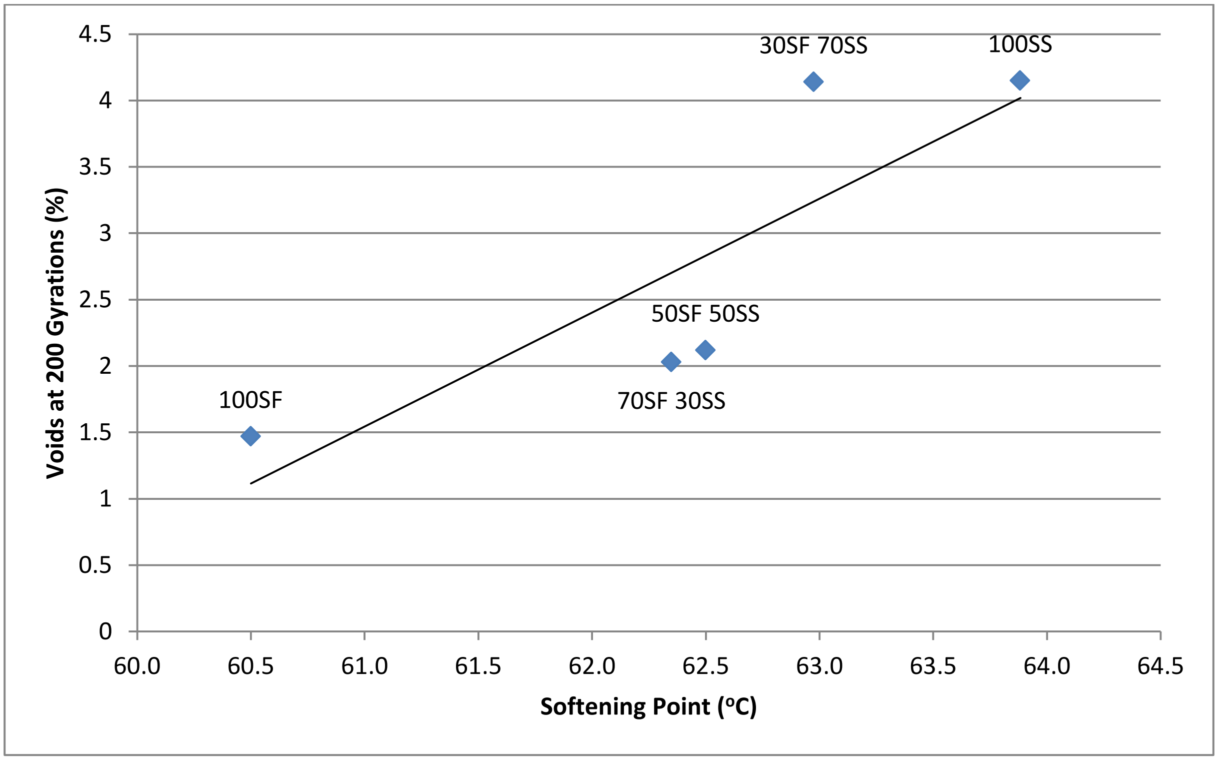


Figure 6.9 – Voids at 200 gyrations against softening point for each mastic

6.4.8 INVESTIGATION OF INDIRECT TENSILE STIFFNESS MODULUS

Introduction

Stiffness is a measure of the resistance of a material to deform under an applied load. Stiffness is an important material property when designing pavements and is both temperature and loading rate dependant.

Stiffness modulus testing is a procedure used to rank bituminous mixtures on the basis of stiffness and it is used as a guide to the relative performance of the material in the pavement and its structural behaviour.

The stiffness modulus of bituminous mixtures can be determined in the laboratory by several test methods such as repeated load beam test, uniaxial repeated load test and indirect tensile test.

In the UK, the Indirect Tensile Stiffness Modulus (ITSM) test method using the Nottingham Asphalt Tester (NAT), which is a non-destructive method, has been widely adopted for determination of stiffness modulus values.

The ITSM was determined for the range of de-icing chemical formulations using the Nottingham Asphalt Tester in accordance with “*BS EN 12697-26:2004 Bituminous Mixtures – Test Methods for hotmix asphalt: stiffness, Appendix C ITCY*”.

The testing principle involves deforming suitable shaped asphalt specimens in their linear range under repeated loads. The amplitude of the stresses and strains are measured together with the phase difference between stresses and strains.

Test Procedure

Testing was carried out on six cylindrical specimens manufactured using the bituminous mixture produced by section 6.4.2.1 and compacted by impact compaction in accordance with "*BS EN 12697–30:2004 Bituminous Mixtures – Test Methods for Hotmix Asphalt: Specimen preparation by impact compaction*". This method was selected due ease of manufacturing a higher number of specimens. A compaction of 50 blows per face was applied. The specimens were manufactured by placing a predetermined weight to give a desired height of 63.5mm into a 100mm steel compaction mould.

Following extrusion, the test specimens were weighed and measured to determine the bulk density and air void content in accordance with BS EN 12697-29:2002 and the test specimens were marked with two diameters at 90 ± 10^{o} to each other.

Testing was carried out using a Cooper's Nottingham Asphalt Testing Machine, comprising of a loading frame containing two stainless steel loading strips suitable for supporting the cylindrical specimen, a Linear Variable Differential Transformer (LVDT) mounting frame with transformers and a load actuator capable of applying the repeated load, see Figure 6.10.

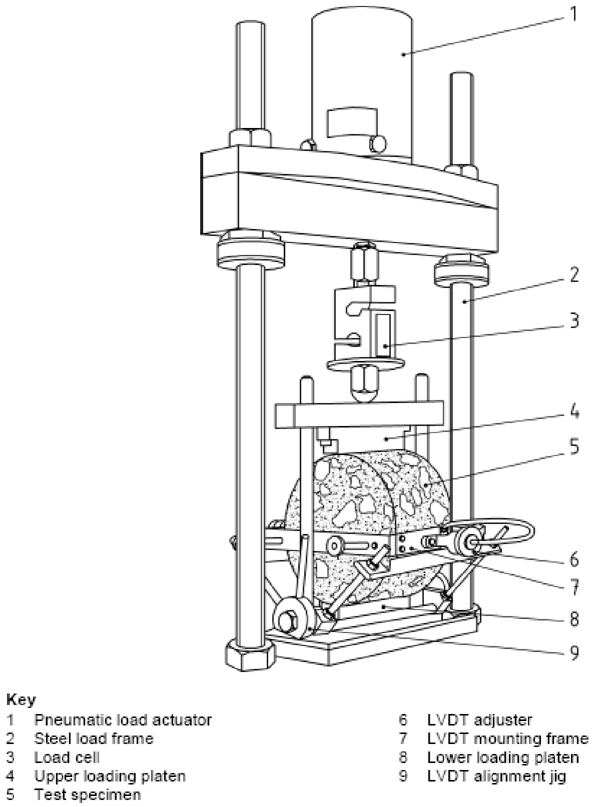


Figure 6.10 - Testing of ITSM using a Nottingham Asphalt Tester

Testing was then conducted in full accordance with "*BS EN 12697-26:2004 Bituminous Mixtures – Test Methods for hotmix asphalt: stiffness, Appendix C ITCY*", by applying the following test conditions:-

- Test temperature 20^{o}C
- Rise time (124 ± 4) ms
- Horizontal deformation (5 ± 2) µm
- Poisson ratio 0.35
- Load area factor of 0.60

Test Results

Indirect tensile stiffness modulus testing was carried out using the Nottingham Asphalt Tester to determine the effect varying chemical formulations have on the stiffness of the material. Testing was carried out on six cylindrical specimens with each specimen tested in two orientations. The results of the test were electronically adjusted to a load area factor of 0.60 and averaged. These results are summarised in Table 6.5.

Additive	ITSM (MPa)	ITSM ratio of chemical additive and control	Standard Deviation
Control – No Additive	4621	-	263
3% 100SF	4281	0.93	248
3% 70SF 30SS	4828	1.04	363
3% 50SF 50SS	6200	1.34	693
3% 30SF 70SS	5316	1.15	439
3% 100SS	6538	1.41	435

Table 6.5 – Indirect Tensile Stiffness Modulus for the specific chemical formulations

Discussion of Test Results

The initial indirect tensile stiffness modulus data for each chemical formulation demonstrates that replacing a percentage of limestone filler with a de-icing chemical formulation does not significantly reduce the stiffness of the material. The chemically modified pavement surface course maintains the ability to spread the load exerted on the pavement surface course by trafficking.

The only reduction observed in Indirect Tensile Stiffness Modulus was for a 3% addition of sodium formate resulting in a 7% reduction in indirect tensile stiffness modulus.

The alternative de-icing chemical formulations have demonstrated varying degrees of increased stiffness, ranging from a 4% increase to a maximum increase of 41%. This increase in stiffness is dependent on the sodium silicate content as demonstrated in Figure 6.11.

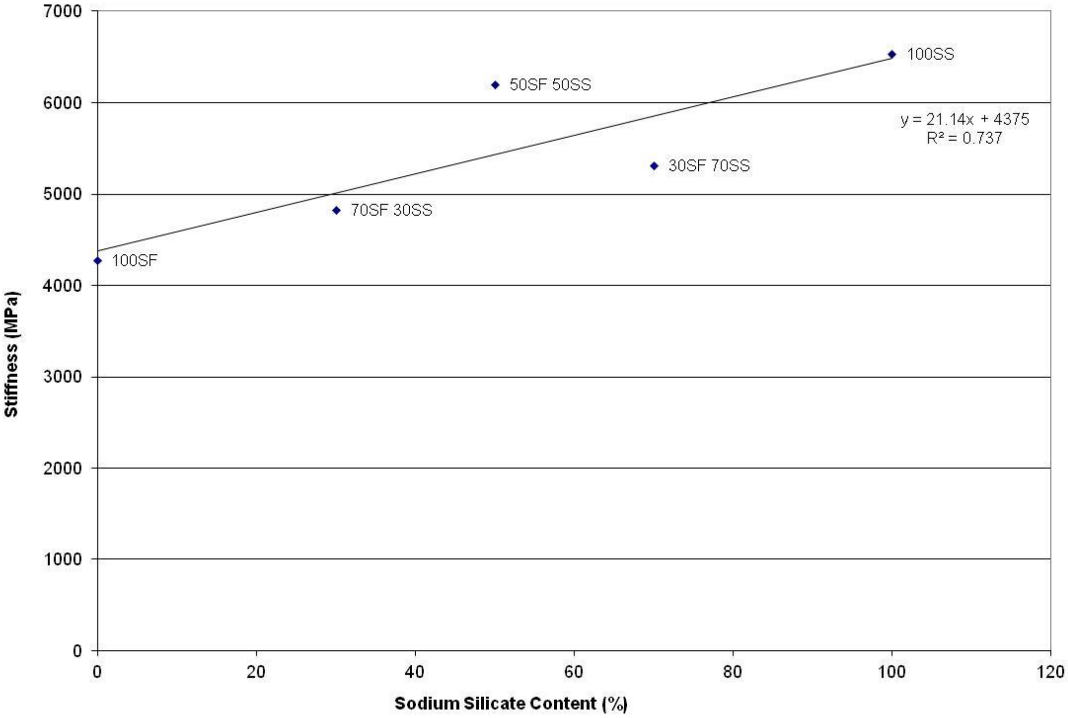


Figure 6.11 Indirect Tensile Stiffness Modulus against sodium silicate content

An increased stiffness is commonly viewed as being beneficial to the load spreading ability and the deformation and/or fatigue resistance of the structure. The increases in stiffness for the de-icing formulations are therefore generally considered positive.

Whilst this is potential positive, it is important to recognise the potential for the material to become overly stiff and exhibit a brittle nature including as the bitumen ages and oxidizes.
As the bitumen becomes brittle its ability to support traffic-induced stresses and strains may significantly reduce, this can lead to cracking. The 41% increase in stiffness for the 100% sodium silicate addition could be considered excessive relative to the control and potentially lead to durability problems.

Considering the aggregate structure is consitent for all mixes, the variations in the asphalt stiffness can be attributed to the stiffening effects that the de-icing chemical formulations have on the bitumen. This relationship is demonstrated in Figure 6.12.

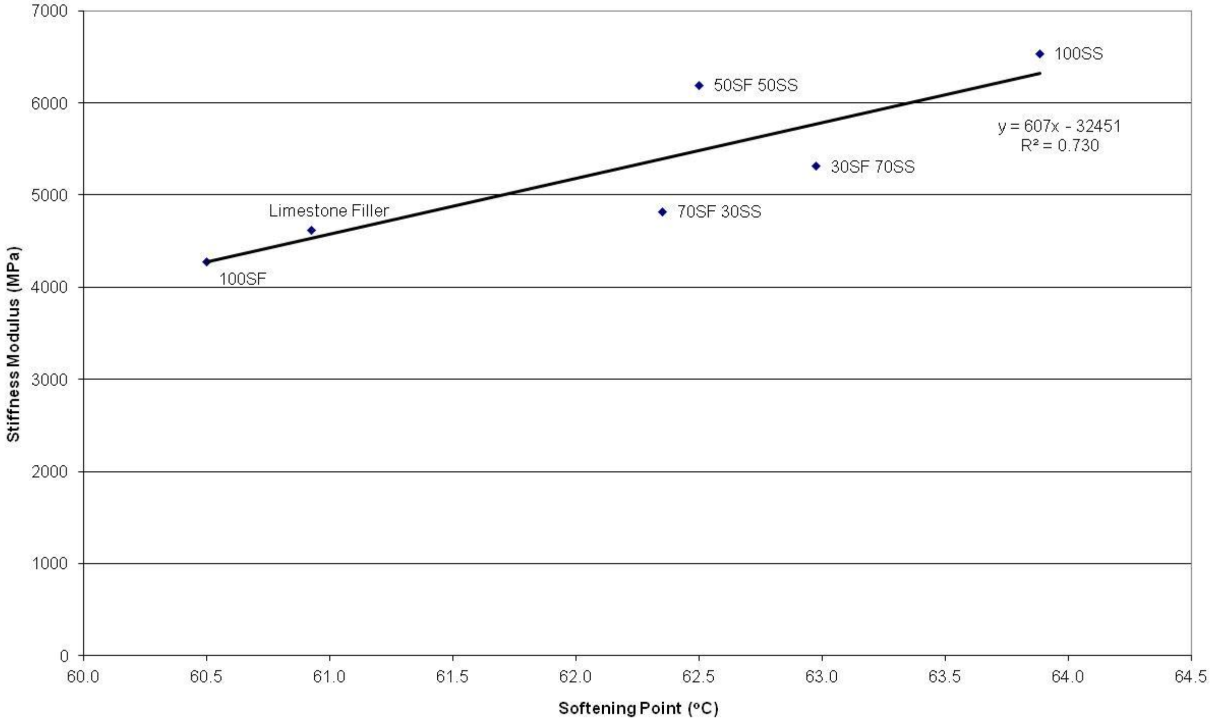


Figure 6.12 – Indirect Tensile Stiffness Modulus against softening point

Figure 6.12 shows a direct relationship between the stiffening effecting that the de-icing chemical formulations have on the bitumen and the stiffness of the bituminous mixture. The reasons for the differences in the stiffening affects the de-icing chemical formulations have on the stiffness of bitumen have been explained previously in section 6.4.4, which concluded:-

- The relatively high maximum packing fraction of sodium formate results in the lowest Delta Ring and Ball value and has the least stiffening affects.
- The lower maximum packing fraction of sodium silicate results in the highest Delta Ring and Ball value and has the greatest stiffening affects.

6.4.9 RESISTANCE TO FATIGUE

Introduction

Fatigue is defined as the `*phenomenon of cracking under the repeated application of a stress that is less than the tensile strength of the material*` (Read and Whiteoak 2003). It consists of two main phases, crack initiation and crack propagation.

Fatigue is one of the main failure modes of a pavement structure which results in degradation of the bound pavement materials and finally the pavement structure. Fatigue cracking of pavement base layers has received more attention from the research community than any other deterioration mechanism.

Resistance to fatigue is a fundamental characteristic of any asphalt surface course and historical evidence suggests this is a particular problem for chemical modified anti-icing surface courses. The two chemical modified surface courses of Verglimit and Grikol, discussed in Sections 3.7 and 3.9 respectively, experienced varying degrees of cracking, resulting in significantly reduced service lives. For this reason, the resistance to fatigue for the asphalt surface courses modified by the various de-icing chemical formulations will form an extensive part of this research project.

Fatigue characteristics of specific mixtures are usually evaluated over a range of traffic and environmental conditions. The charcterisation of fatigue behavior of a bituminous mixture generally involves the application of either a controlled stress or a controlled strain, with the fatigue relationship typically expressed between the initial stress or strain and the number of load repetitions to failure.

It has been suggested by many researchers (Read 1996 and Santucci and Schmidit 1969) that controlled stress mode of loading is applicable to thick bituminous pavements (>150mm), whilst controlled strain tests are applicable to thinner bituminous pavements (<50mm).

In a controlled stress test, a constant repeated load amplitude is applied and the displacement of the specimen is monitored in order that the strain resulting from the applied load can be calculated (Osman 2004). The formation of the initial crack is quickly followed by rapid crack propagation and complete specimen failure.

In a constant stain test the strain amplitude remains constant. As damage accumulates the stress required to maintain the initial strain gradually decreases after crack initiation as the stiffness of the mixture effectively decreases (Osman 2004). In this mode of testing, when the cracks initiates to maintain the same strain level, a reduction in stress occurs around the crack. Crack propagation is therefore relative slow compared with a controlled stress test.

In controlled stress tests higher stiffness results in longer life, where as in controlled stain mode stiffness has the opposite affect (Brown 1978).

The fatigue failure of a specific asphalt mix can be characterised by the slope and relative level of the stress or strain versus the number of load repetitions to failure on a log-log plot, see Figure 6.13.

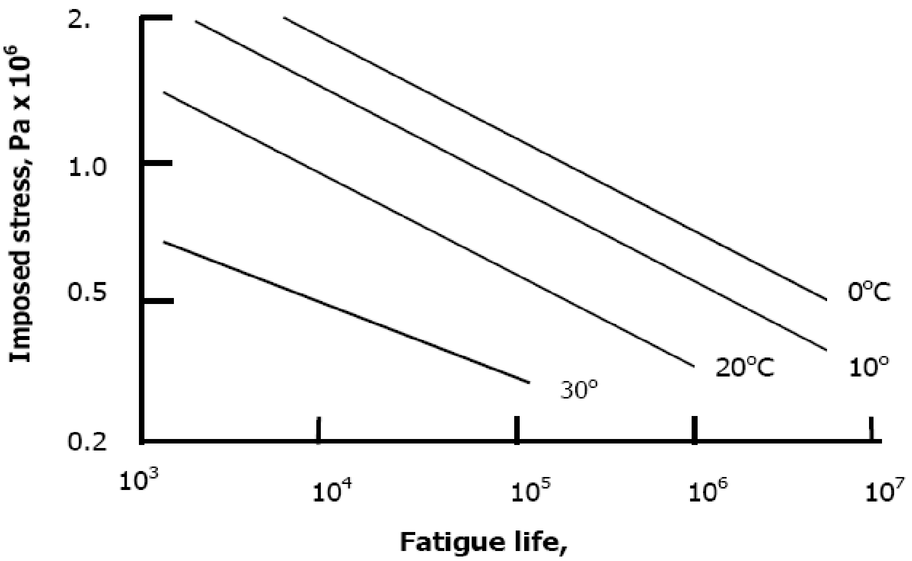


Figure 6.13 – Typical plot of fatigue resistance for various temperatures

The general relationship defining the fatigue life based on crack initiation is typically described using the following equation:

$$Nf = C\left(\frac{1}{\varepsilon t}\right)^{m}$$

(Eq. 6.3)

where:

Nf = number of load applications to initiate a fatigue crack

ε*t* = maximum value of applied tensile strain

c, m = factors depending on the composition and properties of the mixture

A number of different methods of measuring resistance to fatigue are currently used to measure the performance of bituminous materials. These include two point bend on trapezoidal specimens, two, three and four point bending tests on prismatic specimens and indirect tensile testing on cylindrical specimens.

Test Procedure

The indirect tensile fatigue test (ITFT) was conducted to the draft standard *DD ABF – 2000 –* "*Method for the determination of the fatigue characteristics of bituminous mixtures using indirect tensile fatigue*" (BSI, 2000).

Controlled stress testing was carried out at a standard temperature of 20±1^{o}C, with a minimum of ten 100mm diameter specimens. These 100mm diameter specimens were manufactured by impact compaction at 50 blows per face and both faces were cut to a height of 40±5mm.

The test was performed at various stress levels at a rate of 40 pulses per minute. Each specimen was repeatedly loaded until it failed by cracking or deformed by 9mm. The testing procedure is briefly described as follows:

- The indirect tensile stiffness modulus is determined at the target stress level for each specimen.
- The indirect tensile fatigue test is conducted at an initial target stress level of 600kPa. This stress is applied to the first specimen and subsequent stress levels selected in accordance with BSI(2000) to provide cycles to failure that are at least one order of magnitude from the lowest number of cycles to failure.
- The maximum horizontal tensile strain at the centre of each specimen is calculated using Equation 6.3.
- The maximum tensile strains (εx,max) are plotted against the number of cycles to failure (Nf) using logarithmic scales.
- Linear regression analysis is used to describe the resulting fatigue relationship.

The results obtained from ITFT tests can be expressed in the form of a relationship between the maximum tensile horizontal strain and the number of cycles to failure:

$$\varepsilon_{x}\max = \frac{\sigma_{xmax}\ (1+3v)}{Sm} \text{ x } 1000$$

(Eq. 6.4)

where:

$\sigma_x$max = maximum tensile stress at the centre of the specimen (kPa)

v = Poissons ratio (assumed to be 0.35)

Sm = Indirect Tensile Stiffness Modulus at $\sigma_x$max (Mpa)

Test Results

A fatigue line of maximum tensile horizontal strain against number of cycles was plotted for each material, an example of this fatigue line is demonstrated below for the 50SF 50SS formulation:

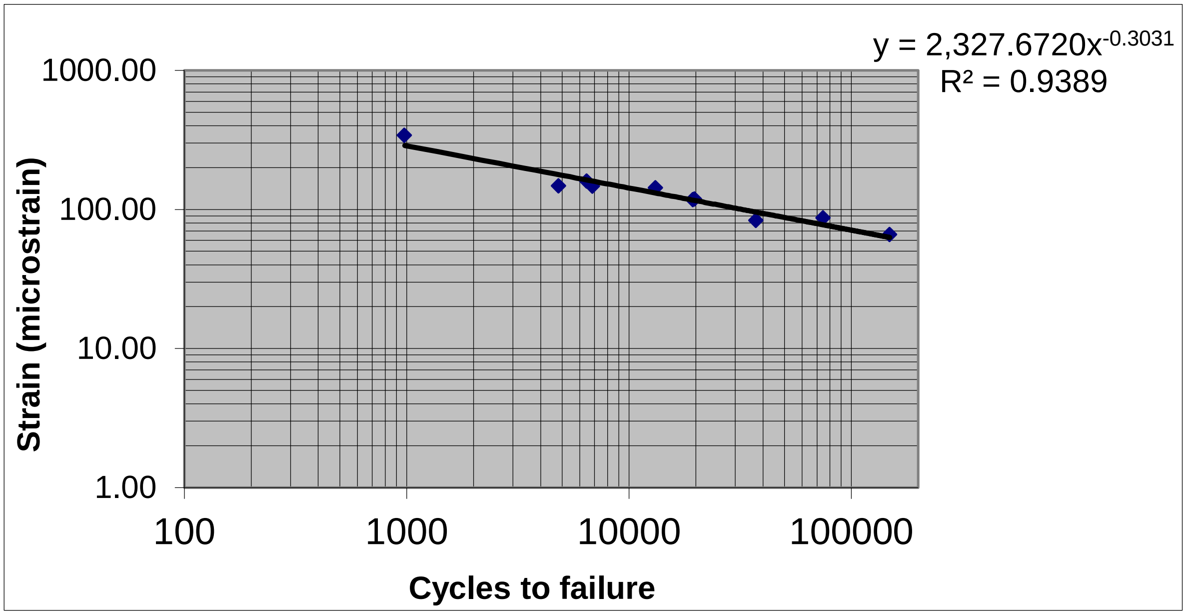


Figure 6.14 – Typical fatigue relationship for the de-icing formulation 50SF 50SS

The number of cycles to failure at the defined strain of 100 was calculated from the fatigue relationship. The quality of the data was statistically analysed using the square of the correlation coefficient (R^2) for the linear regression analysis to establish if the results were statistical significant as shown in Table 6.6. Results are deemed statistical significant if the correlation coefficient (R^2) is greater than 0.90 (BSI, 2000).

Additive	Number of Cycles to Failure at a Strain of 100	Correlation Coefficient (R^2)
Control – No Additive	68,072	0.92
3% 100SF	26,427	0.95
3% 70SF 30SS	35,005	0.88
3% 50SF 50SS	32,345	0.94
3% 30SF 70SS	46,770	0.97
3% 100SS	41,817	0.96

Table 6.6 - Number of cycles to failure at a strain level of 100 for each de-icing chemical formulation

Discussion of Test Results

The test results demonstrate that each of the de-icing additive formulations have a lower fatigue resistance than the control, with the fatigue performance of the 100SF formulation having the least resistance when subjected to a controlled stress.

To compare each of the material formulations directly and to determine the significance of this difference, all of the data was plotted on one chart, as shown in Figure 6.15.

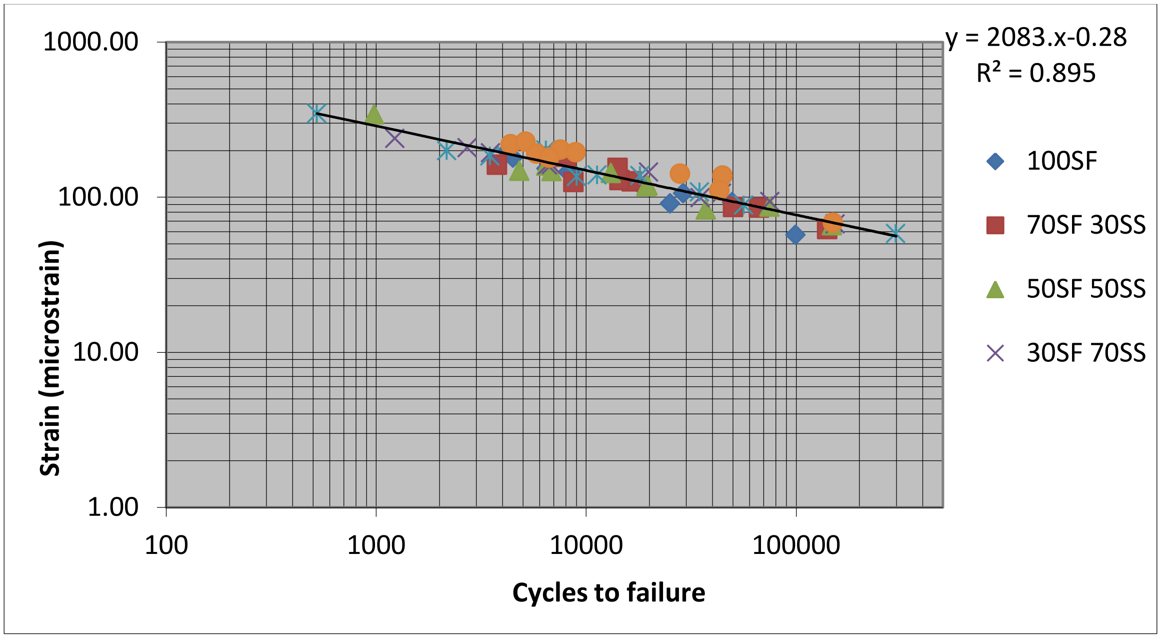


Figure 6.15 - Fatigue relationship for all data

The graph demonstrates the control results are typically above the trend line produced based on the average of all data. In contrast, the high sodium formate specimens were typically below the trend line.

The predicted strain based on all test results (regardless of formulation) was calculated for the varying cycles to failure. A comparison between the actual cycles to failure and the predicted cycles to failure was undertaken and the mean difference for each material was determined, as shown in Table 6.7 below.

Additive	Mean Strain Measured	Predicted Strain from All Data	Mean Difference
Control – No Additive	167.13	139.42	27.70
100SF	128.83	137.62	-8.79
70SF 30SS	129.34	132.00	-2.66
50SF 50SS	140.86	144.04	-3.18
30SF 70SS	147.02	149.22	-2.20
100SS	159.54	161.60	-2.06

Table 6.7 - Mean strain measurement for individual de-icing chemical formulations compared to estimations made for all data

The analysis of the data concludes that the control has greater fatigue resistance in comparison to the average fatigue resistance of all the materials. The 100SF formulation has the least resistance.

Previous research (Collop et al. 1995, Hammooum et. al 2002 and Osman 2004) has highlighted that cracking generally propagates through the binder (bitumen and filler) and does not generally occur through the aggregate particles. This failure takes place in the form of a cohesive failure in the bitumen/filler film. This means that fillers can have a significant role in the fatigue resistance of asphalt.

Visual observations of the tested specimens confirmed that the failures were in the bituminous mastic with the cracks formed running through the bitumen mastic.

The previous research has highlighted that a high number of factors can influence the fatigue resistance of bituminous mixtures. The filler particles can have particular influence and factors such as the particle size, shape, surface properties and stiffening effects can all influence the fatigue resistance.

This high number of factors means that there is no simple explanation for the fatigue resistance results, however a number of factors for both the sodium formate and sodium silicate samples can be attributed to final results.

The 100% sodium formate sample has the least fatigue resistance of all specimens. Delta ring and ball testing in Section 6.4.4 of this report concluded that the sodium formate has the least stiffening effects on the bitumen when compared to sodium silicate and limestone filler. Previous research by Kim et al. (2003) identified that if the filler stiffens the binders, they acted in such a way that they provided better resistance to microcracking and thus an increased fatigue life. Whilst there are likely to be many inter-related factors that could have influenced this reduced fatigue resistance, the reduced stiffness of the mastic relative to limestone and sodium silicate samples is a likely contributory factor to the reduced fatigue resistance.

The 100% sodium silicate samples showed a marginal reduction in fatigue resistance compared to the control specimens.

A review of the delta ring and ball testing indicated that the sodium silicate increased the stiffness of the mastic. Based on the previous research it would have been expected that sodium silicate would have increased the fatigue resistance.

Sodium silicate additions, however, results in reduced asphalt compaction and higher air void contents. Reduced compactability and resultant higher air void content provides an easier route for cracks to propagate and generally results in a reduced fatigue life. Analysis of the air void contents of the sodium silicate specimens confirmed a mean air void content of 8.7%. In contrast the control specimens had a mean air void content of 5.0%. This is consistent with the gyratory compaction results in Section 6.4.7.

The smoother particle surface of the sodium silicate is also likely to have contributed to the reduced fatigue resistance. This because the interlock between particles is reduced creating a greater area of stress around the sodium silicate particles.

The reduced compactability, high air void content and limited particle interlock appears to outweigh the increased stiffness benefits. This results in a marginally lower fatigue resistance for sodium silicate additions relative to the control surface.

The conclusions drawn above are related to the fatigue resistance under a controlled stress test. Controlled stress testing is dependent on the initial asphalt stiffness and the formation of the initial crack is quickly followed by rapid crack propagation and complete specimen failure. The conclusions observed above are strongly related to the initial asphalt stiffness as demonstrated by the reduced fatigue resistance of sodium formate. Rapid specimen failure between cracking initiation and propagation was observed for all formulations indicating that the above results are predominately based on crack initiation.

Under controlled strain testing the stress is reduced as damage accumulates to maintain the initial strain. Controlled strain testing is likely to produce different results than those discussed above, this is because controlled strain testing is typically based on a failure defined by a percentage reduction in the initial stiffness (e.g. a 50% reduction). This would therefore place less emphasis on the initial mixture stiffness, which may have strongly influence the results observed for the sodium formate and sodium silicate formulations. Crack propagation is also relative slow compared with a controlled stress test. The physical properties of the de-icing formulations may influence the rate of crack propagation by varying amounts and could influence the fatigue resistance, which would not have been assessed under the controlled stress method discussed above.

6.4.10 INVESTIGATION OF PERMANENT DEFORMATION

Introduction

Resistance to deformation or rutting under applied loads is a fundamental property of bituminous materials. Deformation in pavements can be restricted to one or more of the asphalt layers or can extend through the entire pavement. The majority of deformation defects result from plastic deformation of the surfacing, which is dependent upon the load application and climatic conditions.

Primarily plastic deformation is dependent upon the composition of the bituminous mixture, for this reason the influence of the de-icing chemical formulations on resistance to permanent deformation needs to be determined.

The resistance to deformation of bituminous materials can be measured through a wheeltracking test. A wheeltracking test measures the susceptibility of bituminous materials to deform by assessing the degree of permanent deformation occurring at repeated passes of a loaded wheel.

Test Procedure

A number of wheel tracking devices exist varying in loading regime from small, large and extra large devices. Testing was carried out in accordance with “*BS EN 12697-22:2003+A1:2007 Bituminous mixtures. Test methods for hot mix asphalt – Wheeltracking*” using a large-size device (BSI, 2007).

This device simulates some of the most severe types of loading experienced by surface courses and is particularly useful for comparing the performance of rut resistant materials.

Prior to testing, two slabs were manufactured using roller compaction in accordance with BS EN 12697-33:2002+A1:2007 *Bituminous mixtures. Test methods for hot mix asphalt – Specimen prepared by roller compaction”*. The principle of roller compaction is that a given mass of bituminous mixture is compacted in a rectangular mould under an applied load.

Test slabs were manufactured by firstly calculating the correct weight to obtain a finished void content of 5.0%. The correctly weighed asphalt was then placed in a ventilated oven at mixing temperature of 155^{o}C, for a minimum of 1 hour. The asphalt sample was placed evenly into a mould of internal dimensions of 500 x 180mm with a desired nominal thickness of 50mm. Light compaction was carried out using a single pneumatic tyre in accordance with the specified sweep plan (BSI, 2007)

Following the manufacturing of the two specimens, they were conditioned for 72 hours at ambient temperature. After the conditioning period, the slabs were weighed and measured in accordance with BS EN 12697-29:2002 and the bulk density and void content calculated. Any specimen with a void content greater than 1.0% from the target was rejected.

The specimens were placed into the same mould in the same orientation and a conditioning run was carried out. The conditioning run was at a temperature between 15^{o}C to 25^{o}C for 1,000 passes at a tyre pressure of 600kPa.

Initial readings were taken at 15 predetermined locations using an analogue depth gauge with an accuracy of ±0.2mm. Following the conditioning run the two specimens were temperature conditioned at the test temperature of 60^{o}C for a period of between 12 to 16 hours prior to testing.

The test was executed by measuring the rut depth at the 15 predetermined locations after the test specimen had undergone the specified load cycles, 100, 300, 1000, 3000, 10000 and 30000. This excludes the number of conditioning cycles.

The mean rut depth was calculated for each specimen based and the mean rut depth for the two specimens calculated at the appropriate number of cycles.

Test Results

The rate of rut development is a good measure of the susceptibility of a material to permanent deformation. The wheel tracking test was conducted on two chemically modified slabs for each de-icing formulation using the large device in accordance with BS EN 12697-22:2003+A1:2007 (E). This was to determine if the chemical additives have an influence on the buildup of permanent deformation.

Test data was analysed by ensuring that the results for the two slabs were within the repeatability conditions stated in Table 3 BS EN 12697-22:2003+A1:2007.

The mean value for each measurement was determined and plotted on a log-log scale for ruts measured and number of cycles. The development of the mean rut depth over 30,000 cycles for the different de-icing formulations are demonstrated in Figure 6.16.

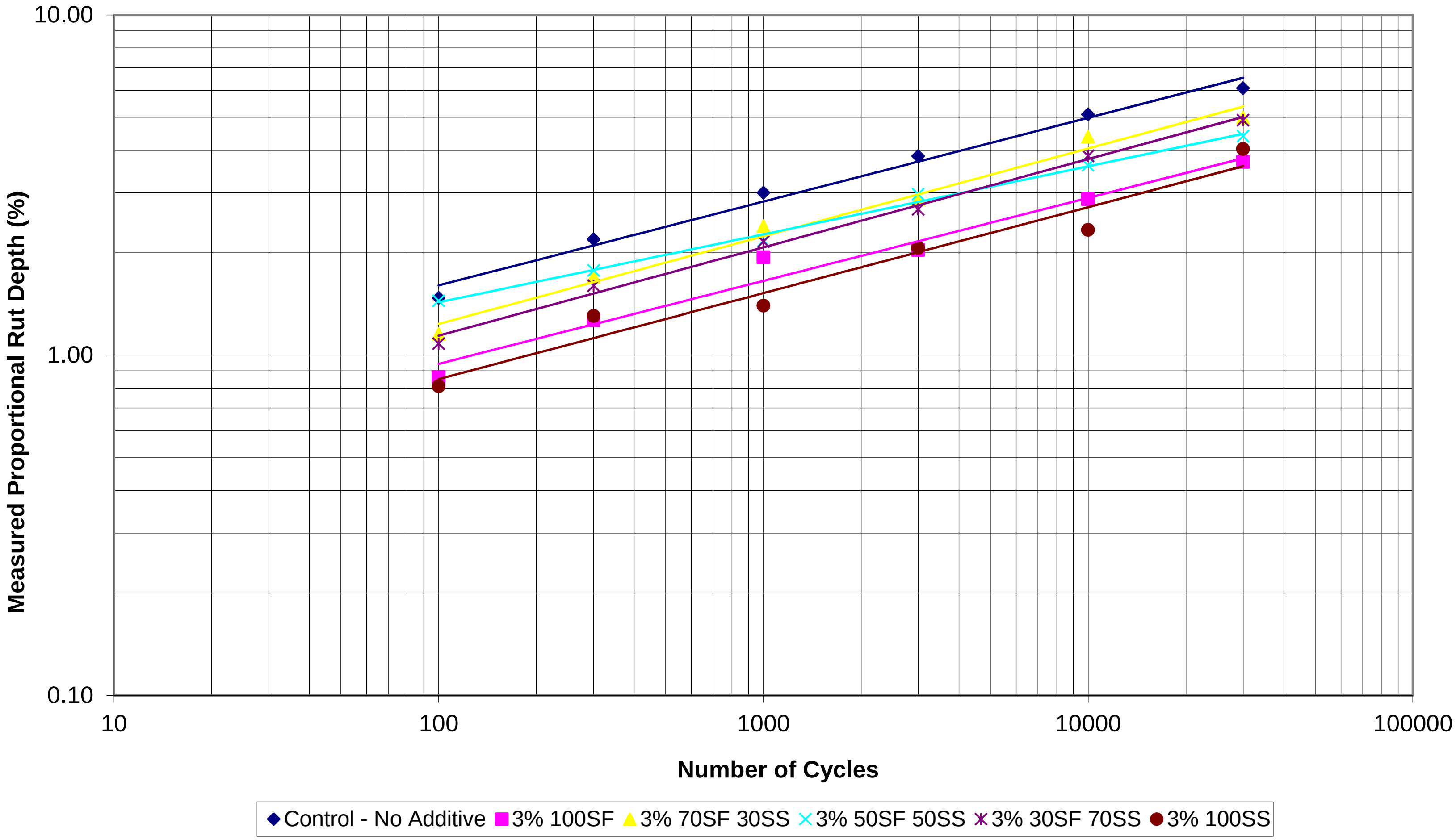


Figure 6.16 – Average measured proportional rut depth against number of cycles for the varying de-icing chemical formulations

Discussion of Test Results

Large wheeltracker testing has demonstrated that all mixtures provided high levels of rut resistance with final rut depths at 30,000 cycles less than 7.5% of the slab thickness. This is indicative of Stone Mastic Asphalt surfaces where the aggregate skeleton of the mixture dominates and provides high level of rut resistance.

The chemical additives of sodium silicate and sodium formate improve the resistance to permanent deformation relative to limestone filler. This improvement is consistent in terms of the early life rut depth, final rut depth and the rate of rut development (see Table 6.8).

Additive	Rut Measured at 100 Cycles (%)	Rut Measured at 30,000 Cycles (%)	Rate of Rut Development (mm/1000 cycles)	Correlation Coefficient (R^2)
Control – No Additive	1.47	6.09	0.165	0.987
3% 100SF	0.86	3.69	0.095	0.973
3% 70SF 30SS	1.15	4.99	0.139	0.985
3% 50SF 50SS	1.44	4.40	0.102	0.995
3% 30SF 70SS	1.08	4.90	0.130	0.994
3% 100SS	0.81	4.03	0.092	0.955

Table 6.8 – Initial and final ruts measured and rate of rutting

The final proportional rut depth measured demonstrated improvements between 1.10% and 2.40% for the de-icing chemical formulations relative to the control specimen after 30,000 cycles. This difference is relatively small but is considered to be significant when considering the precision data stated in Table 3 of BS EN 12697-22:2003+A1:2007 which specifies repeatability and reproducibility conditions of approximately 1.0%.

The 100% addition of sodium formate and sodium silicate demonstrate the lowest final values of ruts measured at 30,000 cycles. This reduction is primarily due to a reduced rate of rut development. The rate of rut formation for 100% sodium silicate and 100% sodium formate at 3% additions are 0.092 and 0.095 mm/1000 cycles respectively.

The differences in the rate of rut formation can be attributed to the de-icing chemical formulations. It has previously been demonstrated in Section 6.4.4 that sodium silicate stiffens the bitumen. Mixtures containing stiffer bitumen mastics have been proven to be less susceptible to permanent deformation.

Sodium formate also demonstrated an improvement in the rut resistance relative to the control sample. Specimens containing sodium formate have been shown in Section 6.4.7 to improve the compactability of the asphalt. The measurements of air voids in the large wheeltracking slab have confirmed this conclusion and the slabs containing sodium formate had on average 0.4% less air voids than the control. Well compacted materials have been demonstrated to be more resistant to permanent deformation. This affect has been demonstrated for sodium formate in terms of reduced initial rutting after 100 cycles and the reduced rate of rut formation.

6.4.11 SENSITIVITY TO WATER (MOISTURE DAMAGE)

Introduction

Moisture damage can be defined as the loss of strength and durability in asphalt mixtures due to the effects of moisture (Little et al. 2003).

The presence of water (or moisture) often results in premature failure of pavements in the form of isolated distress caused by debonding of the bitumen film from the aggregate surface, referred to as stripping, and/or early rutting/fatigue cracking due to reduced mixture strength (Lu and Harvey, 2007).

Moisture can enter the pavement from the surface, from the sides due to poorly constructed shoulders and sometimes from beneath the subgrade because of a rise in the water table. The types of distresses that can be caused by moisture damage include:

- Stripping/debonding
- Fretting and ravelling
- Potholes
- Premature fatigue cracking/rutting

Moisture can deteriorate the asphalt by stripping or debonding the bitumen from the aggregate. The susceptibility of this can be dependent upon the mechanical interlock (lock and key/area of bonding) and physico-chemical factors (surface energy/chemical reactions).

Moisture can also weaken the asphalt mixture by softening or partially emulsifying the bitumen film without removing it from the aggregate surface. During this weakened state, the asphalt pavement layer is subjected to accelerated damage from applied traffic.

A number of test methods have been developed internationally to assess the water (moisture) sensitivity of asphalt. These can be considered as tests of loose coated aggregate and asphalt.

Qualitative tests provide a subjective evaluation of the stripping potential on loose coated aggregate include:

- Boiling water tests
- Rolling bottle tests
- Chemical immersion tests
- Many others

A number of tests have also been designed to look at the water sensitivity of asphalt with regard to a specific parameter such as strength before and after conditioning. These tests include:

- Immersion compression tests
- Indirect tensile tests
- Submerged/Hamburg wheeltracking tests
- Duriez tests
- Freeze-thaw pedestal tests

A number of water sensitivity evaluations have been conducted as part of this research project to determine if de-icing chemical formulations are particularly sensitive to the presence of moisture and the role that the surface energy of the chemical has on the water sensitivity performance.

Water sensitivity conducted as part of this research project includes:

- Work of adhesion and energy ratio calculations
- BS EN 12697-11:2005 - Binder affinity testing using the bottle rolling method
- British Board of Agreement (2004). Appendix A2 – Water sensitivity immersion test
- EN 12697-12:2003 – Indirect Tensile Strength test
- Submerged wheeltracking

6.4.11.1 DETERMINATION OF WORK OF ADHESION AND BITUMEN-FILLER/CHEMICAL BOND ENERGY RATIOS

Introduction

Sensitivity to moisture damage of a particular asphalt mixture is primarily influenced by the interfacial characteristics of the component materials, particularly the binder and the aggregates. These interfacial characteristics (cohesive and adhesive bond strengths) can be determined by using the surface energy properties of the material (Airey et al., 2007).

This section of the report calculates the work of adhesion under dry conditions and in the presence of water, to identify the sensitivity to moisture with the various de-icing chemicals and the tendency for the bitumen to debond (strip) from the chemical in the presence of water.

Calculation Method for Work of Adhesion

Moisture damage depends on the interaction of surface energy components of aggregate, bitumen and water. The adhesive and cohesive bond strength of a bitumen-aggregate system both with and without the presence of water at this interface can be calculated.

As part of this study the interaction of filler and/or chemical powders has been examined by substituting the aggregate component.

Several theories explain the molecular origin of surface free energy of solids. The Good-van Oss-Chaudhury theory is widely applied to explain the surface free energy components of various materials and determine these components by measuring work of adhesion of the material with other liquids or vapors (Bhasin 2006).

According to the Good-Van-Oss-Chandhury theory, the total surface free energy of any material is divided into three components based on the type of molecular forces on the surface. These components are: 1) the nonpolar component, also referred to as the Lifshitz-van der Waals (LW) or the dispersive component, 2) the Lewis acid component, and 3) the Lewis base component. The total surface free energy is obtained by combining these components as follows:

$$\gamma = \gamma^{LW} + \gamma^{AB}$$

(Eq.6.5)

Where the acid/base component is composed of the Lewis acid γ^{+} and the Lewis base γ^{-} components:-

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}}$$

(Eq. 6.6)

The Lifshitz Van der Waals and the Lewis Acid and Lewis Base components have been measured previously for bitumen, limestone filler and chemical additives using a range of techniques dependant on the source material.

The techniques are as follows:

- Bitumen – Contact Angle using Goniometer, see Section 6.6.3.1
- Limestone filler – Dynamic Vapour Sorption, see Section 5.3.2
- Sodium formate and sodium silicate – Washburn Method, see Section 5.3.2.

This testing produced the following surface energy components:

	γ^{LW}	γ^{AB}	γ^{+}	γ^{--}
Limestone Filler	55.3	191.6	51.6	178.1
Sodium Formate	15.1	11.7	2.8	12.4
Sodium Silicate	16.3	6.9	1.8	6.7
Bitumen (40/60 Penetration Grade)	31.1	9.6	1.7	3.4
Bitumen Mastic (40/60 Penetration Grade with 3% Limestone Filler)	31.4	5.8	1.0	2.1

Table 6.9 – Surface energy components of reference materials

The surface energy components above have been used to calculate the work of adhesion of energy ratios.

The bond strength of a material (binder or chemical/filler) is the combination of the Liftshitz-van der Waals (non-polar) and the Lewis acid/base forces.

According to Good-Van-Oss-Chandhury theory, the adhesive bond strength between two materials ‘A’ and ‘B’ in the dry in the absence of water at the interface can be computed in terms of their respective surface free energy components by:-

$$\Delta G^{a}_{BA} = 2\sqrt{\gamma_B^{LW}\gamma_A^{LW}} + 2\sqrt{\gamma_B^{+}\gamma_A^{-}} + 2\sqrt{\gamma_B^{-}\gamma_A^{+}}$$

(Eq. 6.7)

Where B denotes bitumen and A represents limestone or the chemical additive in this case.

In order to quantify the propensity of one material to displace another, use of interfacial energies of these materials is necessary. Bhasin (2006) considered a three phase system comprising of bitumen, aggregate and water, as shown in Figure 6.17.

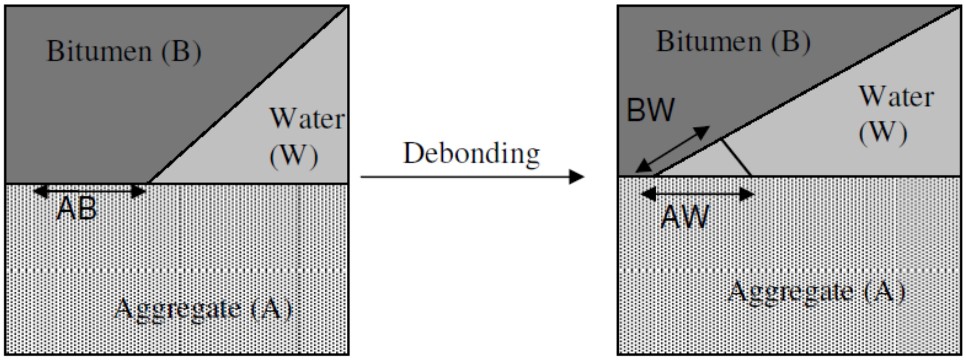


Figure 6.17 – Displacement of Bitumen from Bitumen-Aggregate Interface by Water (Bhasin 2006)

The process of water displaces bitumen from the bitumen-aggregate interface is explained by Bhasin (2006) "The interface of the aggregate with bitumen is lost and is associated with external work, - γ_{AB} , from the definition of interfacial free energy. Similarly, two new interfaces, between water and bitumen, and between water and aggregate are created during this process. The work done for the formation of these two new interfaces is $\gamma_{WB} + \gamma_{WA}$. Therefore, the total work done for water to displace bitumen from the surface of the aggregate is, $\gamma_{WB} + \gamma_{WA} - \gamma_{A}$”.

The work of debonding (adhesive bond strength in the presence of water) at the interface can therefore be given by:

$$\begin{aligned}\Delta G^{a}_{BWA} &= \left\{\left(\left(\sqrt{\gamma_A^{LW}} - 4.67\right)^2\right) + \left(2 \times \left(\sqrt{\gamma_A^{+}} - 5.05\right) \times \left(\sqrt{\gamma_A^{-}} - 5.05\right)\right)\right\} \\ &+ \left\{\left(\left(\sqrt{\gamma_B^{LW}} - 4.67\right)^2\right) + \left(2 \times \left(\sqrt{\gamma_B^{+}} - 5.05\right) \times \left(\sqrt{\gamma_B^{-}} - 5.05\right)\right)\right\} \\ &- \left\{\left(\left(\sqrt{\gamma_B^{LW}} - \sqrt{\gamma_A^{LW}}\right)^2\right) + \left(2 \times \left(\sqrt{\gamma_B^{+}} - \sqrt{\gamma_A^{+}}\right) \times \left(\sqrt{\gamma_B^{-}} - \sqrt{\gamma_A^{-}}\right)\right)\right\}\end{aligned}$$

(Eq. 6.8)

Where W denotes water with the Lifhshtis-van der Waals component and the acid-base components are taken as per the values specified by Bhasin (2006):-

- $\gamma^{LW} = 21.8$
- $\gamma^{+} = \gamma^{-} = 25.5$

Calculation Results - Work of Adhesion

The work of adhesion under dry and wet conditions were calculated for combinations of bitumen with limestone filler, sodium formate and sodium silicate. These results are shown in Table 6.10.

	Work of Adhesion Dry (G_{AB})			Work of Adhesion in Presence of Water (G_{ABW})		
Bitumen	Limestone Filler	Sodium Formate	Sodium Silicate	Limestone Filler	Sodium Formate	Sodium Silicate
40/60 Penetration	144	57	59	-71	41	32
40/60 Penetration with 3% Limestone Filler	131	54	55	-77	45	35

Table 6.10 – Dry and wet work of adhesion values between the filler/de-icing chemicals and bitumen/bitumen mastic

Discussion of Calculation Results

The magnitude of the work of adhesion in the dry for the limestone filler were slightly higher but broadly consistent with the values reported by Bhasin (2006) ranging from 90-126, confirming a high level of adhesion between the bitumen and the limestone was achieved.

The work of adhesion between bitumen and chemical additives show significantly different results when compared to the bitumen and limestone filler. These results indicated that the chemical additive reduced the resistance to adhesive fracture (at the asphalt-chemical interface). This reduction in work of adhesion is typically in the order of 60%, as shown in Figure 6.18.

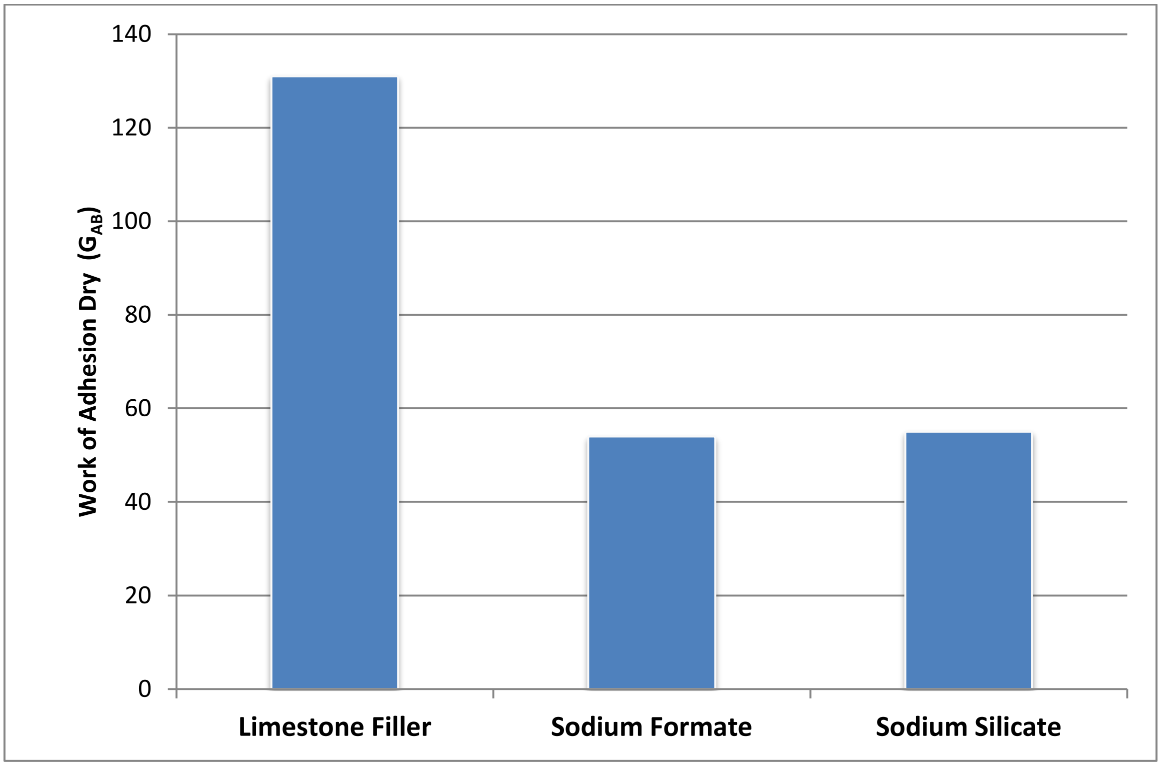


Figure 6.18 – Work of adhesion (dry) between limestone filler/de-icing chemicals and bitumen

When water is present at the interface, the work of adhesion is typically negative. The negative magnitudes show that water will promote debonding along the interface, since it will adhere more strongly than bitumen to the aggregate surface (in this case limestone or chemical additive).

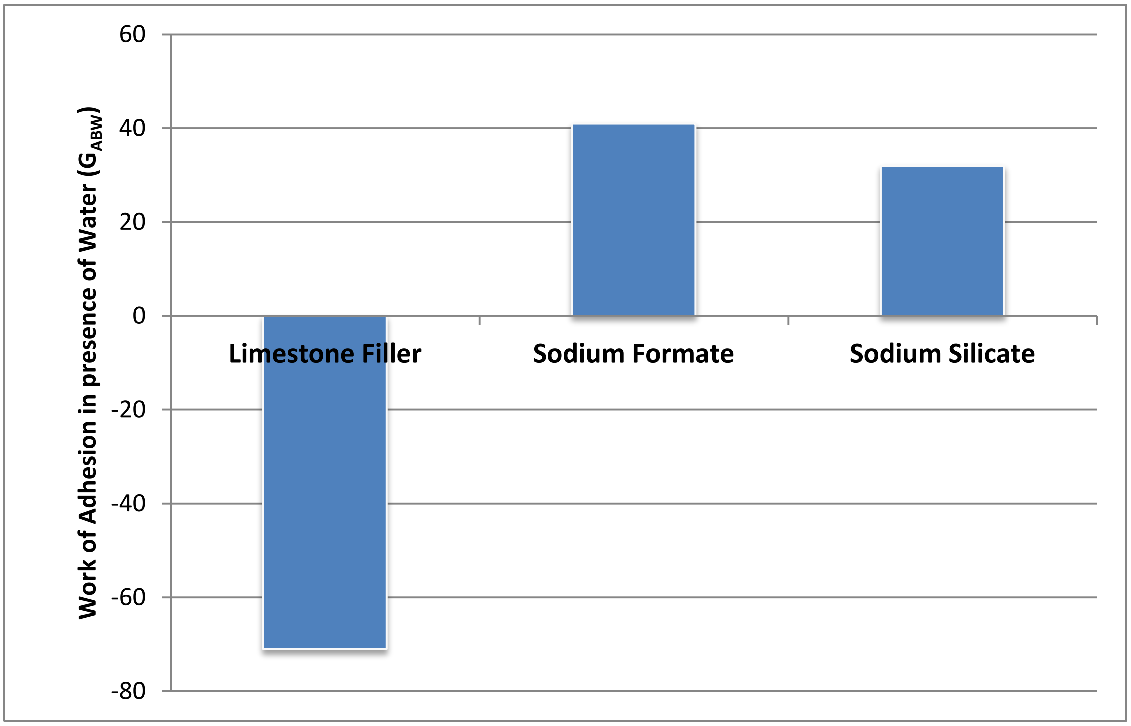


Figure 6.19 – Work of adhesion in presence of water between limestone filler/de-icing chemicals and bitumen

Higher negative magnitudes are indicative of a higher energy potential for disrupting the bitumen-aggregate bonding in the presence of water. The negative value for limestone filler of -71 and -77 are typical for limestone-bitumen combinations (Bhasin 2006) and the use of limestone is generally considered to be less susceptible to moisture damage compared to other aggregate-bitumen combinations. The positive values for sodium formate and sodium silicate show that material may behave differently in the presence of water. To determine how the work of adhesion in the dry conditions and work of adhesion under wet conditions may influence the moisture sensitivity of asphalt containing these different constituents, energy ratio calculations can be performed.

Calculation Method for Bitumen-Aggregate Bond Energy Ratios

The ratio between the adhesive bond energy values under dry conditions (ΔG_{AB}) and in the presence of water (ΔG_{BWA}) can be used to predict the moisture sensitivity of asphalt mixtures (Bhasin 2006). The combination of asphalt binder and aggregate with the highest magnitude of energy parameters will be relatively more resistant to water damage than other combinations.

A higher value of energy ratio, R, indicates better resistance to moisture damage for that bitumen-aggregate combination. It is generally concluded that mixtures with a ratio higher than 1.5 were more moisture resistant than the ones with ratios lower than 0.8.

Four types of moisture sensitivity analysis parameters have been used for each combination of material. In order to represent the moisture damage by a single value, Bhasin et al. (2006) combined the two bond energy parameters as a dimensionless energy ratio.

Parameter No. 1:

$$R_1 = \left| \frac{\Delta G_{BA}}{\Delta G_{BWA}} \right|$$

(Eq. 6.9)

This is the ratio of dry to wet bond strength of the bitumen-aggregate combination.

Aggregates with higher surface roughness and greater surface area are supposed to bond well with bitumen by providing more bond area and better interlocking. In order to accommodate this effect, Bhasin (2006) multiplied the bond energy ratio (Parameter No. 1) with specific surface area-SSA of aggregates.

Parameter No. 2:

$$\left|\frac{\Delta G_{BA}}{\Delta G_{BWA}}\right| \times SSA(Aggregate \cdot Surface \cdot Area)$$

(Eq. 6.10)

Parameter No. 1 is multiplied with the specific surface area of the aggregates to consider the effect of aggregate surface area on the final adhesion.

Wetting/coating of an aggregate with bitumen is not only affected by the surface properties of the two materials. The viscosity or cohesion of the bitumen itself plays a very important role. Bitumen, with lesser cohesion and greater affinity for the aggregates, will have a higher wetability property and will coat the aggregate surface more than bitumen having lesser wetability characteristics. However, a softer bitumen having less cohesion may be more prone to emulsification (decrease in cohesion) in the presence of water. Bhasin (2006) modified the above mentioned bond energy ratio by replacing the bond strength in dry conditions (ΔG_{BA}) with a wetability relationship (ΔG_{BA} - ΔG_{BB}).

Parameter No. 3:

$$R_2 = \left|\frac{\Delta G_{BA} - \Delta G_{BB}}{\Delta G_{BWA}}\right|$$

(Eq. 6.11)

Bitumen cohesive bond strength (ΔG_{BB}) is used in the parameter in order to account for the wetability (ΔG_{BA} - ΔG_{BB}) of the binder.

This bond energy ratio was then multiplied with the square root of the specific surface area of the aggregate in order to accommodate the effect of aggregate micro texture on the final bitumen-aggregate bond strength (Bhasin, 2006).

Parameter No. 4:

$$\left|\frac{\Delta G_{BA} - \Delta G_{BB}}{\Delta G_{BWA}}\right| \times \sqrt{SSA}$$

(Eq. 6.12)

Aggregate specific surface area is again introduced giving a fourth parameter.

Bhasin (2006) compared the results from these parameters with the laboratory test results for different mixtures. It was concluded that the fourth parameter provided best correlation with moisture sensitivity of the mixtures estimated by laboratory testing. For this reason energy Parameter No. 4 will be used to assess the moisture sensitivity of the bitumen and in filler/de-icing chemicals.

Calculation Results – Energy Ratios

The following energy ratio parameters were calculated using the surface energy components of the materials previously and the specific surface areas measured by laser diffraction in Section 5.3.1.

	Limestone	Sodium Formate	Sodium Silicate
Energy Ratio 4	1.76	0.07	0.02

Table 6.11 – Energy ratio parameters for limestone filler and chemical additives using 40/60 penetration bitumen

	Limestone	Sodium Formate	Sodium Silicate
Energy Ratio 4	1.38	0.06	0.02

Table 6.12 – Energy ratio parameters for limestone filler and chemical additives using 40/60 penetration bitumen with 3% limestone filler

Discussion of Energy Ratio Calculation

Energy ratio parameter can be used to identify material combinations which are less susceptible to moisture damage; these are associated with high values of energy ratios.

High values of energy ratios are obtained from high magnitudes of adhesive work of adhesion, which indicate that more work is required to separate the bitumen from its interface with the aggregate and smaller magnitudes of adhesive work of adhesion in wet condition that indicate less thermodynamic potential for water to cause debonding at the bitumen-aggregate interface.

It is generally concluded that mixtures with a ratio higher than 1.5 were more moisture resistant than the ones with ratios lower than 0.8 (Ahmad 2010).

The limestone filler-bitumen combination produced energy ratios of 1.7 with 40/60 Pen bitumen, indicating a moisture resistant mixture.

In contrast the combinations of sodium formate-bitumen and sodium silicate-bitumen produced a low energy ratio of 0.06 and 0.02 with 40/60 Pen bitumen, respectively. These values are well below the 0.8 level indicating very high susceptibility to moisture damage for mixtures containing sodium formate and sodium silicate.

6.4.11.2 BINDER AFFINITY TEST

Introduction

The primary function of bitumen is to act as an adhesive, to bind aggregate particles together or to provide a bond between particles and the existing surface (Read and Whiteoak 2003). This adhesive bond is dependent on both the aggregate, bitumen and mixture properties.

Failure of the aggregate/bitumen bond is commonly referred to as stripping. Stripping is a physiochemical process in which separation of bitumen binder film from aggregate surfaces occurs as a result of prolonged contact with water. Binder and aggregate combinations with a tendency to strip are said to have low binder affinity. The tendency for stripping of the binder film in the presence of water is highly correlated to the surface properties of the asphalt binder, aggregate and filler.

The previous section has demonstrated a susceptibility for a reduced adhesive bond strength between the bitumen and de-icing chemical formulations, in comparison to limestone filler.

A number of tests exist for measuring the affinity of bitumen on loose coated aggregate particles, these include but are not limited to:-

- Static and dynamic immersion tests
- Chemical immersion tests
- Rolling bottle methods
- Boiling water tests

Laboratory testing of binder affinity was carried out to correlate theoretical adhesive bond strength results with physical measurement. This was conducted using the rolling bottle method.

Test Procedure

The rolling bottle method was selected because it provided a measure of binder affinity over specific time periods to indicate the rate at which stripping occurred.

The rolling bottle method was conducted in accordance with "*Section 6.3.5 BS EN 12697-11:2005 Determination of the affinity between aggregate and bitumen.* This part of the European standard specified a method to determine the influence that filler particles or, in this case, had on the binder affinity.

The test procedure involved washing and drying a single size fraction of 6.3/10mm aggregate. The filler or chemicals were then added to aggregate at a rate of 3% by mass to the aggregate.

The blended single fraction of 6.3/10mm aggregate and filler mixture was coated with bitumen to obtain uniform and total coverage. The bitumen coated aggregates were placed loosely distributed on silicone paper until ambient temperature is achieved. This was split into three 150g parts for analysis.

Each part sample was transferred to a bottle filled with deoinised water at 5^{o}C. The bottle was then sealed and placed on a bottle rolling device at 60RPM and rolled at ambient temperature for specific time periods. The time period selected were 6, 24, 48 and 72 hours. At these specific time intervals the degree of bitumen coverage on the aggregate particles was visually estimated by three technicians independently.

Test Results

The mean bitumen coverage results determined visually by the three operators is displayed graphical in Figure 6.20 for each de-icing chemical formulation.

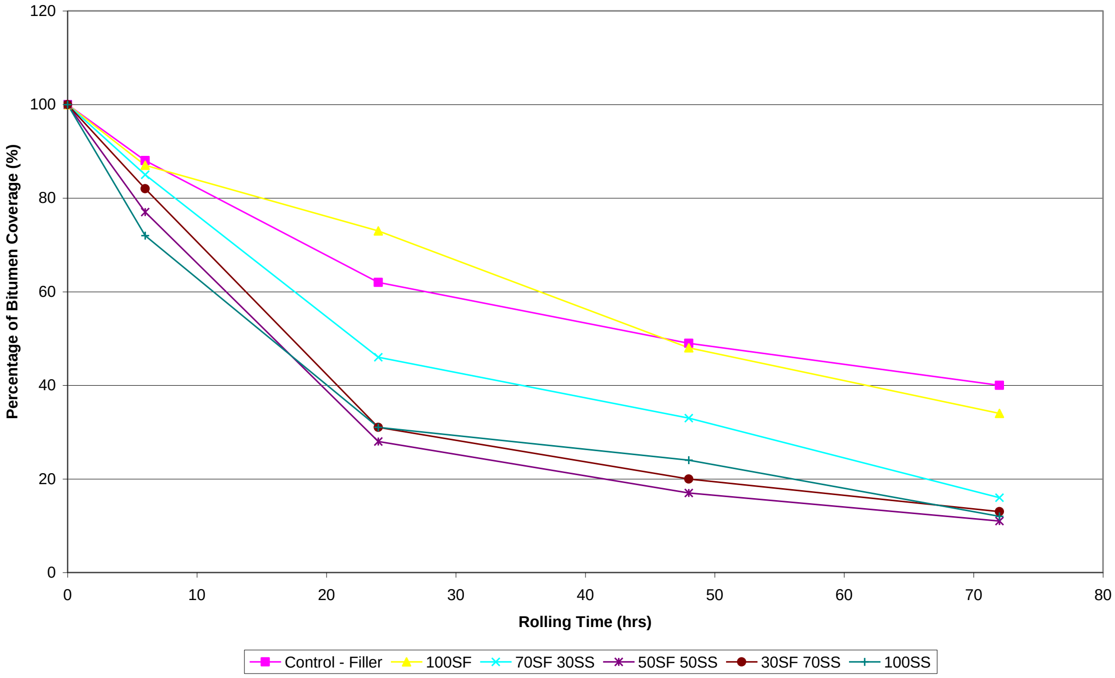


Figure 6.20 – Percentage of bitumen coverage against time for each de-icing chemical formulation

Discussion of Test Results

The rolling bottle method for determining binder affinity demonstrated a strong correlation between reduced binder affinity in the presence of sodium silicate. A substantial reduction in retained bitumen coverage was evident when sodium silicate was incorporated in the mixture after being rolled for a period of 24 hours. This reduction is considered significant based on the precision threshold on the determination of stripping of 2% stated in BS EN 12697-11.

The relationship between binder affinity and sodium silicate content does not appear to be linear. Small proportions of sodium silicate significantly increased the tendency of stripping, as demonstrated in Figure 6.21. In contrast, the retained binder coverage of the sodium formate sample (100SF) is relatively comparable to the control filler (100FF) sample.

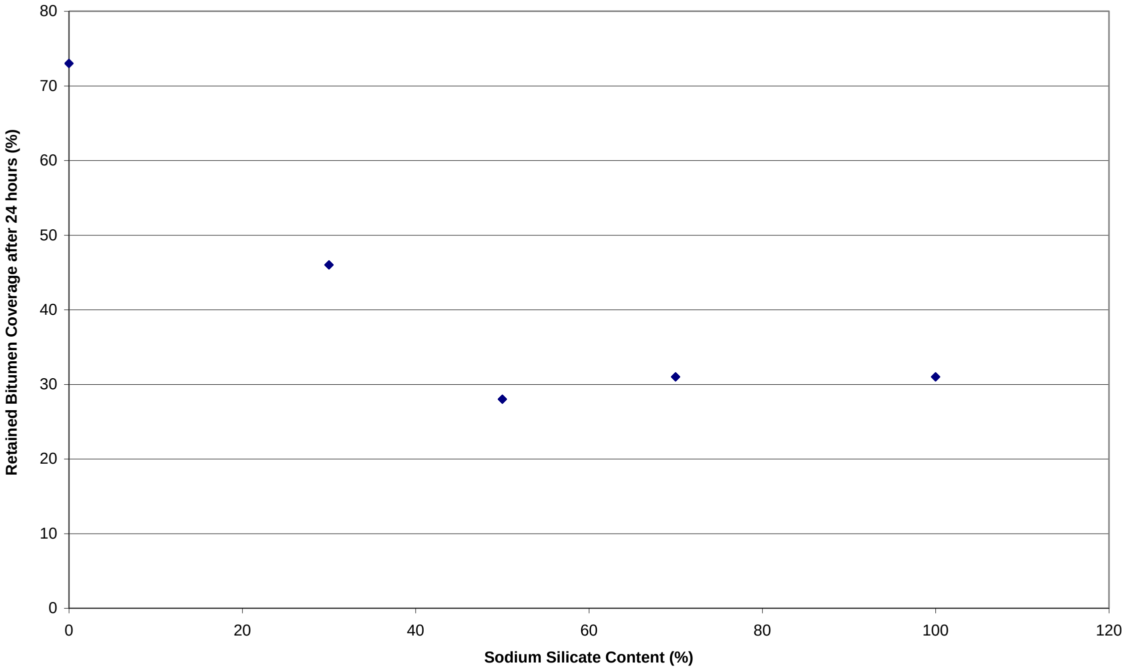


Figure 6.21 – Influence of sodium silicate on retained binder content after rolling for 24 hours.

The poor binder affinity for mixtures containing sodium silicate is consistent with the surface energy ratio calculations indicating an increased susceptibility to deterioration in the presence of water.

In contrast, 100% sodium formate samples retained a bitumen coverage that was comparable to the control sample. This occurred despite the surface energy calculations indicating an increased susceptability to deterioration in the presence of water.

The reason for the difference between the performance of sodium formate and sodium silicate is likely to be related to the mechanical adhesion. Analysis of the particle shape report in Section 5.2.3 show that sodium formate has a very rough surface. This provides a lock and key with the bitumen and a greater area of bonding resulting in a greater force is required to separate the bitumen from the surface.

Sodium silicate has a rounded surface that is very smooth. This means there is very little interlock and area of bonding. The combined effect of this poor adhesion and low surface energy results in the easier removal of bitumen from the particle surface.

The use of the specific surface area from laser diffraction in the energy parameter 4 calculation is likely to have underestimated the specific surface area and surface texture influences for sodium formate. This is because the specific surface area used for the sodium formate calculation was from laser diffraction. Laser diffractions assumes spherical particles and does not allow for variations due to deviations in shape and surface texture. An increase in the specific surface area to account for the surface texture would results in a significantly higher energy ratio parameter 4.

6.4.11.3 INVESTIGATION OF SENSITIVITY TO WATER – BBA HAPAS METHOD

Introduction

Sensitivity to water damage in a bituminous mixture is a measure of potential vulnerability of the bitumen-aggregate interface in the presence of water. Interactions of de-icing chemical formulations on the bitumen-aggregate interface have the potential to impact upon the asphalt service life.

A number of test methods exist to measure water damage, such as Saturation Ageing Tensile Stiffness Tests (SATS), soaking tests and submerged wheeltracking tests. There is no agreement as yet on the most appropriate test to determine susceptibility to water damage.

For practical reasons sensitivity to water testing was conducted by measuring the effect that water saturation and accelerated water conditioning has on the Indirect Tensile Stiffness Modulus for each de-icing chemical formulation in accordance with the BBA HAPAS method.

Test Procedure

The BBA HAPAS method selected is outlined in `*Guidelines Document for the Assessment and Certification of Thin Surfacings for Highways*` BBA 2004 Appendix A.2. This protocol was selected because, at the time of conducting the testing, it was the recommended procedure for assessing surface courses and involves measuring the retained stiffness after water conditioning.

The testing procedure used is based on the Indirect Tensile Stiffness Modulus specimens as previously determined in Section 6.4.4.

The first stage of the test method is to determine the unconditioned Indirect Tensile Stiffness Modulus. The specimens undergo vacuuming in water to remove any entrapped air and promote water into the voids of the specimens. The specimens then undergo a number of water conditioning cycles with the Indirect Tensile Stiffness Modulus measured after each cycle.

This water conditioning cycle comprises:

- Being placed at 60 ± 1^{o}C for 6 ± 1 hours.
- Immediately transferred in a cold water bath at 5 ± 1^{o}C for 16 ± 1 hours.
- Place in water at test temperature of 20 ± 0.5^{o}C for a minimum of 2 hours.

Following each water condition cycle, the specimens were removed from the water bath, surface dried and the Indirect Tensile Stiffness Modulus measured.

The process of water conditioning cycles and stiffness testing was carried out for three cycles in total and the change in stiffness was measured with each cycle.

Test Results

The results of the ITSM unconditioned and after the three conditioning cycles are summarised below in Table 6.13 and Figure 6.22 for each modification:

Additive	Unconditioned ITSM (MPa)	BBA HAPAS Cycle 1 (MPa)	BBA HAPAS Cycle 2 (MPa)	BBA HAPAS Cycle 3 (MPa)
Control – No Additive	4621	5612	5404	5513
3% 100SF	4281	6113	6155	5705
3% 70SF 30SS	4828	6843	7106	6892
3% 50SF 50SS	6200	6726	6697	6132
3% 30SF 70SS	5316	6415	5068	5137
3% 100SS	6538	4894	4157	Specimens too deformed to test

Table 6.13 – Indirect Tensile Stiffness Modulus for each chemical formulation over a number of BBA HAPAS water conditioning cycles.

The influence the de-icing chemical formulations have on the water sensitivity can be presented by determining the ratio of indirect tensile stiffness modulus for each cycle against the unconditioned indirect tensile stiffness modulus for each material. This data is displayed graphically in Figure 6.23 for each chemical formulation.

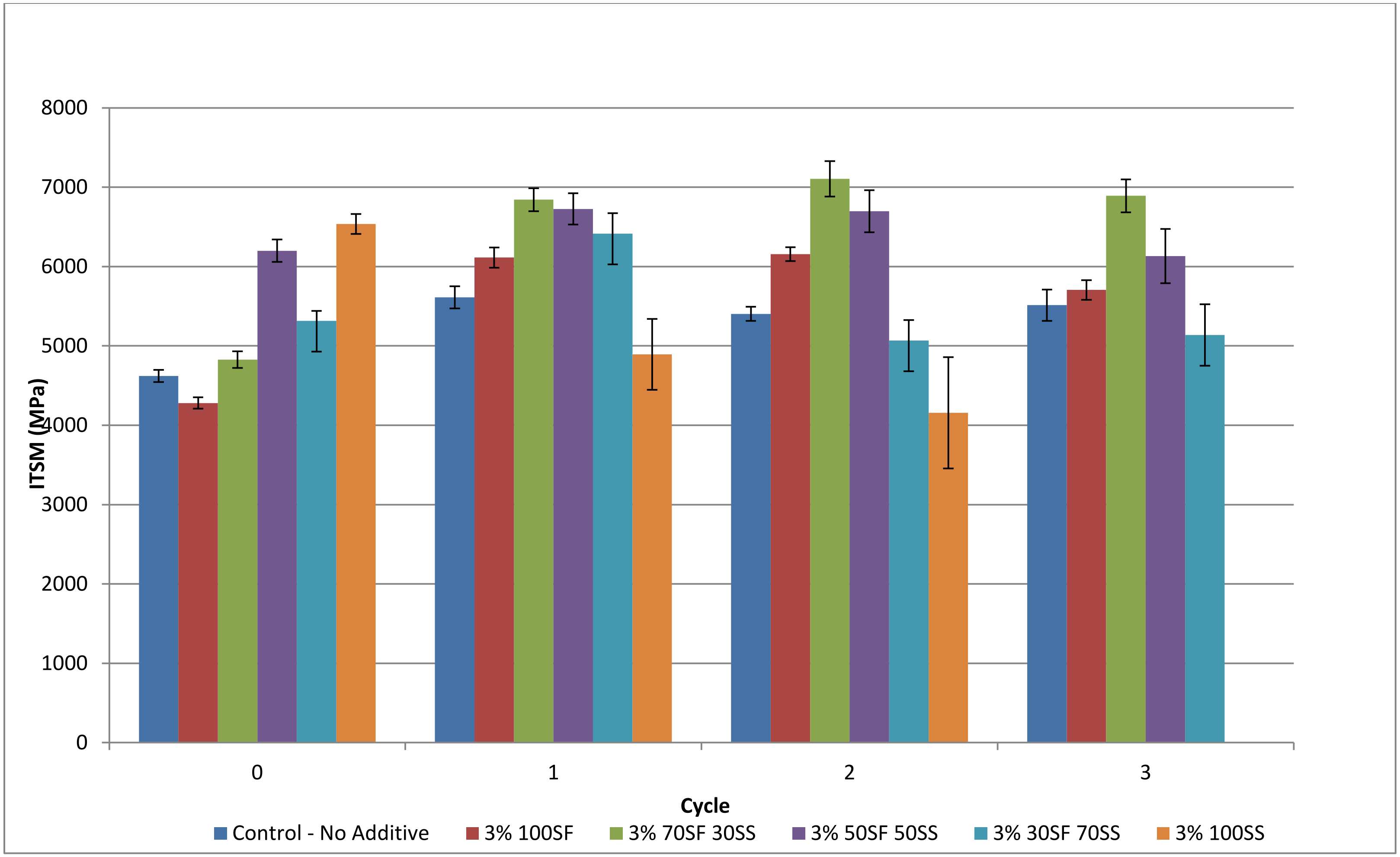


Figure 6.22 - ITSM for the three BBA HAPAS cycles for each chemical formulation

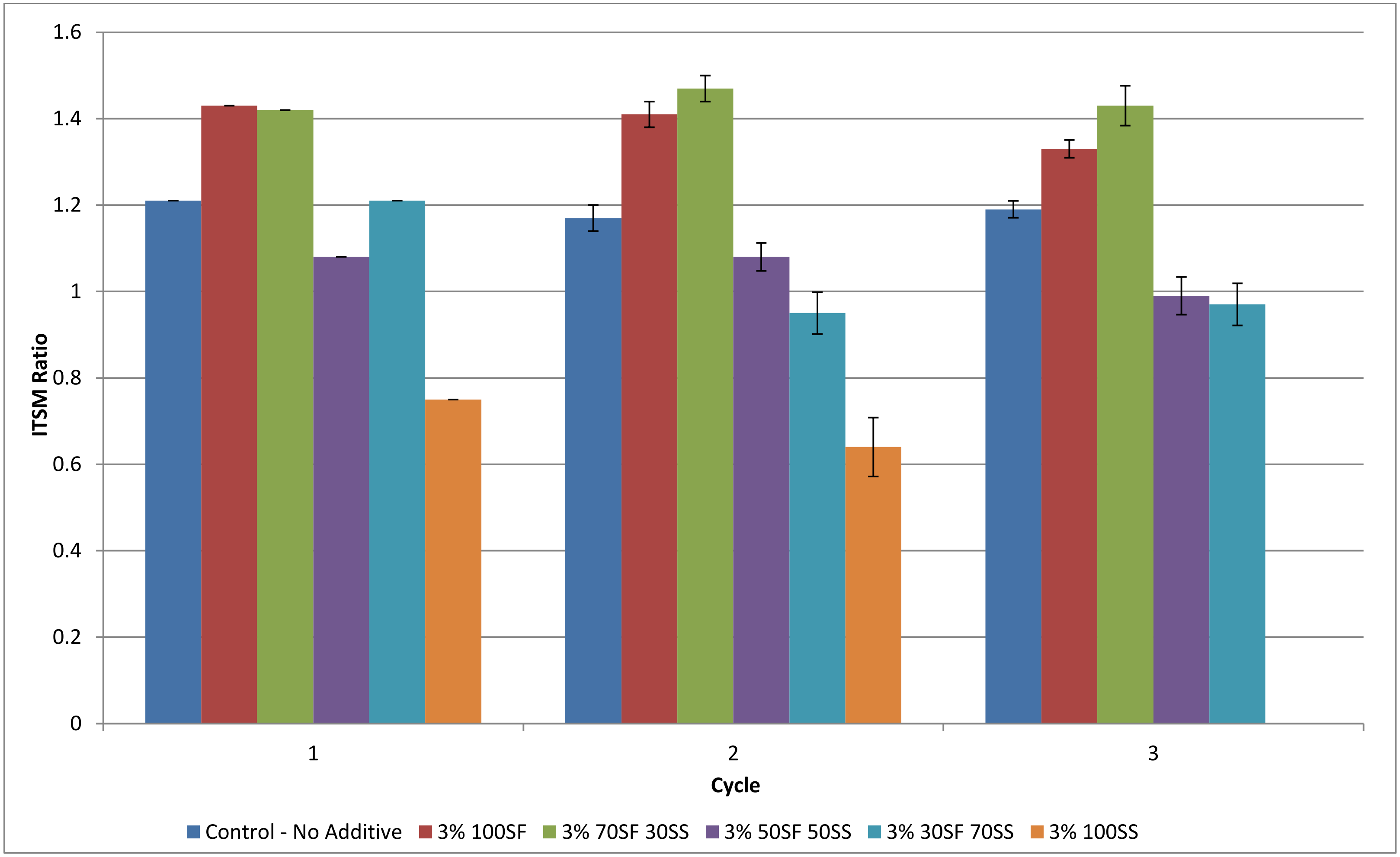


Figure 6.23 – ITSM ratio for the three BBA HAPAS cycles for each chemical formulation

Discussion of Test Results

Analysis of the indirect tensile stiffness modulus data after water conditioning demonstrates that at 3% additions, the majority of the chemically modified specimens passed the BBA HAPAS water sensitivity criteria by retaining at least 80% of the unconditioned indirect tensile stiffness modulus after three cycles.

A number of de-icing chemical formulations demonstrated higher indirect tensile stiffness modulus and water sensitivity ratios after three cycles when compared to the control. This is demonstrated by BBA HAPAS water sensitivity ratios of 1.43 and 1.33 for 3% additions of 70% sodium formate and 30% sodium silicate and 100% sodium formate, respectively. These ratios are a significant improvement on the 1.19 ratio observed for the control and the initial stiffness measurements.

In contrast, sodium silicate contents above 50% for the 3% addition demonstrated reduced indirect tensile stiffness modulus values after three cycles. With the specimen containing 100% of sodium silicate failing the BBA HAPAS criteria after the first water sensitivity cycle. The 100% sodium silicate specimens were of such low stiffness and so deformed by the third water sensitivity cycle that it was not possible to accurately test the specimens.

The conclusion that sodium silicate increases sensitivity to water damage is supported by observations made during testing. Specimens with high sodium silicate content could be deformed by hand and started to significantly disintegrate during testing, with the edges of the samples breaking away and the mastic appearing significantly weakened, see Figure 6.24.

Figure 6.24 - Control specimen (left) and a 3 % addition of sodium silicate (right) showing the difference in edge deformation after 3 BBA HAPAS cycles.

The phenomena of sample deformation and edge disintegration were observed during testing for the following samples:

- 100% sodium silicate after 1 BBA HAPAS cycle
- 30% sodium formate and 70% sodium silicate after 2 BBA HAPAS cycles

Some minor deterioration was visible after three cycles for:

- 50% sodium formate and 50% sodium silicate
- 70% sodium formate and 30% sodium silicate

The control and 100% sodium formate specimens did not exhibit such deterioration after three cycles.

The results and observations from this section are consistent with the binder affinity testing conclusions and support the conclusion that the smooth and low surface energy component has increased water sensitivity due to the reduced adhesion of the bitumen leading to stripping of the bitumen. This results in the disintegration of the aggregate skeleton because the bond between individual aggregate particles is substantially weakened.

6.4.11.4 INVESTIGATION OF SENSITIVITY TO WATER – EUROPEAN STANDARD

Introduction

The BBA HAPAS method for determining sensitivity of water on 100mm specimens containing de-icing chemical formulation has indicated that large variations in the retained stiffness can be obtained for specimens of the same formulation. It is also acknowledged by BBA (2004) that `*The method has yet to be proven and shown to be valid*`.

For these reasons the sensitivity of water to BS EN1297-12:2003 was also conducted. The test assessed the effect of saturation and accelerated water conditioning on the indirect tensile strength, in accordance with BS EN 12697–30:2004 and used different conditioning temperatures and periods to that of the BBA HAPAS method.

Test Procedure

The test procedure requires six 100mm cylindrical specimens manufactured using impact compaction in accordance with BS EN 12697–30:2004, to be divided into two equally sized subsets having approximately the same average length and average bulk density.

The principle of the test is that one subset is maintained dry in a temperature controlled cabinet at 20^{o}C whilst the other subset is saturated and stored in water at an elevated conditioning temperature of 40 ± 1^{o}C for a period of 68 to 72 hours.

After conditioning, the wet specimens were brought to the test temperature of 20^{o}C by placing them in a second water bath at test temperature for a minimum of 2 hours. The Indirect Tensile Strength test was conducted on each of the two subsets in accordance with BS EN 12697-23:2003 using a Controls compression testing machine. This machine loads the specimen diametrically along the direction of the cylinder axis with a constant speed of displacement of 50mm/min until it breaks using two loading strips. The peak load observed during loading is recorded.

The indirect tensile strength for each specimen was then calculated using the following formula:

$$ITS = \frac{2P}{\pi DH} \qquad \text{(Eq. 6.13)}$$

- ITS = Indirect Tensile Strength expressed in GPa, rounded to three significant figures
- P = Peak Load expressed in kN, rounded to three significant figures
- D = Diameter of the specimen expressed in mm, to one decimal place
- H = Height of the specimen expressed in mm, to one decimal place

The ratio of the indirect tensile strength of the water conditioned subset compared to that of the dry subset was determined and expressed as a percentage.

Test Results

Water sensitivity tests to the European standard BS EN 12697-12:2003 were conducted on the different de-icing chemical formulations in response to concerns over the accuracy of the BBA HAPAS method.

The test method involves determining the indirect tensile strength of a dry subset and a wet subset and measuring the indirect tensile strength ratio of the two subsets. The results of the dry and wet indirect tensile strength tests and the water sensitivity ratio (ITSR) are tabulated in Table 6.14.

Additive	Av.ITSd (KPa)	Av. ITSw (KPa)	ITSR Ratio
Control – No Additive	1571	1334	84.86
3% 100SF	1317	1074	81.53
3% 70SF 30SS	1347	865	64.22
3% 50SF 50SS	1424	839	58.95
3% 30SF 70SS	1357	821	60.48
3% 100SS	1299	590	45.46

Table 6.14 – Water sensitivity to European standard BS EN 12697-12:2003

Discussion of Test Results

The measurements of water sensitivity by the European standard method are not consistent with the BBA HAPAS method, however similar conclusions regarding the influence that each chemical has on the water sensitivity can be drawn from the results.

The test confirm the reduction of the indirect tensile strength ratio (water sensitivity) is directly linked to the addition of sodium silicate to the bituminous material. This coincides with conclusions made previously by the BBA HAPAS method.

The test results also support the conclusion that the addition of 100% sodium formate is not significantly detrimental to the water sensitivity of the mixture. The 100% sodium formate passed the 80% water sensitivity ratio criteria, however a reduction of water sensitivity ratio by 3.5% was observed for the 100% sodium formate when compared to the control.

The main difference between the European standard method and the BBA HAPAS method is that the European standard method indicates that the water sensitivity of the bituminous mixture is strongly related to the inclusion of sodium silicate.

Each de-icing chemical formulation containing sodium silicate failed to retain 80% of the dry subset strength when subjected to the European standard method.

The inclusion of small amounts of sodium silicate significantly reduced the water sensitivity ratio. For example, the 3% addition of a blend of 70% sodium formate and 30% sodium silicate reduces the water sensitivity by approximately 20.5% when compared to the control.

This trend continues for increasing sodium silicate contents with the exception of a 30% sodium formate and 70% sodium silicate blend, which shows a marginal improvement when compared to a 50/50 blend of sodium formate and sodium silicate.

This effect is demonstrated below in Figure 6.25, which shows the ITSR ratio against sodium silicate additions where sodium formate makes up the additional additive.

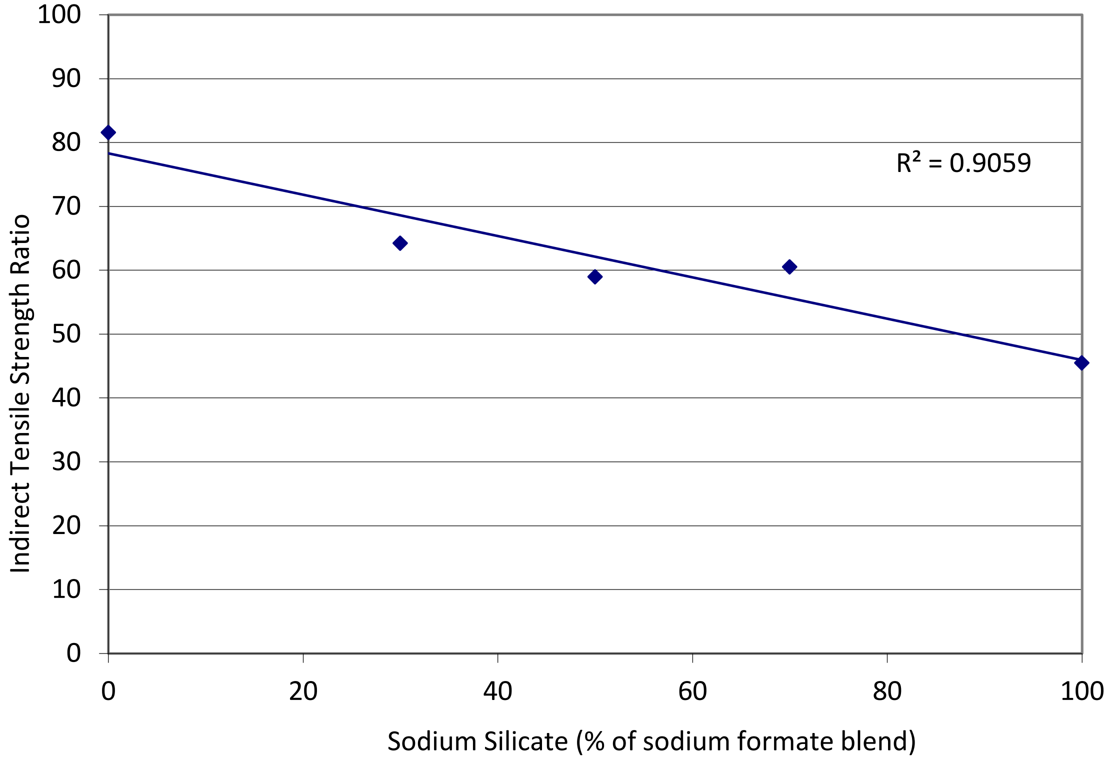


Figure 6.25 – Indirect Tensile Strength ratio against sodium silicate addition

By plotting the dry and the wet indirect tensile strengths separately, it can be seen that the reduction caused in the indirect tensile strength ratio for the de-icing chemical formulations containing sodium silicate is primarily due to the reduction in the wet indirect tensile strength. The dry indirect tensile strength remains relatively constant for all de-icing chemical formulation, as demonstrated in Figure 6.26.

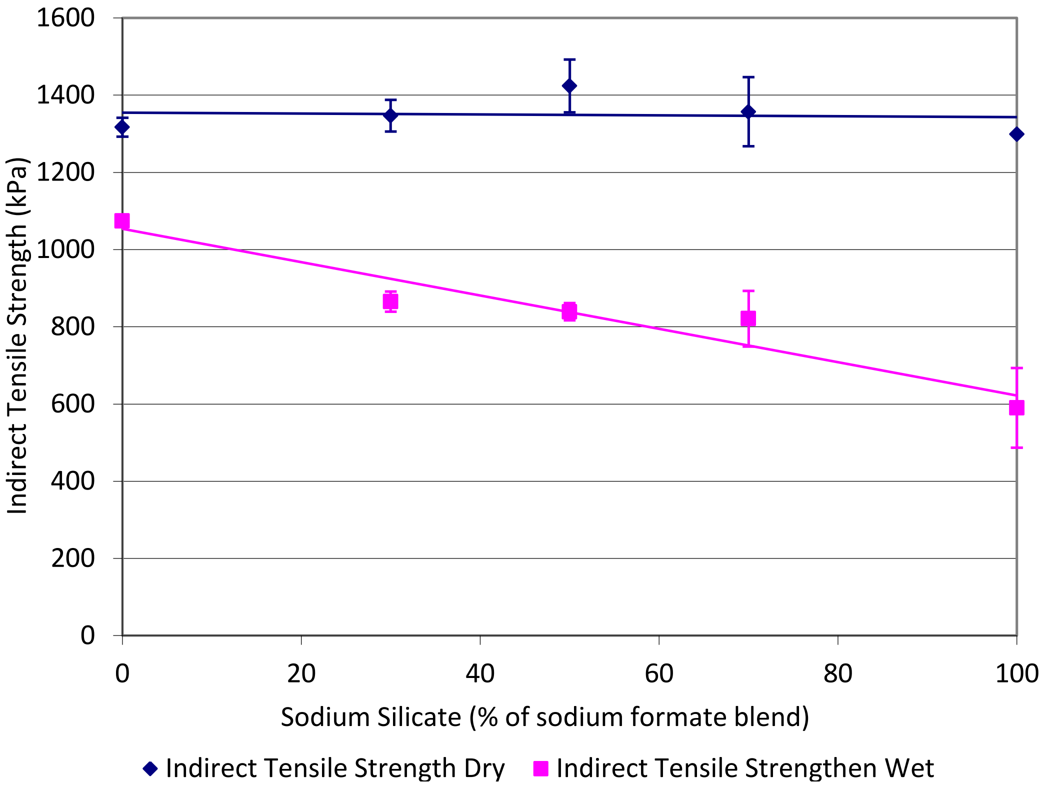


Figure 6.26 – Wet and dry Indirect Tensile Strength values for each sodium formate and sodium silicate blend

Observation of the asphalt briquettes after testing provide an indication of the failure mechanism. Sodium silicate samples after water conditioning failed by means of "deformation" as defined in the BS EN 12697-12:2003. This is indicative of failure through the mastic and around the aggregate particles. In contrast the dry specimens and the wet control and 100SF specimens failed by "combination", indicating a combined influence of the aggregate interlock and bituminous mastic.

The conclusions from the European standard testing are supportive of the conclusions drawn in the previous sub-sections indicating an increased susceptibility of deterioration in water when sodium silicate is present.

6.4.11.5 SUBMERGED WHEELTRACKING

Introduction

A submerged wheeltracking test can be used to assess the premature failure susceptibility of bituminous materials due to weakness in the aggregate structure, inadequate binder stiffness, moisture damage and other factors including adhesion between the aggregate and bitumen.

The principle of the test is to apply a repeated load using the same loading and loading rate as the wheeltracking small device when the specimen is submerged under water. The application of this test method is considered to closely resemble actual loading (trafficking) and environmental conditions exerted on a pavement surface course.

Test Method

The submerged wheeltracker used was based on the standard small device wheeltracking device with a compartment to maintain a controlled volume of water, see Figure 6.26. This compartment held 600ml of water and fully submerged the specimens.

In total, three slabs of the same material were loaded into the chamber for each test. These slabs were manufactured to a void content of 5%. The specimens were loaded by means of a 7kN load axle at a frequency of 26.5 load cycles per 60s. The slabs were submerged and continuously loaded for 12 hours at a constant elevated temperature of 60°C. The testing was restricted to 12 hours to prevent the evaporation of water from the test chamber.

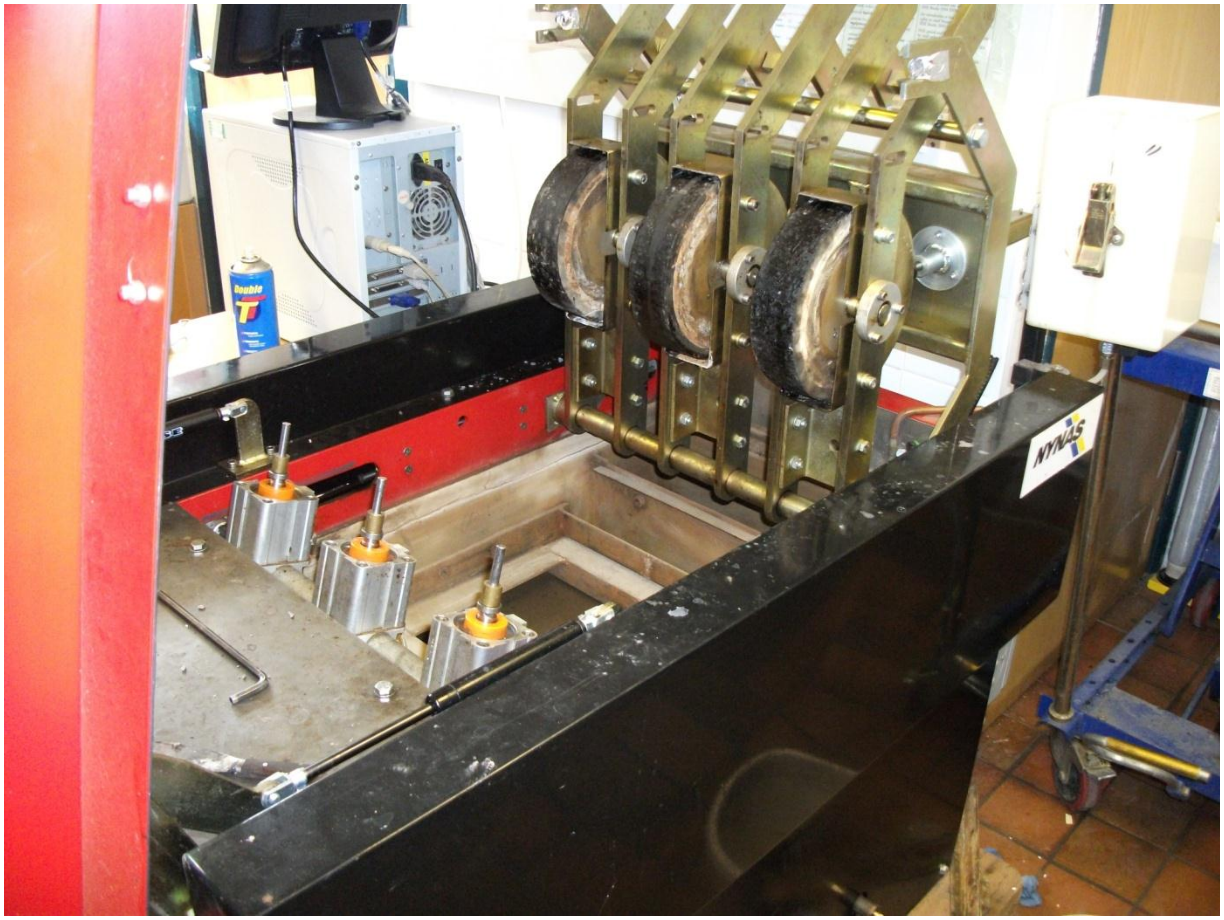


Figure 6.27 - Submerged wheeltracker equipment used for testing

Throughout the duration of the test the mean rut depth was measured every 25 cycles for each of the three tracks. The slabs were also visually observed and any defects in the specimens recorded.

Test Results

The mean rut depth for each de-icing chemical formulations over a period of 12 hours is displayed graphically in Figure 6.28.

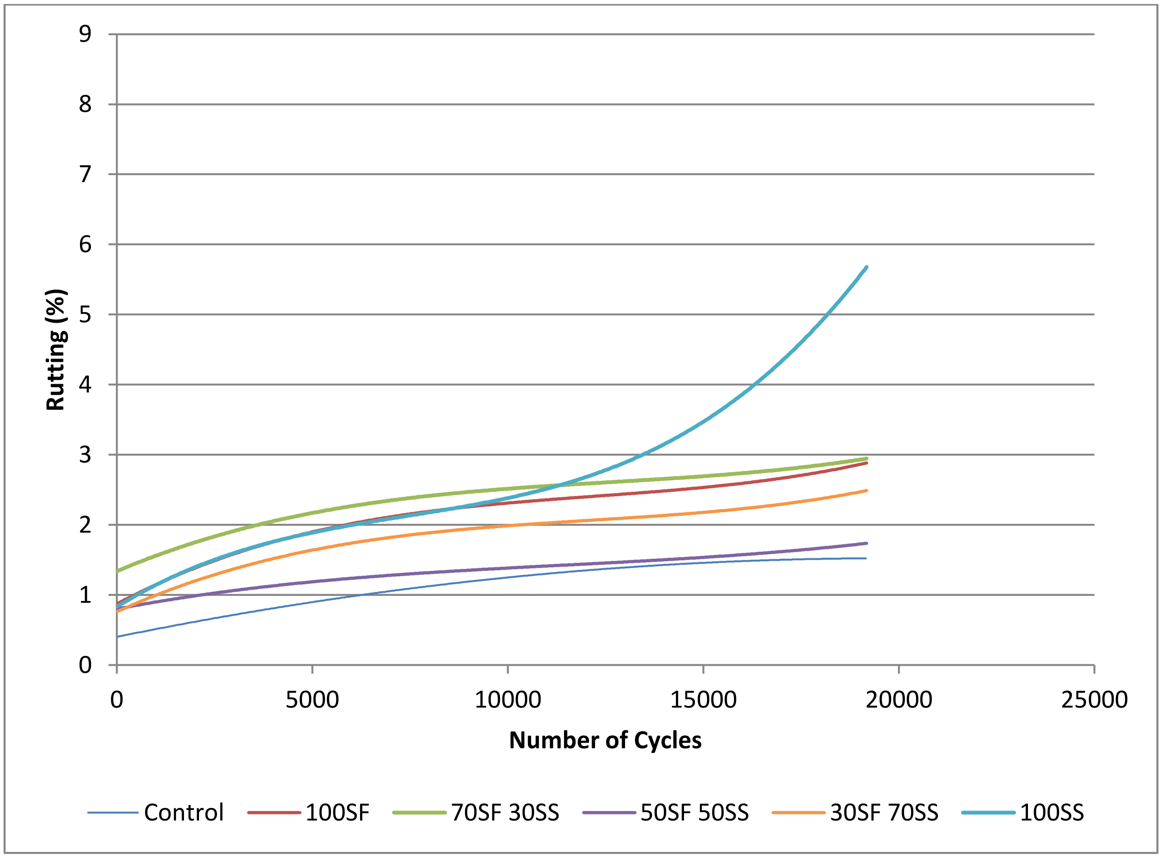


Figure 6.28 – Mean rut depths measured by submerged wheeltracker testing for each de-icing chemical formulation

Discussion of Test Results

The submerged wheeltracking test results show no significant difference between the control and the majority of the de-icing chemical formulations had ruts between 1 to 3% after 20,000 cycles. As per the previous water sensitivity testing regimes, the exception to this was the 100% sodium silicate formulation which rutted by over 6%.

Close inspection of high sodium silicate specimens after 12 hours of wheeltracking demonstrated the significant stripping of bitumen from the aggregate surface. The aggregates particle on the surface had little or no bitumen coverage, as shown in Figure 6.29. This is in contrast to the control specimen (Figure 6.30), which showed no bitumen stripping or aggregate loss. This confirms the results demonstrated by the binder affinity testing.

Further examination of the high sodium silicate mixes demonstrated signs of fretting breakdown of the aggregate structure. Rounding of the stripped aggregate particles were also observed, which have been attributed to abrasion between the aggregate particles during testing.

To assess the degree of disintegration the 100SS specimen was allowed to dry and the loose aggregate particles were lightly brushed from the surface. This process demonstrated the signification disintegration of the asphalt surface and breakdown of the aggregate structure (as demonstrated in Figure 6.31).

Further visual observations would indicate that other high sodium silicate specimens would have also failed if the test could have been conducted for a longer period.

This significant level of deterioration is unacceptable and highlights that high sodium silicate mixes are unsuitable modifications. Considering these conclusions and observations, the use of submerged wheeltracker can be considered to be a suitable single test to highlight the weakness of low surface energy materials.

Figure 6.29 – Photograph demonstrating the stripping of surface aggregate on the 100% sodium silicate sample after 12 hours of wheeltracking

Figure 6.30 – Photograph of control sample surface after 12 hours of wheeltracking

Figure 6.31 – Photograph demonstrating the disintegration and breakdown of aggregate structure of the 100% sodium silicate sample shown in Figure 6.29 after drying and the removal of loose aggregate

6.4.11.6 DISCUSSION OF WATER SENSITIVITY

A number of water sensitivity evaluations have been conducted including work of adhesion calculations, binder affinity testing and a range of immersions tests (BBA HAPAS/ EN 12697-12:2003) and submerged wheeltracking.

Each of the evaluations has conclusively demonstrated poor water sensitivity for the 100% sodium silicate formulation.

A number of tests have shown that inclusions of this material at various concentrations in de-icing chemical formulations can significantly reduce the performance of the asphalt. This is due to the relatively smooth rounded surface providing limited interlock and bonding area and the low surface energy nature of this material.

Considering the test results and visual observations it would appear that high sodium silicate samples are unacceptable modifications. This is due to water sensitivity and deterioration by two principle mechanisms.

The first mechanism is the adhesive failure due to stripping. Stripping is a physiochemical process in which separation of bitumen binder film from aggregate surfaces occurs as a result of prolonged contact with water. Evidence of the stripping of bitumen was provided by the binder affinity testing and submerged wheeltracking tests, with limited binder coverage remaining on the aggregate surfaces of high sodium silicate content de-icing chemical formulations. A significant amount of research has been conducted on the tendency for stripping of the binder film in the presence of water and the tendency is highly correlated to the surface properties of the asphalt binder, aggregate and filler.

As stripping starts to occur a second and more cohesive failure mechanism can occur due to the loss of the mixture stiffness and breakdown of the aggregate structure. Studies by (Martins et al. 2003) postulated that the strength of asphalt significantly decreases, as stripping starts to occur and this overshadows the aging-stiffening effect of the bitumen, see Figure 6.32.

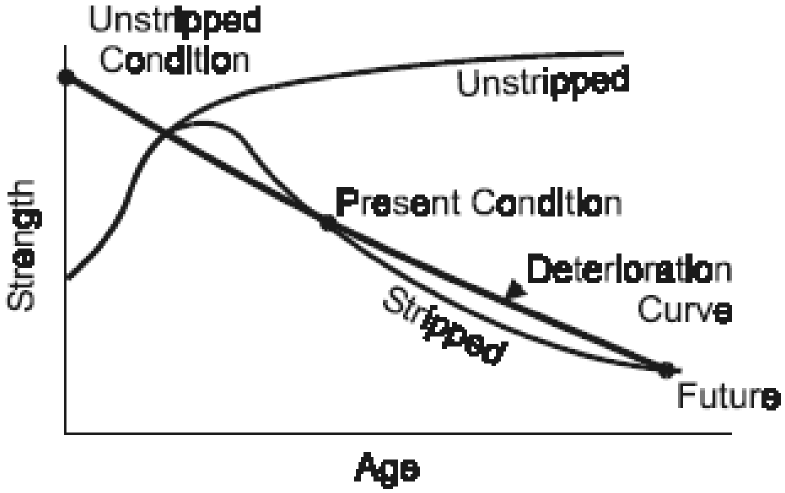


Figure 6.32 – Deterioration curve of asphalt field cores (Martins et al. 2003)

This rapid deterioration was observed for 100SS de-icing chemical formulation with reduced performance and disintegration after only one cycle of the BBA HAPAS test and high levels of disintegration of the submerged wheeltracking specimens. These observations indicate that there is an increased risk of early life failure and reduced service life of the pavement surface course with high concentrations of sodium silicate and possibly other low surface energy materials.

Based on the surface energy calculations, it was anticipated that sodium formate would also exhibit poor water sensitivity, however this was not measured in any of the water sensitivity tests conducted. This may be attributed to the good mechanical adhesion achieved due to the surface roughness providing a lock and key with the bitumen and a greater area of bonding. It is recommended that these factors are considered in addition to surface energy parameters when considering future suitable chemicals.

6.4.12 INVESTIGATION OF SKID RESISTANCE

Introduction

Skid resistance is a property of the trafficked surface which limits the relative movement between the contact patch of a vehicle tyre and the surface. It is an essential design parameter of road surfaces for safety reasons. Previous experience and concerns regarding the slipperiness of the Verglimit product indicated that skid resistance is an essential parameter to consider when selecting de-icing additives.

Test Procedure

Initial laboratory assessment of skid resistance was determined using the pendulum tester. It incorporates a spring loaded slider comprising of a standard rubber attached to the end of a pendulum. On releasing the pendulum from a horizontal position, the loss of energy as the slider assembly passes over the test surface is measured by the reduction in length of the upswing using a calibrated scale.

The pendulum tester measures skid resistance in terms of the Pendulum Test Value (PTV). The Pendulum Test Value (PTV) is defined as the loss of energy when the standard rubber coated slider assembly slides across the test surface providing a standardised value of skid resistance.

This method measures the slip/skid resistance of a small area of a surface (approximately 0.01 m^2). The methodology was selected because it is the most practical measure of skid resistance of a surface under laboratory conditions because the device remains stationary at the test location. Testing was conducted on slabs manufactured as in Section 6.3.7.

Testing was conducted within the wheel track of these specimens in accordance with Procedure 9.2 Measurements in Laboratory stated in BS EN 13036-4:2003 `*Road and Airfield Surface Characteristic Test Methods – Method for measurement of slip/skid resistance of a surface – The Pendulum Test*` using a TRL rubber slider.

Laboratory specimens, water for wetting the surface, the pendulum tester and the slider were kept in a room at controlled temperature of 20 ± 2°C for at least two hours before the test started and remained for the duration of the test. The test procedure was performed five times, with copious amounts of water applied to the surface before testing. If the first five readings differed by more than three units, the test was repeated until three successive readings were constant and this value was recorded.

Due to concerns that the soluble chemicals could leech to the surface under heavy rainfall conditions leading to a reduction in the overall skid resistance, a second phase of testing was conducted. For this second phase of testing water was maintained on the test surface for 1 hour after the initial test prior to the skid resistance being re-measured. To ensure consistency of the results, testing for each testing phase was conducted on the same contact patch.

Test Results

Skid resistance was measured in terms of the Pendulum Test Value (PTV) conducted in accordance with BS EN 13036-4:2003 under wet conditions and after a second phase of soaking the test specimens.

Mean Pendulum Test Value for the de-icing formulations are demonstrated in Table 6.15.

De-Icing Formulation	Mean PTV Wet	Mean PTV Wet (1 hour soaking)
Control – No Additive	68	66
3% 100SF	68	72
3% 70SF 30SS	70	71
3% 50SF 50SS	70	69
3% 30SF 70SS	71	70
3% 100SS	70	72

Table 6.15 – Pendulum Test Value of modified asphalt slabs

Discussion of Test Results

The pendulum test values demonstrate that the skid resistance of the de-icing chemical formulations are comparable to that of a control surface when wet and soaked conditioning procedures employed. With Pendulum Test Values ranging from 66 to 72.

In general, the Pendulum Test Values measured remained consistent between the wet and soaked conditions, indicating that the prolonged presence of water did not affect the results and that early life leeching is not a concern. This is likely to be due to the aggregate particles protruding above the water level that can be maintained on the surface.

TRL (1969) specifies minimum Pendulum Test Values for sites at intervals of 10PTV. Any observed differences can be considered minimal and it can be concluded that the de-icing chemical formulations do not significantly affect skid resistance when measured by the pendulum skid resistance tester under the above conditions.

6.5.0 PHASE 2 – DETERMINATION AND INFLUENCE OF MOISTURE ABSORPTION ON THE MECHANICAL PROPERTIES OF ASPHALT

Moisture absorption is a key parameter when considering the suitability and effectiveness of a de-icing chemical modification of an asphalt surface course.

The absorption of moisture from the atmosphere will allow a chemical formulation to enter into a solution quicker and enhance the anti-icing performance. However, a moisture absorption rate that is too high could lead to caking in shipments and/or expansion and cracking of the asphalt pavement around the chemical. At high rates of humidity, there is also potential for the surface to become slippery because the moisture contained within the asphalt surface and/or the transferred chemical.

Concerns with previous products have been related to early life cracking, decomposition and reduce skid resistance with some suggesting that the issues may be related to moisture absorption. Despite these suggestions, the role of moisture absorption does not appear to have been previously examined by researchers.

The extent of moisture absorption during the high humidity of the winter period was evident at trial sites, as discussed later in this report (Chapter 7.0). *"The anti-icing surface course maintained a damp appearance in contrast to dry control surface courses."* This degree of moisture absorption has the potential to influence the service life of the asphalt, especially considering that it has been demonstrated in Phase 1 of testing that the specific de-icing chemical formulations are susceptible to moisture damage. This part of the thesis will provide new research and provide understanding of how moisture absorption can influence this type of pavement surface.

This phase of testing evaluates the susceptibility of de-icing chemical formulations to damage through moisture absorption at high relative humilities. The phase of testing considers the levels absorbed by:

- The de-icing chemicals
- Chemically modified asphalt briquettes

The chapter then examines the influence that the moisture absorption has on the following asphalt properties:

- Indirect tensile stiffness modulus
- Indirect tensile strength
- Resistance to fatigue
- Skid resistance

6.5.1 MOISTURE ABSORPTION - CHEMICAL ADDITIVES

Introduction

The determination of the moisture absorption of individual chemical concentrations will quantify the potential of each chemical to draw moisture from the atmosphere and provide an indication of the chemical's suitability.

Previous work by Baum et al. (1992) measured the moisture pick up of single chemical solutes over a period of 6 weeks. The methodology used is principally based on the previous work undertaken by Baum et al. (1992) with comparisons made between the two studies.

Test Procedure

Approximately five grams of each chemical formulation were weighed under ambient conditions to the nearest 0.001g and placed into cylindrical metal containers approximately 50mm diameter by 20mm deep. The chemical formulations were dried at 100^oC for a period of 12 hours until constant mass had been achieved. The specimens were cooled and immediately weighed.

A glass dessicator was used as a humidity chamber, with the lower section below the perforated shelf filled with a saturated sodium chloride solution. The sodium chloride solution was selected for comparative purposes with the study by Baum et al. (1992) and designed to achieve humidity of 75%. This solution was allowed to equilibrate in the dessicator for a period of one week prior to testing.

The samples were weighed five days a week for a period of 6 weeks and the weights recorded. The percentage of weight gain was then calculated using the following equation:

$$\text{Weight Gain (\%)} = \frac{\text{Hydrated Weight of Sample Time(n)} - \text{Initial Dried Weight of Sample}}{\text{Initial Dried Weight of Sample}} \times 100 \qquad \text{(Eq. 6.14)}$$

Test Results

Test results for moisture absorption over an 6 week period at 75% humidity are displayed in Figure 6.33.

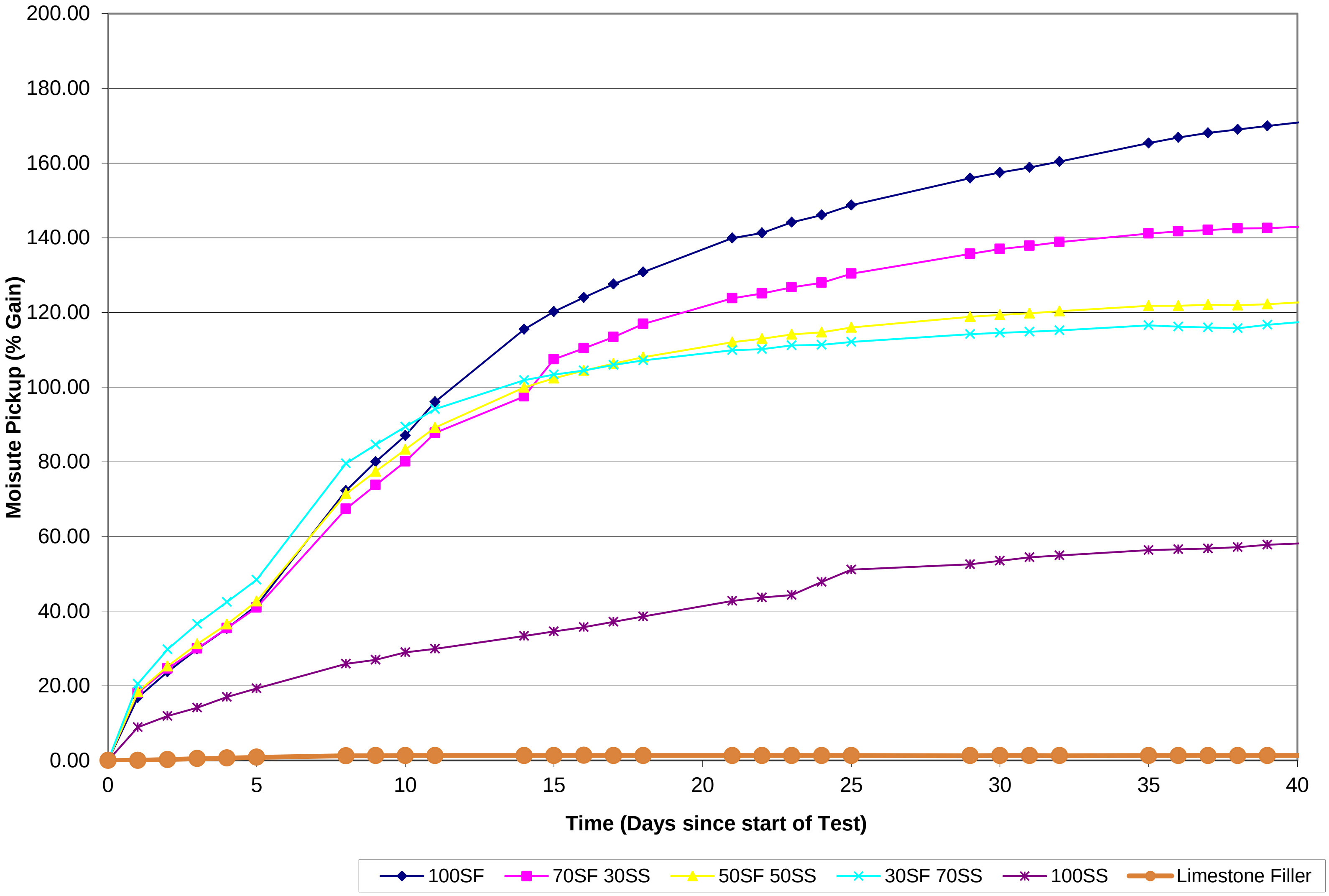


Figure 6.33 - Moisture absorption of chemical samples at 75% humidity for 6 weeks

Discussion of Test Results

The results demonstrate that sodium formate absorbs significantly greater quantities of moisture relative to sodium silicate. This is due to the hydroscopic nature of sodium formate. The results for the sodium formate powder are consistent with those presented by Baum et al. (1992). After 6 weeks moisture absorption values of 170% were measured in comparison to the 177% measured by Baum et al. (1992).

De-icing chemical formulations of sodium formate and sodium silicate demonstrated initial moisture absorption rates comparable to sodium formate when used independently. After ten days, the rate of moisture absorption of the sodium formate/sodium silicate de-icing chemicals formulations had reduced relative to sodium formate when used independently. This resulted in lower levels of moisture absorbed after a period of 6 weeks.

The level of moisture absorption after 6 weeks appears to be heavily related to the sodium formate content of the de-icing chemical formulation. This relationship does not appear linear and the small inclusions of sodium formate significantly increased moisture absorption.

All de-icing chemical formulations gained in excess of 100% weight gain after an 6 week period. In contrast, the limestone filler absorbed only small amounts of moisture, with a total gain in weight of 1.35% after 6 weeks.

The testing has demonstrated that prolonged and continuous exposure of the de-icing chemicals to high humidity levels can result in excessive levels of moisture being absorbed. The presence of this moisture and any volumetric expansion may influence the asphalt service life. The limestone filler did not absorb significant quantities of moisture and it is anticipated that the control specimens are not susceptible from moisture gain at high relative humdities.

6.5.2 MOISTURE ABSORPTION – CHEMICALLY MODIFIED ASPHALT

Introduction

The independent moisture absorption of chemicals may not necessarily reflect the moisture absorption when the chemical forms part of the bituminous mixture. When the chemical particles are encased by bitumen and compacted in a bituminous material the moisture absorption is likely to reduce due to a reduced exposure to the atmosphere.

This section of the report aims to quantify the potential of each de-icing chemical formulation to absorb moisture from the atmosphere when it forms part of the bituminous mixture, thereby providing further indication of the chemical's suitability. The section will also consider the relationship between the moisture absorption of chemical particles and the moisture absorption of the chemically modified bituminous material.

Test Procedure

Standardised asphaltic specimens were produced to ensure factors such as surface texture, void content and chemical dispersion were comparable for each specimen. This was achieved by manufacturing 100mm cylindrical specimens by impact compaction of 50 blows per face, in accordance with BS EN 12697–30:2004.

To ensure a direct comparison, the chemical was added to the aggregate at 3% by mass. This was to ensure continuity from previous work on sections considering the mechanical properties of asphalt. Specimen void content was maintained between 6.0% ± 1.0% air voids and any specimen outside this range was discarded. Mixing times were kept consistent and used a high mixing speed of 50rpm to ensure consistent chemical dispersion.

Following manufacture, the asphalt briquettes were weighed to the nearest 0.1g and placed in a dessicator to achieve a humidity of 75%. This was to ensure comparative purposes with the study by Baum et al. (1992) and assessments of the moisture absorbed by the de-icing chemical particles in section 6.5.1. This solution was allowed to equilibrate in the dessicator for a period of a week prior to testing.

The six asphalt briquettes were weighed each week for a period of 30 weeks and the moisture gain calculated for the briquettes each week. The moisture absorption for the quantity of chemical in the briquette was then adjusted by assuming that the chemical represents 2.81% of the asphalt briquette by mass (3% of aggregate by mass). This is based on the assumption that correct dispersion of the chemical had occurred and uniform samples had been taken.

The mean moisture absorption of the chemical particles in each of the six briquettes was calculated on a weekly basis, these results are presented in Figure 6.34.

The moisture absorption is strongly dependent upon the void content, which enables a passage for moisture to enter and increases the surface area of the briquettes. As the void content varied up to 1% for each sample, the results were normalised to the mean void content of 6% by assuming a linear relationship between moisture absorption and void content. These results are presented in Figure 6.35.

Test Results

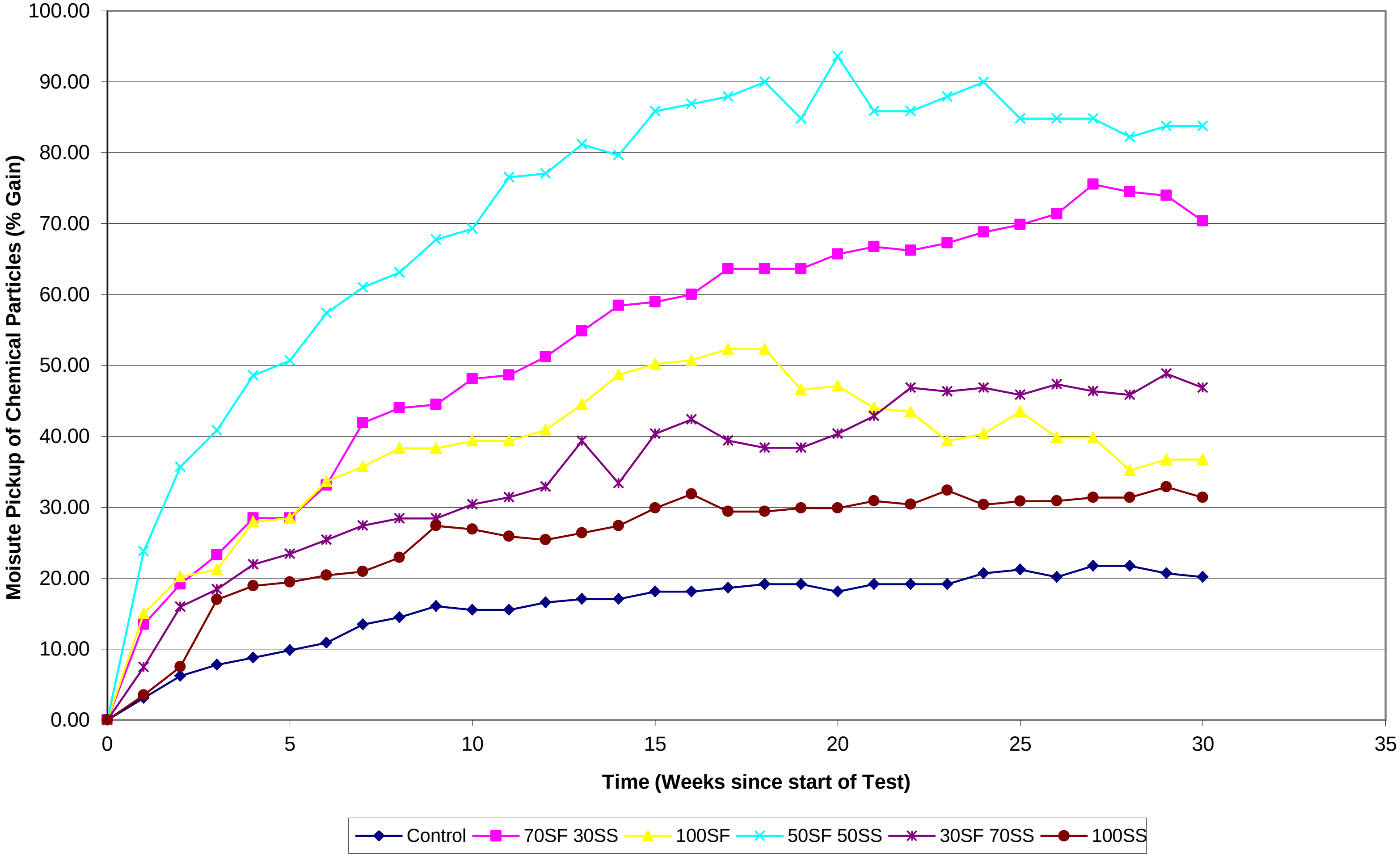


Figure 6.34 - Moisture absorption of chemical within asphalt briquettes at 75% humidity for 30 weeks

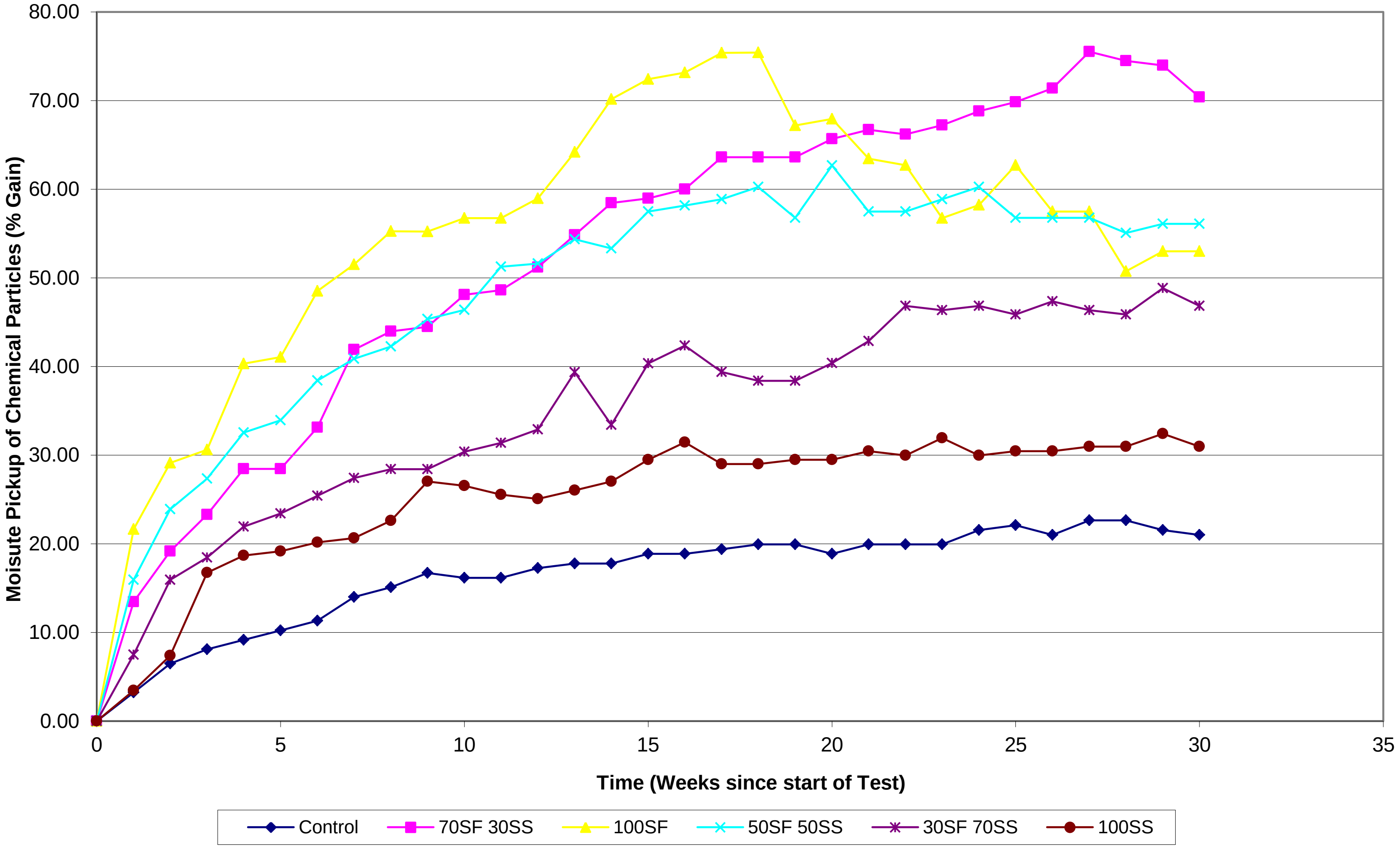


Figure 6.35 - Moisture absorption of chemical within asphalt briquettes at 75% humidity for 30 weeks – adjusted to 6.0% air void content

Discussion of Test Results

Measurement of moisture absorption is based on the mean results of the six briquettes normalised to a target air void content of 6.0%

The experimental data demonstrates that the de-icing chemical formulations absorb significant amounts of moisture in comparison to the control bituminous mixture. The results show a consistent trend to moisture absorption experiments of the chemical additives presented in Section 6.5.1, with high sodium formate formulations absorbing the highest levels of moisture.

Comparison of moisture absorption measurements of chemicals and modified briquettes demonstrated that the incorporation of the chemicals into modified pavement surface courses reduces the rate of moisture absorption, in comparison to chemical solutes. A significant amount of moisture is still absorbed with the chemical particle increasing in mass by up to 70%, see Figure 6.35. This will typically be absorbed by chemical exposure at the surface of the pavement and through the voids.

Comparing the chemical additive moisture absorption and the chemically modified asphalt moisture absorption results, enables the reduction of moisture absorbed by chemicals when incorporated into a bituminous mixture to be calculated. A comparison of absorption over a five week period is displayed in Figure 6.36.

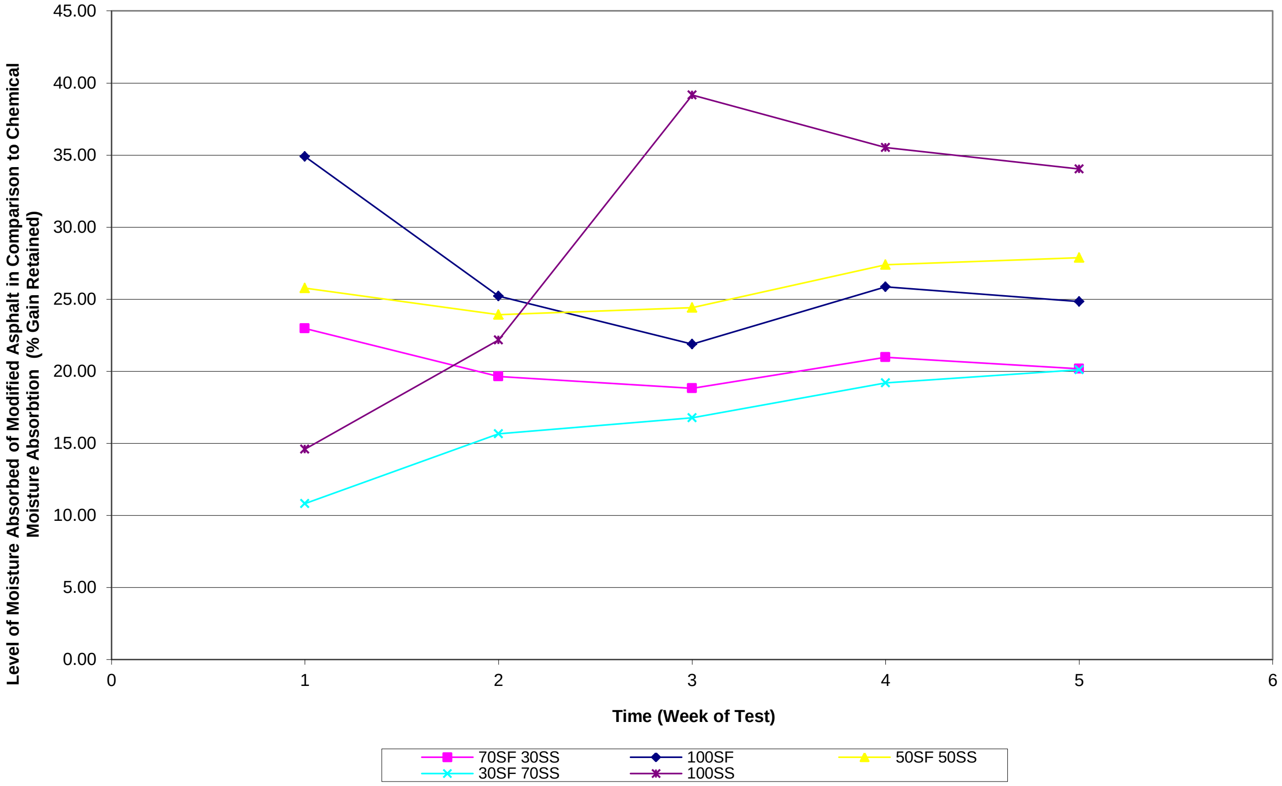


Figure 6.36 – Comparison of moisture absorbed between modified briquettes and de-icing chemical solutes

The results demonstrate that over the first five week period the chemically modified asphalt absorbs between 15-25% of the levels of moisture absorbed by the chemical particles. It can be concluded that incorporating the chemical into a pavement surface course reduces the levels of moisture absorbed. This is due to the combined effect of encasing the de-icing chemicals in bitumen and compacting the bituminous mixture. The net effect is that moisture is restricted in reaching the de-icing chemical particles.

6.5.3 MOISTURE PICK UP – INDIRECT TENSILE STIFFNESS MODULUS

Introduction

It has been established that the specific chemical de-icing formulations still absorb significant quantities of moisture when encased in a bituminous mixture. It has been suggested that a moisture pick up which is too high can lead to expansion and cracking of the asphalt pavement around the chemical and/or early life pavement failures. However, no measure of the potential of absorbed moisture to influence the pavement service life has been confirmed and early life failures of previous products have been attributed to a wide range of causative factors.

An indicative parameter for overall pavement service life is stiffness. Stiffness is a measure of the resistance of a material to deform under an applied load and it is a fundamental material property when designing pavements. This experiment procedure will quantify the influence of moisture absorption has on the Indirect Tensile Stiffness Modulus of bituminous materials.

Test Procedure

Testing of Indirect Tensile Stiffness Modulus was conducted simultaneously with *Section 6.5.2 Moisture Pick Up – Chemical Additives* test procedure using the same asphaltic specimens. Specimens were maintained in a glass dessicator at 75% humidity stored in a temperature controlled cabinet a 20^{o}C. Initially, and on a weekly basis, the Indirect Stiffness Modulus for each briquette was determined in accordance with *BS EN12697-26:2004(E) Appendix C* and as stated in *Section 6.4.4 Investigation of Indirect Tensile Stiffness Modulus*.

The Indirect Stiffness Modulus for each week was taken as the mean of the six briquettes on each test in two orientations. Testing was conducted for a period of 30 weeks, in order to establish the influence of long term moisture absorption while maintaining a practical test procedure within the time restrictions.

The retained Indirect Tensile Stiffness Modulus was plotted against the number of weeks of accelerated condition and against the level of moisture absorption due to the varying quantities of moisture absorbed.

Test Results

Measurements of Indirect Tensile Stiffness Modulus were conducted each week after conditioning at 75% humidity. The results are displayed in Figure 6.36 and are based on the mean results of six briquettes.

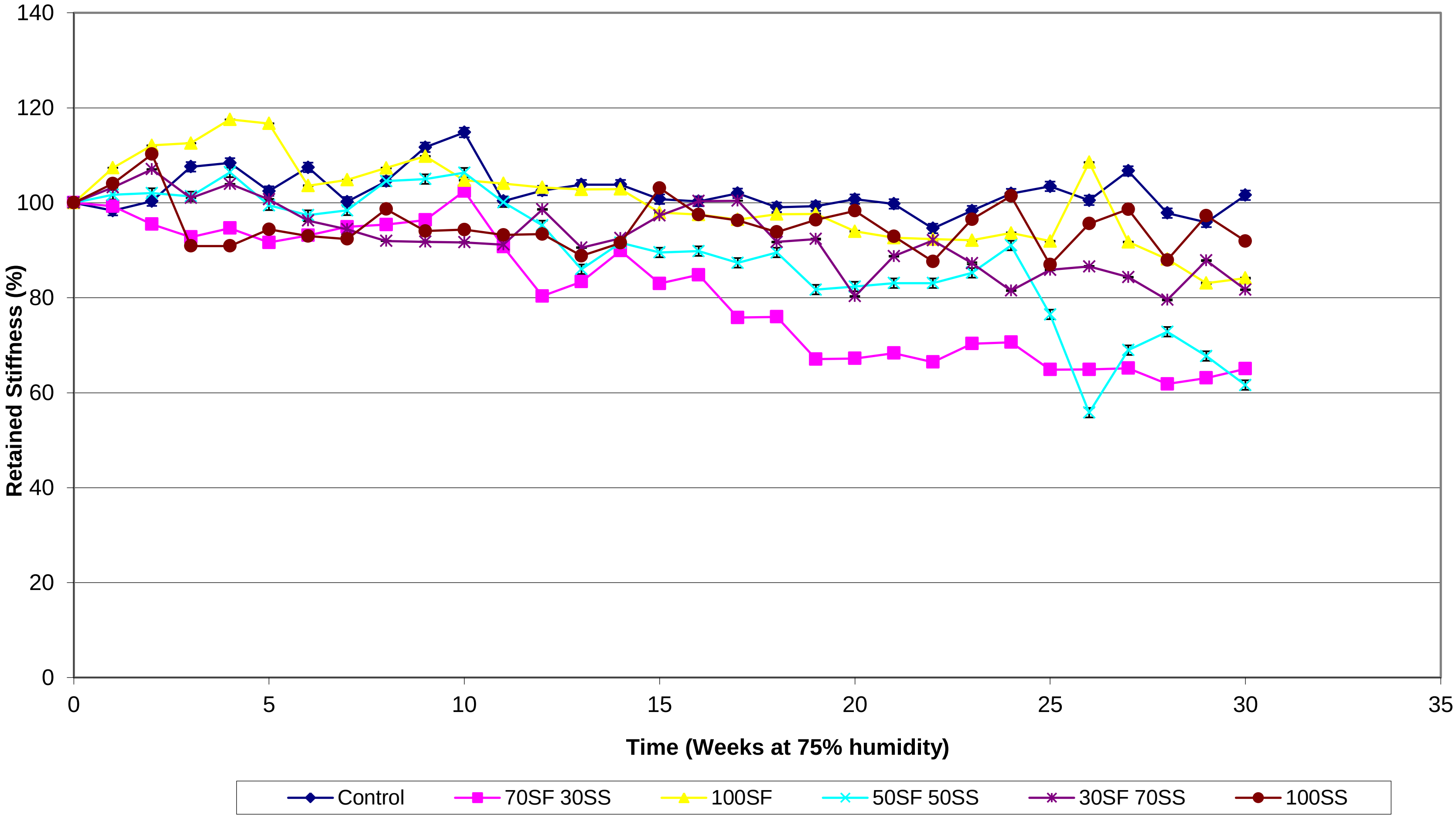


Figure 6.37 - Retained Indirect Tensile Stiffness Modulus per week at 75% humidity for 30 weeks

Discussion of Test Results

The results demonstrate a degree of fluctuation in the retained stiffness modulus each week, which is typically due to the combination of the test method and the pavement surface course features such as the alignment of voids and presence of moisture at the contact points. Despite the localised fluctuations, testing over a long period (30 weeks) has enabled an overall trend to be established and the following conclusions to be made.

The control surface demonstrates a degree of fluctuation around the equilibrium point of 100% retained stiffness. This confirms that the standard asphalt surface course material’s stiffness is not affected by high humidity conditions or the limited moisture absorption.

The formulations of 100% sodium formate and 30% sodium formate and 70% sodium silicate retained stiffness over a 30 week period reduced to approximately 80%. This level is not considered critical, however the effect may become more significant over a longer period, e.g. in excess of 30 weeks.

The low surface energy material of sodium silicate has a retained stiffness which fluctuated between 90-100%. This would indicate that despite the susceptibility for 100SS specimens to deteriorate when submerged in water as demonstrated in section 6.4.11, the levels of moisture absorbed during the period were not at a level to significantly reduce the stiffness performance.

In contrast, the modified asphalt of 70% sodium formate 30% sodium silicate and 50% sodium formate 50% sodium silicate are susceptible to the moisture absorbed at high humidities.

The results demonstrate a consistent but relatively minor reduction in the early life stiffness. Following approximately 10-15 weeks of accelerated moisture conditioning, the reduction in stiffness appears to increase. After the 30 week period both of the chemical formulations demonstrated a 40% loss in stiffness.

This is a significant decrease and it can be attributed to the combined effect of:

- The hydroscopic and high moisture absorption of sodium formate, which draws moisture from the atmosphere at high relative humidities in the bituminous mixture through the asphalt surface and surface voids.
- The inclusion of the water sensitive chemical of sodium silicate, which leads to an increased tendency for the bitumen to strip from the chemical surface and cohesive failure of the mastic, as concluded in section 6.4.11.6.

Combinations of the two attributes above can deteriorate significantly under the environmental conditions of high relative humidity alone. This is occurs as moisture is drawn into the pavement by the sodium formate particles. The prolonged presence of water in the vicinity of sodium silicate particles leads to stripping and the weakening of the mastic resulting in reduce asphalt stiffness.

Asphalt containing combinations high moisture absorption (such as sodium formate) and low surface energy materials (such as sodium silicate) should be used with caution. Standard test methods do not take this phenomena into account and therefore the mix design process for de-icing chemical formulations should be revised to account for deterioration due to moisture absorption.

6.5.4 MOISTURE PICK UP – INDIRECT TENSILE STRENGTH

Introduction

In addition and in support of the Indirect Tensile Stiffness Modulus measurements, an experiment measuring the effects of moisture absorption on Indirect Tensile Strength was conducted. Indirect Tensile Strength is an assessment of the level of stress which can be withstood prior to fracture. It is anticipated that any deterioration of the bituminous mixture due to increased humidity would be reflected in the Indirect Tensile Strength results in a similar manner to the Indirect Tensile Stiffness Modulus testing presented in the previous section of this report

Test Procedure

The Indirect Tensile Strength is a destructive test. This test method involves applying an indirect load and measuring the peak load to fracture. The horizontal stress applied at the centre of the specimen is then calculated in accordance with the standard equation.

The Indirect Tensile Strength was measured on a set of six cylindrical specimens compacted to target void content of 6.0% and tested in accordance with `*BS EN 12697-23:2003 Determination of the Indirect Tensile Strength of Bituminous Specimens*`.

The testing was measured on an unconditioned set of cylindrical samples. A second set of samples were conditioned at 75% humidity and tested after a period of 30 weeks.

Test Results

The test results for the unconditioned and 30 week specimens at 75% relative humidity are demonstrated in the Table 6.16.

	Mean Indirect Tensile Strength (KPa)					
Weeks	Control	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
0	1571	1317	1347	1424	1357	1299
30	1645	1403	955	909	1514	1934
	Retained Indirect Tensile Strength (%)					
-	105	107	71	64	112	149

Table 6.16 - Indirect Tensile Strength against moisture adsorption

Discussion of Test Results

The test results and trend for the Indirect Tensile Strength are relatively comparable for the 70% sodium formate 30% sodium silicate and 50% sodium formate 50% sodium silicate chemical formulations to the Indirect Tensile Stiffness Modulus results presented in the previous section. These test results confirm that the combination of high moisture absorption chemicals and low surface energy materials deteriorate the bituminous mixture in the presence of high relative humidities, as explained in the previous section.

The Indirect Tensile Strength results for the remaining chemical formulations are comparable to the control specimen. These results differ from the Indirect Tensile Stiffness Modulus results which demonstrated a slight decrease in the modulus measured.

The exception to the results is the 100% sodium silicate, which demonstrated a significant increase in retained indirect tensile strength. No explanation for this significant increase can be provided. The results do support the overall conclusion that the levels of moisture absorbed during the period were not at a level to significantly reduce the performance of the asphalt containing only 100% sodium silicate.

6.5.5 MOISTURE PICK UP – FATIGUE

Introduction

Resistance to fatigue is a fundamental characteristic of any asphalt surface course and historical evidence suggests this is a particular problem for chemical modified anti-icing surface courses. The two chemically modified surface courses of Verglimit and Grikol, discussed in Sections 3.4.1 and 3.4.2 respectively, experienced varying degrees of cracking, resulting in significantly reduced service lives. Evidence of moisture absorption has also been identified on chemical modified pavement surface course with specific Verglimit sites being acknowledged as absorbing significant levels of moisture.

It is currently unknown if a relationship exists between the moisture absorption and the susceptibility of surface course cracking. This section aims to compare fatigue performance against moisture absorption.

Test Procedures

In order to be able to compare with previous fatigue testing conducted in Section 6.4.9 of this report and to UK practice the Indirect Tensile Fatigue Test (ITFT) to the draft DD ABF:2000 standard was conducted using the controlled stress methodology previously reported.

Test samples were conditioned at 75% humidity and the stiffness and number of cycles to failure tested after 30 weeks. The results were compared to the standard unconditioned fatigue results presented in Section 6.4.9 by calculating the number of cycles to failure at a strain of 100.

Test Results

The test results comparing the number of cycles to failure at a strain of 100 for the unconditioned and moisture conditioned specimens are presented below:

Additive	Number of Cycles to Failure at a Strain of 100	
	Standard	30wk at 70%RH
Control – No Additive	68,072	152,290
3% 100SF	26,427	30,866
3% 70SF 30SS	35,005	10,877
3% 50SF 50SS	32,345	42,641
3% 30SF 70SS	46,770	20,493
3% 100SS	41,817	36,497

Table 6.17 – Number of cycles to failure at a strain of 100 for standard and after 30 weeks conditioning at 70% relative humidity.

Discussion of Test Results

The number of cycles to failure at a strain of 100 under the standard test methodology (unconditioned – controlled stress) and after 30 weeks humidity conditioning at a relatively humidity of 70%, indicated variable results with some de-icing chemical formulations having increased fatigue resistance and others showing a decreased fatigue resistance. These test results were unexpected because previous performance testing indicated that the de-icing chemical formulation were susceptible to moisture damage and there did not appear to be a trend for one chemical to have the best or worse fatigue resistance.

A further review of the data was conducted and it has been identified that the stiffness of the de-icing chemical formulations was significantly less on the 30 week relative humidity specimens compared to the unconditioned set. These results were consistent with the stiffness measurements conducted on a 30 week basis as outlined in Section 6.5.3.

Analysis of strain against cycles to failure identified that the differences in stiffness significantly skewed the data. This is because stiffness is taken into account when converting the test stress to a value of strain, when undertaking a controlled stress test as discussed previously in Section 6.4.9.

To remove the influence of stiffness, the number of cycles to failure was compared for each test stress, as shown in Table 6.15. Analysing the data on a stress basis highlights the significant reduction in the number of cycles to failure when subjected to high periods of relative humidity. Figures 6.38 and 6.39 highlight the differences in the number of cycles to fail on moisture conditioned specimens for a 100% sodium silicate formulation at stresses of 550kPa and 450kPa, respectively.

The data shows a significant reduction in the number of cycles to failure for all anti-icing modified specimens in comparison to the control and signifies a reduction in fatigue resistance and increased susceptibility to cracking. The combination of the reduced stiffness and fatigue resistance highlight that the chemicals of sodium formate and sodium silicate are highly susceptable to moisture damage. This is due to the hydroscopic nature of sodium formate and low surface energy and moisture susceptability of sodium silicate.

In contrast, the control surface showed an increase in the number of cycles to failure at a number of stresses. This increase was shown at target stress levels of 500, 450, 350 and 300KPa. Analysis of the stiffness data showed an increase in stiffness for the briquettes tested after 30 weeks in comparison to the unconditioned specimens. This may be an indication of the onset of binder ageing. Previous research has demonstrated that initial binder ageing and the onset of stiffening can result in increased fatigue resistance.

The conclusions drawn above are related to the fatigue resistance under a controlled stress test. Controlled strain testing may be more appropriate for any future assessment of fatigue resistance of de-icing chemical formulations following prolonged moisture absorption. This is because it has been established that the stiffness of the modified asphalt can reduce in the presence of moisture. This difference in stiffness significantly skewed the strain data when converting from the test stress to strain. As discussed in section 6.4.9, under a controlled strain test as damage accumulates the stress required to maintain the initial strain gradually decreases after crack initiation, as the stiffness of the mixture effectively decreases.

In addition to this many research have defined fatigue failure by monitoring changes in the stiffness modulus, for example, failure defined when the stiffness of the sample drops to 50% of the initial stiffness. This would therefore take into account the reduced initial stiffness of moisture absorbed specimens.

Controlled strain tests would also place further emphasis on the propagation of cracking after initiation. This is because controlled stress testing generally leads to a rapid failure after crack initiation.

Stress (kPa)	Control				100SF				70SF 30SS			
	Standard	30wk	Difference	Percentage Change (%)	Standard	30wk	Difference	Percentage Change (%)	Standard	30wk	Difference	Percentage Change (%)
600	4378	4456	78	1.8	4226	121	-4105	-97.1	6751	867	-5884	-87.2
550	5158	5156	-2	0.0	6504	98	-6406	-98.5	3773	4289	516	13.7
500	5801	18134	12333	212.6	8424	930	-7494	-89.0	16511	1619	-14892	-90.2
450	8947	30278	21331	238.4	18132	3579	-14553	-80.3	8735	6536	-2199	-25.2
400	28031	26713	-1318	-4.7	29057	3121	-25936	-89.3	14450	5000	-9450	-65.4
350	44742	56611	11869	26.5	49705	4122	-45583	-91.7	66856	42522	-24334	-36.4
300	43182	150933	107751	249.5	25143	19854	-5289	-21.0	50194	5254	-44940	-89.5
Mean	**20034**	**41754**	**21720**	**108.4**	**20170**	**4546**	**-15624**	**-77.5**	**23896**	**9441**	**-14455**	**-60.5**

Stress (kPa)	50SF 50SS				30SF 70SS				100SS			
	Standard	30wk	Difference	Percentage Change (%)	Standard	30wk	Difference	Percentage Change (%)	Standard	30wk	Difference	Percentage Change (%)
600	980	6213	5233	534.0	1231	284	-947	-76.9	522	743	221	42.3
550	6470	4815	-1655	-25.6	3518	557	-2961	-84.2	18097	2038	-16059	-88.7
500	6874	1287	-5587	-81.3	6563	1199	-5364	-81.7	6446	2460	-3986	-61.8
450	19436	5837	-13599	-70.0	6852	724	-6128	-89.4	9047	7888	-1159	-12.8
400	13172	5920	-7252	-55.1	44268	270	-43998	-99.4	11305	8008	-3297	-29.2
350	37284	6811	-30473	-81.7	75314	2357	-72957	-96.9	56446	8009	-48437	-85.8
300	74889	7037	-67852	-90.6	153973	8246	-145727	-94.6	34832	9229	-25603	-73.5
Mean	**22729**	**5417**	**-17312**	**-76.2**	**41674**	**1948**	**-39726**	**-95.3**	**19528**	**5482**	**-14046**	**-71.9**

Table 6.18 – Number of cycles to failure at each test stress for standard and after 30 weeks conditioning at 70% relative humidity and the percentage change in the number of cycles to failure.

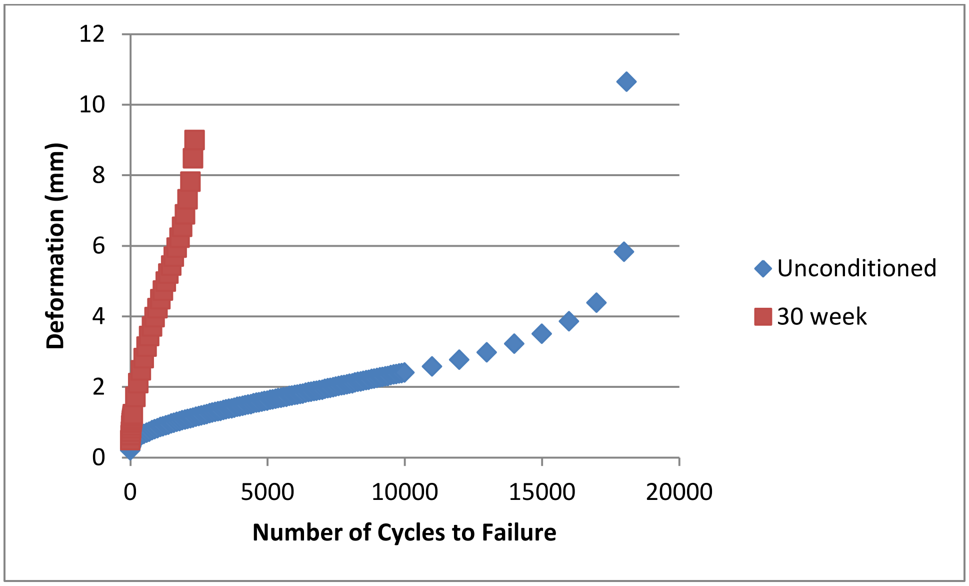


Figure 6.38 – Number of cycles to fail 100% sodium silicate specimen at a stress 550kPa for unconditioned and after 30 weeks at a relative humidity of 70%.

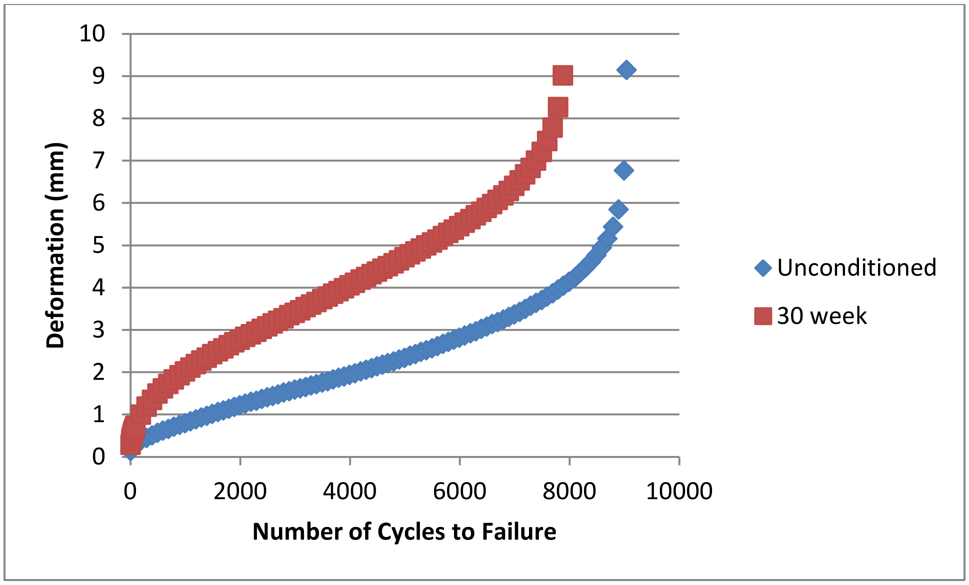


Figure 6.39 – Number of cycles to fail 100% sodium silicate specimen at a stress 450kPa for unconditioned and after 30 weeks at a relative humidity of 70%.

6.5.6 MOISTURE PICK UP - SKID RESISTANCE

Introduction

Skid resistance testing is typically conducted under wet conditions because the skid resistance measured is typically lower than under dry conditions and therefore represents the worse case scenario experienced on the highway network. One concern is that absorption of moisture by the chemical particles will create a damp surface, which may have a reduced skid resistance and the potential to become slippery under specific conditions. Such concerns have been raised by previous proprietary anti-icing road surface.

Standard skid resistance testing conducted previously in Section 6.4.12 has not measured this potential; this is because water is applied to the pavement surface prior to testing in accordance with BS EN 13036-4. A revised conditioning protocol has been developed.

Test Procedure

Skid resistance testing was determined using the Pendulum Tester on asphalt slabs as per the procedure stated in Section 6.4.12 with appropriate changes to the condition period employed. The asphalt slabs were initially tested in their dry state and then placed in a dessicator at 75% humidity. These slabs were tested on a fortnightly basis using the pendulum but without applying water to the surface of the slab.

Throughout testing laboratory specimens, the pendulum tester and the slider were kept in a temperature controlled room at 20 ± 2°C. The test procedure was performed five times. If the first five readings differed by more than three units, the test was repeated until three successive readings were constant and this value was recorded. Testing for each testing regime was conducted on the same contact patch to ensure consistent results and the mean Pendulum Test Value (PTV) recorded every two weeks.

Test Results

Skid resistance was measured in terms of the Pendulum Test Value (PTV) conducted in accordance with BS EN 13036-4:2003(E) under dry conditions and after periods at 75% relative humidity. The change in skid resistance against the number of days at 75% relative humidity are presented in Figure 6.40 and 6.41 for the 38 week period.

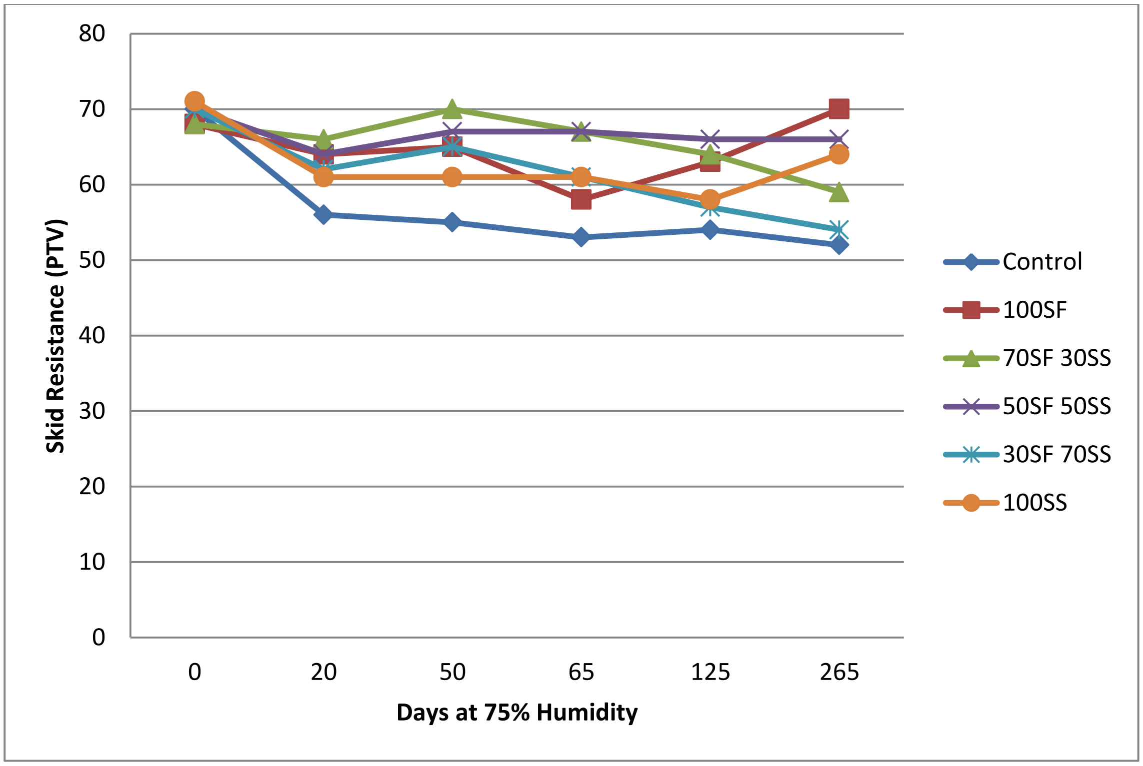


Figure 6.40 – Skid Resistance over a 38 week period

Discussion of Test Results

The skid resistance testing over a 38 week period demonstrated that the de-icing chemical formulations are consistent or above the skid resistance of the control surface. This would indicate that the moisture absorption by the de-icing chemicals does not appear to be detrimental.

The skid resistance of all formulations and the control typically reduce over a 38 week period. This reduction is typically in the order of 5-25%, as shown in Figure 6.41.

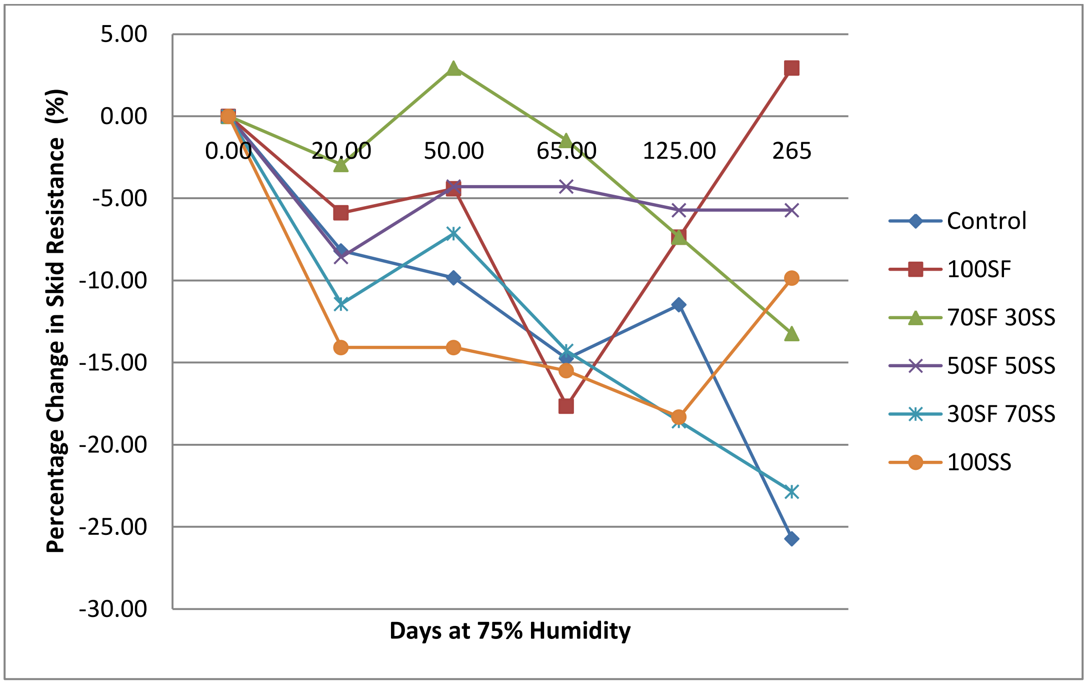


Figure 6.41 – Percentage change of Skid Resistance over a 38 Week Period

There does not appear to be any correlation between the reduction in skid resistance and the different formulations.

The reduction of the skid resistance of the control was not anticipated as this surface absorbs very little moisture and no explanation for this difference can be provided.

It is important to recognise that skid resistance testing using the pendulum tester on laboratory specimens can be subject to a degree of variations due to the limited test small area of a surface (approximately 0.01 m^2) and small variations in the test location leading to a variable interaction between the rubber foot and test specimen.

6.6.0 PHASE 3 – INFLUENCE OF THE CHEMICAL ADDITIVE ON THE PHYSICAL PROPERTIES OF ICE AND THE ICE PAVEMENT BOND

The influence that chemical additives have on the formation of ice is fundamental to the anti-icing of any chemically modified surface course. The purpose of phase three of this testing programme is to determine the anti-icing performance and contributing physical mechanisms that occur when a select range of anti-icing additives are added to the pavement surface course.

The testing phase will address the issues by undertaking a range of tests on both the chemical solutes and modified pavement surface. Such tests have been specifically designed to determine:

- The method of chemical transfer
- The reduction in freezing point
- The influence the chemical additive has on the ice pavement bond strength

This phase of testing will be considered in terms of initial performance and after conditioning periods to reflect the conditions experienced on the highway network.

6.6.1 CHEMICAL TRANSFER

There is currently a limited understanding of how the chemical is transferred through the bituminous mixture to the pavement surface.

Previous products have shown a degree of anti-icing performance, however no substantial data has been provided to explain how the products work or the transfer mechanism.

A more detailed understanding of the mechanism by which the chemical is transferred to the pavement surface and the effects of environmental conditions and pavement characteristics on the anti-icing performance would be a significant step forward.

This thesis aims to establish a new understanding of the chemical transfer mechanism. The testing in this phase consists of:

- Environmental Scanning Electron Microscope testing of chemically modified mastics
- Visual observations of chemically modified asphalt before and after soaking
- The measurement of interconnecting voids of bituminous mixtures
- Leachate testing of solutions after submerged wheeltracking of chemically modified asphalt

6.6.1.1 ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE

Introduction

Scanning Electron Microscopy (SEM) is a rapid and non-destructive technique used to investigate the microstructure, morphology and elemental composition of materials.

Environmental Scanning Electron Microscopy (ESEM) is a form of scanning electron microscopy enabling imaging and elemental analysis of samples incompatible with high vacuum, such as nonconductive, hydrated and delicate samples.

Scanning Electron Microscopy uses the following techniques to assess a number of material parameters:

- High-resolution secondary electron imaging of topographic surfaces to examine microstructure and particular features such as size and morphology in a sample
- Backscatter electron (BSE) imaging for identification of phases with differences in composition
- EDX analysis to determine elemental composition of morphological and textural features in a sample
- Multi-element digital X-ray maps for spatial distribution and relative concentrations of elements

The ESEM technique utilises a controlled flow of gas into the sample chamber to maintain the pressure at levels much higher than conventional SEM. As part of this technique, water vapour can be admitted to the chamber to produce relative humidities up to 100%. The variable temperature peltier sample stage can then be used to control evaporation and condensation.

Test Procedure

Environmental Scanning Electron Microscope testing was conducted using a Philips XL30 FEG device under varying conditions. A cycled conditioning protocol was employed to assess the surface topography and chemical transfer from the mastic in relation to the influence of moisture absorption.

The conditioning protocol employed was to image a large proportion of the sample area when dry under vacuum conditions to replicate initially laid material. The relative humidity was then increased by increments of 10% to replicate moisture absorption from 0% up to 100% relative humidity. At 100% relatively humidity the sample was fully submerged by adjusting the partial pressure and temperature of the Peltier stage. This was followed by a reverse procedure by decreasing the relative humidity to dry the specimen and encourage the deposition of the chemical. This conditioning process was conducted twice for each mastic.

At each 10% relative humidity increment, specific particles of interest were imaged to identify the particle features and morphology of the particles. Specific particles were selected and the position electronically recorded. The particles were then analysed using an EDX detector to determine the elemental composition of the particle and mapped for specific elements. The major elements of interest to this study were sodium and silicon from the chemical formulations. Calcium, carbon and oxygen were used to identify limestone. Carbon, hydrogen and sulphur form the large proportion of the bitumen.

Elemental mapping techniques were employed to determine the spatial distribution of elements before and after wetting to provide an idea of how the particles are mobilised and then deposited.

Testing was carried out on mastics modified with the three formulations of 100% sodium formate, 50% sodium formate and 50% sodium silicate and 100% sodium silicate. Alternative sodium formate and sodium silicate formulations were not tested, as it was considered the qualitative data output and small scale of the measurements would not demonstrate any distinguishable differences from a 50% sodium formate and 50% sodium silicate blend.

The proportions and components for the three formulations tested are presented in Table 6.1. These formulations were mixed by using the protocol presented in section 6.4.1.1 "*Experimental Setup – Mastic Specimens*". The blended mastics were then poured directly onto silica paper in droplets approximately 5mm in diameter and 1-2mm in thickness. These were then cooled and carefully removed to form the test specimen.

Test Results and Discussion of Test Results

Initial Observation (Before Conditioning)

Initial observations of the three mastic samples were conducted at a pressure of 1.5Torr at ambient temperature.

Observations of the chemically modified mastics identified a relatively flat and smooth surface with numerous particles protruding from the sample surface. The particles varied in shape and size and were typically below 20 microns, see Figure 6.42.

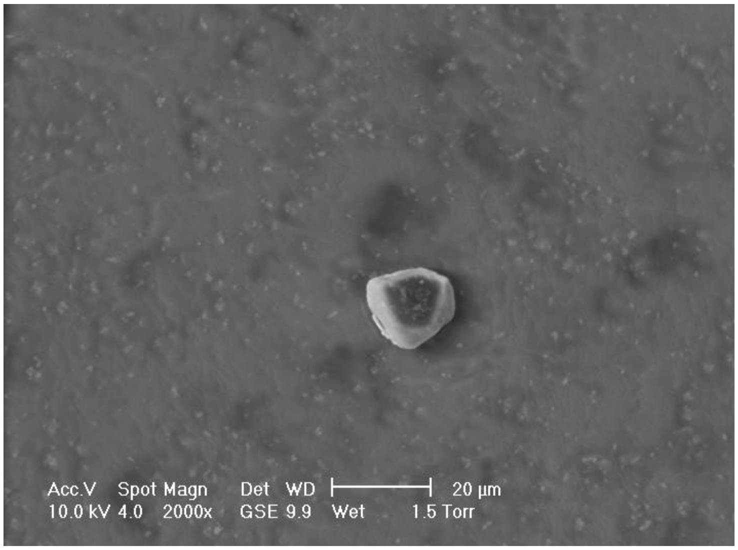


Figure 6.42 – Image of surface topography of mastic pre-wetting

Analysis of various particles present at the surface using EDX analysis identified that the particles were typically composed of calcium, carbon and oxygen indicating the presence of the limestone filler, see Figure 6.43.

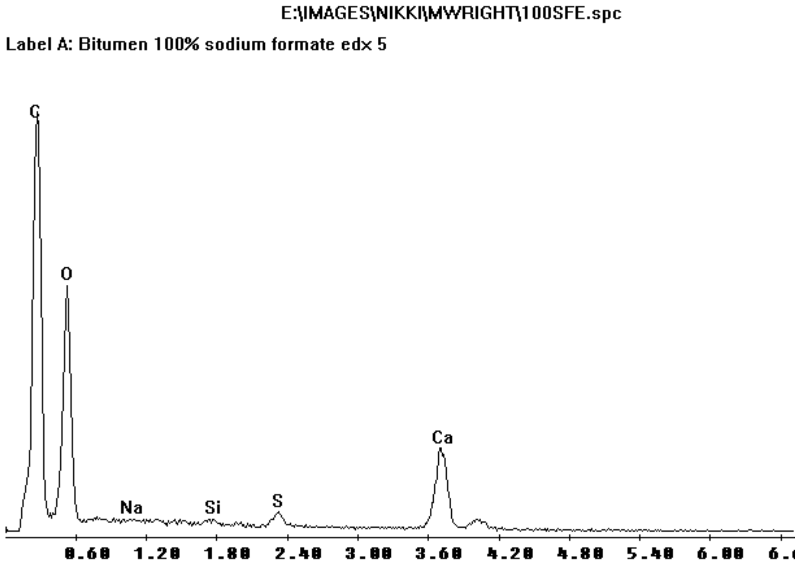


Figure 6.43 – EDX analysis of particles typically detect at the mastic surface

Analysis of the background between particles indicates this was primarily composed of carbon, hydrogen and sulphur, which is consistent with the presence of bitumen, see Figure 6.44.

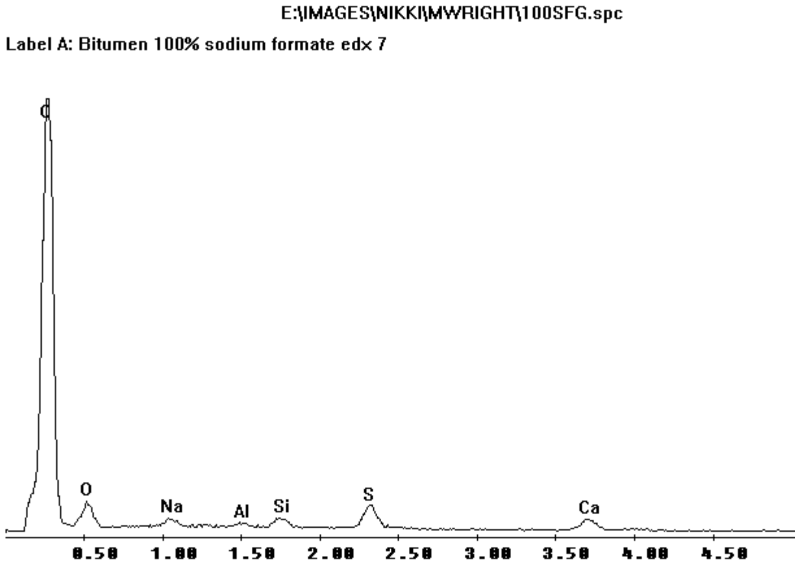


Figure 6.44 – EDX analysis of background typically detect at the mastic surface

Only a very limited number of particles exhibiting the elemental composition of sodium formate or sodium silicate were detected at the surface of the mastic. The limited particles detected were generally at the sample edges or the cut face of the mastic.

This would indicate that the chemical is maintained in the body of the mastic and that a bitumen film covers the sodium formate and sodium silicate particles. This bitumen film is likely to be at least five microns in thickness to prevent detection using EDX analysis. It can therefore be concluded that the chemicals are not initially present at the surface of the bitumen mastic.

Cycle 1 - Incremental Increase in Relative Humidity (20% to 100% RH)

Up until relative humidities of 60%, there was no significant change to the appearance of the particles being imaged. At a relative humidity of 60% there were first signs of wetting on the 100% sodium formate mastics and a significant number of droplets on sodium silicate particles. Wetting was signified by a discrete dark region defining a water droplet.

With increasing relative humidity the number of water droplets increased with the wetted area spreading to cover a wider area. This was particularly evident for sodium formate particles above a relative humidity of 70%, see Figure 6.45. When 100% relative humidity had been achieved, the surface of the entire mastic was fully wetted with a thin layer of water preventing any observation of the surface and defined droplets present on the mastic surface, see Figure 6.46.

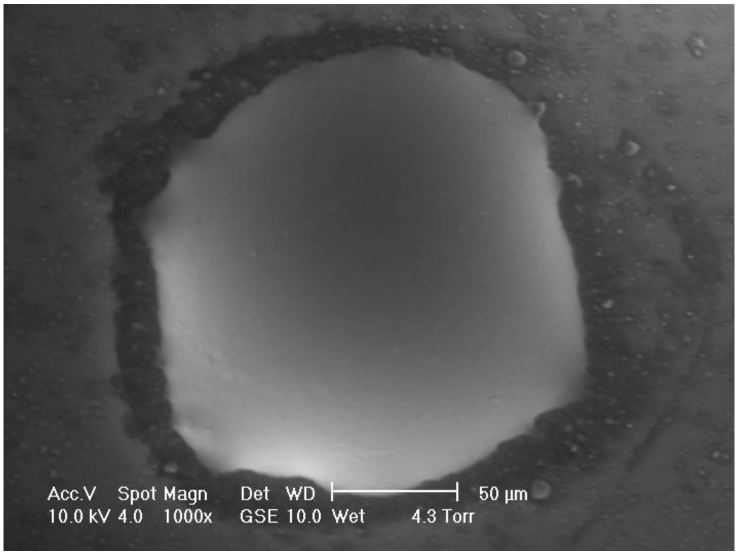


Figure 6.45 - Water droplet forming on the 100SF mastic surface

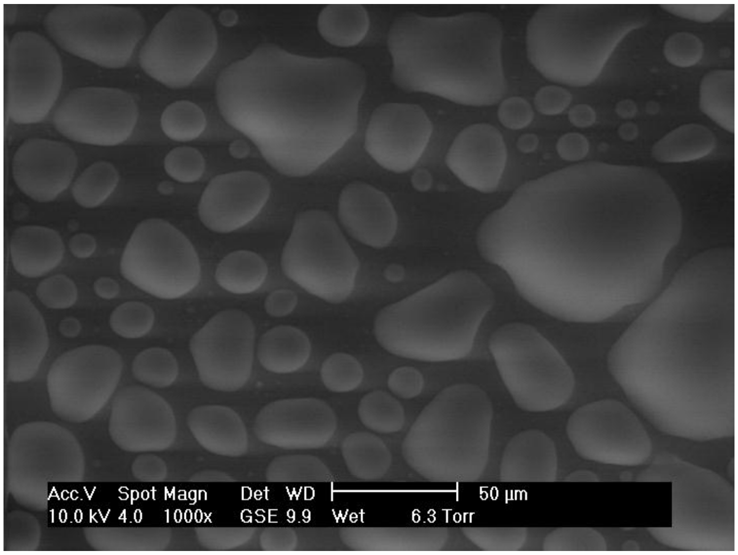


Figure 6.46 - Overview of the 100SF mastic surface at 100% relative humidity

Cycle 1 - Decreasing of Relative Humidity (100% to 3.5%RH)

As the humidity decreased below 60% the first sign of defined particles emerged at the surface of the mastic where the water droplet had previously been. As the humidity continually decreased the particles continued to dry and the chemical structure became visible.

For the sodium formate particles, a proportion of the particles were well rounded and typically of 100 micron in size, see Figure 6.47. However, a number displayed a significantly different appearance on the surface of the mastic. The particles were of an angular spikey appearance, on occasions originating from a central point and typically in excess of 200 micron in size, see Figure 6.48. These particles were of similar appearance to a salt crystal and displayed strong peaks of the element sodium when subjected to EDX analysis, see Figure 6.49.

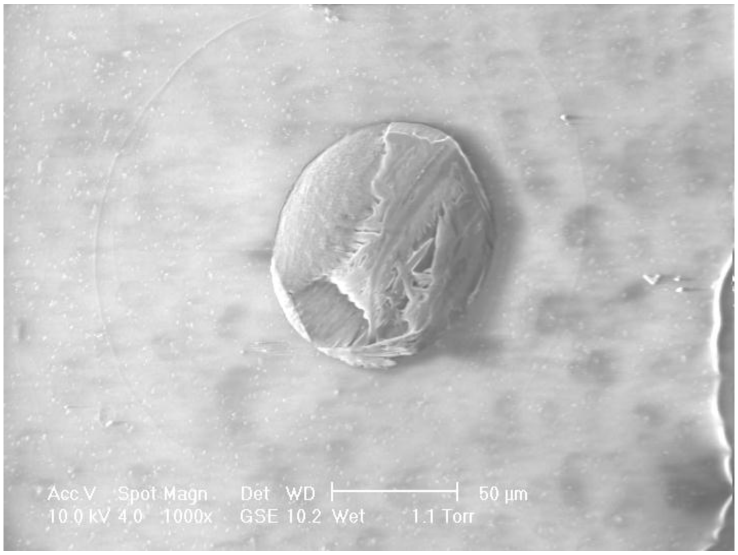


Figure 6.47 - Example of defined particle of sodium formate

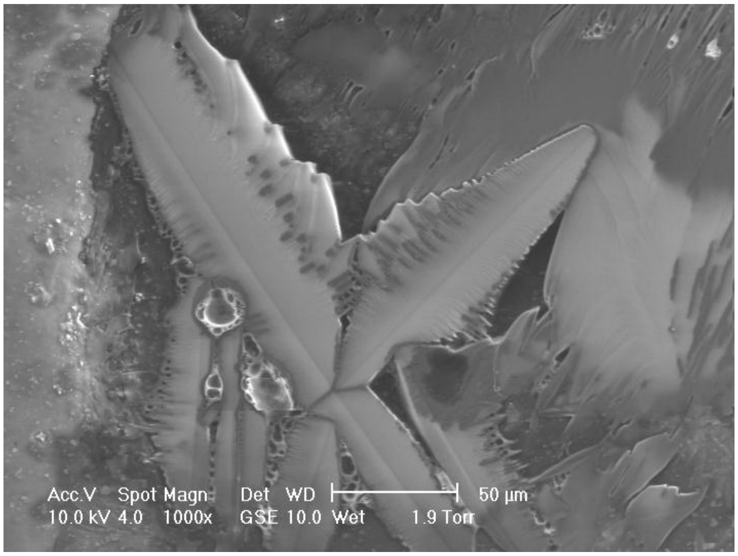


Figure 6.48 - Example of angular crystalline formation of deposited sodium formate

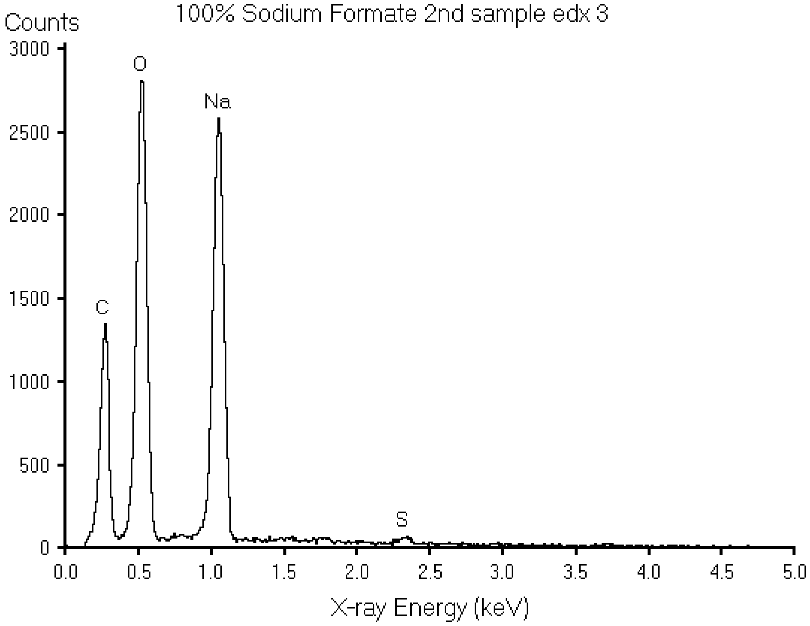


Figure 6.49 – EDX analysis of sodium formate particle

In contrast the deposited sodium silicate appeared in general to be smooth and well defined particles in the region of 50-100micron in size, see Figure 6.50. There were strong sodium, silicone and oxygen signals produced from the EDX analysis, see Figure 6.51.

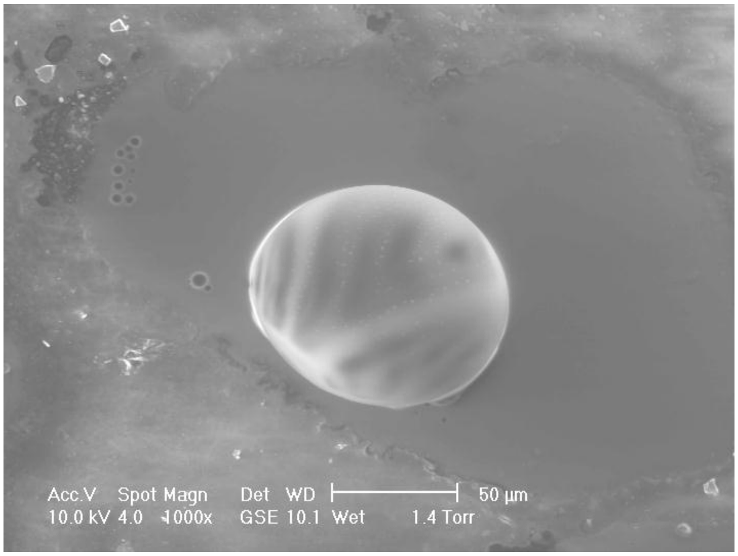


Figure 6.50 – Structure of deposited sodium silicate particles

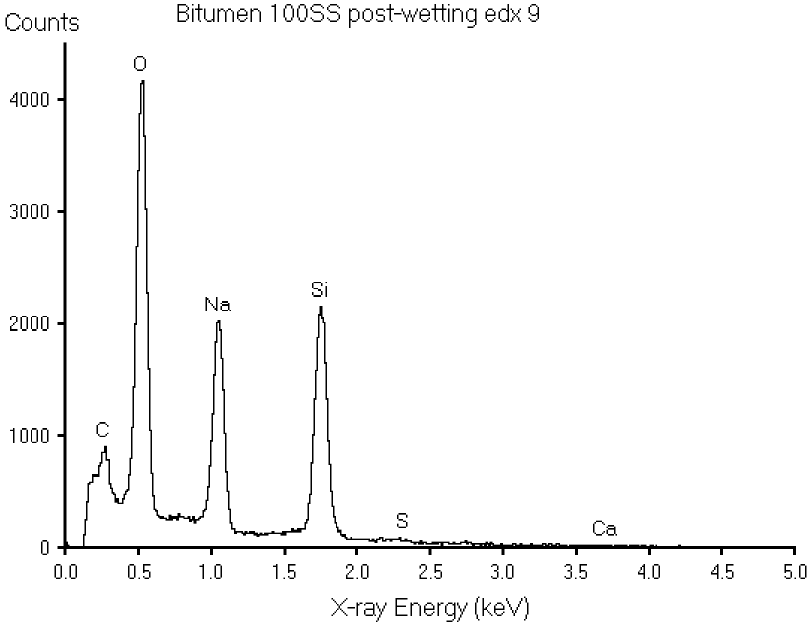


Figure 6.51 – EDX analysis of sodium silicate particle

A number of particles on the 50% sodium formate 50% sodium silicate mastics demonstrated traces of a very strong sodium peak and a minor silicon peak. This response would indicate either a combination of the two chemicals or the deposition of one chemical component around or over the other chemical component. Particles omitting this response had various topography and structures, an example of which is demonstrated below in Figure 6.52 and EDX analysis shown in Figure 6.53.

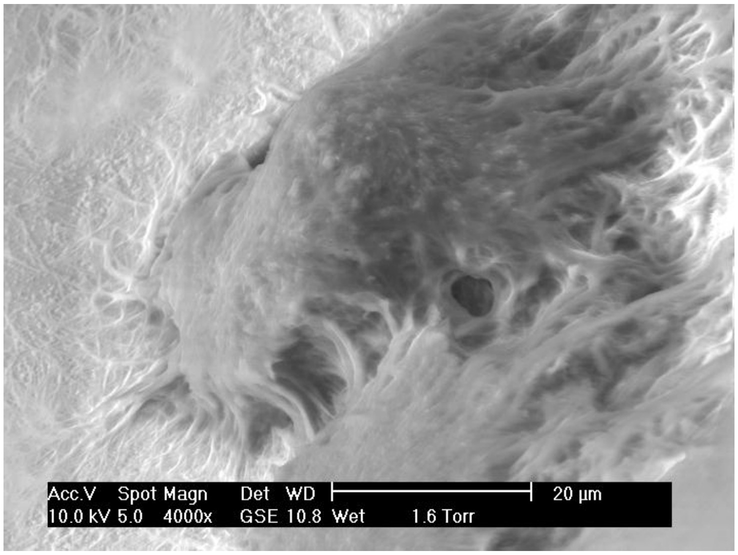


Figure 6.52 – Structure of particle consistent with sodium formate and sodium silicate

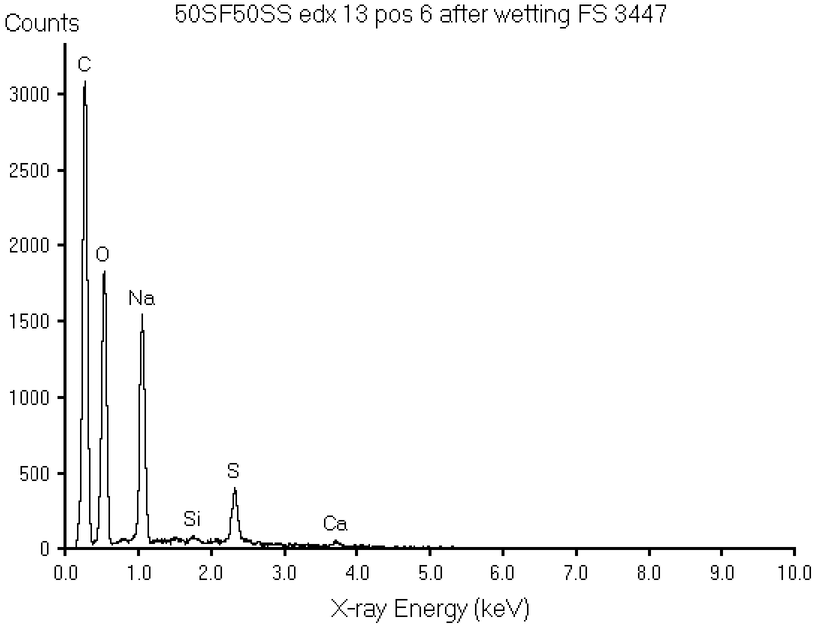


Figure 6.53 – EDX analysis of sodium formate and sodium silicate trace

The first cycle of this phase of testing demonstrates that both sodium formate and sodium silicate are typically not present at the mastic surface but can be transferred through a bitumen film to the surface of the mastic. This transfer occurs at high relative humidities under the presence of moisture. The individual particles are deposited or dispersed over a proportion of the mastic surface.

Cycle 2 - Incremental Increase in Relative Humidity (20% to 100% RH)

After a number of particles were exposed on the mastic surface, the levels of relative humidity was re-increased at 10% increments through changes in temperature and pressure and specific particles imaged. Until relative humidities of 60% there was no significant change to the appearance of the particles being imaged. At a relative humidity of 60% the initial wetting of a number of sodium formate particles and the majority of sodium silicate particles was observed as they absorbed moisture. Wetting was signified by a dark region limited to the edge of the particle with bubbles and particle protruding from the particle surface.

At 70% relative humidity all of the particles identified as sodium formate were demonstrating some form of wetting, with increasing intensity and spreading of the wetted area. At relative humidities of 80% there was full water coverage for all de-icing chemical particles identified. This was limited to the area that the particle previously occupied. This remained constant for 90% relatively humidity with increases in the water film indicated by the darker and defined edges of the water droplet. At this humidity the proportion of discrete droplets converging to form much larger droplets was evident.

When 100% relative humidity had been achieved the surface of the entire mastic was fully wetted, with a thin layer of water preventing any observation of the surface.

The assessment of the surface topography in relation to increases in relative humidity demonstrates that particles of sodium formate and sodium silicate absorb moisture from the atmosphere when exposed at the surface of the mastic. This point, at which wetting is initiated, appears to be in the region of 60% relative humidity for mastics containing sodium formate and sodium silicate individual or combined.

This value appears consistent with the level of relative humidity at which chemicals are transferred from the body of the mastics to the surface. The exact relative humidity appears related to the physical properties of the individual particle, for example particle size and the distribution of the particle within the mastic. With the smaller particles, with greatest surface in close proximity to the surface appearing to wet first.

Increases in relative humidity increase the spreading of the wetting area until the particle is fully covered and the thickness of the water film present. The initial absorption of moisture and associated wetting is primarily confined to the area of the individual chemical particles with very limited spreading beyond the particle boundary. It can be concluded that the moisture absorbed is initially confined to individual particles and that any deterioration measures in Section 6.5.0 - Phase 3 Deterioration and Influence of Moisture Absorption on the Mechanical Properties of Asphalt, is attributed to deterioration around the individual chemical particles. At higher humidities the discrete water droplets covering individual particles converge to form large water droplets.

Cycle 2 - Decreasing of Relative Humidity (100% to 3.5%RH) and Analysis of Spatial Distribution of Elements

The relative humidity was again decreased with chemical particles being deposited on the surface with clearly defined structures in a similar manner as cycle 1. Topographical assessments were made of the particles deposited and Elemental Spatial Distribution was conducted for individual particles exposed after conditioning cycle 1 and comparisons made to the distribution after conditioning cycle 2.

A number of sodium formate particles produced from the 100% sodium formate mastic demonstrated relatively limited changes in the spatial distribution after being exposed from cycle 1 and re-deposited after cycle 2, an example of which is presented in Figure 6.54 with sodium and oxygen overlays shown in Figures 6.55 and 6.56, respectively. These particles maintained a strong sodium response around the nucleus of the original particle, with discrete elements being transferred from the centre of the particle or forming through the mastic.

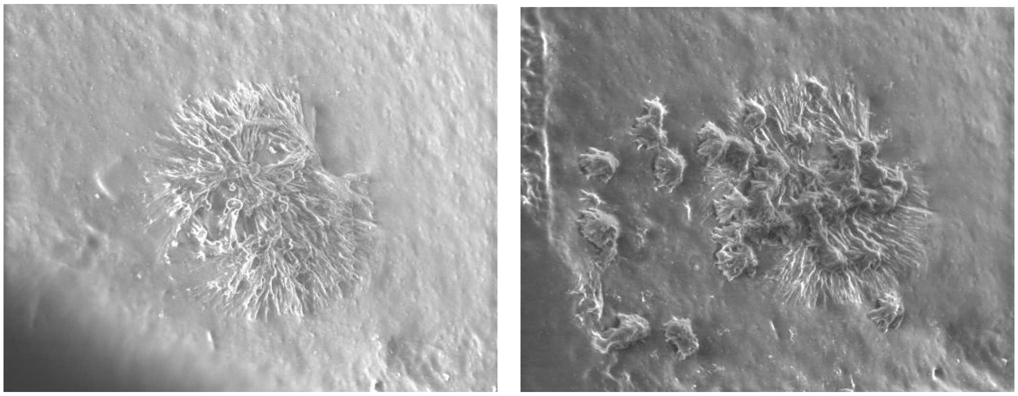


Figure 6.54 - Image of initial exposed particle after cycle 1 (left) and deposited after conditioning cycle 2 (right) 1000x magnification

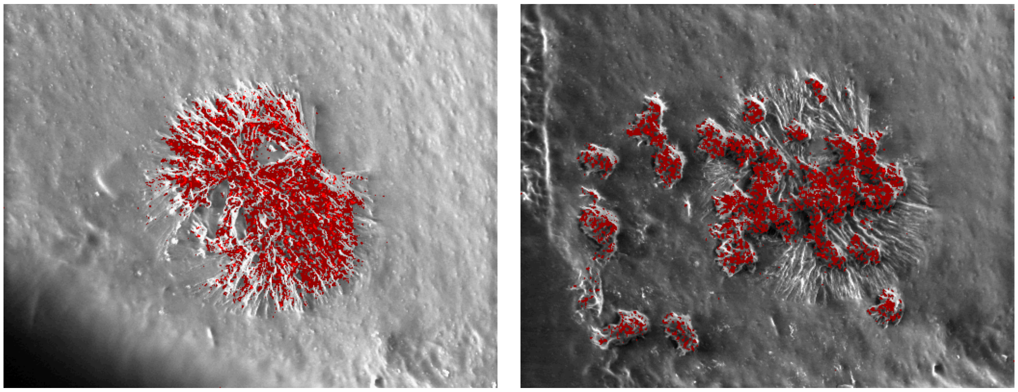


Figure 6.55 - Filter overlay of sodium element to above images 1000x magnification

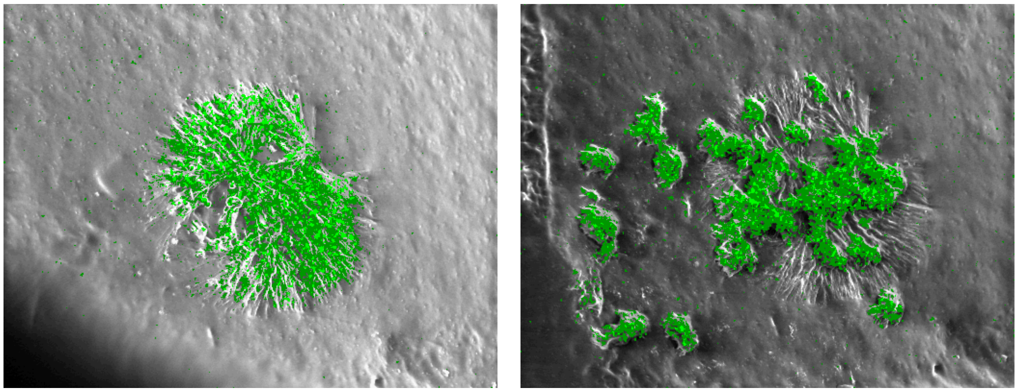


Figure 6.56 - Filter overlay of oxygen element to above images 1000x magnification

The 50% sodium formate and 50% sodium silicate sample observed demonstrated a range of elemental spatial distributions. A number of particles were spread over a wide range of the surface in excess of 200 microns. These particles had a spikey nature and produced a very strong sodium peak with limited or no silicon count, see Figure 6.57.

One particle of interest appeared to have a different structure. This particle initially demonstrated high sodium and oxygen peaks and only a limited silicon count. After re-wetting and drying, the particle spread significantly over the surface of the surrounding mastic, with the element of sodium detected around the centre where the particle was initially and a significant increase in the silicon detected over a wide area of the surface. The protruding particle from cycle 1 to the completion of cycle 2 had disappeared and instead there was a sizeable pit in the surface of the mastic, see Figures 6.57, 6.58 and 6.59. Spatial mapping of the particle in question between cycles 1 and 2 showed a significant increase in silicon, indicating the transfer or emergence of sodium silicate, as shown in Figure 6.61.

The 100% sodium silicate sample appeared to have spread and precipitated over a wider area than the original particle between cycles 1 and 2 with a smooth glassy surface finish. The change between cycles 1 and 2 for the sodium silicate particle is shown in Figure 6.62.

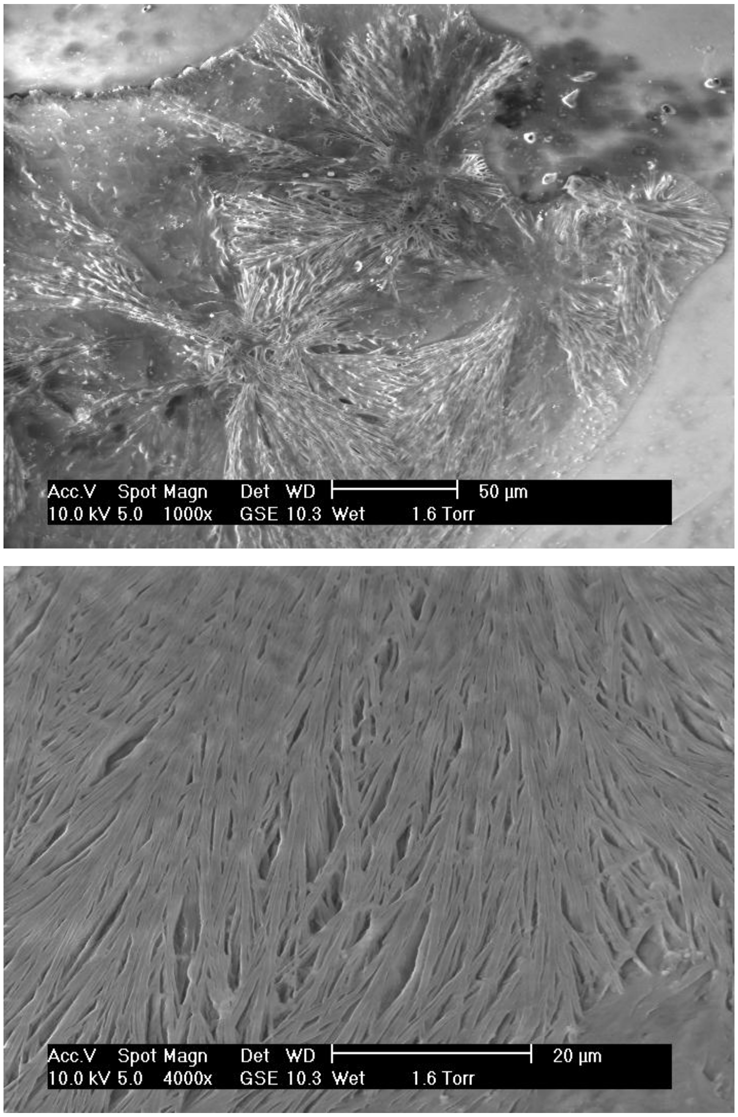


Figure 6.57 -An area of the 50% sodium formate 50% sodium silicate sample after cycle 2 at 1000x magnification (top) and 4000x magnification (bottom)

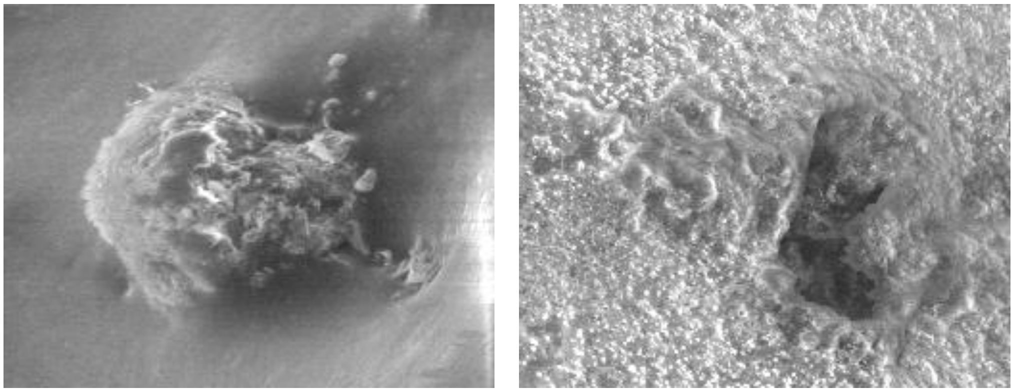


Figure 6.58 -Image of initial exposed particle (left) and deposit after conditioning (right) 1000x magnification

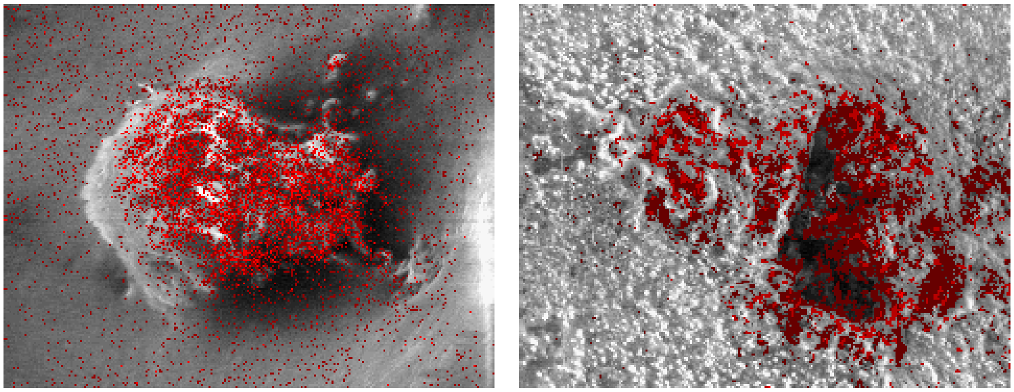


Figure 6.59 - Filter overlay of sodium element to above images 1000x magnification

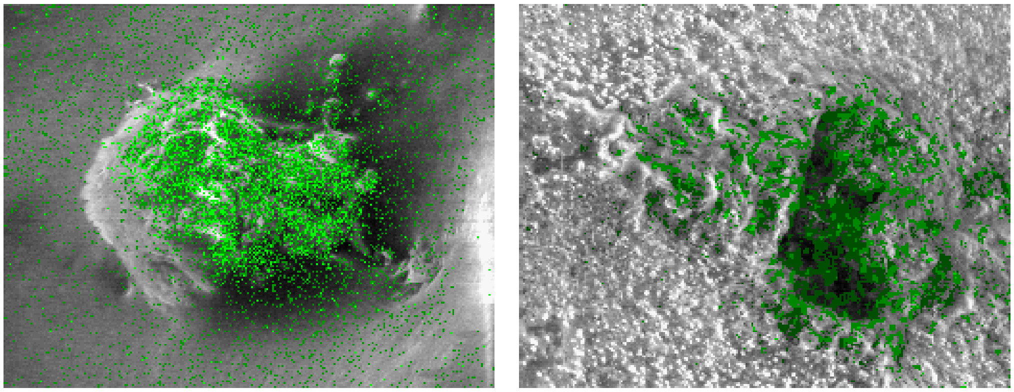


Figure 6.60 - Filter overlay of oxygen element to above images 1000x magnification

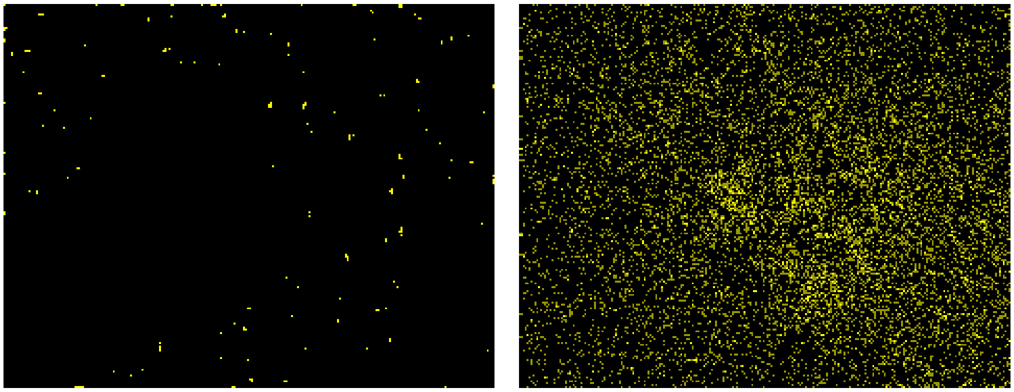


Figure 6.61 - Elemental mapping of silicon on initial exposed particle (left) and deposit after conditioning (right) 1000x magnification

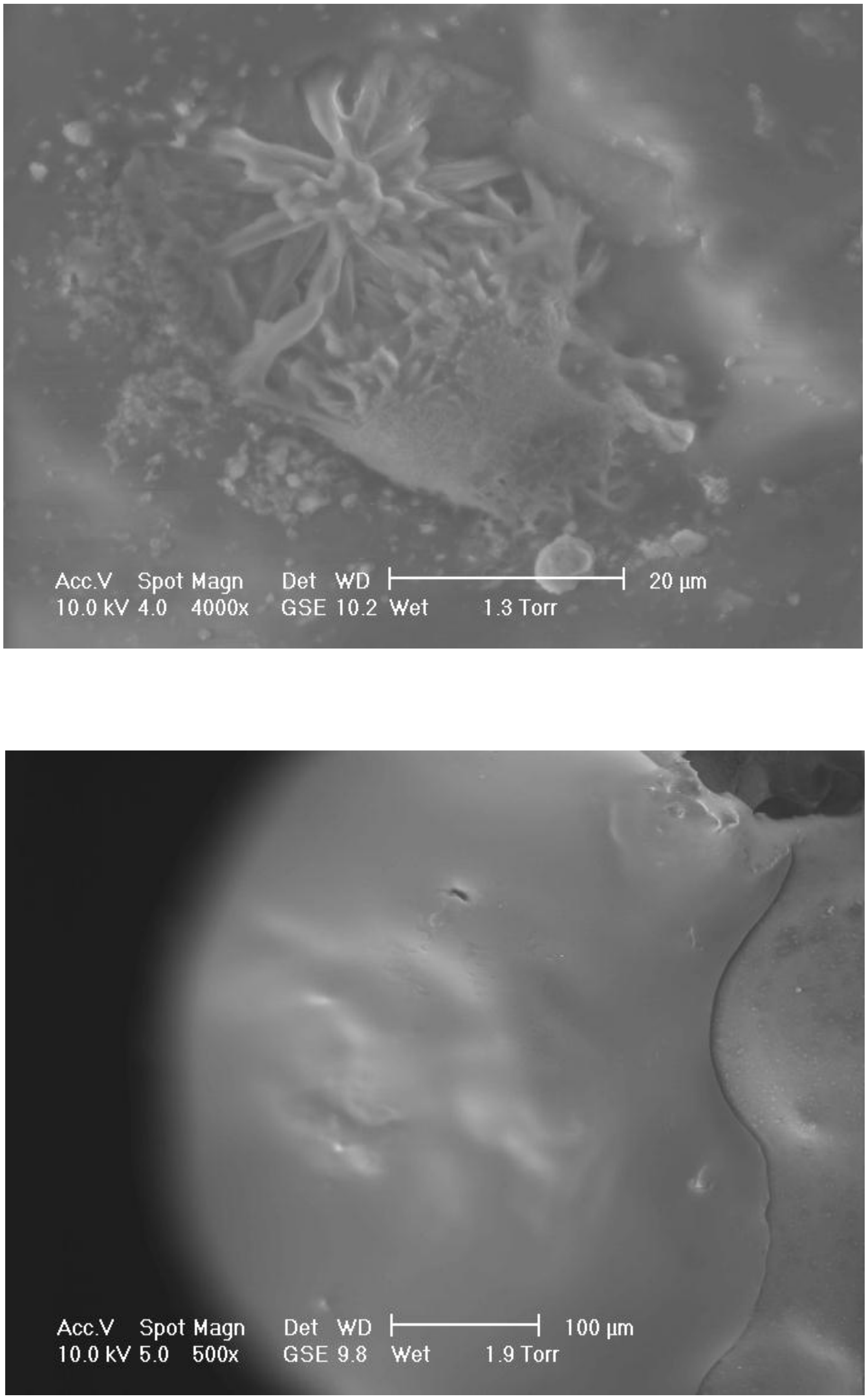


Figure 6.62 – Structure of deposited sodium silicate particles after cycle 1 (top image) and structure of deposited sodium silicate particles after cycle 2 (bottom image).

OBSERVATIONS OF FINISHED SAMPLES

Samples were also observed after the completion of cycle 2 to determine if such effects were representative over the complete mastic surface. On the surface of the 100% sodium formate a limited number of white particles were noted, see Figure 6.63.

Figure 6.63 – Photograph of 100% sodium formate sample after cycle 2

Then the 100% Sodium Silicate sample was removed from the microscope chamber it had a roughened pitted appearance. There were also numerous holes observed, see Figure 6.64.

Figure 6.64 – Photograph of 100% sodium silicate sample before cycle 2 (left) and after cycle 2 (right) demonstrating pitting on the surface

6.6.1.2 VISUAL OBSERVATIONS OF SUBMERGED ASPHALT

Introduction

The de-icing chemicals of sodium formate and sodium silicate can be transferred from a thin layer of mastic to the pavement surface when subjected to specific humidity conditions. To assess whether the chemicals can be transferred to the surface of a bituminous mixture, samples from the BBA HAPAS testing outlined in 6.4.11.3 were allowed to dry in air and the dried surface was observed.

Test Methodology

The samples from the BBA HAPAS testing outlined in 6.4.11.3 underwent 3 conditioning cycles comprising of:

- Being placed at 60 ± 1^{o}C for 6 ± 1 hours
- Immediately transferred to a cold water bath at 5 ± 1^{o}C for 16 ± 1 hours
- Place in water at test temperature of 20 ± 0.5^{o}C for a minimum of 2 hours

After the three submersion periods, the specimens were allowed to air dry gradually over a period of days.

This process of immersing the specimen in water and gradual drying mirrors the process of precipitation and evaporation of the road surface.

Test Results

The control material showed no change in colour or chemical deposition. On the 100% sodium formate sample, there was very limited chemical deposited in the voids. The higher sodium silicate content in the mixture generated higher amounts of a white chemical powder on the surface of the specimens, as shown in Figure 6.65.

Figure 6.65 – Specimens after drying showing the control (top left), 100% sodium formate (top right), 50% sodium formate and 50% sodium silicate (bottom left) and 100% sodium silicate (bottom right)

Discussion of Test Results

These observations confirm that the chemical can be transferred through the bituminous mixture to the surface when immersed in water with the high sodium silicate specimens showing the highest quantity of chemical on the surface.

Further observation of the samples, identified that the greatest chemical concentrations were present in the surface voids of the bituminous mixture. This would indicate that the air voids might provide the primary route for transferring the de-icing chemicals to the pavement surface.

6.6.1.3 INTERCONNECTING VOIDS AND PERMABILITY ASSESSMENTS

Introduction

The visual observations conducted in the previous chapter and the moisture absorption experiment results of asphalt, indicate that the air voids provide a route for moisture to enter the bituminous mixture and provide a path for the de-icing chemicals to be transferred to the pavement surface. To examine the role of the air voids in the chemical transfer process, interconnecting voids and permeability assessments were conducted.

Test Methodology

The interconnecting voids and permeability assessments were conducted with the assistance of Eurovia Management at the Research Center of Mérignac.

Two standardised asphaltic specimens were produced for each formulation to ensure factors such as surface texture, void content and chemical dispersion were comparable for each specimen. This was achieved by manufacturing 100mm cylindrical specimens by gyratory compaction to a set air void content of 5.0%, in accordance with BS EN 12697–31:2007. These were then transferred to the Research Center of Mérignac for testing.

Testing was conducted in two phases:

- Phase 1 - Interconnecting Voids
- Phase 2 - Permeability

Phase 1 – Interconnecting Voids

The structure and interconnectivity of the air voids was assessed using a vacuum resin impregnation method. This method involves injecting a Ultra-violet resin in to the asphalt specimens. The specimens were then cut in the vertical direction and analised under natural and ultraviolet light. A visual assessment of the void arrangement and connectivity was then conducted.

Test Results

Images of the air void arrangement through the depth of the briquette were produced for each de-icing chemical formulation under classic and ultra violet light. Examples of the images produced are shown in Figures 6.66 and 6.67.

The images show a high level of surface voids. These connect the upper 10-20mm of the bituminous mixture to the surface.

The voids within the body of the material itself are limited, for example Figure 6.66 highlights the voids in the body of the material (white circle). These are independent air voids with no interconnectivity.

These observations were consistent for all de-icing chemical formulations and it was concluded that there was no connectivity between the body of the material and the surface.

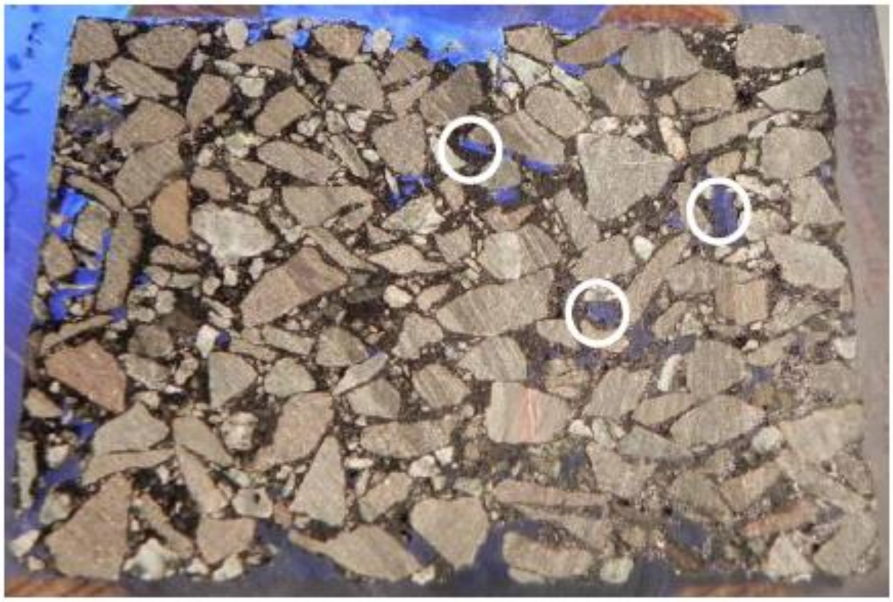


Figure 6.66 – Natural light image of control sample

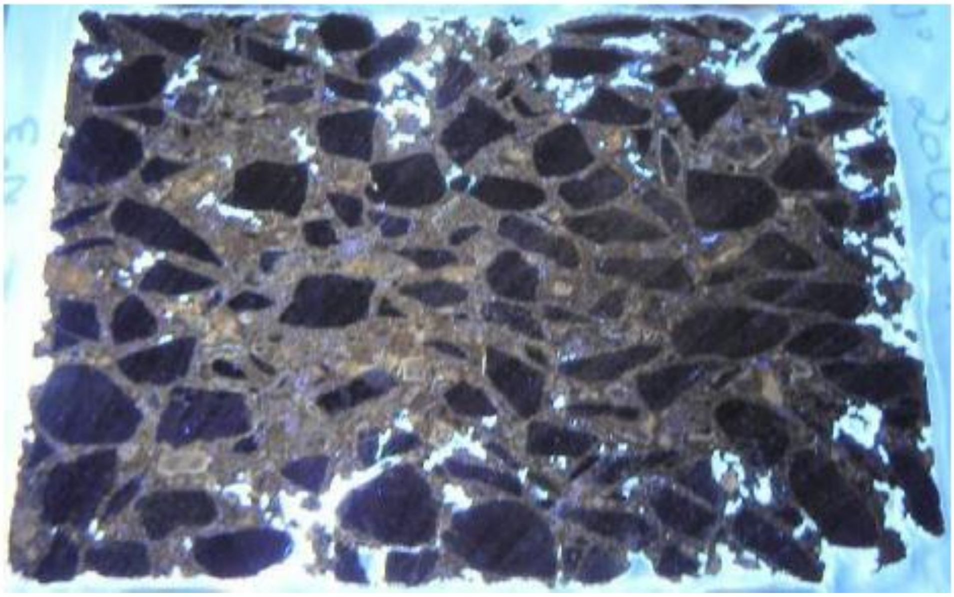


Figure 6.67 – Ultraviolet light image of 50% sodium formate and 50% sodium silicate sample

Phase 2 – Permeability Testing

The second specimen was subjected to a permeability test based on a modified version of the standard French permeability test NF P98-254-2. This test involved placing a water column on the surface of the asphalt specimen and sealing and encasing the asphalt and water with hot bitumen. The bitumen was then allowed to cool to perform a perfect seal with no route for the water to escape, see Figure 6.68.

The water column was then filled to a height of 1 metre and the water permeability was measured over a 24 hour period.

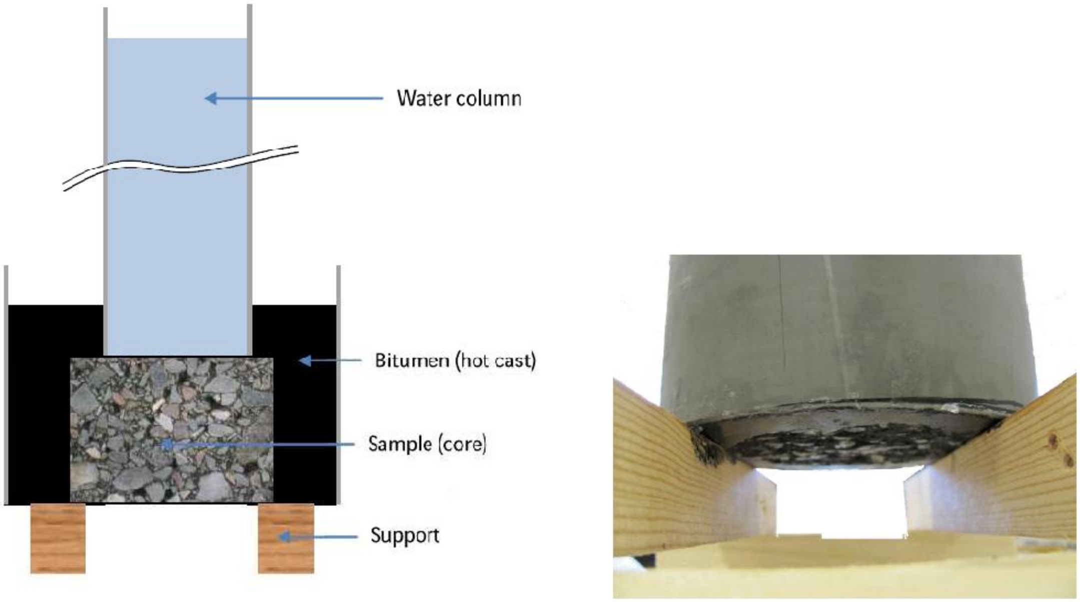


Figure 6.68 –Diagram showing permeability test arrangement and sealing of sample

Test Results

The water column height did not decrease during the test time and no water was visible at the base of all specimens. This indicates that there was no permeability on any specimens after 24 hours.

Discussion of Test Results

The interconnectivity void and permeability analysis conducted with the assistance of Eurovia Management at the Research Center of Mérignac has indicated that there is no interconnectivity from the body of the material to the surface of the asphalt. This was confirmed by permeability testing.

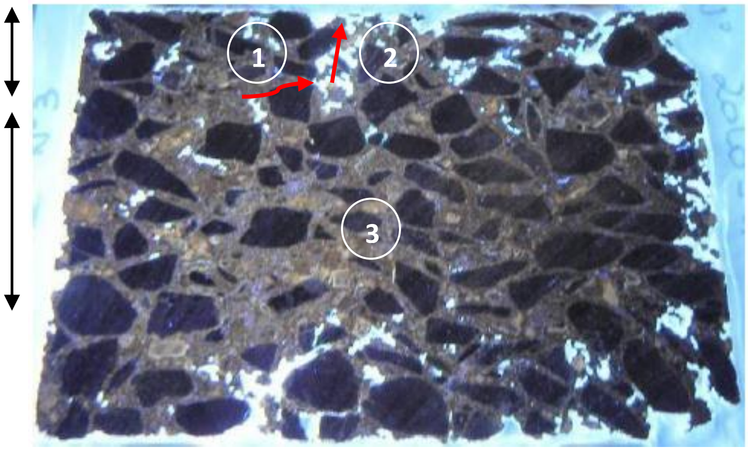
The lack of interconnecting voids and restricted permeability of the stone mastic asphalt surface considered as part of this study at 5% total air void content is consistent with the conclusions by Zube (1962). Zube (1962) concluded "that hot mix asphalt mixture became permeable to water at air voids contents of approximately 8 percent…..above this percentage, the permeability rapidly increases." The conclusion that 8 percent air voids content appears to be critical is also support by Brown et al. (1989) and Santucci et al (1985).

The limited interconnectivity would indicate that the transfer of the de-icing chemicals contained with the body of the asphalt may be severely restricted and/or prevented. This is because there does not appear to be:

- A clear route for moisture/water to enter the specimen
- A clear interconnecting air void path for the chemicals to be easily transferred to the surface
- An aggregate particle structure that would result in a long and obstructed path if the chemical is transferred through the bituminous mastic

Based on published literature it would be anticipated that higher void surface courses in excess of 8% air voids, such as porous asphalt, would have significantly greater levels of permeability and interconnecting voids. In theory this would allow greater chemical utilisation and easier chemical transfer due to the greater number of transport paths for the chemical to pass from within the asphalt to the surface of the pavement.

Whilst the test results do provide evidence of interconnecting voids, the interconnecting void images have shown significant surface voids in the top 10-20mm of the surface of the asphalt specimens. This means that the upper 20mm of the asphalt will provide an easy path for the chemical to be transferred through the bitumen film via the surface voids to the pavement surface, see Figure 6.69.



Surface Features

Surface voids in upper 20mm of specimen

Limited interconnectivity at centre of specimen – Restricted

Proposed Transfer Mechanism

1). Chemical is transferred through bitumen mastic at high relative humidities

2). Chemical transferred to the pavement surface via surface voids

3). Limited interconnecitivity restricts chemical utilisation

Figure 6.69 –Proposed Chemical Transfer Mechanism of SMA surface (5% air void content)

The upper 20mm of the asphalt specimen equates to 20% of the total specimen depth analysed. Considering that Section 6.5.2 "*Moisture Absorption of Chemically Modified Asphalt*" concluded that "*over the first five week period the chemical modified asphalt absorbs between 15-25% of the levels of moisture absorbed by the chemical particles*" it could be postulated that only the surface voids allow moisture absorption and that the de-icing chemicals are only transferred and utilised in and around the surface voids.

Confirmation of the role of the air void content and interconnectivity would be subject to further work, see Section 8.3.

6.6.1.4 LEACHANT ANALYSIS OF SUBMERGED WHEELTRACKER SOLUTION

Introduction

It has been established that the de-icing chemicals can be transferred through a bitumen mastic and that surface air voids provide an easy transport path from a bituminous mixture to the pavement surface.

To identify if the chemicals can be transferred to the pavement surface to form a solution with water on the pavement surface and the ease/longevity of the chemical transfer, leachate analysis of a submerged wheeltracking solutions were conducted.

Test Procedure

A number of factors are likely to determine the rate of chemical leaching from a pavement surface. These include environmental conditions such as:

- Water depth
- Relative humidity and temperature
- Duration of standing water

Loading conditions could also impact upon the rate of chemical leaching, including:

- The number of wheel passes
- Wheel/loading type
- Loading weight

In order to best replicate the highway environment a submerged wheel tracker was used. The submerged wheeltracker simulates loading conditions and environmental conditions on the pavement surface under a standard and controlled procedure.

The submerged wheeltracker was based on the standard small device wheeltracking device with a compartment to maintain a controlled volume of water. This compartment held 600ml of water. This level of water provides complete submersion and is far in excess of the water content experienced on pavement surfaces.

In total three slabs of the same material were loaded into the chamber for each test. These slabs were manufactured to a void content of 5.0%. The specimens were loaded by means of a 7kN load axle at a frequency of 26.5 load cycles per 60s. The slab was submerged and continuously loaded for 24 hours at an ambient temperature of 20^{o}C.

After the completion of the submerged loading, the solution was drained from the controlled chamber. This solution was then tested by the external laboratory LPD Laboratory Service using a range of wet chemical techniques and infra-red spectroscopy.

Sodium formate was measured by ion chromatography using sodium formate standards. Sodium silicate was determined by a colorimetric method based on the formation of a heteropolymolybdate species. The method was calibrated using the sodium silicate salt supplied.

Test Results

Test results for the sodium silicate and sodium formate contents are demonstrated in Table 6.19.

Sample	**pH**	**Conductivity (mS/cm)**	**Sodium Silicate Content (mg/l)**	**Sodium Formate Content (mg/l)**
Control	6.4	1.785	4.3	None found
100SF	6.7	1.661	4.5	None found
70SF 30SS	7.0	1.772	44	None found
50SF 50SS	7.0	1.894	75	None found
30SF 70SS	7.3	2.230	77	None found
100SS	7.6	1.381	123	None found

Table 6.19 – Analysis of leachant samples

Discussion of Test Results – Sodium Silicate

Leachant analysis of the submerged wheeltracking solution after 24 hours demonstrates significant leaching of sodium silicate. This leaching increased linearly with the sodium silicate content. A background sodium silicate level was detected within the control and the 100% sodium formate sample.

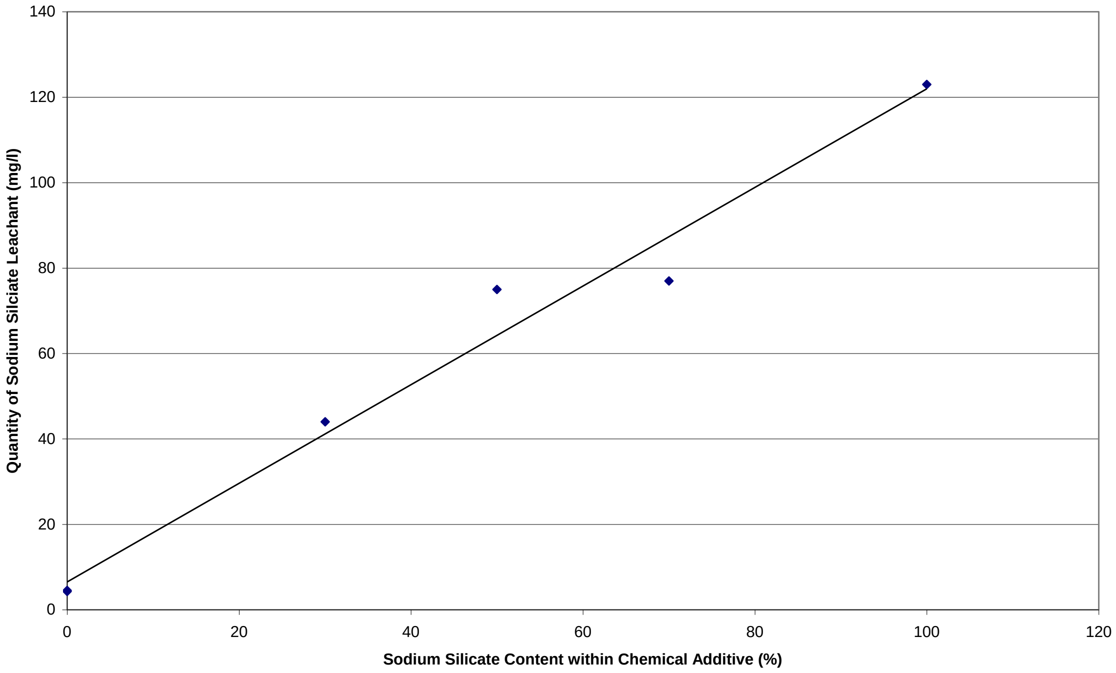


Figure 6.70 – Quantity of sodium silicate leachant against the percentage of sodium silicate in the chemical de-icing formulation after 24 hours.

The level of leachant in respect to the amount of sodium silicate available has been assessed below based on the assumption of even particle distribution and controlled water volume of 600ml.

Formulation	Sodium Silicate Available in Slab (g)	Total Amount of Sodium Silicate Leachant (g)	Total Amount of Sodium Silicate Remaining in Slab (g)	Percentage of Sodium Silicant Leachant (%)	Percentage of Sodium Silicant Remaining (%)
Control	0	2.6	-2.6	-	-
100SF	0	2.7	-2.7	-	-
70SF 30SS	120	26.4	93.6	22.0	78.0
50SF 50SS	200	45.0	155.0	22.5	77.5
30SF 70SS	280	46.2	233.8	16.5	83.5
100SS	400	73.8	326.2	18.4	81.6

Table 6.20 – Calculated sodium silicate leachant and percentage of sodium silicate remaining

The results demonstrate a relative consistent rate of leaching, with approximately 80% of the chemical still available within the asphalt after 24 hours of submerged wheeltracking.

Theory 1 – Linear Rate of Leaching

It is assumed a constant linear rate of sodium silicate leaching with time, based on an average 20% of sodium silicate leaching over a 24 hour period.

Based on an assumed constant leaching rate, the total longevity of the de-icing chemical is estimated at five days based on the laboratory submersion of constant submersion and wheeltracking.

This theory does not take into account that the leaching rate would slow as the chemical levels in the water increase and/or less free chemical particles being available.

Theory 2 – Surface Voids Active Only

The interconnecting voids analysis and permeability assessment has indicated that only the first 20mm (20% of specimen depth) has voids connected to the surface, which provide an easy path to the surface. The body of the bituminous material has limited or no void connectivity to the surface.

Based on this theory, it would mean that all or nearly all of the 20% of sodium silicate has leached from the surface voids leaving little or no sodium silicate available at the surface voids for transfer. The significant chemical available in the body of the bituminous material could be inactive with no direct route to the surface, resulting in an estimated life of 24 hours, based on the laboratory submersion of constant submersion and wheeltracking.

The chemical usage and deterioration of supply will result in reduced anti-icing performance and/or a need for a conventional winter service treatment to prevent the formation of ice on the pavement surface. Further research is required to establish the relationship between the utilisation of chemical, longevity of the de-icing chemicals and the interconnecting void/air void arrangement.

Discussion of Test Results – Sodium Formate

No sodium formate could be found in the samples using ion chromatography. This may indicate that sodium formate is not leached from the pavement surface.

Alternatively, formate is a ‘biocide’ at high concentrations but is biodegraded at low concentrations. When diluted formate can be broken down in the environment to carbon dioxide and water. Published literature results on the biodegradability of sodium formate such as those by CABOT (2009) reproduced below shows the high rate of biodegradation of sodium formate. Biodegradation may explain why no sodium formate was detected.

Time (days)	Sodium Formate Concentration	
	11.8 mg/l	31.2 mg/l
7	13% Biodegraded	8% Biodegraded
14	89% Biodegraded	92% Biodegraded
21	91% Biodegraded	94% Biodegraded

Table 6.21 - Biodegradtion of sodium formate (reproduced from CABOT 2009)

6.6.2.0 FREEZING POINT

Depressing the freeze point using chemical additives is a fundamental principle in preventing the formation of a strong layer of small ice crystals directly on the pavement surface. The freezing point is depressed by interfering with hydrogen bonds and changing the inherent structure of water, see Section 3.3.1 Freeze Point Depressant. This is the method by which chemical de-icers used in current practice as precautionary and reactive winter road treatments principally work.

The ability to depress the freezing point of a pavement surface course is dependant on:

- The de-icing chemical ability to interfere with the hydrogen bonds
- The interaction with the pavement surface course material
- Solubility of the chemical
- Ability to be released when required and maintained for future winters

This section details the freezing point measurement of chemical additives, chemically modified mastics and the freezing point measurements of the residue from briquettes.

6.6.2.1 FREEZING POINT MEASUREMENT – CHEMICAL ADDITIVES

Introduction

The determination of the freezing point of individual chemical concentrations will quantify the potential of each chemical to depress the freezing point.

Measurements of the freezing point of chemical formulations were carried out using a methodology consistent with the method used by Baum et al. (1992). Comparisons are made from the chemical formulations considered within this study with the Baum et al. (1992) results.

The experiment was designed to create freezing point diagrams for each de-icing chemical blend at different concentrations with water. In order to cover the full spectrum of results over the phase diagram, the concentrations of the solution used were 3%, 5%, 10% 20% and 30% of de-icing chemical formulation added by weight to dionised water. The control specimen of 100% dionised water was tested to check methodology and as a comparison.

Test Procedure

Testing was based on a simple freezing experiment for various chemical solutions based on the method as described by Baum et al. (1992).

Samples for testing were prepared in 200ml batches of solution. This quantity was selected to reduce the uncertainty of weighing out specimens with sampling the test solution. The process of manufacturing the solution was to first weigh out the de-icing chemical formulation to the nearest 1mg followed by adding a specific weight of dionised water directly into the beaker. The sample was stirred mechanical for approximately 5-10 minutes until the solute was no longer visible. Two samples were then drawn from the solution using a 20ml syringe.

Twenty millilitres of each solution were placed in a test tube. A thermocouple was centred in the solution approximately one centimeter below the meniscus. The test tube was immediately placed in a freezer with a constant temperature set to -25^{o}C. The temperature of the solution was recorded every ten seconds, until the freezing point had been established. Two freezing point curves were developed for each solution and the mean freezing point averaged.

The determination of the freezing point was established by the phenomenon known as ‘under cooling’ or ‘super cooling’ presented on the cooling curves. Super cooling occurs when a liquid or solution is cooled towards its freezing point and the temperature will drop below the freezing point before any phase change occurs. The freezing point is derived from the maximum, or plateau, in the discontinuity which follows the super cooling definition. The plateau or maximum at the freezing point is caused by the energy change occurring as the phase of the mixture changes from liquid to solid. Effectively the thermal energy being removed from the liquid is offset by the energy required for the phase change to occur and the temperature remains constant during the time taken for the sample to change from a liquid to a solid. In the absence of super cooling the freezing point is derived from the plateau in the cooling curve.

Test Results

For each chemical a freezing point curve was created by plotting the temperature of the solution against time. The freezing point was determined by the process of super cooling or from the point of stabilisation where the super cooling curve did not exist. An example of the freezing point determination is displayed in Figure 6.71.

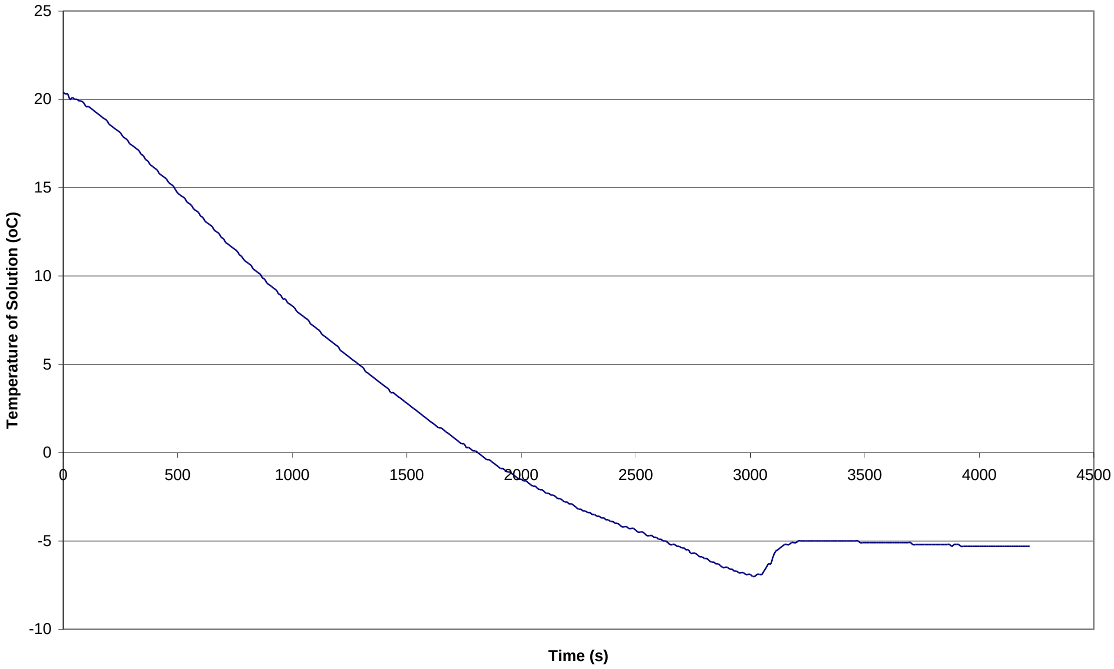


Figure 6.71 - Freezing Point Curve for an experiment of 10% 100SF to 90% Water

A diagram of freezing point against chemical concentration was plotted for each de-icing solution, as demonstrated in Figure 6.72.

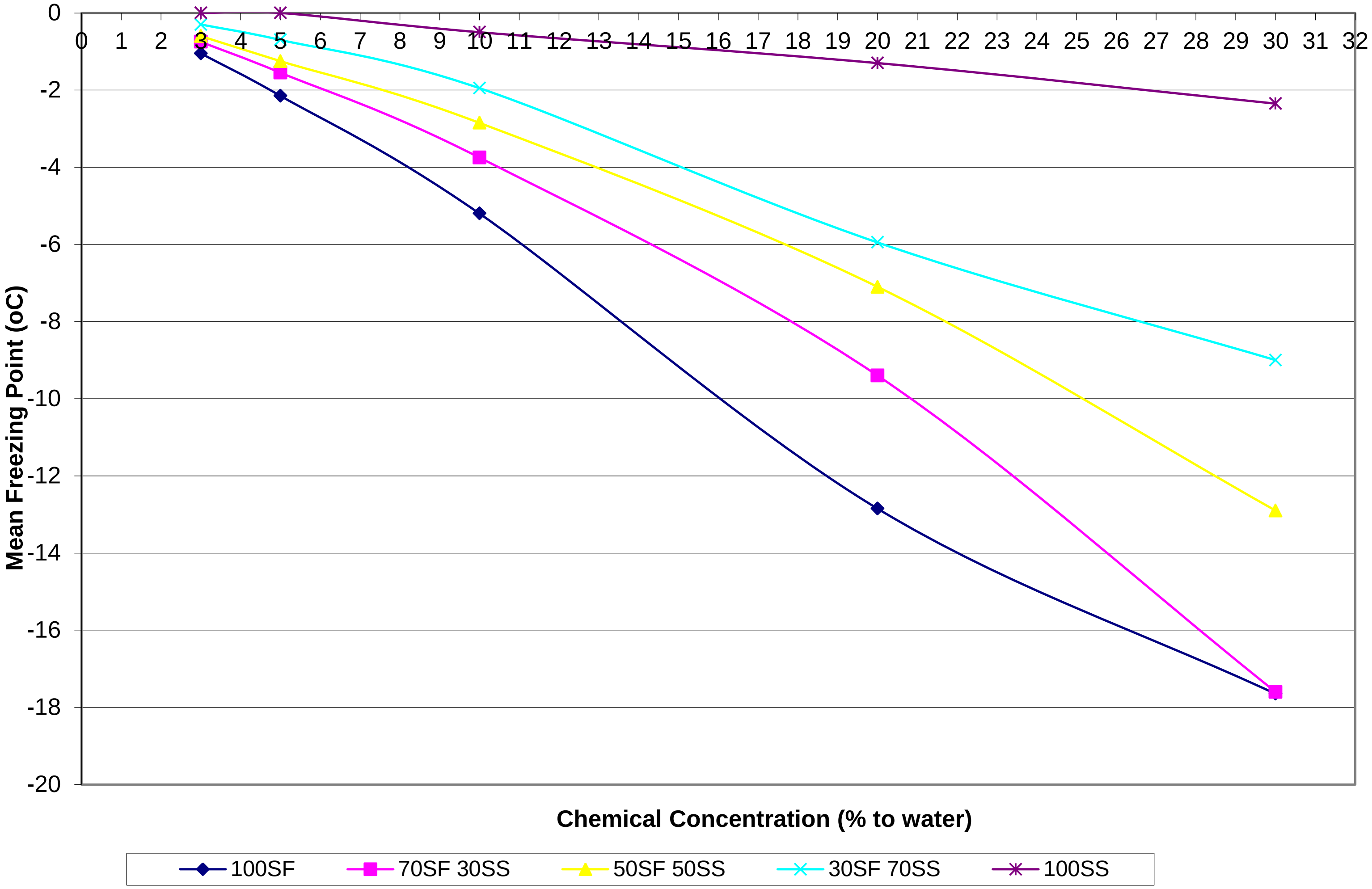


Figure 6.72 – Freezing point against chemical concentration for the de-icing chemical solutions

Discussion of Test Results

Freezing point measurements of chemical solutions confirm the freeze depressant ability of sodium formate. The chemical of sodium silicate has significantly less potential to reduce the freezing point.

Various chemical formulations of the two chemicals demonstrate freezing points between the results for the single chemicals, with the freezing point strongly related to sodium formate concentration. Small inclusions of sodium formate can significantly lower the freezing point.

6.6.2.2 FREEZING POINT MEASUREMENT – CHEMICALLY MODIFIED MASTICS

Introduction

The next phase of freezing point testing considers the freezing of a thin layer of water on to the surface of the chemically modified mastics. This testing process would take into account the encapsulation of the chemicals with bitumen, the rate of chemical transfer and chemical features such as solubility.

A thin layer of water was used to assess the freezing point to reflect the typically water film thickness on pavement surfaces.

Test Procedure

Mastics specimens were manufactured in accordance with Section 6.4.1 Experimental Setup – Mastic Specimens. A T-Junction Wire Thermocouple with an accuracy of ±0.2°C was then placed in the centre of a 95mm diameter petri-dish and secured to the base. Approximately 35g of mastic was then poured directly into petri-dish fully covering the thermocouple and placed on a flat surface to self-level. The specimens were then cooled at room temperature for 16-24 hours.

The specimens were then placed in a temperature controlled cabinet and 25ml of water placed onto the mastic surface. A further T-Junction wire probe was placed into the water at the bitumen/water interface and secured in place.

The specimens were cooled to an air temperature of 5°C for a period of 1 hour equilibrium temperature. The air temperature was then reduced by increments of 0.5°C every 30 minutes. Temperature measurements of air, water, and mastic temperature were taken at each increment.

Visual observations of the onset of freezing, ice formation and ice characteristics were recorded and the level of the ice bond determined through probing the interface with a spatula. It is acknowledged that the exact point of freezing may be difficult to identify due to the visual determination of the initial on set of freezing and the time delay to when the water has fully frozen. For this reason a rating scale was devised to assist with the semi-quantitive test method.

This rating scale was as follows:

Rating	Description
1	Onset of freezing visible
2	Thin layer of ice visible with no bond formed at the interface
3	Moderate ice layer formation with a weak interface bond
4	Moderate ice layer formation with a moderate interface bond
5	Large ice layer formation with a moderate interface bond
6	Large ice layer formation with a strong interface bond
7	Full depth ice formation with moderate interface bond
8	Full depth ice formation with strong interface bond

Table 6.22 - Semi-quantative rating scale used to assess ice formation

Test Results

Time (mins)	Air Temperature (°C)	Freezing Point Rating											
		100SF		70SF 30SS		50SF 50SS		30SF 70SS		100SS		Control 100% Filler	
0	4	-											
30	3.5	-											
60	3	-											
90	2.5	-											
120	2	-											
150	1.5	-											
180	1	-										1	
210	0.5	-										1	
240	0	-						1		1	*	2	*
270	-0.5	-				1	*	2	*	2		3	
300	-1	1		1	*	2		3		3		5	
330	-1.5	2		2		3		3		3		5	
360	-2	2	*	2		3		3		5		6	
390	-2.5	4		4		6		6		5		8	
420	-3	7		7		8		8		7		8	

Table 6.23 - Freezing rating for chemically modified mastics

* Denotes the temperature at which ice formation is indicated by increasing water temperature.

Discussion of Test Results

The freezing points measured for the chemically modified mastics ranged from 0°C to -2°C. The 100% sodium formate sample provided the lowest freezing point. The 100% sodium silicate sample had the same freezing point of the control filler sample at 0°C, however the bond between the ice and substrate was judged to be slightly less. The freezing points of the various chemical formulations were in between the two individual chemicals and dependent on the sodium formate content.

Generally the freezing points measured were consistent with the freezing points of chemical solutions at a concentration of between 3 and 5%, based on Figure 6.70, confirming that the chemical could be easily transferred from a mastic sample.

All de-icing chemical formulations demonstrated the onset of initial freezing, such that full depth ice formation had occurred with a moderate/strong bond to the mastic surface at -3°C.

6.6.2.3 FREEZING POINT MEASUREMENT – CHEMICALLY MODIFIED ASPHALT

Introduction

The previous experiments have determined the potential of each chemical if they were to be added directly to water on the pavement surface or bituminous mastics, the test methodology does not take into account the transfer of the chemical additives from asphalt.

The transfer of the chemical from the asphalt into solution is dependant on a number of chemical, asphalt, environmental and site factors. The rate of chemical transfer may depend on:

- Chemical - solubility, availability and dispersion
- Asphalt - void content, texture and binder film thickness
- Environmental - water film thickness, quantity of water, duration water is present on the pavement surface, temperature and relative humidity
- Site related factors - induced pore pressure from moving vehicles and rate of vehicle passes.

This section investigates the ability of asphalt specimens modified with different chemical formulations to depress the freezing point for different climatic environmental factors. These are achieved by submerging asphalt specimens in water for different periods of time.

To ensure comparative results, standardised asphalt specimens were manufactured for the different de-icing chemical formulation. Site factors were omitted due to limitations in the laboratory and no measure of traffic and traffic loadings were conducted as part of this experiment.

Test Procedure

Standardised asphaltic specimens were produced to ensure factors such as surface texture, void content and chemical dispersion were comparable for each specimen. This was achieved by manufacturing 100mm cylindrical specimens using the bituminous mixture produced by Section 6.4.8 and compacted by impact compaction at 50 blows per face, in accordance with BS EN 12697–30:2004. To ensure a direct comparison, the chemical was added to the aggregate at 3% by mass to ensure continuity from previous work on the sections considering the mechanical properties of asphalt. Specimen void content was maintained between 6.0% ± 1.0% air voids and any specimen outside this range was discarded. Mixing times were kept consistent and used a high mixing speed of 50rpm to ensure consistent chemical dispersion and asphalt sampling procedures were employed to ensure representative samples were taken.

Following the manufacture of the asphaltic specimens, the 100mm briquettes were placed in a 500ml beaker and submerged in 350ml of deionised water to completely cover the specimens for set time periods, representing a fully saturated pavement surface.

The time periods for submersion selected were 1, 7, 15, 36 and 72 hours. No previous studies have been undertaken to determinine the length of time water is held within a pavement surface course. As a result, a wide range of times were selected from short term (e.g. 1 to 7 hours) to replicate prolonged rainfall events, to a much longer period of time (e.g. 15 to 72 hours) to represent large quantity of water fully submerging the asphalt specimen.

Following this submersion period, the briquettes were carefully removed from the water, ensuring any remaining water contained within the specimen voids was drained back into the beaker. The solution was then mechanically stirred and a representative 20ml sample was taken.

Measurements of the freezing points of these samples were immediately conducted using the methodology based on previous work by Baum et al. (1992) and as stated in Section 6.6.2.1 Freezing Point Measurement - Chemical Additives. This approach was taken to enable comparisons to be made between the freezing point of the chemicals independently and as part of a modified asphaltic material. Freezing point diagrams for each de-icing chemical formulation for the different submersion times were plotted.

It was decided to conduct freezing point measurements on the sample solution rather than on the surface of the briquettes themselves, because the porous nature of asphalt specimens meant a significant amount of water drainage occurred through the asphalt specimen. This significantly reduced the ability to control the water film thickness and it is commonly acknowledged that water film thickness strongly affects the freezing point due to the quantity of water present to change phase.

Test Results

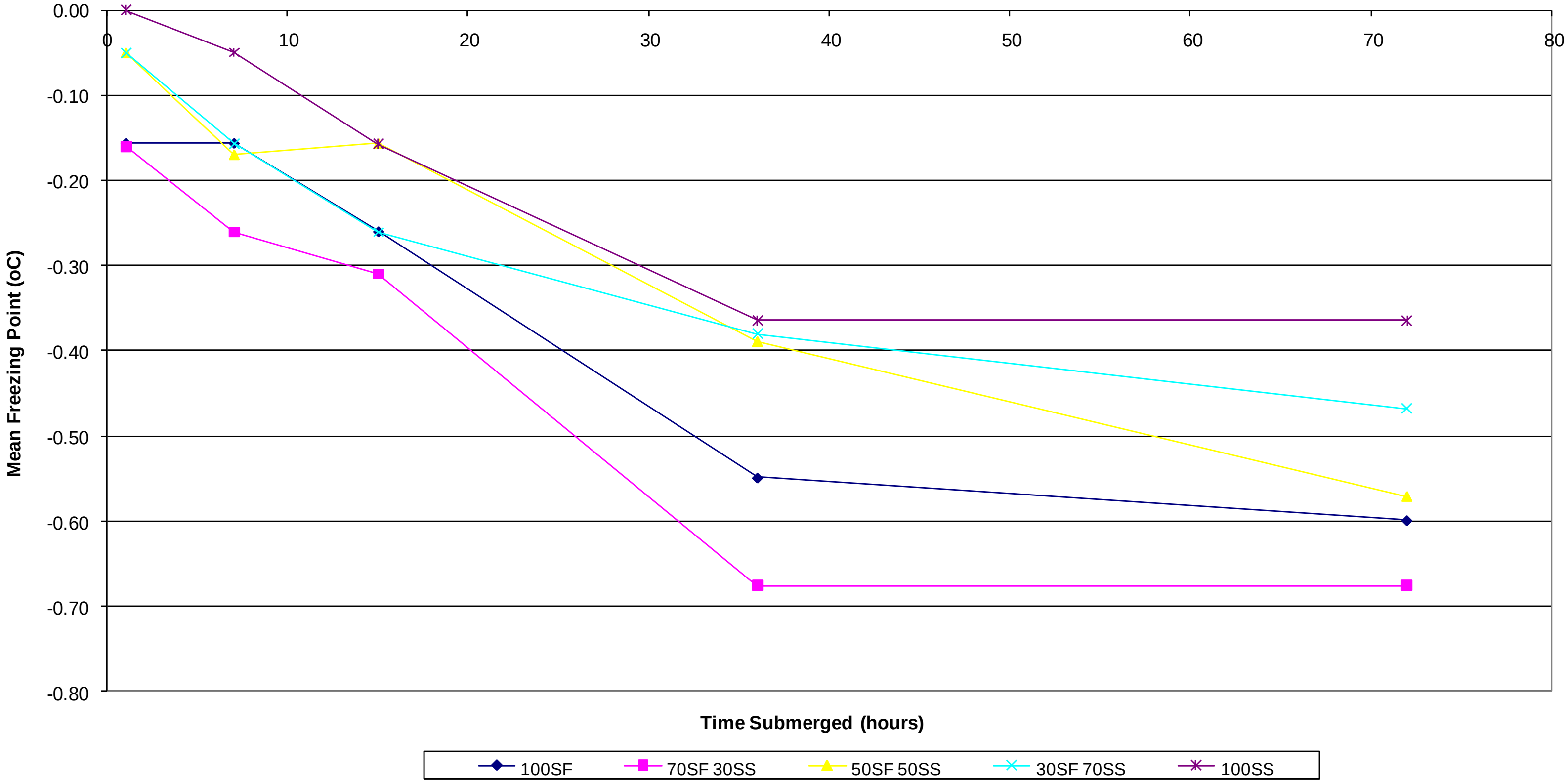


Figure 6.73 – Freezing point against chemical modified asphalt submersion time

Discussion of Test Results

The freezing point measurements of submerged asphalt samples have shown a similar trend to the freezing point measurements of chemical solutions and chemically modified mastics.

High sodium formate specimens have the lowest freezing point. This confirms sodium formate has the ability to reduce the freezing point and the chemical can be leached from the asphalt samples to form a solution with water. The chemical of sodium silicate has significantly less potential to reduce the freezing point of the water.

Generally the freezing point depressing ability was related to the sodium formate content of the specimen. The 70% sodium formate 30% sodium silicate specimen lowered the freezing to a greater extent than the 100% sodium formate sample. However, this difference is not significant as it was less than 0.1^{o}C and within the accuracy of the thermocouple used for measurement.

The test has demonstrated that the screening test conducted by Baum et al. (1992) to analyse and highlight potential of chemical additives to reduce the freezing point is still valid when the chemicals are incorporated into asphalt.

The testing has also confirmed that the freezing point depression is much less than when the chemicals are added directly to the water, indicating that the encapsulation in a bituminous material restricts the freezing point depression.

It has been calculated that there was 1g of de-icing chemical contained within the asphalt for every 11.6ml of water used in this experiment. If the entire chemical was activated then this would equate to an 8.6% de-icing chemical concentration.

By comparing the freezing point depression results after 36 hours with the freezing point depression results of the chemical solutions at different concentrations, it is possible to estimate the chemical concentration after 36 hours. The results of which are shown in Table 6.24.

	Estimated Concentration of Chemical to Water if the Chemical in the Briquette is Utilised	Freezing Point of Asphalt Solution after 36 hours (°C)	Predicted Equivalent Chemical Concentration based on Figure 6.72	Chemical Utilised
100 SF	8.6%	-0.55	1.6%	18.6%
70SF 30SS	8.6%	-0.68	2.7%	31.4%
50SF 50SS	8.6%	-0.39	2.0%	23.3%
30SF 70SS	8.6%	-0.38	3.4%	39.5%
100SS	8.6%	-0.38	8.6%	100%

Table 6.24 – Calculated chemical usage based on freezing point result of submerged asphalt after 36 hours compared to freezing point of chemical solutions at known concentrations

The results in Table 6.24 shows that between 18-40% of the chemical is utilised after a 36 hour period of constant submersion. This is consistent with the level of active surface voids on the upper surface (estimated at 20%), because water had access to the specimens from the sides in addition to the upper surface.

The relatively flat line between 36 hours and 72 hours submersion in Figure 6.72, indicates that no significant rate of change in the freezing point during over this period. This supports the theory that only surface voids contribute the chemical transfer, as the freezing point did not continue to decrease with submersion time.

The 100% sodium silicate results indicates that all of the sodium silicate is transported and utilised. This is much higher than the results established in Section 6.6.1.4. The utilization of the chemical will inevitably result in a deterioration in the chemical supply, leading to reduced anti-icing performance and/or a need for a conventional winter service treatment to prevent the formation of ice on the pavement surface.

6.6.3 ICE ADHESION

Introduction

In general terms ice adhesion relates to the physical and chemical bonding of ice with a substrate. The bond established between ice and a highway pavement material is a complex function of many parameters including temperature, rate and direction of freezing and the physical and chemical conditions of the substrate surface. Several fundamental features of both the pavement and the ice lead to excellent bonding between the two, as explained in Section 3.2.2 Ice Bond Strength and Influencing Factors. The result being that bond prevention is difficult.

Surface energy is most commonly used to predict adhesion between two materials and is dependant upon the surface energies of the two substances which meet to form an interface. Creation of a low energy surface is an approach widely investigated for de-icing purposes of ships, leading edges of airplane wings and overhead telephone wires. In order to lower the ice adhesion as much as possible, surface energy components must be made as small as possible. The lower the values of these components, the lower the overall forces that hold the ice to the surface will be, and the more easily it can be removed.

It is therefore logical to consider the potential of lower energy surface for pavement de-icing purposes, which justifies the specific inclusion of sodium silicate into this study. This section will assess whether the varying surface energy of de-icing chemical formulations impact upon the adhesion of ice to the pavement surface, by considering surface energy testing and ice bond measurements over a period of time.

6.6.3.1 SURFACE ENERGY- CONTACT ANGLE WITH WATER

Introduction

The methods used to compute work of adhesion and surface energy involve contact angles made by well characterised probe liquids on the solid surface of interest. Contact angles provide a measure of interaction between a solid and a liquid. The exact value of the contact angle made by a probe liquid on the surface of a solid is as a direct result of intermolecular interaction between them. A contact angle value close to zero indicates that there is a strong adhesion between the liquid and the solid, and the liquid wets the surface of the solid. A contact angle value greater than ninety degrees indicates the hydrophobic characteristic of the solid.

Observations from freezing point measurements of chemically modified mastics indicate that a weaker bond at the ice/mastic interface is achieved for specific chemical modifications. Surface energy testing was conducted in two phases.

The first phase measured the surface energy at ambient temperature to determine whether chemically modified mastics would instantaneously influence the interaction between the mastic and probe liquids. Secondly and following the conclusion of the first phase of testing, a study of the influence of the contact angle of water droplets on conditioned mastics at high humidities relative to unconditioned mastics was conducted.

Phase 1 - Test Procedure

The first phase of the experiment is designed to measure the instantaneous surface energy of chemically modified mastics. Surface energy testing was carried out by a method of measuring contact angles using a Goniometer. A Goniometer is an instrument that measures the contact angles and it can rotate an object to a precise angular position. The measurement of the contact angle is based on the sessile drop method. This method is used to estimate the wetting properties of a localised region of a solid surface. The angle between the baseline of the drop and the tangent of the drop is measured. The contact angle is specific for any given system and is determined by the interactions across three interfaces.

Testing was carried out using the same proportions and components in Table 6.2. These formulations were mixed by using protocol presented in Section 6.4.2 Experimental Setup – Mastic Specimens. The testing sample was produced by heating the mastic to 180^{o}C for a further two hours to ensure uniform temperature and stirring the sample to ensure a uniform blend. The mastic was poured directly onto a glass slide in a manner that ensures a level uniform surface of the sample.

The glass slides were conditioned to test temperatures at room temperature of 23±2^{o}C and humidity 50±5% for 24 hours. Following this conditioning period, the glass slide was clamped to the stage of the Goniometer with the edge of the panel flush with the front of the stage plate.

Measurement of the contact angles was based on the use of Glycerol, Diiodomethane and Distilled Water reagents with 99% purity. A micro-syringe was filled with the selected reagent for the test and subsequently fastened so that the syringe is 2±1mm above the specimen, in accordance with BS EN 828:1998. The filling of the micro-syringe was carried out by pouring the reagent into a sample tube and a test portion was taken from the sample tube. This was carried out to avoid contamination of the reagent.

A drop of the liquid reagent approximately 5-6µl was deposited onto the surface of the mastic using automated dispensing, see Figure 6.74. This procedure consisted of using Drop Volume control software to accurately dispense the drop. The stage supporting the substrate was raised to carefully take the drop ensuring the drop does not split.

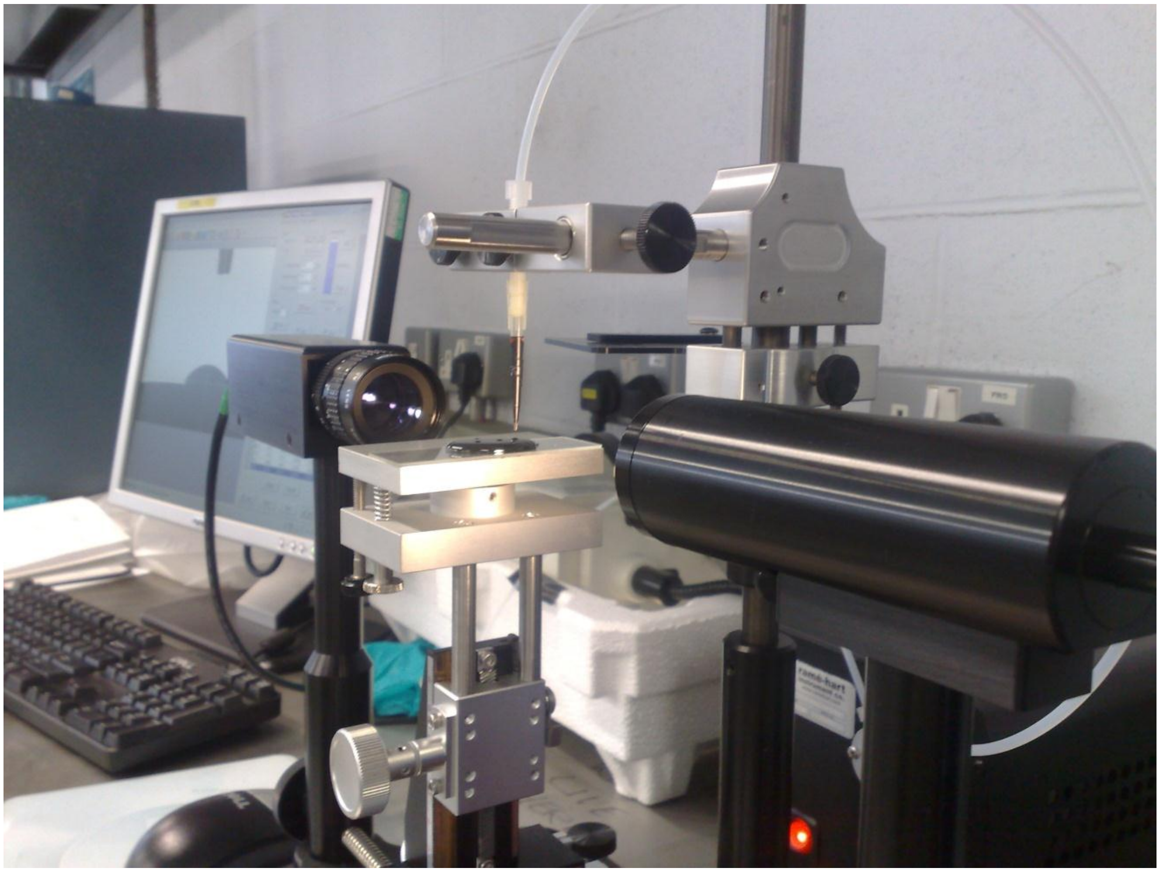
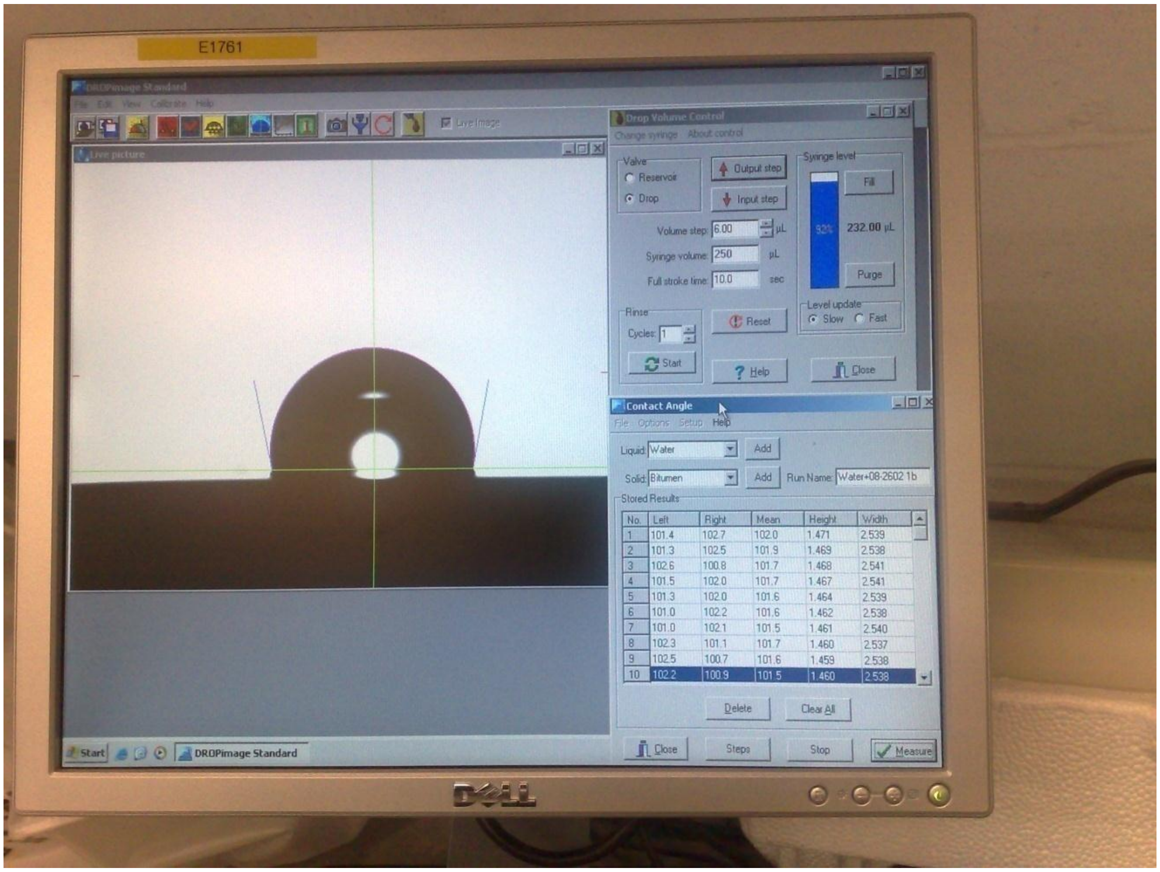


Figure 6.74 – Equipment setup of Goniometer

Following the dispensing of the drop, the microscope was re-focused onto the drop. The baseline was defined by adjusting the sample stage angle to get a good clear reflection of the drop, see Figure 6.75. Measurements for distilled water and glycerol were taken 10 times at intervals of 5s. Measurements for diiodomethane were taken at 15s intervals (50 in total), due to uncertainty regarding the potential for diiodomethane to degrade the bitumen.

These measurements were repeated 3 times on each slide, with 3 slides in total used for each individual reagent and mastic combination.



Valve: ○ Reservoir ● Drop

Volume step: 6.00 µL

Syringe volume: 250 µL

Full stroke time: 10.0 sec

Syringe level: 232.00 µL

Level update: ● Slow ○ Fast

Rinse Cycles: 1

Liquid: Water

Solid: Bitumen

Run Name: Water+08-2602 1b

Stored Results

No.	Left	Right	Mean	Height	Width
1	101.4	102.7	102.0	1.471	2.539
2	101.3	102.5	101.9	1.469	2.538
3	102.6	100.8	101.7	1.468	2.541
4	101.5	102.0	101.7	1.467	2.541
5	101.3	102.0	101.6	1.464	2.539
6	101.0	102.2	101.6	1.462	2.538
7	101.0	102.1	101.5	1.461	2.540
8	102.3	101.1	101.7	1.460	2.537
9	102.5	100.7	101.6	1.459	2.538
10	102.2	100.9	101.5	1.460	2.538

Figure 6.75 – Measurement of contact angles

Analysis of the measurements was undertaken using the acid based test (Van Oss theory). This test takes into account three probe liquids, one with a non-polar and two with polar characteristics. The two polar components used were distilled water and glycerol, and diiodomethane is non-polar. Three liquids were selected because three gives good repeatability compared to a lower number of liquids, as demonstrated by Van Oss, Chaudhury and Good (1998).

Test Results

The measured contact angles and computed surface energy for individual mastics are demonstrated in Table 6.25.

	Contact Angle Measured						
Reagent	Bitumen	Bitumen Filler	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
Water	101.8	102.7	103.4	101.5	103.2	102.9	102.2
Glycerol	99.9	97.4	97.9	95.3	97.2	95.6	97.5
Diiodomethane	55.8	54.9	56.7	52.3	54.1	53.5	51.8
Surface Energy	26.3	28.4	28.0	29.9	30.3	30.3	30.3

Table 6.25 – Computed surface energy for de-icing mastic formulations

Discussion of Test Results

Analysis of Table 6.22 indicates that the chemical composition of the mastic does not significantly influence the instantaneous contact angle of probe liquids and therefore does not significantly affect the surface energy.

Despite the varying surface energy of the chemicals (see Section 5.3.2 – Surface Energy), the mastic surface energy is not instantaneously affected due to the presence of a thin binder film between the modification and the probe liquid. This theory is supported by the ESEM observations which detected no traces of the chemical additives at the mastic surface until they were exposed to high levels of relative humidity. This would indicate that the surface energy would not be reduced until the de-icing chemical particles are exposed or transferred to the pavement surface by forming an aqueous solution.

Phase 2 – Test Procedure

The second phase of testing was designed to condition the chemically modified samples and thereby transfer the chemical particles from within the mastic to the mastic surface.

Contact angle measurement was conducted using the same procedure employed for the first phase of testing. The conditioning period selected for this experiment was a period of one week at a relative humidity of 75%. This conditioning period was selected to transfer a number of chemical particles to the mastic surface, without excessive transfer which could significantly increase the surface roughness and influence the contact angle measurements. The relative humidity of 75% is consistent with previous experiments.

Analysis of the contact angle measurements with water was conducted to assess if the de-icing chemical particles have the ability to change the wetting properties of water and therefore influence the adhesion of ice on the mastic surface.

Test Results

Contact angle measurements of water were conducted using a Goniometer on unconditioned and conditioned mastics. The results of the experiment are presented in Table 6.26.

	Unconditioned		**Conditioned (1 week)**		
	Mean Contact Angle (°)	**Standard Deviation**	**Mean Contact Angle (°)**	**Standard Deviation**	**Change in Contact Angle (°)**
Bitumen	101.8	1.40	103.5	1.09	1.7
Bitumen Filler	102.7	1.24	103.6	2.20	0.9
100SF	103.4	0.88	105.4	4.07	2.0
70SF 30SS	101.5	1.29	107.8	9.08	6.3
50SF 50SS	103.2	1.44	105.9	2.68	2.7
30SF 70SS	102.9	1.10	105.4	3.96	2.5
100SS	102.2	1.35	109.2	13.36	7.0

Table 6.26 – Contact angle of mastic surfaces with water before conditioning and after 1 week condition at 75% relative humidity

Discussion of Test Results

The contact angle measurements indicate that the conditioning procedure and the associated transfer of the chemical particles to the mastic surface can change the contact angle measurements with water.

The overall trend for the chemically modified mastics to increase the contact angle confirms that the chemical modifications can be transferred to the pavement surface, thereby influencing the contact angle and surface free energy when they are transferred to the mastic surface.

The increase in contact angle with water signifies a reduction in the overall surface free energy with increase in the contact angle of up to 7.0 degrees measured. A direct trend towards one chemical having the greatest influence or the magnitude of the chemical particles on the contact angle is not conclusive.

The nature of the test procedure and measurement of discrete droplets on the surface of the mastic means that a change in the contact angle will only be measured when the droplet is placed in the vicinity of a chemical particle. If no chemical particle is present the droplet is likely to have a contact angle as per the unconditioned state.

Analysis of the standard deviation indicates a higher variability in the chemically modified mastics contact angles relative to the unconditioned and control specimens. This relative increase supports the theory that the contact angle measured is dependent on the vicinity of the chemical transferred and that droplets located in the vicinity of chemical particles may have a more significant influence than the mean contact angles presented above.

6.6.3.2 SURFACE ENERGY CALCULATION TO DETERMINE ICE BOND STRENGTH

Introduction

The adhesion between two surfaces can be calculated from the surface energy parameters of individual materials. Experimental work has shown that the de-icing chemicals can be transferred to the pavement surface and can alter the contact angle and wettability of water.

This section will calculate the work of adhesion between ice and de-icing chemical particles based on the surface energy parameters of each material to determine if the de-icing chemicals can weaken the adhesion and theoretically allow easier removal of ice from the pavement surface.

Calculation Procedure

The bond strength of a material is the combination of the Liftshitz-van der Waals (non-polar) and the Lewis acid/base forces. Using the same principle as in Section 6.4.11.1, the adhesive bond strength between two materials can be computed using Equation 6.7, reproduced below:

$$\Delta G_{BA}^{a} = 2\sqrt{\gamma_B^{LW}\gamma_A^{LW}} + 2\sqrt{\gamma_B^{+}\gamma_A^{-}} + 2\sqrt{\gamma_B^{-}\gamma_A^{+}}$$

(Eq. 6.7)

Where B denotes ice and A represents limestone or the chemical additive.

Using the calculation above, the bond strengths between ice and the limestone filler/chemical additives were calculated.

The surface energy parameters of ice used for the calculation were γ^{LW} = 29.6 mJ/m^2, γ^+ = 14 mJ/m^2 and γ^- = 28 mJ/m^2 based on research conducted by Van Oss et. al (1992). The surface energy parameters for limestone filler and the chemical additives were determined previously in Section 5.3.2.

Calculation Results

Using Equation 6.7 and the surface energy parameters of ice presented by Van Oss et. al (1992), the work of adhesion between ice and limestone fillers/chemical additives has been calculated. These are presented in Table 6.27.

	Calculated Work of Adhesion with Ice	Reduction in Ice Adhesion relative to Limestone Filler
Limestone Filler	257	-
Sodium Formate	77	70%
Sodium Silicate	86	67%

Table 6.27 – Calculated work of adhesion between limestone filler/chemical additives and ice

Discussion of Calculation Results

The test results demonstrate that the low surface energy properties of sodium formate and sodium silicate substantially reduced the theoretical adhesion with ice by 70% and 67%, respectively. The high surface energy properties of limestone filler indicates a strong adhesion would be achieved with ice.

The surface energy properties of the limestone filler are in the same order of a number of aggregates used in bituminous mixtures; the calculation results demonstrate that if the chemical particles are transferred to the pavement surface, the bond achieved between ice and the chemical particles will be significantly less than aggregate/filler particles. Theoretically this will allow for easier ice removal under trafficking.

6.6.3.3 MEASUREMENT OF ICE BOND STRENGTH

Introduction

Surface energy results have demonstrated the ability of chemical particles to influence the contact angle of water on a bituminous surface and theoretically influence the bond strength between the two surfaces.

In order to further examine this factor, ice-bitumen bond strength measurements were conducted using a modified torque bond experiment.

Test Procedure

The principles behind this experimental procedure is based around Baum et al. (1992) utilising a ice disc bound to a bituminous surface.

Ice bond strength measurements were assessed in terms on the torque required to fully break the interfacial bond.

The equipment used for this research was a specifically designed testing rig that composed of a fixed base for holding the bituminous sample and a freely rotating upper component which rotated a pre-bonded ice disc. The ice bond strength was measured used a hand held torque meter. The equipment and setup is demonstrated in Figure 6.76.

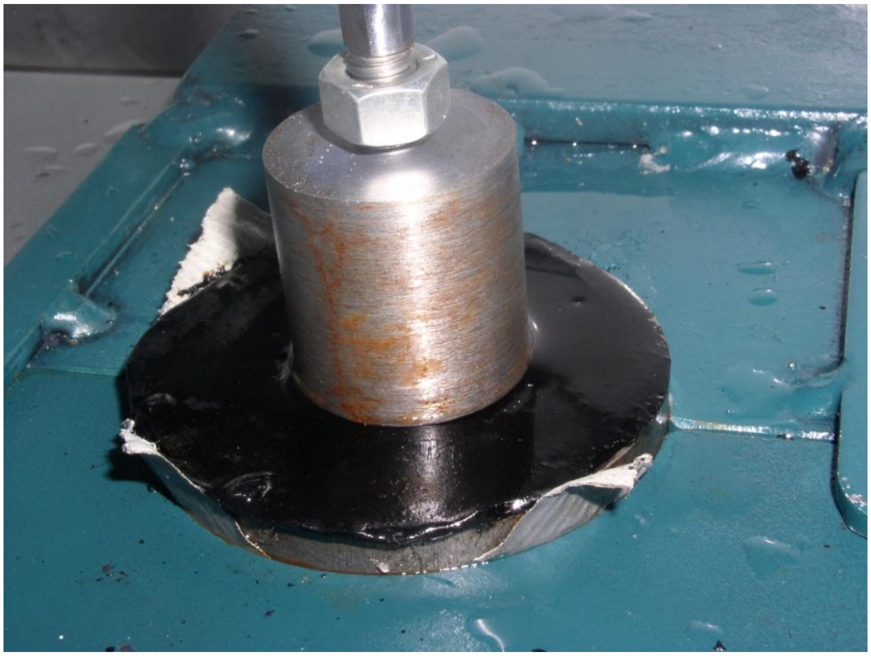


Figure 6.76a – Photograph of equipment setup

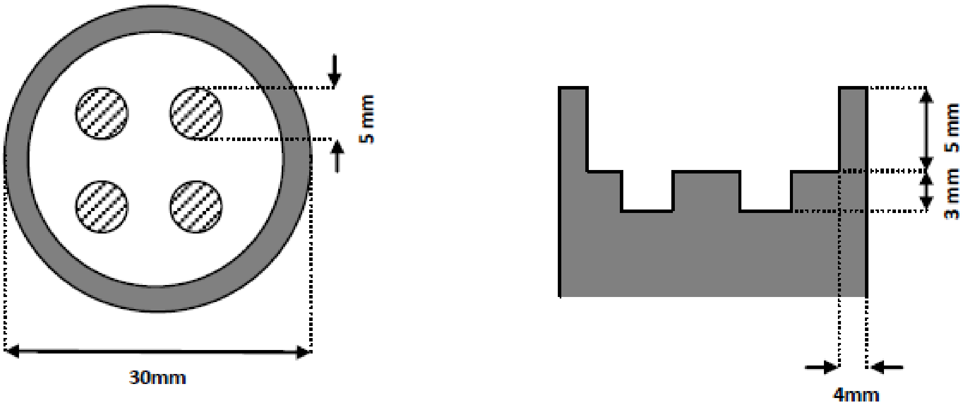


Figure 6.76b – Schematic of test head and dimensions

Chemical solutions were manufactured at concentrations of 1, 3 and 5% by weight for the various formulations. These were then poured into a metal test head cylinder and frozen at -20°C for a minimum of 12 hours.

The test heads were specially designed with a notched insert to ensure the ice disc created inside could not rotate or move in any way. At the same time a bitumen disc was frozen at -20°C for a minimum of 12 hours, placed and secured to the base of the testing equipment. The two components were then bonded together by placing 5ml of the solution on the bitumen disc and lowering the ice disc onto the bitumen surface. The entire unit was then frozen at various temperatures for a period of 45 minutes and the ice bond measured using a torque meter.

The bond established between ice and a material surface is a complex function dependent on temperature, rate and direction of freezing, and the physical and chemical conditions of the substrate surface. Special attention was therefore given to ensure samples and the test procedure conditions were constant and that no external variables were introduced.

Test Results

The mean ice bond strength was calculated for each de-icing solution at 1%, 3% and 5% concentrations between -1°C to -5°C. These results are presented in Table 6.28, 6.29 and 6.30 and Figures 6.77 to 6.79 inclusive. The error bars represent the standard deviation of the ice bond strength measurements.

Test Temperature	Mean Ice Bond Strength – N/mm (lb/in)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	2.59 (14.8)	2.24 (12.8)	2.22 (12.7)	2.29 (13.1)	2.35 (13.4)	2.38 (13.6)
-3°C	2.77 (15.8)	2.66 (15.2)	2.70 (15.4)	2.66 (15.2)	2.68 (15.3)	2.70 (15.4)
-5°C	3.34 (19.1)	3.19 (18.2)	3.19 (18.2)	3.20 (18.3)	3.24 (18.5)	3.24 (18.5)

Table 6.28 – Mean ice bond strength at a 1% concentration

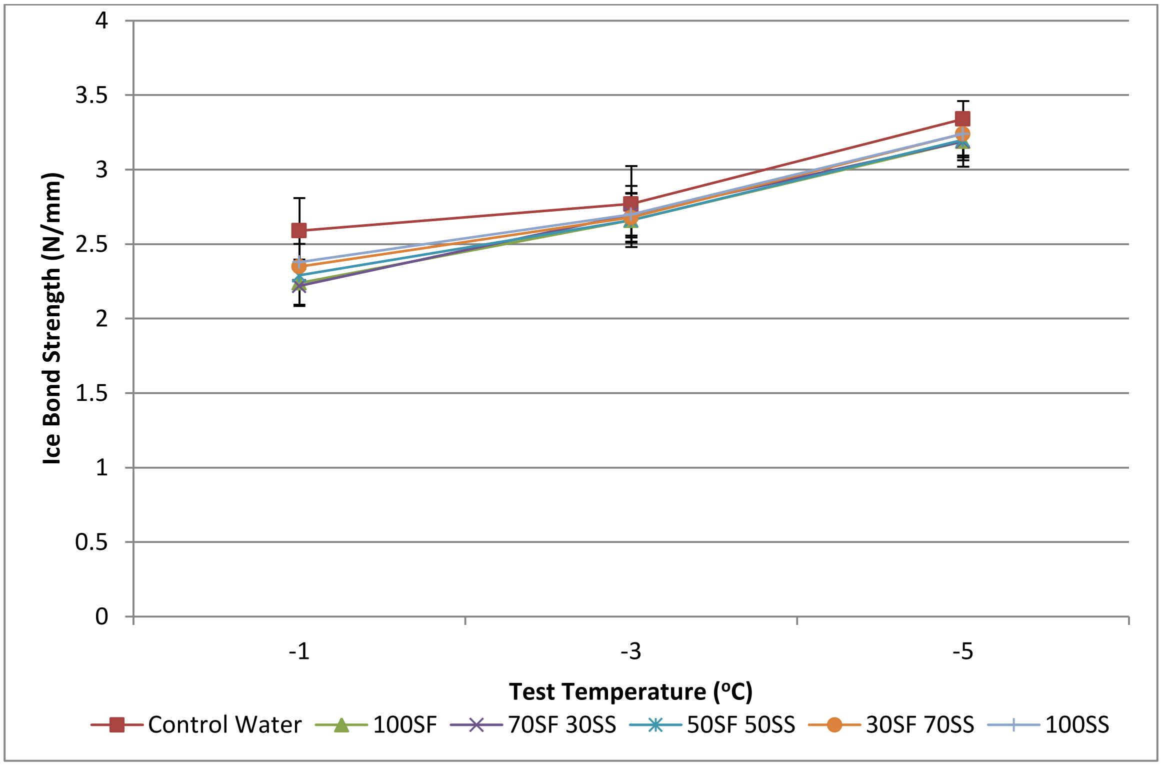


Figure 6.77 – Mean ice bond strength at a 1% concentration

Test Temperature	Mean Ice Bond Strength – N/mm (lb/in)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	2.59 (14.8)	1.96 (11.2)	2.00 (11.4)	1.96 (11.2)	1.98 (11.3)	1.98 (11.3)
-3°C	2.77 (15.8)	2.12 (12.1)	2.42 (13.8)	2.61 (14.9)	2.63 (15.0)	2.61 (14.9)
-5°C	3.34 (19.1)	2.82 (16.1)	2.85 (16.3)	2.91 (16.6)	2.87 (16.4)	2.94 (16.8)

Table 6.29 – Mean ice bond strength at a 3% concentration

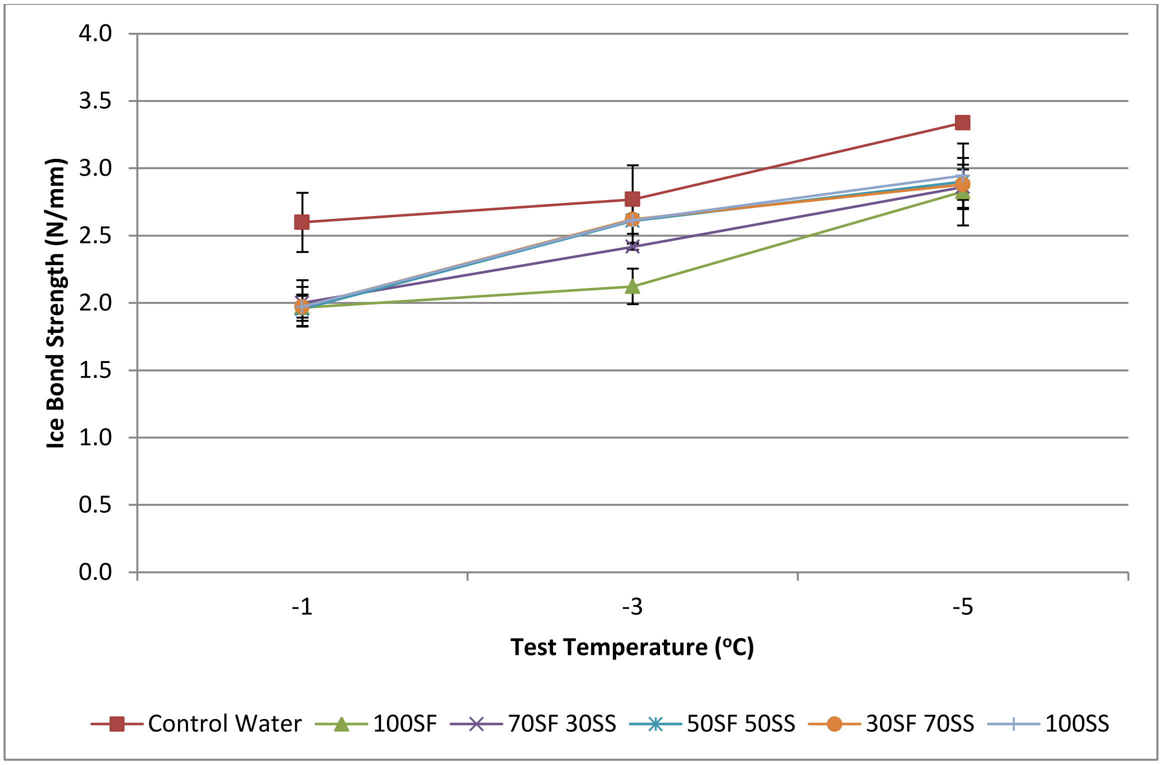


Figure 6.78 – Mean ice bond strength at a 3% concentration

Test Temperature	Mean Ice Bond Strength – N/mm (lb/in)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	2.59 (14.8)	1.68 (9.6)	1.66 (9.5)	1.65 (9.4)	1.79 (10.2)	1.84 (10.5)
-3°C	2.77 (15.8)	1.65 (9.4)	1.82 (10.4)	1.77 (10.1)	1.94 (11.2)	2.15 (12.3)
-5°C	3.34 (19.1)	1.77 (10.1)	1.86 (10.6)	1.79 (10.2)	1.94 (11.1)	2.19 (12.5)

Table 6.30 – Mean ice bond strength at a 5% concentration

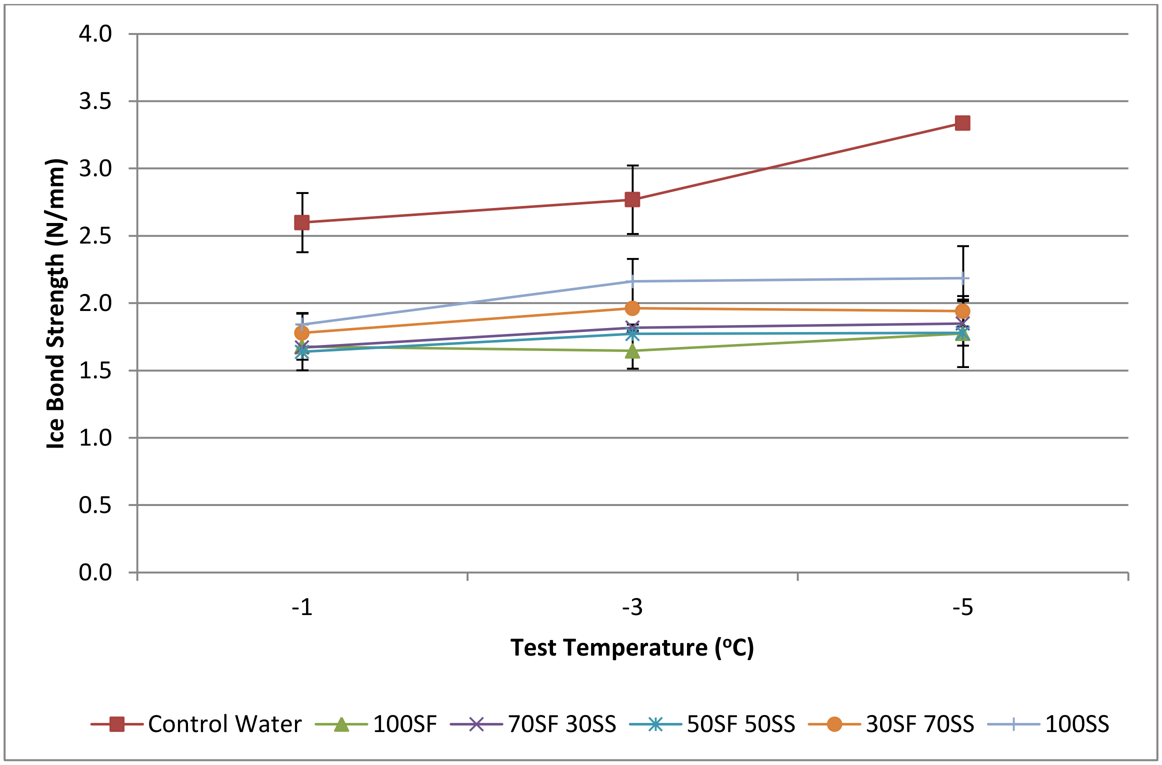


Figure 6.79 – Mean ice bond strength at a 5% concentration

Discussion of Test Results

The results demonstrate a reduction in the bond strength between all of the de-icing chemical solutions and the bitumen mastics' surface in comparison to the bond strengthen between water (control) and the bitumen surface. This difference is most evident as the chemical concentration is increased from 1% to 5%, as shown in Tables 6.31, 6.32 and 6.33. Typically:

- At a 1% concentration the de-icing chemicals solution have bond strength with bitumen which is typically 2.5-14.6% less than the bond strengthen with water.
- At a 3% concentration the de-icing chemicals solution are more effective with reductions ranging from 5.4-24.8% less.
- At 5% concentration the bond strength measured is up to 46.8% less than water.

This confirms that de-icing chemicals can weaken the bond and that the bond strength is directly related to the amount of de-icing chemical that can be transferred.

Generally, the results for sodium formate and sodium silicate are similar across all temperatures and concentrations. This appears consistent with the theoretical work of adhesion calculations conducted in the previous section.

The de-icing chemicals typically provide similar reductions in the ice bond strength regardless of the temperature the test was conducted under. The exception to this is the de-icing chemical concentrations at -5^{o}C as shown in Figure 6.79, where the control water sample bond strength increased but the de-icing chemical bond strengths remained constant.

Overall, the testing confirms that the inclusion of lower surface energy de-icing chemicals can weaken the bond between ice and a bituminous surface and confirms that work of adhesion calculations provide a good estimate for highlighting potentially effective chemicals. The test method developed has proved to be an accurate method of measuring ice bond strength in the laboratory with an average standard deviation of less than 0.2 N/mm over 324 individual tests.

Test Temperature	Mean Percentage Bond Strength Reduced relative to Control (%)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	-	13.8	14.6	11.9	9.6	8.4
-3°C	-	3.9	2.5	3.9	3.2	2.5
-5°C	-	4.4	4.4	4.1	2.9	2.9

Table 6.31 – Mean percentage bond strength reduced relative to the control at a 1% concentration

Test Temperature	Mean Percentage Bond Strength Reduced relative to Control (%)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	-	24.4	23.0	24.8	24.1	24.1
-3°C	-	23.3	12.7	5.7	5.4	5.6
-5°C	-	15.3	14.3	13.1	13.7	11.8

Table 6.32 – Mean percentage bond strength reduced relative to the control at a 3% concentration

Test Temperature	Mean Percentage Bond Strength Reduced relative to Control (%)					
	Control Water	100SF	70SF 30SS	50SF 50SS	30SF 70SS	100SS
-1°C	-	35.4	35.7	36.9	31.5	29.1
-3°C	-	40.5	34.3	36.0	29.2	21.9
-5°C	-	46.8	44.6	46.7	41.9	34.5

Table 6.33 – Mean percentage bond strength reduced relative to the control at a 5% concentration

7.0 SITE TRIALS

7.1 INTRODUCTION

Experimental results in the previous phases of the research project have identified that the different chemical blends of sodium formate and sodium silicate have the potential to be suitable anti-icing modifying chemicals. However, it is widely acknowledged that laboratory testing does not provide an exact replica of real life conditions. This is especially important for determining anti-icing performance where factors such as water film thickness, traffic and relative humidity cannot be easily incorporated into laboratory experimental designs.

To provide a measure of the in-service anti-icing performance, a number of site trials using the perceived most promising chemical blend were constructed at various stages throughout the research project. This chemical blend was a 3% addition comprising of 70% sodium formate and 30% sodium silicate. This blend was selected based on the initial gyratory compaction, stiffness, resistance to permanent deformation, water sensitivity (BBA HAPAS only) and freezing point of chemical additives.

Experimental trials of other chemical blends were not incorporated as part of this study due to the substantial cost of chemical products, measurement devices and site limitations.

The first trial (started at the end of year 1 in November 2008) was conducted at Bow Depot in Central London. A decision to carry out the trial before completion of all the laboratory experiments was primarily based on the time constraints of the research project. It was necessary to assess the modified material over multiple years.

The primary objective of this trial was to check that the material could be satisfactorily produced, laid and to ensure the in-service performance was satisfactory prior to transferring the system to the highway network. This was especially important considering the failings of previous products.

A second phase of trials was conducted after year 2 in June 2009 of the research project. This phase was designed to measure the performance of the material under highway trafficking. The objectives of this set of trials were to quantitatively measure the anti-icing and mechanical performance of surface course under varying conditions over a period of 2 years.

7.2 CHEMICAL BLEND AND PRODUCTION

To replicate the laboratory experiments and to ensure no external variables were introduced, the chemical suppliers and type of product from the laboratory experiments were used for the site trial. The chemicals were first sieved to remove any elements of caking from the chemicals. The two components were then mechanically blended to form a uniform powder.

Following this process, the blended chemical was weighed into low density polyethylene bags at a weight of 2kg, see Figure 7.1. The chemical was added in bag format because no powder system was available at the desired production facility. The low weight of 2kg bags was selected due to the size constraints of the entrance into the mixer box. This bagging process took place under vacuum conditions to ensure no air was introduced and to prevent caking. These bags were then heat sealed.

Figure 7.1 – Production of chemical formulation

7.3 SURFACING SELECTION AND ASPHALT PRODUCTION

The selection of the asphalt surface course was kept consistent for all site trials, this was the 0/10mm Stone Mastic Asphalt surface course comprising of the same aggregate and bitumen suppliers as used in the laboratory studies. This ensured the number of external factors introduced during production were minimised.

The only new variable introduced for the sites trials was the low density polyethylene bags used for producing the chemical formulation. It was calculated that the polyethylene bags constituted 0.53% to the bitumen by mass, which is likely to modify the penetration grade bitumen. In France, bitumen modification using polyethylene is typically based on 0.4% to 0.6% polyethylene to bitumen by mass to improve the properties of the bitumen.

The asphalt surface course was produced using a standardised production method by means of an asphalt batch plant in 3T batches. A schematic of an asphalt batch plant is shown below in Figure 7.2.

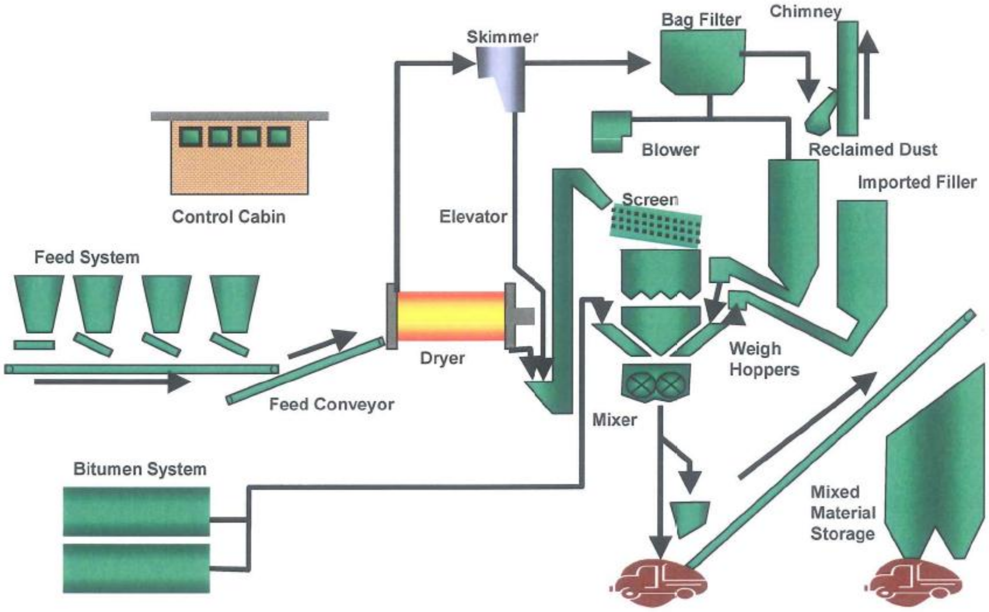


Figure 7.2 – Schematic of asphalt batch plant

This process dries the aggregates through a drum heater at temperatures of approximately 210°C. The dry aggregate is then discharged and transported vertically to a screening unit, where the aggregates are separated and stored in hot storage bins.

From the hot storage bins, the mixing sequence commences by discharging the correct mass of each aggregate size into the mixer box. The chemicals were added cold to the blended aggregates in the mixer box. For health and safety reasons this had to take place through a RAP conveyor belt which directly dropped into the mixer. This meant that the 42 2kg chemical bags had to be placed on a conveyor belt at a rate of one bag per 5 seconds to ensure the RAP opening did not block. The chemical and aggregate were mixed for a further 90 seconds. This time was selected after production trials to ensure the chemical was uniformly distributed based on visual observations. The loose fibres (as used in the laboratory mixes) were blown directly into the mixer box at 0.3% mass addition.

The bitumen was added at the correct mass via the bitumen kettle and the batch mixed for a further 25 seconds. The batch was discharged into an insulated hopper. This process was repeated until the appropriate tonnage of anti-icing material was produced where it was discharged.

Following the discharge of the material it was visually examined to ensure a homogenous batch had been produced. During this visual inspection it was noticed that the anti-icing surface course material appeared duller in comparison to the control surface and of a grey appearance.

The output temperature was also measured in multiple places, producing an average output temperature of approximately 170°C, which is within the specified temperatures for Stone Mastic Asphalt surface of this type. This confirmed that the moisture content of sodium silicate did not reduce the output temperature of the mix.

7.4 SITE TRIAL LOCATION AND DESIGN REQUIREMENTS

The selection of the site location is fundamental to the quality and effectiveness of any site trial. To fully achieve the objectives of establishing the anti-icing performance and mechanical performance of the modified anti-icing surface course a strict criteria for the site trial location was developed. The site location criteria were as follows:

- The site had to be of new construction or a structurally sound pavement structure
- Able to accommodate at least two sections comprising of the modified anti-icing surface course and a control surface course
- Located within range of a suitable asphalt production plant
- Situated on a low risk site with appropriate control measures in relation to vehicle movements, carriageway characteristics and appropriate speed limit, in response to concerns raised from previous chemically modified surface courses
- Located on a section where salting does not occur or could be managed to ensure an appropriate level of anti-icing data could be recorded
- Allow routine testing and installation of remote testing equipment to take place, where appropriate.

7.5 TRIAL 1 - BOW SITE TRIAL

7.5.1 INTRODUCTION

The first trial was conducted at Bow Depot in Central London at the end of year 1. A decision to carry out this trial at the end of year 1 and not after the completion of all laboratory experiments was primarily based on the time constraints of the research project.

The aims and objectives of this site trial were:

- To ensure that anti-icing chemically modified asphalt could be satisfactorily produced using conventional production methods.
- To monitor skid resistance and in-service performance to ensure that future site trials do not generate an increased risk for road users.
- To provide visual observations of the anti-icing process and effectiveness.

7.5.2 SITE TRIAL DESIGN

The selected site location that met the above criteria was the construction of a new car park as part of Ringway Jacob’s depot in Bow (London). A car park location was selected in favour of a local minor road for the initial site trial for health and safety reasons. The car park location eliminated the risk to the general public and the salting of the depot could be controlled and delayed until the formation of ice. The new construction of the depot meant that the site design and construction methods could be closely controlled to ensure a direct comparison.

The chemical blend selected for the first site trial was a blend of 70% sodium formate and 30% sodium silicate. This chemical blend was selected based on initial mechanical performance and physical anti-icing performance.

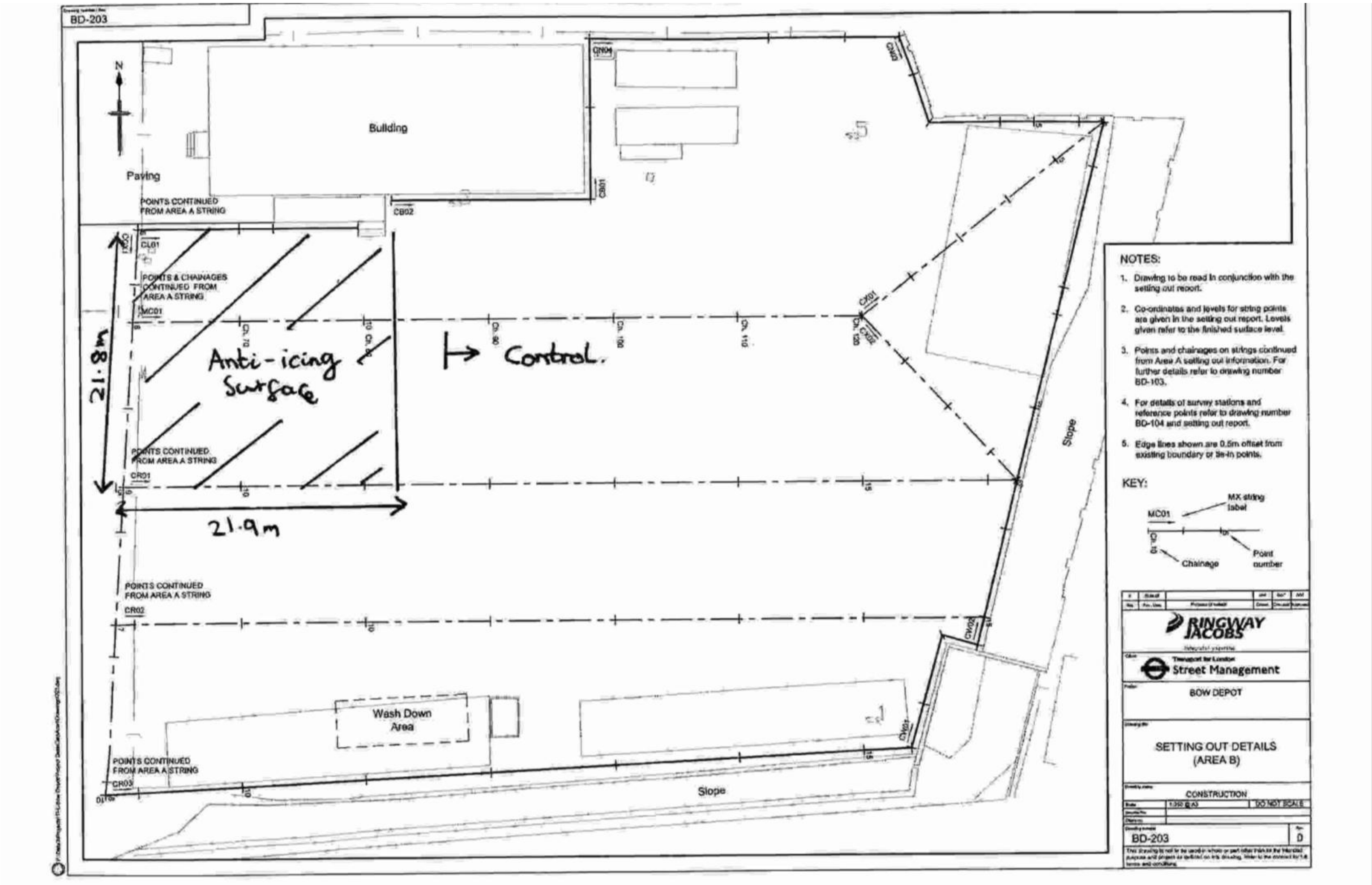
The site design incorporated 20T of the anti-icing surface course (3% addition 70% sodium formate 30% sodium silicate) providing an area of 400m^2. This was laid adjacent to 60T of control surface course creating a control area of 1200m^2.The control surface course consisted of the same bitumen and aggregate composition, with 3% limestone filler replacing the chemical additive.

The location of the surface course sections were designed to ensure a direct comparison between the two surface courses. The design of the site trial surface is shown in Figure 7.3.

Firstly, the surface course sections were designed to ensure equal trafficking across each section. This was achieved by laying the anti-icing surface course and the control perpendicular to the depot's one-way system. This meant that every traffic movement must cross each surface course section to enter and leave the depot car park.

Secondly, the surface sections were located adjacent to each other between the building and the central gully. Laying the sections adjacent to each other limited any micro-climate variations and ensured the levels and crossfalls for both sections were consistent.

The larger area of the control surface allowed for a buffer zone to be created. This provided a clear seperation preventing any chemical contamination on the observation/test area of the control surface from the anti-icing surface course.



NOTES:

1. Drawing to be read in conjunction with the setting out report.
2. Co-ordinates and levels for string points are given in the setting out report. Levels given refer to the finished surface level.
3. Points and chainages on strings continued from Area A setting out information. For further details refer to drawing number BD-103.
4. For details of survey stations and reference points refer to drawing number BD-104 and setting out report.
5. Edge lines shown are 0.5m offset from existing boundary or tie-in points.

Figure 7.3 - Schematic of site trial design

7.5.3 SITE TRIAL CONSTRUCTION

The anti-icing surface course and the control surface course were constructed directly on top of a 60mm layer of AC20 HDM 40/60 base. This was supported by 150mm of recycled asphalt planings complying with the Type 1 aggregate specification. Both the anti-icing surface course and the control surface course were laid at a target depth of 40mm. No bond or tack coat was applied between the base course and the surfacing.

Both the control and the chemically modified anti-icing surface course were laid using a Titan Paver in a direction perpendicular to the building, see Figure 7.4. Areas around iron work and roadside obstacles were hand laid. These were then immediately compacted using a Bomag 120AD roller with between 6-8 passes made on each section. A wacker plate was used to compact restricted areas.

Each 20T load of surface course was laid within one hour of the final batch being produced.

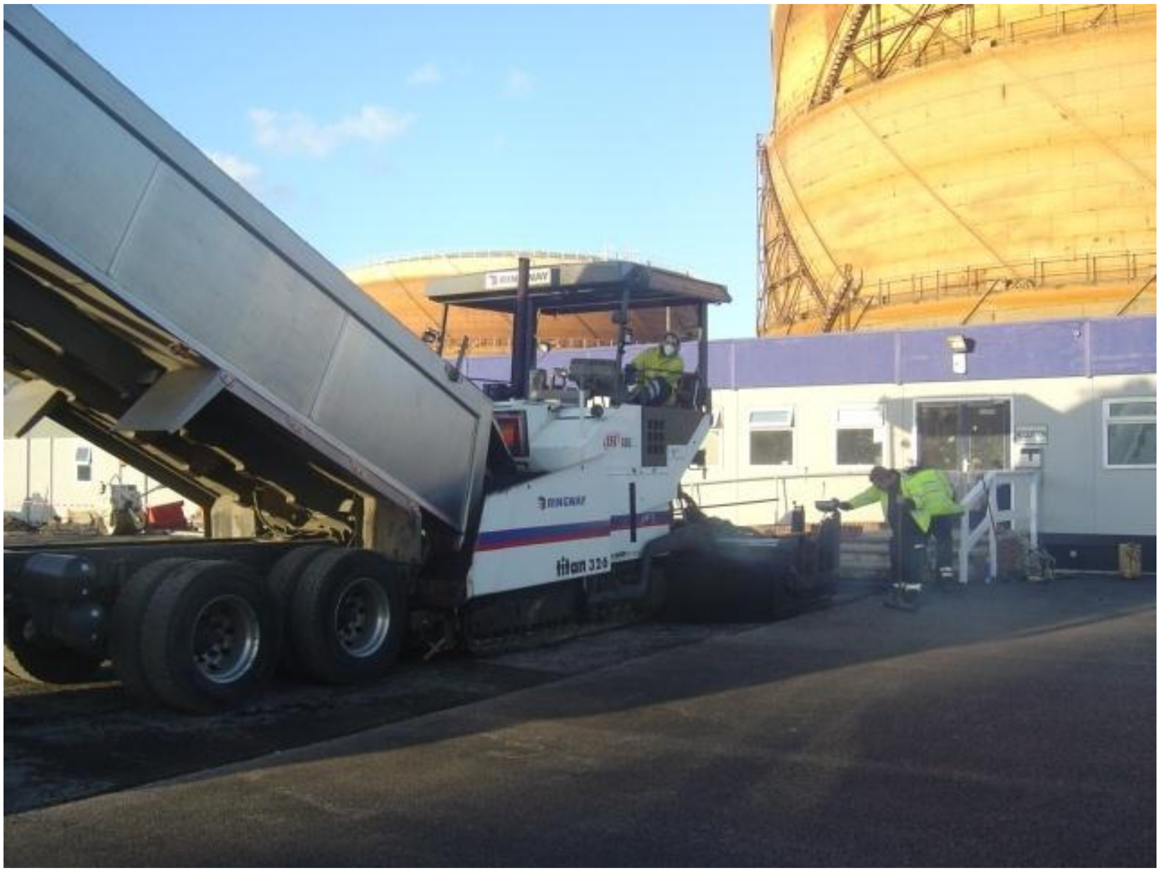


Figure 7.4 – Laying and compaction of anti-icing surface course material

The anti-icing surface course and control surface course were laid during November (2008) under suitable laying conditions on a clear/sunny day, with air temperatures of 11^{o}C and average wind speed of 17mph.

Throughout laying of both surface courses it was noted that the control and anti-icing surface course materials performed similarly. The only notable difference was the increased workability of the anti-icing surface course, especially when hand laid.

7.5.4 TESTING PROCEDURE

The primary purpose of the trial was to monitor skid resistance and in-service performance to ensure that future site trials do not generate an increased risk for road users. The site testing programme measured in-service performance by means of skid resistance testing, macro-texture measurements and visual inspections.

Skid resistance is a property of the trafficking surface which limits the relative movement between the contact patch of a vehicle tyre and the surface. It is an essential design parameter for road surfaces for safety reasons.

Skid resistance was measured using a Pendulum Skid Tester as displayed in Figure 7.5 and tested in accordance with BS EN 13036-4:2003(E) `*Road and Airfield Surface Characteristic Test Methods – Method for measurement of slip/skid resistance of a surface – The Pendulum Test*`. In total ten locations were selected for testing on each surface, which were typically 5m apart with testing conducted in both directions. Testing was conducted in the wheel tracks at locations representative of the overall surface. In total, 5 consistent swings were recorded for each location and the mean value of skid resistance was temperature corrected for the conditions at the time of testing. A micro-griptester was also used to measure the skid resistance in dry mode.

Macrotexture refers to the overall texture of the pavement surface. It is an essential characteristic to ensure satisfactory skid resistance under wet conditions. Sudden increases in macrotexture can provide an indication of the deterioration of pavement surface courses due to aggregate particle loss and fretting.

Macrotexture measurements were conducted in accordance with BS EN 13036-1:2002 `*Road and Airfield Surface Characteristic Test Methods – Measurement of pavement surface macrotexture depth using a volumetric patch technique*`. Macrotexture measurements were conducted at specific chainages to coincide with the skid resistance results and to allow comparisons to be made over time. Measurements were typically conducted on a monthly basis for the first year (weather dependent) and at yearly intervals thereafter.

Figure 7.5 - Pendulum skid tester and volume patch equipment

Testing to determine anti-icing performance was based on the qualitative information provided by detailed visual inspections. No attempt to instrument the site trial was made for this initial trial due to the cost implications.

7.5.5 ANALYSIS OF SITE TRIAL

Analysis of the performance of the anti-icing section for the Bow site trial is considered in terms of the mechanical performance of the asphalt and anti-icing performance.

7.5.6 ANTI-ICING AND CHEMICAL TRANSFER OBSERVATIONS

Visual inspections of the site trial section and control section were undertaken on a monthly basis and throughout winter weather events. This included recording the frost or ice formation on the control surface or anti-icing surface course and the temperature at which the event occurred.

Winter weather records for the site were intermittent and not every winter weather event was recorded. Particular events to note were on the 8th of December 2008, when it was noted that the surface of the control was damp with signs of hard frost in areas. The anti-icing surface course remained clear from ice and frost. Further detailed inspections were made between the 9th and 10th of December when air temperatures dropped to -2°C. The control surface had a thin layer of ice covering the surface whilst the anti-icing surface course was free from frost and ice.

Consistent observations were also made over the following two winters 2009 and 2010. An interesting observation was made on the 16th January 2009 which recorded significant snow deposits at a temperature of 1°C on the control surface and whilst snow was starting to settle on the chemically modified section, it was significantly less than the control. However, on one occasion a conflicting report of frost forming on both surfaces was recorded.

These observations suggest that a degree of anti-icing performance is maintained for over three winters. However, the performance of the chemically modified pavement surface has some limitations to when it is fully effective.

Detailed site observations provided significant evidence of the principles by which such anti-icing chemical systems work.

An observation continuously made throughout the winter period (2009 and 2010) is that the anti-icing surface course maintained a damp appearance and only rarely became fully dry over the entire section, see Figure 7.6. This is in contrast to the control surface course, which quickly dried out after periods of precipitation or high humidity.

This observed effect is due to the hydroscopic nature and moisture absorption of the chemical modification. These continued observations correlate with the laboratory moisture absorption testing conducted in phase 3 and confirm that moisture absorption can occur over prolonged periods of time in the field.

Figure 7.6 - Visual difference between surface courses due to moisture attraction damp anti-icing surface course (top) and dry control surface (bottom)

Visual observations also confirmed that the chemical can be transferred to the surface of the pavement and are deposited when the relative humidity decreases.

The best evidence of this process was on the 15th of June 2009 when the visual inspection identified further and significant chemical transfer. This assessment followed two weeks of high temperatures (typically 23 deg.C) and low humidity, representing the first prolonged summer weather system following the winter period.

Inspection of the chemical identified significant deposits in the particle voids located around aggregates particles, see Figure 7.7.

Figure 7.7 – Chemical deposits on surface during low humidity

An inspection on the 19th of June 2009 was conducted under dry and sunny conditions following a short rainfall event. At this inspection, the chemical deposits were less pronounced, indicating significant removal of the chemical from the surface, see Figure 7.8.

The removal of the chemical is likely to happen via two mechanisms. Firstly, a mechanism by which the chemical may have formed a solution and been transported to adjacent surfaces and/or the drainage system.

Secondly, the formation of a solution and deposition of the chemical deep into the upper air voids in the pavement surface course upon humidity and temperature changes.

Figure 7.8 - Chemical deposits on surface 15/06/09 (left) and surface after a rainfall event 19/06/09 (right)

These observations support the findings of the laboratory testing experiments designed to examine the chemical transfer mechanism and confirm:-

- The chemical can be transferred from the bituminous materials to the pavement surface
- The transfer mechanism and chemical deposition is related to the relative humidity
- The surface voids provide a chemical transport path and can collect significant quantities of chemical particles when the chemicals are deposited

7.5.7 MECHANICAL PERFORMANCE

The primary purpose of the trial was to monitor skid resistance and in-service performance to ensure that future site trials do not generate an increased risk for road users.

Skid Resistance

Skid resistance testing was conducted on a monthly basis at predetermined locations for the first year of the site trial and at yearly intervals thereafter. The mean results for each month are displayed in Table 7.1 and Figure 7.9.

Surface/Months	Mean Pendulum Test Value (Temperature Corrected)													
	1	2	3	4	5	6	7	8	9	10	11	12	24	36
Control - Wheelpath	67.5	71	70.5	68.5	65	64.5	65	71	62	63	64	67.5	64	57
Anti-icing Surface - Wheelpath	69.5	70	73.5	70	69	69.5	69	74.5	63	65	66	68	66	64

Table 7.1 – Mean Pendulum Test Value (BS EN 13036-4:2003) from November 2008

The results show high skid resistance typically between 65 to 75. Comparing the two surfaces, the skid resistance of the anti-icing surface course is comparable to the control surface throughout the year, with marginal improvements generally observed. Both surfaces display traditional skid resistance characteristics, with an increase in skid resistance in the early life due to the removal of the binder film. This is followed by cycles of polishing in summer periods reducing skid resistance and weathering in winter periods increasing skid resistance. Skid resistance reductions at 36 months were observed and may be attributed to polishing of the aggregate particles, see Figure 7.9.

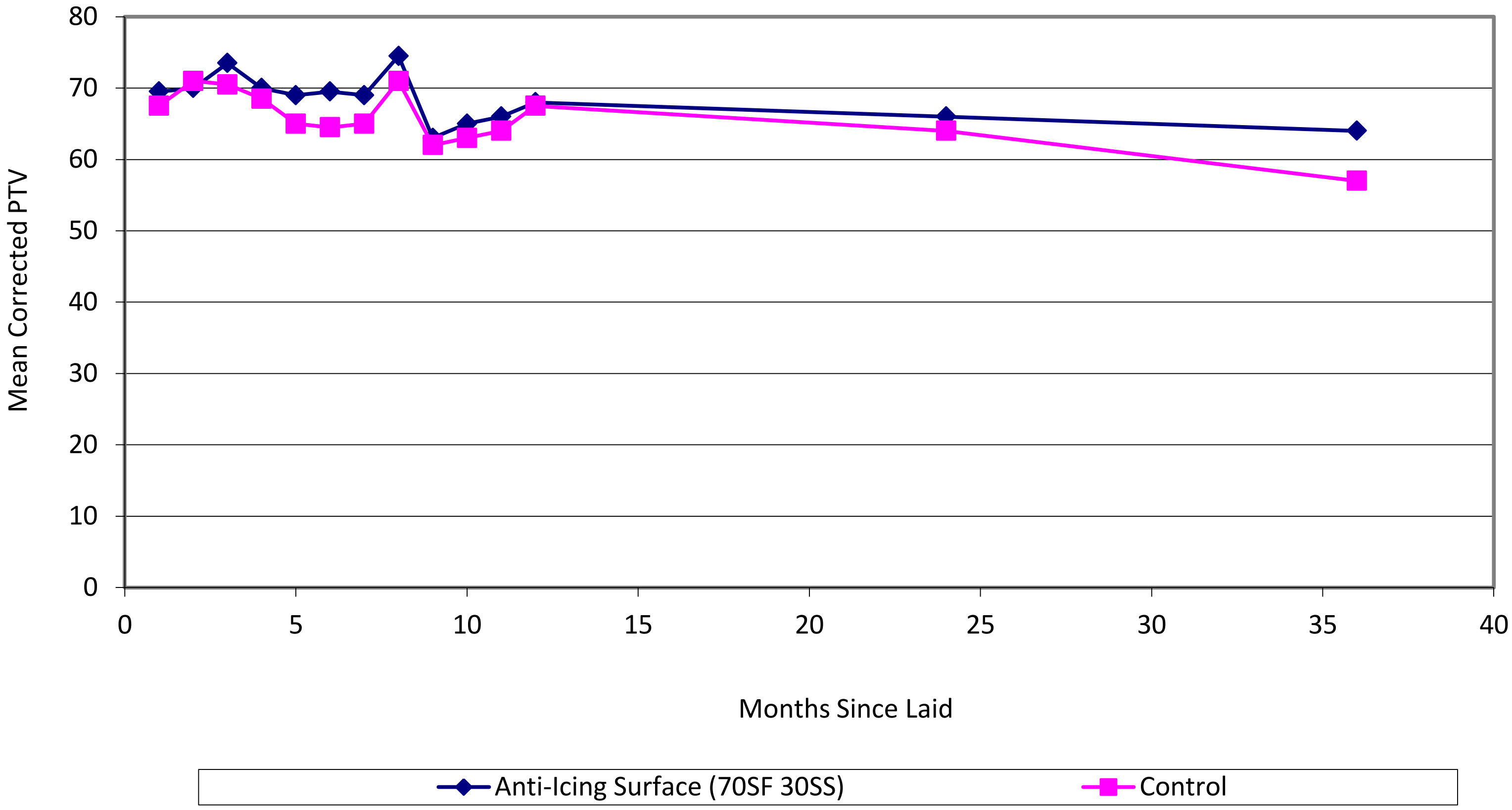


Figure 7.9 - Determination of Skid Resistance (BS EN 13036-4:2003) from November 2008

The pendulum test requires water to be placed on the surface prior to testing. Any effects of moisture absorption on skid resistance may not necessarily be detected. To assess if the moisture absorption of the anti-icing surface course resulted in a reduced skid resistance, a micro Griptester was used in its dry mode without adding any extra water to the surface.

The micro Griptester is based on the same principle as the Griptester (Findlay Irvine 2010) and measures the skid resistance in terms of the Grip Number. The micro Griptester was operated in accordance with manufacturer Findlay Irvine's recommended instructions and a walking test speed of 0.7m/s. The micro Griptester testing was conducted during November 2011 after a period of high humidity and the results in terms of the Grip Number are shown in Figure 7.10.

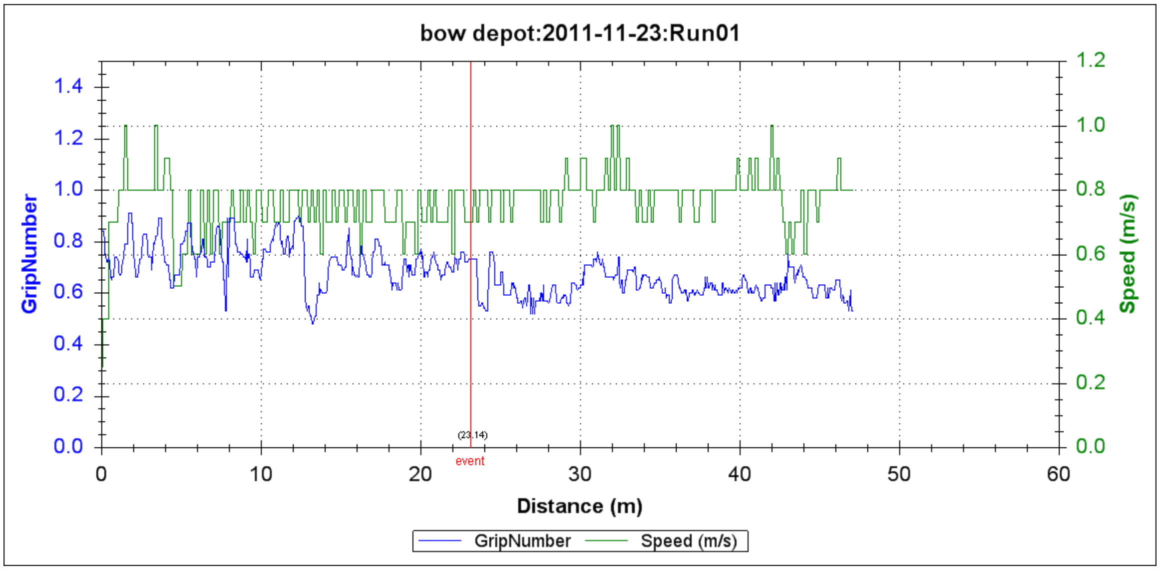


Figure 7.10 – Grip number results for anti-icing surface course (distance 0-23m) and control surface (23-47m)

The test results show that the anti-surface course does not have a lower skid resistance than the control despite the higher moisture absorption. The mean Grip Number across the section for the anti-icing surface course was 0.73 and control surface mean was considerably less at Grip Number 0.63. No explanation for the increase in Grip Number could be provided.

Macrotexture

Macrotexture measurements were conducted on a monthly basis for the first year of the site trial and at yearly intervals thereafter at the same predetermined locations. The results are shown in Table 7.2 and Figure 7.11.

Surface/Months	Mean Surface Macrotexture							
	1	4	5	7	8	9	24	36
Control - Wheelpath	1.30	0.95	0.95	0.95	0.95	1.00	0.95	0.90
Anti-icing Surface - Wheelpath	1.20	1.05	1.00	1.05	1.05	0.95	1.00	0.95

Table 7.2 – Mean Macrotexture (BS EN 13036-1:2002) from November 2008

Macrotexture results have consistently indicated no change to the texture of the anti-icing section between month 4 and month 36.

The results are comparable with the control signifying no deterioration or fretting being measured at these locations on the surface.

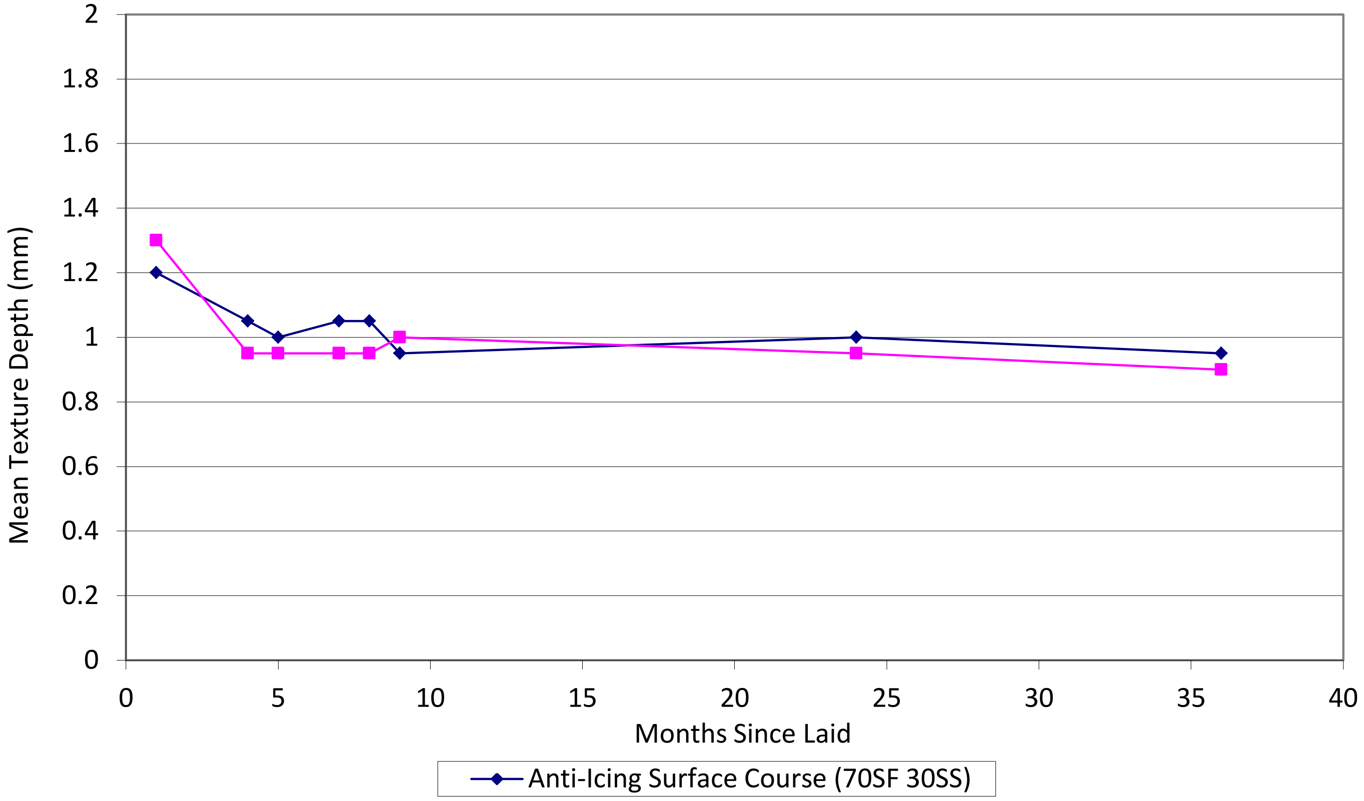


Figure 7.11 - Determination of surface Macro Texture (BS EN 13036-1:2002) from November 2008

Visual Inspections

Visual inspections were conducted on a monthly basis for the first year and annually thereafter. The visual inspections were conducted in accordance with TRL inspection panel methodology, Nicholls (1997) and the surface rating and any defects recorded in accordance with Table 7.3.

Mark	Description	
E (Excellent)	No discernible fault	Termed
G (Good)	No significant fault	Serviceable
M (Moderate)	Some defects but insufficient serious problems	
A (Acceptable)	Several defects but would usually be just acceptable	
S (Suspect)	Seriously defective, but just serviceable in the short term	Termed
P (Poor)	Requires remedial treatment	Unserviceable
B (Bad)	Requires immediate remedial treatment	
Where Suffix: - represents loss of chippings/aggregate s represents stripping v represents variable		

Table 7.3 - TRL inspection panel methodology (Nicholls 1997)

The inspection panel mark for each year of visual inspection is shown in Table 7.4.

Surface/Year	Inspection Panel Mark			
	2008	2009	2010	2011
Control	E	E	E/G-	G-
Anti-icing Surface	E	E	E/G-	G-

Table 7.4 – Visual inspection of the Bow test surface conducted in accordance with TRL inspection panel methodology (Nicholls 1997)

The inspections confirmed that there was no visible deterioration of the anti-icing pavement surface or on the control surface.

An inspection during August 2010 and November 2011 identified some signs of minor fretting in small localised areas on both surfaces, however the overall condition was still deemed to be good. The visual inspections to date have concluded that the anti-icing surface course on this site has performed well and the overall condition is consistent with the control surface.

7.6 TRIAL 2 – THE RIDGEWAY ENFIELD

7.6.1 INTRODUCTION

A second trial was conducted in August 2009 on the Ridgeway in Enfield. The Ridgeway is a 60mph, heavily trafficked road situated off junction 24 of the M25. It is on a salting route and the application of sodium chloride will be conducted on both sections as per standard practices.

The decision to conduct this trial was made on the basis that it was required to evaluate the anti-icing chemical formulation under heavier trafficking.

The aims and objectives of this site trial were:

- To provide visual observations of the chemical transfer under trafficking.
- To visually assess the mechanical asphalt performance on a heavily trafficked high speed road.

7.6.2 SITE TRIAL DESIGN

The selected site for this trial was in the London Borough of Enfield. The Ridgeway site was selected because it was the main site for winter maintenance decisions within the area and contained an existing weather station system, providing climatic information including temperature, humidity and precipitation.

The site trial formed part of the current re-surfacing programme within Enfield and incorporated 10T of anti-icing SMA (3% addition 70% sodium formate 30% sodium silicate) laid directly in front of the weather station in one lane.

An extensive control surface surrounds the test section which extends for a significant length. The control surface course consisted of the same bitumen and aggregate composition, with 3% limestone filler replacing the chemical additive, as per the Bow depot trial.

The chemical blend was selected based on laboratory studies conducted pre-August 2009 and to ensure consistency with previous trials.

7.6.3 SITE TRIAL CONSTRUCTION

The anti-icing surface course and the control surface course were constructed as part of the London Borough of Enfield resurfacing programme. This involved the 40mm plane and replacement of the entire surface course over this section.

Both the control and the chemically modified anti-icing surface course were laid using a Titan Paver. Areas around iron work and roadside obstacles were hand laid. These were immediately compacted using a Bomag 161 tandem roller using between 6-8 passes made on each section, and a Bomag 130 roller used for final polishing. The anti-icing surface course was laid within one hour of the final batch being produced and arrived on site at approximately 170°C.

The anti-icing surface course and control surface course were laid during the night on the 4th of August (2009) under suitable laying conditions on a clear/sunny night, with air temperatures of 18°C. Throughout the laying of both surface courses, it was noted that the control and anti-icing surface course materials performed similarly.

7.6.4 TESTING PROCEDURE

The evaluation of the site consisted of visual inspection of the chemical transfer under trafficking and visual inspections of the surface condition in accordance with TRL inspection pannel methodology (Nicholls 1997). These were made on a monthly basis.

Measurement of skid resistance and texture depths were not possible due to the speed and traffic of the road restricting access to the site.

As the road was on a salted site no anti-icing performance data was collected.

7.6.5 ANALYSIS OF SITE TRIAL

7.6.6 ANTI-ICING AND CHEMICAL TRANSFER OBSERVATIONS

Visual observations indicate that there was no significant chemical transfer visible in the summer after hot weather periods, as demonstrated in Figure 7.12. This is in contrast to observations made during the Bow site trial and may indicate that the chemicals are not deposited under heavier traffic nor are they deposited without a period of high humidity prior to warm/dry weather conditions.

Figure 7.12 – Photograph of the Ridgeway site with the control surface (left lane) and modified surface (right lane)

7.6.7 MECHANICAL PERFORMANCE

The visual inspection of the Ridgeway site was conducted on a monthly basis and the inspection panel mark for each month is shown in Table 7.5.

Surface/Year	Inspection Pannel Mark							
	Aug 2009	Sept 2009	Oct 2009	Nov 2009	Dec 2009	Jan 2010	Feb 2010	Mar 2010
Control	E	E	E	E	E	E	E	E
Anti-icing Surface	E	E	E	E	G v-	M v-	M v-	A v-

Table 7.5 – Visual inspection of the Ridgeway test surface conducted in accordance with TRL inspection panel methodology (Nicholls 1997)

No significant defects were observed in the first five months after the product had been laid.

After the severe and prolonged snow fall during December 2009/January 2010, a pothole was observed on the anti-icing surface on the 16th of January 2010 and subsequently a patch repair was constructed. This failure of the material was localised to one specific area and the remainder of the surface was in an acceptable condition at this time.

A further inspection on the 13th of March 2010 recorded minor fretting at one end of chemically modified section, see Figure 7.13.

Figure 7.13 – Photograph of patch repair and onset of minor fretting (March 2010) on anti-icing surface (bottom lane) and control surface (top lane)

The combination of these minor defects on this heavily trafficked and high speed road led to a decision to remove the anti-icing section and replace the trial section in June 2010 with a conventional surface material. At the time of replacement the anti-icing section was still in a serviceable condition and the fretting was not widespread over the full trial section.

The durability of the anti-icing surface course was considered to be considerably less than the control surface. The rate of deterioration of the anti-icing surface was considered to be significant and in excess of typical deterioration rates for thin surface course presented by Nicholls et al. (2010), which estimates that a 10mm Stone Mastic Asphalt surface course serviceable life is greater than 14 years.

7.7 TRIAL 3 – NORFOLK AVENUE, ENFIELD

7.7.1 INTRODUCTION

A trial was conducted in November 2009 in Norfolk Avenue, Enfield. Norfolk Avenue is a 30mph lightly trafficked street, which is fairly exposed to the North. The site represents the first non-salted highway site trial.

The aims and objectives of this site trial were:

- To scientifically measure the anti-icing performance of the chemical modified section under typical highway conditions.
- To provide visual observations of the chemical transfer under trafficking.
- To visually monitor and assess the mechanical asphalt performance on a lightly trafficked low speed road.

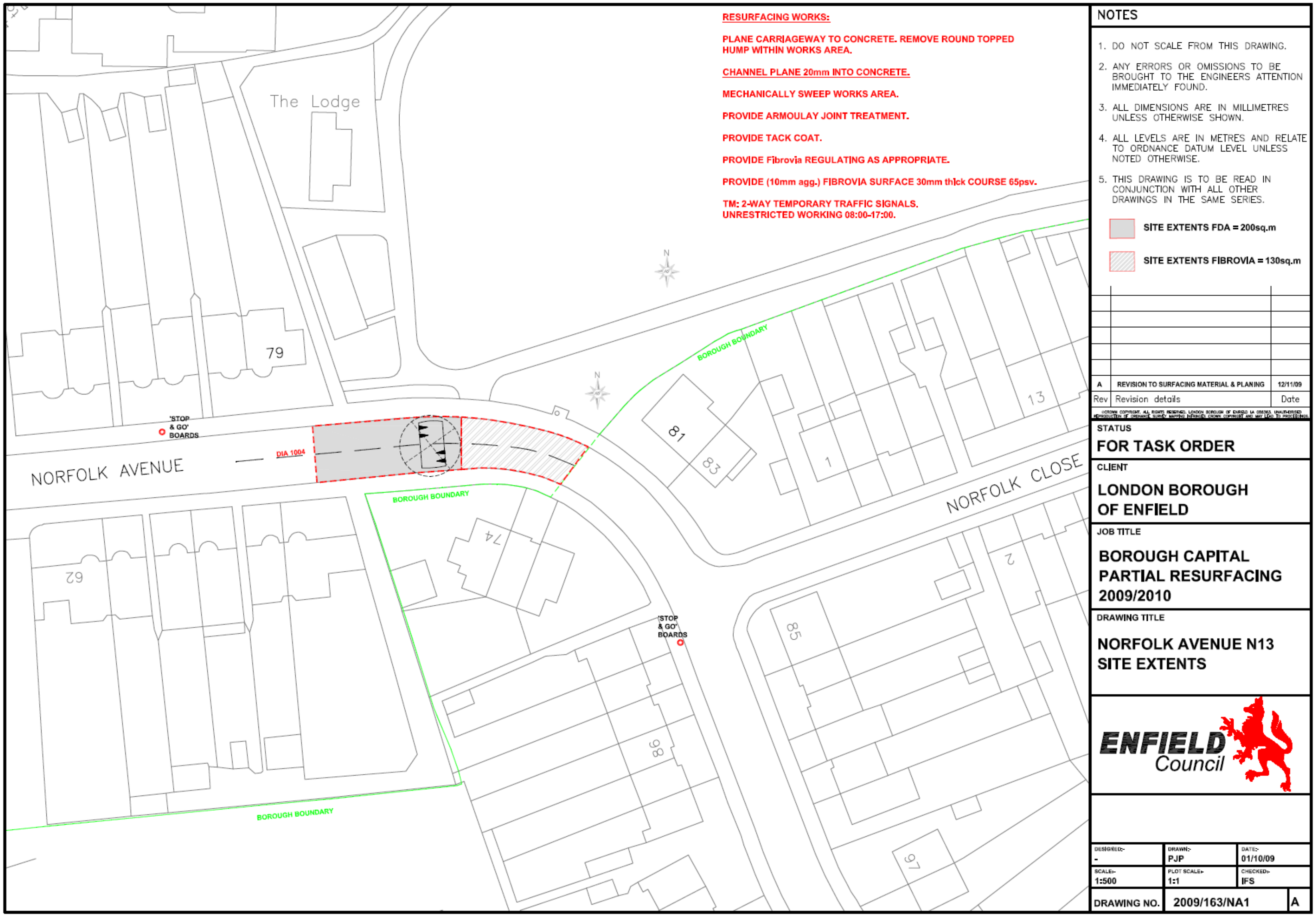
7.7.2 SITE TRIAL DESIGN

The selected site for this trial was in the London Borough of Enfield and the Norfolk Avenue site was selected because it was an open and exposed site, on a relatively low trafficked road, unsalted and could accommodate road surface monitoring equipment.

The site trial formed part of the current re-surfacing programme within Enfield and incorporated 15T of anti-icing SMA (3% addition 70% sodium formate 30% sodium silicate) laid throughout both carriageway lanes for an approximate length of 20m. This was adjacent to 15T control surfacing laid throughout both lanes for the remainder of the scheme. The control surface course consisted of the same bitumen and aggregate composition, with 3% limestone filler replacing the chemical additive.

The chemical blend selected for this phase of trial was the blend of 70% sodium formate and 30% sodium silicate as per previous sites trials.

The surface course sections were located to ensure the installation of an appropriate monitoring system, reduce the impact of parked cars on the monitoring equipment and to ensure comparative conditions, see Figure 7.14.



RESURFACING WORKS:

PLANE CARRIAGEWAY TO CONCRETE. REMOVE ROUND TOPPED HUMP WITHIN WORKS AREA.

CHANNEL PLANE 20mm INTO CONCRETE.

MECHANICALLY SWEEP WORKS AREA.

PROVIDE ARMOULAY JOINT TREATMENT.

PROVIDE TACK COAT.

PROVIDE Fibrovia REGULATING AS APPROPRIATE.

PROVIDE (10mm agg.) FIBROVIA SURFACE 30mm thick COURSE 65psv.

TM: 2-WAY TEMPORARY TRAFFIC SIGNALS.
UNRESTRICTED WORKING 08:00-17:00.

NOTES

1. DO NOT SCALE FROM THIS DRAWING.
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DRAWING TITLE
NORFOLK AVENUE N13 SITE EXTENTS

DESIGNED:- -	DRAWN:- PJP	DATE:- 01/10/09
SCALE:- 1:500	PLOT SCALE:- 1:1	CHECKED:- IFS

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Figure 7.14 – Schematic of Norfolk Avenue site trial with anti-icing surface (shaded) and control surface (hatched)

7.7.3 SITE TRIAL CONSTRUCTION

The anti-icing surface course and the control surface course were constructed as part of a resurfacing programme involving the 40mm plane out and replacement of the entire surface course over this section, see Figure 7.15. The existing carriageway joints were treated prior to resurfacing and an appropriate tack coat used.

Both the control and the chemically modified anti-icing surface course were laid using a Titan Paver. Areas around iron work and roadside obstacles were hand laid. These were immediately compacted using a Bomag 161 tandem roller with between 6-8 passes made on each section, and a Bomag 130 roller used for final polishing, see figure 7.16. The anti-icing surface course was laid within one and a half hour of the final batch being produced and arrived on site at approximately 170^{o}C.

The anti-icing surface course and control surface course were laid on the 17th of November (2009) under suitable laying conditions on an overcast day, with air temperatures of 12^{o}C. Throughout the laying of both surface courses, it was noted that the control and anti-icing surface course materials performed similarly.

Figure 7.15 - Construction of the anti-surface course second lane

Figure 7.16 – Compaction of anti-icing surface course

7.7.4 TESTING PROCEDURE

The site trial testing programme was designed to scientifically measure the anti-icing performance of the chemical modified section under typical highway conditions through the installation of an appropriate road weather station. An instrumented field trial was required as it is commonly acknowledged that laboratory conditions do not take into account every variable experienced on the highway network. Current research has not extended to instrumented site trials and the testing programme was designed to provide a new understanding of how de-icing surfaces perform in the field.

The road weather surface monitoring equipment used as part of the site trial was the state of the art equipment provided by Vaisala. After numerous discussions with Vaisala regarding the measurement of such a unique surface it was decided that remote measurements rather than embedded sensor would produce the highest quality of data. This is because remote surface sensors measure the mean surface properties of an area typically in 80cm diameter, see Figure 7.17. In contrast the alternative embedded sensor replicate a standard road surface and would rely on the chemical being transferred from the surrounding pavement to the surface of the sensor. This may therefore not provide an accurate measurement of the anti-icing surface conditions.

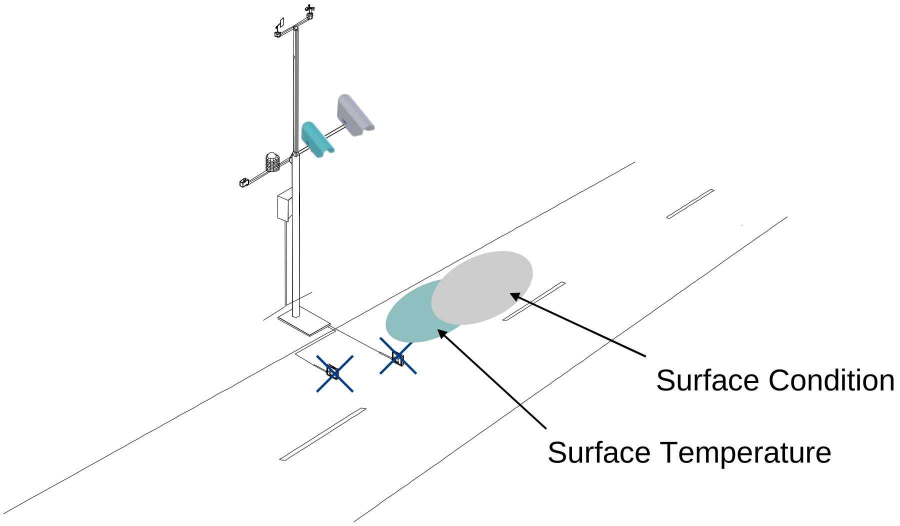

Figure 7.17 – Selection of remote surface sensors over embedded sensors

The road surface sensors used as part of this study were the Vaisala DSC111 and DST111, which were installed towards the end of winter period, the 9th of March 2010.

The combination of the Vaisala DSC111 and DST111 remote surface state uses spectroscopic measuring principles and infrared radiation measurements to accurately measure:-

- Surface state – dry, moist, wet, snow/frost, ice, slush
- Layer thickness of water, ice and snow to a resolution of 0.01mm
- Level of grip – based on scale of 0.01 to 100
- Road surface temperature to an accuracy of 0.1^{o}c
- Air temperature
- Relative humidity

The parameters of surface state and layer thickness were used to determine the anti-icing performance at specific road/surface temperatures and relative humidities.

The site trial was designed so that one of pair of DSC111/DST111 sensors was focused on the anti-icing surface and a second pair focused on the control surface. The sensors were targeted towards the centre line between the two carriageways in order to eliminate the risk of parked cars preventing the measurement of the road surface properties. The design of the site trial and instrumentation enable equal trafficking and were positioned to prevent the risk of contamination from the anti-icing surface to the control surface. The parameters above were measured at 20 minute intervals throughout the year.

The remote measurement was assisted by visual observations of the chemical transfer under trafficking and the surface condition typically taken on a monthly basis.

Figure 7.18 – Vaisala road surface sensors installed at Norfolk Avenue, Enfield.

7.7.5 ANALYSIS OF SITE TRIAL – 2009/2010

Analysis of the performance of the anti-icing section for the Norfolk Avenue site trial is based on visual observations of chemical transfer and surface condition, with the road weather station becoming operational in March 2010.

7.7.6 ANTI-ICING AND CHEMICAL TRANSFER MECHANISMS OBSERVATIONS

Visual observations made between November 2009 and March 2010 indicated that there was no significant chemical transfer visible in the summer after hot weather periods. This is in contrast to observations made during the Bow site trial and may indicate that despite changes in relative humidity, the chemicals are not deposited or are removed under heavier traffic.

Visual inspections on 21st of December 2009 and 12th of January 2010, both following a prolonged period of snowfall and temperature below -5°C, highlighted that during these prolonged snowfall and sub-zero temperatures, ice and snow formed on both sections.

On the 12th of January 2010 the snow and ice was only situated at the sides of the carriageway and there was marginally less on the anti-icing surface compared to the control, see Figure 7.19.

Figure 7.19 – Photograph showing less ice formation on anti-icing surface (front) and control surface (back) on the 12th January 2010.

Further inspection of the ice formations on both dates identified that the ice on the anti-icing surface could be easily removed. This ice formation could be easily removed by foot and delaminated in large pieces with a smooth/flat base, see Figure 7.20.

In contrast, the ice on the control section was well bonded to the pavement surface and could not be removed easily. These observations indicate that ice on the anti-icing section is less adhered to the pavement surface. This is consistent with the ice adhesion testing in the laboratory and if the side of the carriageway was trafficked, this reduced bond could potentially lead to more ice removal from the anti-icing section.

Figure 7.20 – Plate of ice that was easily removed from the anti-icing surface.

The installation of the road weather station was delayed until the end of March 2010 and since the installation no frost, ice or snow events occurred on either surface for the winter 2009/2010.

7.7.7 MECHANICAL PERFORMANCE

The visual inspection of the Norfolk Avenue site was conducted on a monthly basis and the inspection panel mark for each month is shown in Table 7.6.

Surface/Year	Inspection Panel Mark				
	Nov 2009	Dec 2009	Jan 2010	Feb 2010	March 2010
Control	E	E	E	E	E/G
Anti-icing Surface	E	E	G v-	M v-	S sv-

Table 7.6 – Visual inspection of the Norfolk Avenue test surface conducted in accordance with TRL inspection panel methodology (Nicholls 1997)

Visual inspections between November 2009 and February 2010 during winter weather conditions identified no significant differences between the control and the anti-icing surface, with no defects present on either surface.

On the 15th of February 2010 a report of the first signs of distress and fretting on the anti-icing surface was received. No deterioration was present on the control surface. These reports were received as the temperatures returned to above 0^oC.

A further inspection on the 15th of March 2010 confirmed the anti-icing surface course was in a poor condition with the control surface still serviceable with no significant defects; see Figures 7.21, 7.22 and 7.23.

The anti-icing surface course demonstrated signs of major fretting and disintegration of the surface course over the entire section. Significant amounts of aggregate had been lost from the surface course, which had built up at the side of the carriageway. This aggregate was completely clean with no signs of bitumen present. On two small locations the surface had disintegrated through the full depth and the underlying concrete was visible.

Figure 7.21 – Photograph showing the widespread fretting of the anti-icing surface course

Figure 7.22 – Photograph showing the localised disintegration of the anti-icing surface course through to the underlying base

Figure 7.23 – Photograph showing the condition of the control surface.

From the review it can be concluded that surface course is in a poor condition and this distress has occurred rapidly and coincided with the end of a severe winter with prolonged sub zero conditions. The failure mechanisms and site observations indicate that the deterioration may be primarily due to environmental factors, as the deterioration was not confined to the wheel paths. The clean aggregate and major fretting appears to indicate binder stripping and water sensitivity issues.

This sudden failure was consistent with the signs of initial deterioration observed on the Ridgeway site trial and it can be concluded that the use of this chemical blend at a 3% addition on trafficked sites are less durable than the control road surface and has an increased risk of early life failure.

7.7.8 ANALYSIS OF SITE TRIAL – 2010/2011

The serviceability of the Norfolk Avenue site was considered to be unsatisfactory by August 2010 and the anti-icing material section was replaced. At this point in time greater knowledge of the chemical transfer method and the effects of the chemicals on the durability of the asphalt had been gained.

A decision was taken when re-installing the site trial section, that a change in the chemical composition and surfacing type would be tried to prevent the problems experienced with durability. This change in material type consisted of:

- Reducing the chemical additive from a 3% addition to a 2% addition – to reduce the moisture absorption and the effects of sodium silicate on water sensitivity
- Closing up the Gap Grading of the SMA surface to reduce the void content to less than 5%. This reduced the surface voids with no inter-connecting voids as per the previous design. This thereby restricted the amount of chemical transferred, moisture absorption and reduced the rate of water infiltration into the pavement surface
- Maintain a chemical blend of 70SF 30SS for comparative purposes.

7.7.9 ANTI-ICING AND CHEMICAL TRANSFER MECHANISMS OBSERVATIONS

The anti-icing performance of the surfaces for the winter of 2010/2011 were assessed using the Vaisala DSC111/DST111 road surface sensors, in order to provide a quantitative assessment. These sensors reported surface and climatic conditions at 10 minute intervals for both surfaces. This data was then aligned and the performance of the anti-icing surface was compared to the control where data measurements were also taken at each 10 minute interval.

The Vaisala DSC111/DST111 road surface sensors monitor and classify the surface state and provide detailed information with regards to the water/ice/snow depth and grip levels.

This Section assesses the anti-icing and chemical transfer mechanism in three key sections:

- Data validation
- High level surface state and snow depth analysis
- Assessment of the performance of the anti-Icing surface during individual winter weather events.

7.7.10 DATA VALIDATION

The first stage of the data assessment was to validate the site trial design and ensure there were no micro-climatic differences which the surface observations could be attributed to. The mean air temperature, surface temperature, dew point and relative humidity were analysed for both sites on a monthly basis, as demonstrated in Table 7.7.

The assessments confirmed that the surfaces were subjected to comparable climatic conditions with the mean temperatures air and surface temperatures varying by less than 0.1°C over a period of a month and the mean relative humidity typically within 2% for both surfaces.

	November 2010			December 2010			January 2011		
	Anti-icing Surface	Control	Difference	Anti-icing Surface	Control	Difference	Anti-icing Surface	Control	Difference
Mean Surface Temperature (^{o}C)	4.92	4.84	0.08	0.02	0.03	0.01	3.98	3.95	0.03
Mean Air Temperature (^{o}C)	5.34	5.33	0.01	1.08	1.07	0.01	4.90	4.93	-0.03
Dew Point (^{o}C)	3.13	2.95	0.19	-0.52	-0.50	0.03	2.59	2.55	-0.04
Relative Humidity (%)	85.24	84.13	1.11	89.35	89.36	0.01	85.25	85.18	-0.17

Table 7.7 – Mean climatic conditions for the anti-icing surface and control surface on a monthly basis

7.7.11 SURFACE STATE

The Vaisala DSC111/DST111 road surface sensors monitor and classify the surface state of the road surface in terms of dry, moist, wet, slush, frost, ice and snow at ten minute intervals.

High-level analysis was conducted by quantifying the number of ten minute intervals recorded for each surface state type, the results are shown in Table 7.8. For the purposes of this analysis winter weather events relate to a slushy, frost, ice or snow surface state.

Surface State Observed	November 2010		December 2010		January 2011	
	Control	Anti-icing Surface	Control	Anti-icing Surface	Control	Anti-icing Surface
Dry	1453	1378	2521	1921	2461	2989
Wet	179	202	172	202	487	408
Moist	98	148	112	604	118	227
Slush	14	19	20	24	0	0
Frost	0	0	0	0	40	22
Ice	0	2	2	21	0	0
Snow	12	7	449	504	606	66
Total 10 minute measurements	1756	1756	3276	3276	3712	3712
Total Winter Weather Events	26	28	470	550	646	88

Table 7.8 – Number of 10 minute observations for each surface state observed on monthly basis

The majority of winter weather events were recorded between November 2010 and January 2011 as a result of a prolonged period of snowfall. With only a limited number of marginal frost and ice events recorded.

The surface state of the pavement surface is summarised on a monthly basis below:

November 2010

During November there were only a limited number of winter weather events recorded and the surface was predominantly dry on both sections.

Measurements of the surface state on the anti-icing surface indicated a very slight reduction in the number of snowfall events than the control surface; however an increased number of icy/slushy surface states were recorded. This difference would appear to indicate that the anti-icing surface had some influence on the effect on the surface state but the performance was not enough to prevent icy/slushy conditions forming.

An increased number of moist events were recorded on the anti-icing surface in comparison to the control surface. This difference was of the order of 10% and occurred when the control surface was recorded as dry. This would appear consistent with the conclusions made regarding the moisture absorption in the laboratory.

December 2010

In December the anti-icing surface appeared to have performed poorer than the control surface with a significant number of increased snow surface state observations being made, when assessed on surface state measurements alone. The higher frequency of the surface state recorded as snow for the anti-icing surface in December appeared to be related to one winter weather event which occurred between the 22nd of December 19:10 and the 23rd December 9:10.

During this period, 83 surface state observations were made and, on average, the anti-icing surface was recorded as having a 0.02mm of snow on the surface and the control surface was recorded as dry. This depth of snow fall is considered to be minimal and can be attributed to the variability in measuring a small area of road surface and external factors. It is important to acknowledge that the effects of this one weather event on the overall surface state trend.

During December an increase number of moist events were also recorded on the anti-icing surface in comparison to the control surface. The difference in the December was more significant than during November, with approximately 6 times the number of moist events recorded on the anti-icing surface in comparison to the control surface. Whilst, for the majority of these events the control surface was dry. The increase in number of moist surface state measurements was consistent with an increase in the mean relative humidity by 5%. These measurements further support the conclusions regarding moisture absorption and the relationship with relative humidity.

On a limited number of records the control surface was recorded as snow when the anti-icing surface state was recorded as moist. This would indicate that on these occasions the anti-icing surface was effective at removing the snow.

January 2011

During January a high number of individual snow fall events were recorded, typically lasting between 2 to 5 hours. The surface state records during these events showed a significant difference in surface state.

The control surface had snow covering the surface for a total period of 6,060 minutes (approximately 101 hours) and the anti-icing surface only had snow covering the surface for 66 minutes (approximately 1 hour). This significant difference demonstrates the anti-icing potential of the anti-icing surface course during snowfall events.

A number of frost events were also recorded during January. The anti-icing surface course reduced the number of frost surface state observations by approximately 45%.

Equally, the anti-icing surface appeared to be in a moist condition almost twice as long as the control surface. In previous months, the increase in moist surface state for the anti-icing surface appeared to occur when the control surface was dry. However, during January a moist condition was typically recorded when there was snow on the control surface. This shows that the anti-icing surface was effective at reducing the winter weather events.

Surface State – Winter 2010/2011

The surface states measurements were also collated and assessed over the period between November and January to reduce the effects of individual winter weather events. The number of 10 minute intervals for each surface state were recorded throughout this period and are shown in Table 7.9.

Surface State Observed	Control Surface		Anti-Icing Surface	
	Number of Events	Percentage Occurrence (%)	Number of Events	Percentage Occurrence (%)
Dry	6435	73.59%	6288	71.91%
Wet	838	9.58%	812	9.29%
Moist	328	3.75%	979	11.20%
Slush	34	0.39%	43	0.49%
Frost	40	0.46%	22	0.25%
Ice	2	0.02%	23	0.26%
Snow	1067	12.20%	577	6.60%

Table 7.9 – Number of 10 minute observations and percentage breakdown for each surface state observed between November 2010 and January 2011

The data collected throughout the winter 2010/2011 appears to indicate two significant differences in the surface states, these are:

- The anti-icing surface has an increased tendency to be in a moist condition when the control surface is either dry or has a snow covering. When the control surface is dry the moist surface state of the anti-icing can be attributed to the ability of the anti-icing surface to absorb moisture from the atmosphere. When the control surface has snow present, the moist surface state of the anti-icing surface can be attributed to the anti-icing chemical changes in the properties of the snow turning the snow into a liquid.

- The anti-icing surface has demonstrated a degree of anti-icing performance to reduce the number of surface states observations recorded as snow. The surface did not provide a complete anti-icing performance as frost, ice and snow still formed on the anti-icing surface, however a significant reduction in the number of snow surface states were recorded in comparison to the control surface.

Anti-Icing Performance under Snow Surface State

The most frequent winter weather surface state recorded over the winter period was snow.
To directly compare the performance of the anti-icing and the control surfaces, 10 minute observations were identified when snow was recorded on both surfaces.

The mean snow depth and maximum snow depth was determined on a monthly basis for each 10 minute observations when snow was recorded on both surfaces. The results are shown in Table 7.10.

	November		December		January	
	Control	Anti-icing Surface	Control	Anti-icing Surface	Control	Anti-icing Surface
Number of Observation	5		420		12	
Mean Snow Depth (mm)	0.40	0.29	2.04	1.16	0.10	0.04
Maximum Snow Depth (mm)	0.84	0.53	3.24	2.04	0.18	0.05

Table 7.10 – Depth of snow when both recorded as having snow on the surface

The analysis identifies that the anti-icing surface was more effective than the control when snow was present on both surfaces, as demonstrated by the reduced mean snow depth and reduced maximum snow depth on a monthly basis. The anti-icing surface has the ability to reduce the depth of the snow layer by up to 1mm.

This data indicates that even when snow forms of both surfaces, the anti-icing surface course has an ability to reduce the depth of snow on the surface.

7.7.12 INDIVIDUAL WINTER WEATHER EVENTS

Individual winter weather events have also been analysed in order to demonstrate the differences in performance between the anti-icing surface and the control surface. A number of representative extracts are discussed in this chapter.

A winter weather event on the 23rd of January 2011 provided an indication of the behavioral differences between the two surface courses under snowfall. During this event the air temperature at the pavement was relatively steady around 5°C and the relative humidity remained around 85% to 95%.

Snowfall was first recorded on the control surface at 2:30am reaching a nominal depth of 2.0mm by 2:40am. Snow remained on the surface until 7:40am with the depth typically between 2.0mm to 3.0mm during this period, with the exception of what is believed to be an erroneous value at 7:30am. In contrast, the anti-icing surface remained snow free during the entire period, as shown in Figure 7.24. The erroneous result could be attributed to the passing trafficking altering the result for a single ten minute period.

Analysis of the water depth provided further information on how the anti-icing surface course was performing, as shown in Figure 7.25. During this period the anti-icing remained in a moist/wet surface state, as shown by the increase in water depth to a depth of approximately 0.03mm. This is indicative of a reaction between the anti-icing surface course and falling snow resulting in a change of state of the snow-fall and subsequent increased water depth. The depth of water formation is considered to be limited due to the high air voids of the surface course providing drainage paths for the water.

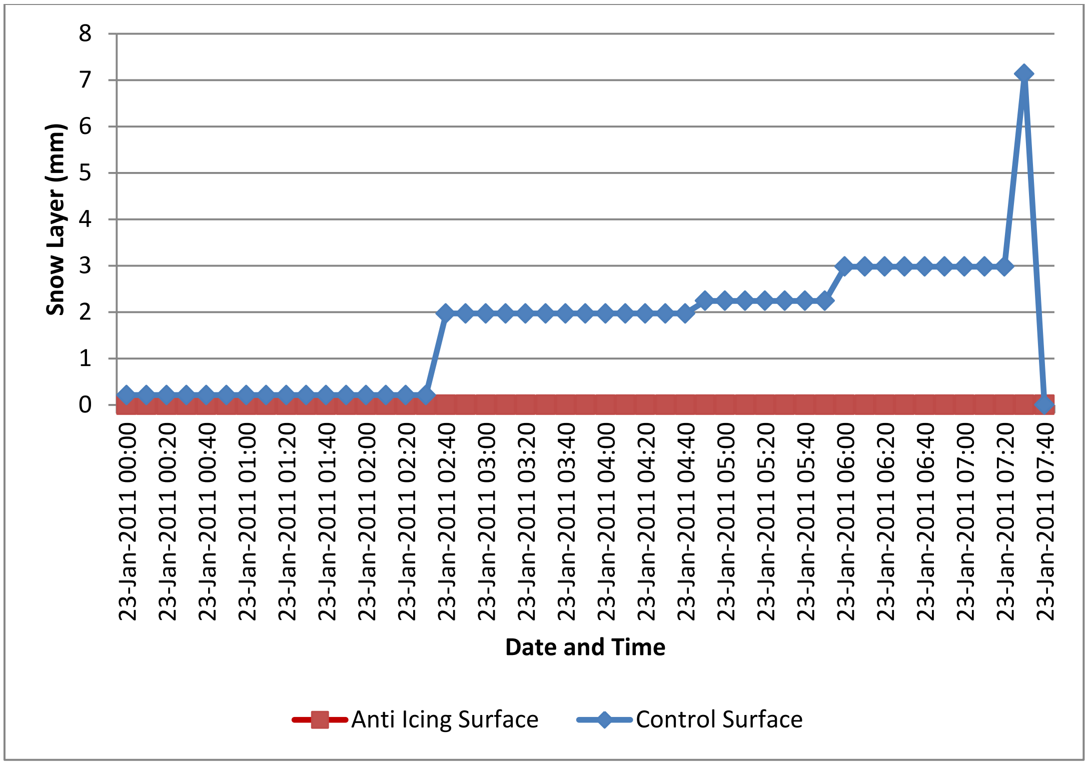

Figure 7.24 – Chart showing snow depth between 00:00 and 7:40 on 23rd January 2011

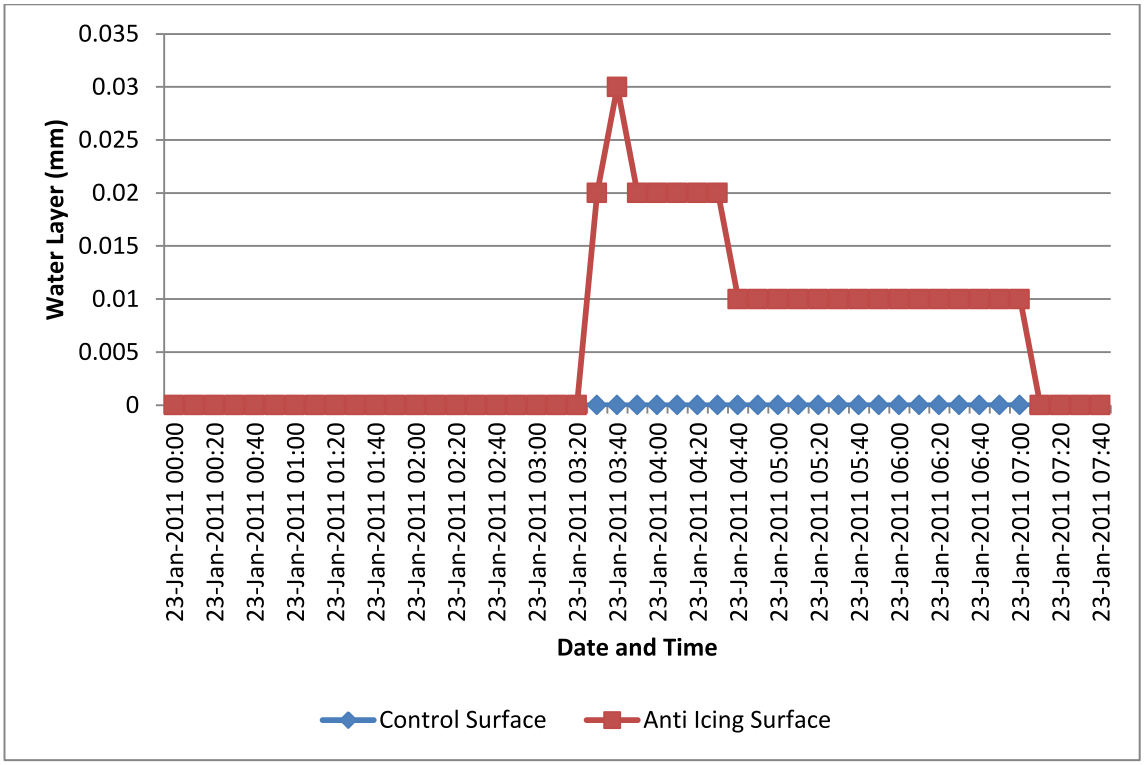

Figure 7.25 – Chart showing water depth between 00:00 and 7:40 on 23rd January 2011

A second winter weather event that occurred over a 24 hour period from 4:20am on the 19th of December to 4:20am on the 20th December 2010 provided a good comparison of how the two anti-icing surface courses perform under heavier snow fall and much lower temperatures, typically between -5°C and -8°C.

During this winter weather event approximately 1.5 to 2.0mm of snow settled on the anti-icing surface course, indicating that the anti-icing surface was unable to prevent snow from settling under these severe conditions.

In contrast, a much greater amount of snow typically between 2.0 and 3.0mm, was recorded on the control surface, as shown in Figure 7.26. This indicates that the anti-icing surface provided some performance benefits on this occasion.

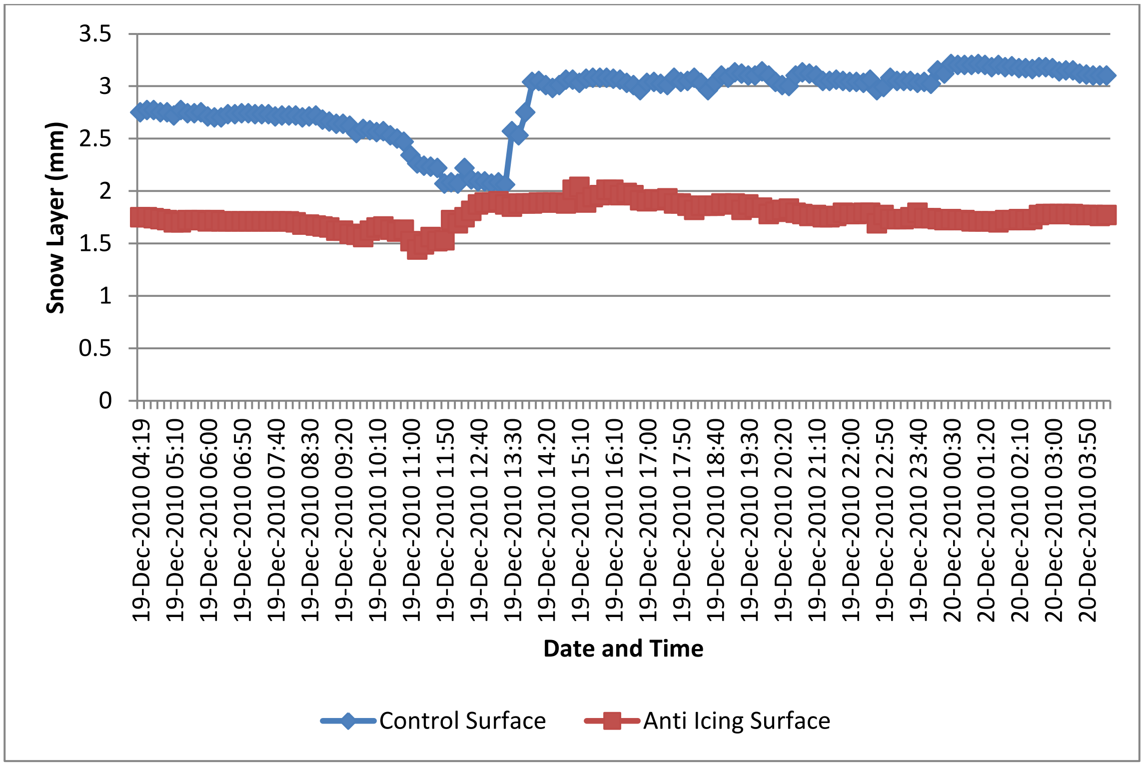

Figure 7.26 – Chart showing snow depth over a 24 hour period from 4:20 on 19th December 2010

Examination of the surface state and relative humidity also indicated the tendency of the anti-icing surface to absorb moisture in comparison to the control surface. An example of this was seen between 1:00am on the 24th of December and 1:00am on the 25th December as shown in Figure 7.27a.

The two charts show a consistent relative humidity for the two surfaces, Figure 7.27b. The control surface remains in a dry surface state and the anti-icing surface course has an increased tendency to have a moist surface state at such high humidities.

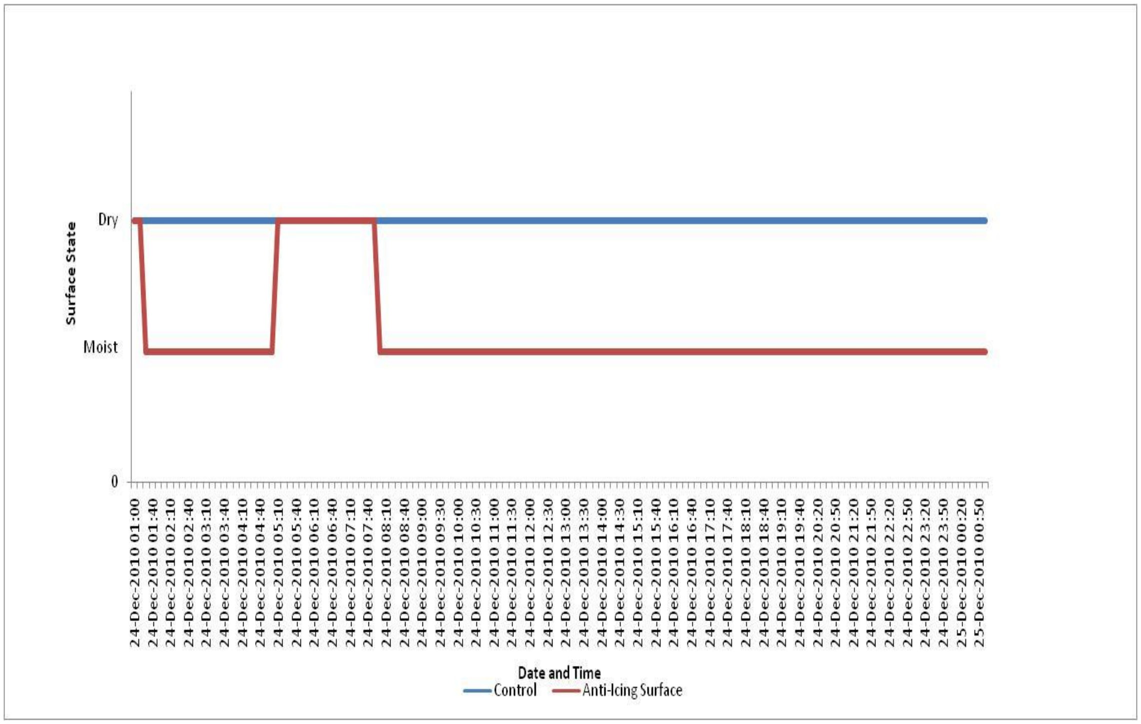

Figure 7.27a - Chart showing surface state over a 24 hour period from 1:00 on 24th December 2010

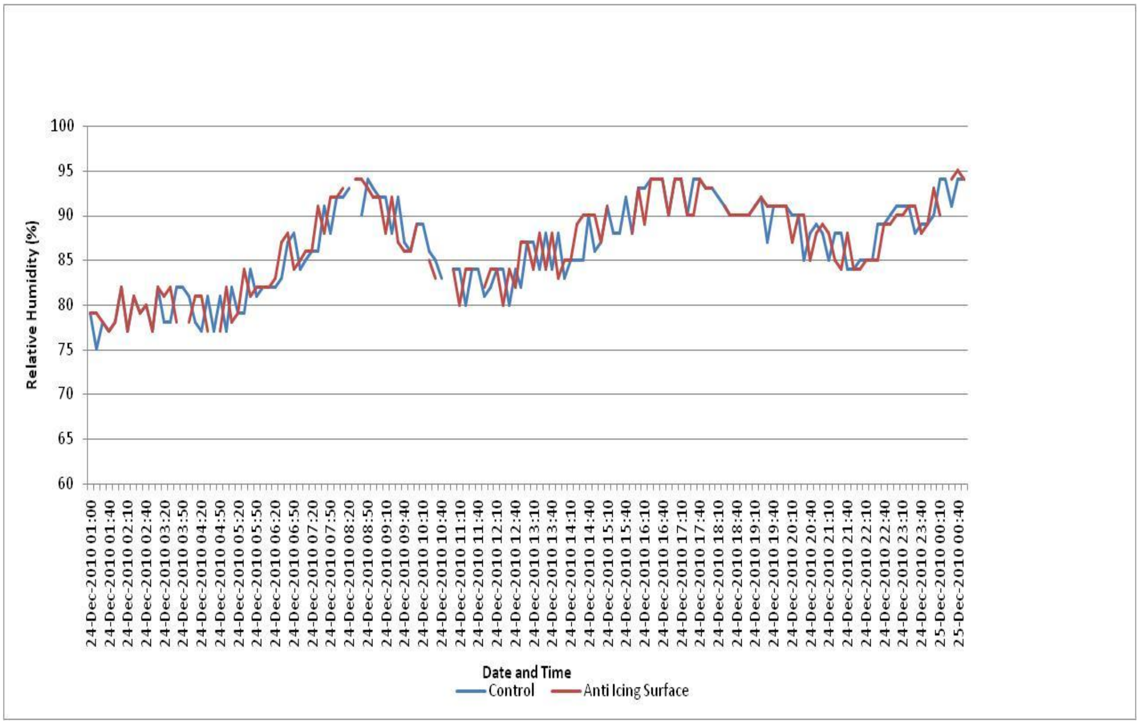

Figure 7.27b - Chart showing relative humidity over a 24 hour period from 1:00 on 24th December 2010

7.7.13 MECHANICAL PERFORMANCE

A visual inspection of the Norfolk Avenue site was conducted on a monthly basis and the inspection panel mark for each month is shown in Table 7.11.

Surface/Year	Inspection Pannel Mark							
	Aug 2010	Sept 2010	Oct 2010	Nov 2010	Dec 2010	Jan 2011	Feb 2011	Mar 2011
Control	E	E	E	E	E	E	E	E/G
Anti-icing Surface	E	E	E	E	E	G v-	G v-	S sv-

Table 7.11 – Visual inspection of the Norfolk Avenue test surface conducted in accordance with TRL inspection panel methodology (Nicholls 1997)

Visual inspection between August 2010 and December 2010 (during winter weather conditions) identified no significant differences between the control and the anti-icing surface, with no defects present on either surface.

On the 2nd of February 2011, evidence of minor fretting was apparent on the anti-icing surface with no defects present on the control surface. The fretting was apparent in the wheeltracks and in locations where parked cars turned. It can be concluded that the onset of fretting on the anti-icing material is accelerated by traffic, see Figures 7.28, 7.29 and 7.30 . An inspection of the aggregate particles being plucked from the pavement surface course had some degree of bitumen retained in comparison to the aggregate particles inspected the previous year at Norfolk Avenue which had no bitumen coverage.

The severity of the fretting also appeared to be less severe than the previous year at Norfolk Avenue with no apparent potholes; however the overall condition was considered unsatisfactory for the age of the pavement surface course. Similar to the previous failure at Norfolk Avenue in 2010, the defects appeared as the temperatures returned to above 0^{o}C.

As this fretting was expected to continue and in order to prevent the carriageway from becoming unserviceable, the anti-icing section was removed in March 2011.

Figure 7.28 – Photograph showing the onset of fretting particularly in the wheeltracks

Figure 7.29 – Photograph showing the onset of fretting distribution over the lane width

Figure 7.30 – Photograph of minor fretting located in areas where traffic is turning.

7.7.14 DISCUSSION AND CONCLUSIONS OF SITE TRIALS

The sites trials at Bow Depot (London), the Ridgeway (Enfield) and Norfolk Avenue (Enfield) have shown a number of consistencies across all three site trials regarding the mechanical performance of asphalt and anti-icing abilities. Equally a number of significant differences have been identified across the three site trials. These areas are discussed below.

Mechanical Performance of Asphalt

The production and laying of the anti-icing surface course has demonstrated that the chemically modified surface course can be produced, transported and laid using conventional plant and equipment, with no compactability concerns as was identified with previous proprietary anti-icing products.

The mechanical performance of the asphalt and the overall durability of the surface course have shown varying results across the three site trials. The Bow Depot trial showed equal in-service performance and durability in comparison to the control surface. In contrast, the Norfolk Avenue and Ridgeway sites experienced significant early life deterioration (within the first six months) in the form of fretting, potholes to full disintegration of the surface course. The differences in the durability between the Bow Depot site trial and the site trials in Enfield is considered significant. A number of factors have been controlled to ensure consistency between the site trials including the production method, laying and arrangement of surfaces. However, there are a number of differences that cannot be fully controlled including climate, pavement and trafficking. The most significant differences between these two set of sites is the trafficking. The Bow Depot is a lightly trafficked car park with some Heavy Good Vehicle usage and in contrast the two sites in Enfield had much higher trafficking. The Ridgeway is a principal road with frequent Heavy Good Vehicle usage and the Norfolk Avenue site has a high frequency of light vehicles.

The site trials have shown significant durability concerns and rapid early life deterioration. The concerns and generally unsuccessful performance identified above are consistent with water sensitivity problems identified in the laboratory experiments. These durability concerns will be required to be solved prior to any widespread use of similar anti-icing surface courses.

Moisture Absorption

The Bow Depot and Norfolk Avenue site trials have both provided indications of increased moisture absorption on the anti-icing surface course. A number of visual observations at Bow Depot identified that the anti-icing surface course remained moist and damp when the control surface looked dry.

Equally the road weather station surface state measurements recorded a number of moist states on the anti-icing surface when the control surface was recorded as being dry. These surface state measurements were not consistent and no conclusions can be made linked to the relative humidity, however the increased number of events indicated a difference in the behaviour between the two surfaces.

The site trial observations and measurements support the laboratory study findings and confirm that anti-icing surface course can absorb moisture under site trials.

Chemical Transfer and Anti-Icing Performance

The Bow Depot and Norfolk Avenue site trials have both provided some evidence of anti-icing performance and reduced winter weather events in terms of surface condition measurements and visual observations.

The Bow Depot trial showed a degree of anti-icing performance over three consecutive winters in terms of preventing ice forming and when snow formed there was visibly less snow on the anti-icing surface in comparison to the control surface. Visible signs of the anti-icing chemicals were also observed at the pavement surface following significant decreases in humidity at the

Bow Depot trial. It is important to note that on a limited number of winter weather events there appeared to be no or very limited visible differences between the two surfaces.

The Norfolk Avenue road weather station results showed a similar trend, with a reduced frequency of snow fall surface states on the anti-icing surface in comparison with the control. Snow did form on the anti-icing surface course on a significant number of occasions, however on a number of occasions the snow depth was significantly reduced compared to the control.

During the monitoring period of this study, there were not enough marginal frosty and icy nights when the anti-icing surface courses are likely to have been most effective.

Overall, the site trials have provided evidence that chemically modified pavement surface courses can provide a degree of anti-icing performance and could have a future role in winter service provision. The site trials have demonstrated that this anti-icing performance is not an absolute performance and have emphasised that anti-icing surface courses are unlikely to prevent all winter weather events. The need for conventional winter service treatments are likely to still be required even if anti-icing surfaces are put in place.

8.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

This final chapter summarises the main topics in the thesis and draws conclusions based on the findings of the laboratory and site investigations. A number of recommendations for future work are outlined.

8.1 SUMMARY

8.1.1 ANTI-ICING SURFACE COURSES

A limited number of proprietary anti-icing pavement surface courses have previously been trialled. The concept of these products is to act as a preliminary anti-icer by reducing the temperature at which ice forms. Early experience with chemically modified pavement surfaces has demonstrated a degree of anti-icing performance; however problems of low skid resistance and poor service life have generated significant concerns.

The only significant study on chemical additives undertaken by Baum et al. (1992) identified a number of promising chemical additives which have the potential to solve such problems; however these do not appear to have been investigated further.

This study considers two potential de-icing chemical additives, these are sodium formate, the perceived `most promising` anti-icing modification from Baum et al. (1992), and sodium silicate (a low surface energy material with the potential to reduce ice adhesion).

The study aims to assess if the de-icing chemicals can be effectively added to asphalt and determine the resultant anti-icing performance and durability of modified pavement surface courses.

8.1.2 EXPERIMENTAL PROGRAMME AND MANUFACTURE

A standard 10mm Stone Mastic Asphalt surface was specified for the experimental study, due to its open aggregate structure. This bituminous surface was manufactured in the laboratory in accordance with "*BS EN12697-35:2004 Bituminous Mixtures – Test Methods for Hotmix Asphalt: Laboratory Mixing*" using a Freundl laboratory mixer.

The de-icing chemical formulations of sodium formate and sodium silicate were added at 3% by weight as a direct replacement for 3% limestone filler.

The experimental programme consisted of three phases. Phase one considered the effects of the de-icing chemical on the mechanical performance of asphalt. Phase two considered the role of moisture absorption. Phase three investigated how the de-icing chemicals can be transferred and the anti-icing performance.

Mechanical Performance of Asphalt

The first phase of testing was designed to assess the influence chemical additives have on the mechanical properties of the asphalt, thereby identifying if any reduction in the service life of the surface course is caused by de-icing chemical additives.

The testing comprised of standard national and European test methods. They examined how the de-icing chemicals influence a number of key material parameters including compactability, stiffness, strength, fatigue, resistance to deformation, skid resistance and sensitivity to water.

Moisture Absorption

The second phase of testing was designed to assess if modified de-icing chemical pavement surface course absorbs moisture from the atmosphere and the levels of moisture absorbed. This was achieved by conditioning chemical and asphalt samples at high humidity over a prolonged period of time.

The mechanical performance of moisture conditioned asphalt was also measured and comparison made to unconditioned samples. This showed how the stiffness, strength, skid resistance and fatigue properties were affected by prolonged moisture absorption.

Chemical Transfer and Anti-Icing Performance

The final phase of laboratory testing was designed to determine the anti-icing performance and contributing physical mechanisms that occur when a select range of anti-icing additives are added to the pavement surface course.

The chemical transfer mechanism has been assessed and characterised using Environmental Scanning Electron Microscope testing of chemically modified mastics, visual observations of submerged asphalt, interconnecting void measurements of asphalt briquettes and leachate testing of solutions after submerged wheeltracking of chemically modified asphalt.

The anti-icing performance was considered in terms of freezing point depression and ice adhesion. Depressing the freeze point by the use of chemical additives is a fundamental principle for preventing the formation of a strong layer of small ice crystals directly on the pavement surface. Freezing point measurement of chemical additives, chemically modified mastics and the leachate from chemically modified asphalt have been made as part of this study.

Ice adhesion in general terms relates to the physical and chemical bonding of ice and a substrate. Theoretical surface energy calculations and physical ice bond strength measurements using modified torque bond equipment have been made.

8.1.3 SITE TRIALS

To provide a measurement of the in-service and anti-icing performance a number of site trials of the perceived most promising chemical blend were constructed at various stages throughout the research project. This chemical blend was a 3% addition comprising of 70% sodium formate and 30% sodium silicate.

The first trial was conducted at Bow Depot in Central London. This trial was to check that the material could be satisfactorily produced and laid and to ensure the in-service performance was satisfactory, prior to transferring the system to the highway network.

Based on the positive results of the trial at Bow Depot, a second phase of trials were conducted. This phase was designed to measure the performance of the material under full highway trafficking conditions. The objectives were to quantitatively measure the anti-icing and mechanical performance of surface course under varying conditions. This phase of site trials consisted of a trial on the Ridgeway and Norfolk Avenue in Enfield.

8.2 CONCLUSIONS

This section of the thesis summarise the conclusions which have been reached following the work undertaken as part of this study.

8.2.1 MECHANICAL PERFORMANCE OF ASPHALT

- The study set out to assess what the influence de-icing chemicals have on the durability of the pavement surface course and the mechanical properties of the asphalt.

- The study has concluded that the addition of de-icing chemical formulations of sodium formate and sodium silicate do not significantly reduce the asphalt performance in terms of compactability, stiffness, permanent deformation and skid resistance, when subjected to a number standard British and European asphalt testing methods.

- The study has however highlighted significant concerns regarding the sensitivity of chemically modified asphalt in the presence of water. Asphalts modified with specific de-icing chemical formulations have an increased susceptibility to deterioration in the presence of water. This was particularly evident when concentrations of the relatively low surface energy sodium silicate were incorporated into the bituminous mixture.

- A reduction in fatigue resistance for the de-icing chemical formulations relative to the control was also measured as part of the study.

- Any observed variations in these individual performance areas were typically attributable to the physical and surface properties of the chemicals that were characterised prior to commencing the study.

- The physical properties of sodium formate and relatively high maximum packing fraction resulted in the lowest Delta Ring and Ball value for all modifications. This demonstrates sodium formate has the least stiffening effects on the bitumen mastic relative to other modifications. Asphalt performance testing has demonstrated that this reduction in mastic stiffness resulted in slightly lower asphalt stiffness and reduced fatigue resistance. The reduced mastic stiffness did aid the compactibility of the bituminous mixture. Improved compactability and reduced air void content has been demonstrated to improve the resistance to permanent deformation. Despite the lower surface energy of sodium formate, poor water sensitivity results were not measured in any of the water sensitivity tests conducted. This may be attributed to the good mechanical adhesion achieved due to the surface roughness providing a lock and key with the bitumen and a greater area of bonding.

- The physical properties of sodium silicate provided the greatest increase in the softening point and increased stiffness of the sodium silicate mastic due to the lowest maximum packing fraction of the chemical. This resulted in an increase in the asphalt stiffness and resistance to permanent deformation. The stiffer mastic reduced the viscosity of the bitumen resulting in reduced compactability and subsequently poorer fatigue resistance. The most significant performance reduction for sodium silicate was observed in the presence of water. This was due to the low surface energy nature of this material combined with the relatively smooth rounded surface. This provided limited interlock and bonding area between the bitumen and the chemical surface, which allowed the bitumen to be easily stripped in the presence of water. This significant deterioration means high sodium silicate concentrations are unacceptable modifications.

- Whilst the site trials demonstrated that chemically modified pavement surfaces can be manufactured and laid successfully, a number of the sites experienced significant early life deterioration and generally failed within the first six months.

- The failure occurred rapidly over a short period and included fretting and potholes and on some sites full disintegration of the surface course. The defect types and observation of binder stripping were indicative of a failure due to the poor water sensitivity of the anti-icing surface course.

- The deterioration discussed above was not observed at all the site trials. The first site trial conducted at Bow Depot did not not shown signs of deterioration even after 3 years in service (as at August 2012). The differences in the performance and durability of the anti-icing surface on the Bow Depot site trial compared with this other sites may be associated with the lower traffic levels relative to the Norfolk Avenue and the Ridgeway sites in Enfield.

- The incorporation of low surface energy materials with poor mechanical adhesion properties, as a filler into pavement surface, has proved to be problematic and the risk of early life failure and reduced service life of the pavement surface course increases on trafficked sites.

- On this basis, the thesis has shown that the concept of adding combinations of the freeze point depressant of sodium formate with the low surface energy material of sodium silicate as a filler replacement is not workable.

- Subsequent research studies and screening programmes for identifying suitable de-icing chemical formulations should place particular emphasis on the performance of asphalt in the presence of water, in order to prevent such early life failures.

- Skid resistance concerns with previous proprietary products do not appear to be a concern for the selected water soluble de-icing formulations.

8.2.2 MOISTURE ABSORPTION

- The de-icing chemical formulations considered as part of this study absorb moisture from the atmosphere at humidity levels greater than 70%.

- This was particularly evident for sodium formate because of the hydroscopic nature of the chemical. Sodium silicate independently only absorbs minor levels of moisture.

- Testing has demonstrated that this level of absorption by the chemical particles is significant and the de-icing chemical formulations can gain over 100% by mass as a result of moisture absorption when subjected to continued periods of high humidity.

- When the de-icing chemical formulations are incorporated into asphaltic specimens the moisture absorption is reduced due to the encapsulation of the chemical particles by bitumen and compaction of the bituminous mixture.

- The level of moisture absorbed is still significant despite this encapsulation and compaction. Between 15-25% of the levels of moisture absorbed by the chemical particles are absorbed when incorporated into asphalt specimens compacted to a 6.0% void content.

- The presence of increased moisture has been observed during site trials with a significant number of moist surface state conditions observed for the chemically modified surface relative to the control surface.

- Further laboratory testing has determined moisture absorption can reduce the mechanical performance of chemically modified asphalts when subjected to prolonged periods of high humidities relative to control samples. This is a new phenomenon specific to chemically modified asphalts.

- Accelerated conditioning at high humidity demonstrated significant reductions in stiffness, strength and fatigue performance of the chemically modified asphalts in comparison to control specimens.

- This reduced performance was particularly evident for combinations of sodium formate and sodium silicate. Sodium formate has been demonstrated to absorb significant quantities of moisture. Bitumen has been demonstrated to be susceptible to stripping when the low surface energy sodium silicate is present. Combinations of the two chemicals result in water being present at the sodium silicate/bitumen interface leading to stripping and water sensitivity failure methods.

- The accelerated moisture conditioning experiments conducted as part of this thesis provide significant evidence that the concept of adding combinations of the freeze point depressant and the low surface energy materials as a filler replacement is not workable.

- High moisture absorbing chemicals should not be incorporated with low surface energy materials unless the formulations can be proven not to be detrimental to the asphalt performance.

- Laboratory and site skid resistance testing did not appear to indicate any reduced levels of performance due to the presence of this moisture within the surface.

8.2.3 CHEMICAL TRANSFER AND ANTI-ICING PERFORMANCE

- This research project aimed to determine the anti-icing performance and contributing physical mechanisms that occur when a select range of anti-icing additives are added to the pavement surface course.

- The study has provided new evidence and concluded that de-icing chemical formulations can be transferred from within the bitumen mastic to the pavement surface.

- The mechanism by which the chemicals are transferred to the pavement surface has been established to be heavily dependent on the relative humidity. The transfer of the de-icing chemical formulation typically occurs at relative humidity above 70%. Humidity levels above this level are consistent with the point at which the de-icing chemicals absorb moisture from the atmosphere.

- As the relative humidity is decreased the chemicals are re-deposited on the surface with very limited movement or loss of the chemical particles.

- Visual observations of laboratory specimens that have undergone cycles of wetting and drying and site trials support the above conclusion and indicate that the levels of chemical transferred and re-deposited on the pavement surface are greatest in the surface voids.

- Interconnecting void analysis on asphalt specimens indicated that there is very limited void connectivity and permeability throughout the depth of the pavement surface course when manufactured at a void content of 5.0%. This evidence is consistent with the type of material and published literature. The lack of interconnecting voids restricts any chemical transfer from the lower layers of the pavement to the very top of the surface course.

- The chemical transfer mechanism on most surface courses (excluding porous asphalt) may be heavily dependent on the number and arrangement of surface voids rather than interconnecting void structure.

- The transfer of the chemical to the surface is required for anti-icing purposes. Analysis of solutions produced from submerged wheeltracking indicates that the de-icing chemical formulations leach over time and as required. This transfer also results in the loss of de-icing chemical formulations from the pavement surface course and the anti-icing performance is likely to diminish over time.

- Freezing point measurements of chemical solutions confirm the freeze depressant ability of sodium formate. Sodium silicate has significantly less potential to reduce the freezing point.

- The test data indicates that freezing can be prevented to temperatures as low as -1.6°C and -2.1°C for specific chemical formulations and concentrations of 3% and 5%, respectively. This reduction would be considered to be effective at reducing the number of winter weather events that would require treatment in a maritime climate, such as the UK.

- Freezing point measurements of bituminous mastics modified with de-icing chemical formulations at a concentration of 3% by weight, gave comparative levels of freezing point depression when a thin layer of water was applied to the surface of the chemical solutions. This supports the view that the chemical can be readily transferred through the bituminous mastic.

- In contrast, compacted asphalt specimens were not as effective at reducing the freezing point in comparison to the bituminous mastic specimens.

- It can be concluded that the structure and compaction of asphalt specimens reduces the chemical available to form a solution with water to lower the freezing point. This reduces the overall anti-icing performance. This reduced ability supports the view that a lack of interconnecting voids may have a limiting role in transferring the chemical for the surface courses examined as part of this experiment.

- Site trials have provided some evidence of anti-icing performance and reduced winter weather events of ice and snow in terms of surface condition measurements and visual observations, and could have a future role in winter service provision. The site trials have demonstrated that this anti-icing performance is not an absolute performance and have emphasised that anti-icing surface courses are unlikely to prevent all winter weather events and need for conventional winter service treatments are likely to remain a requirement.

- Surface energy testing and theoretical calculations of the adhesion strength of ice to the surfaces have indicated that the adhesion of ice to various de-icing chemical surfaces is significantly less than for filler and aggregate particles.

- Physical testing of the ice bond strength to mastic surfaces has demonstrated a reduction in the bond strength between ice and bituminous mastics modified with de-icing chemical formulations. This reduction may be of the order of 20% to 40% when compared to standard bituminous mastics.

- The reduced adhesion of ice to the anti-icing pavement surface in comparison to the control surface was visually observed during the site trial programme.

8.3 RECOMMENDATIONS FOR FUTURE WORK

The report makes the following four recommendations for future work:

1). Mix Design Process

The laboratory testing programme has demonstrated that bituminous materials modified with de-icing chemical formulations can be highly susceptible to water damage. De-icing chemicals formulations can also absorb significant amounts of moisture from the atmosphere. The combined effect can significantly reduce the durability and service life of the pavement surface course.

It is recommended that a mix design process is developed specifically for bituminous materials which are chemically modified for de-icing purposes.

This mix design process should include a number of tests to assess the moisture absorption and water sensitivity of the bituminous materials. For example:-

- Level of moisture absorption at high relative humidity
- Impact of moisture on the mechanical performance (principally stiffness after 30 weeks of high relative humidity)
- Water sensitivity testing. For example, the use of the submerged wheeltracker can be considered a suitable single test to highlight the moisture susceptibility of low surface energy materials.

Performance limits should be set for each design property, which have been correlated with field trials to ensure a high probability of survival and good material durability.

For example, based on this study and associated site trials, the probability of survival can be increased by the following properties (indicative values):-

- Moisture absorption levels of chemically modified asphalt briquettes of less than 50% after 30 weeks
- Retained stiffness values in excess of 80% following moisture condition after 30 weeks
- Retained strength in excess of 80% following water sensitivity testing in accordance with BS EN 12697
- Mean rut depths less than 2.0% when subjected to 15,000 cycles on a submerged wheeltracker

In addition to the test method highlighted above, it is recommended that Freeze thaw testing such as the Texas Freeze-Thaw Pedestal test is conducted. This test method is recommended to further understand how ice forms and thaws in the surface voids at low temperatures (e.g. less than -5^{o}C) to establish if repeated freezing and thawing influenced the early life deterioration on site trials.

It is recommended that further testing of a wide range of de-icing chemical formulations is undertaken along with a site trial programme to establish precise performance limits as part of the mix design process

It is recommended that the mix design process considers specifying a minimum bitumen richness modulus to achieve a less water susceptible asphalt. A minimum and maximum air void content/texture is also recommended (see recommendation 3) to ensure the chemical can be transferred for anti-icing purposes, whilst maintaining durability.

Allowance for the provision for adhesion promoting agents, hydrated lime or polymer modified bitumen is also recommended for improving water sensitivity.

2). Review of Alternative Chemicals and New Way of Incorporating Low Surface Energy Materials

The time constraints of this project have meant that only a limited number of de-icing chemical formulations have been considered in the laboratory and under site trial conditions. The research by Baum et al. (1992) recommended two further promising chemicals of sodium acetate and calcium magnesium acetate. These two chemicals should be further evaluated using the mix design process developed above. Equally, site trials have focused on only one de-icing chemical formulation (70SF 30SS) on moderately trafficked carriageways.

Based on the full laboratory test results and conclusions, it is recommended that a 3% inclusion of sodium formate (100SF) without the use of sodium silicate is further considered under site trial test conditions. This is because the 100SF formulation has shown a good level of anti-icing performance, equivalent mechanical performance and no significant reduction in performance when subjected to water conditioning protocols compared to control specimens.

The incorporation of low surface energy mixture as a filler into pavement surface has been demonstrated to be problematic and the risk of early life failure and reduced service life of the pavement surface course increased on trafficked sites. Despite these problems, low surface energy materials have been demonstrated to reduce the ice adhesion to the pavement surface, thereby allowing the ice to be easily removed.

It is recommended that alternative ways of incorporating low surface energy materials are further explored. Such alternative methods may consider introducing adhesion agents to prevent the durability problems when including a low surface energy material as a filler, or applying the low surface energy material as a coating to the surface of the asphalt pavement surface course.

It is also recommended that the de-icing chemical formulations are trialed in less severe applications, such as footway materials.

In particular, slurry seals may provide a cost effective solution because:-

- De-icing chemical formulations could be easily incorporated into slurry seals:
- The slurry seal would provide a high number of surface voids to transfer the de-icing chemicals when required and ensure all of the chemical is accessible from the surface
- The treatment depth of slurry surfacing limits the quantity of chemical required
- A repeat treatment could be readily applied when the entire chemical addition has been utilised.

3). Role of The Pavement Surface and Specifically The Air Void Content

To date, the research has only considered Stone Mastic Asphalt surface course with air void contents typically in the region of 5.0% to 6.0% air voids. The air void content of the pavement surface course is likely to significantly affect a number of key parameters, these include:

- How the chemical is transferred to the pavement surface
- The rate of chemical transfer
- The level of moisture absorbed
- The durability of the pavement surface course

Laboratory testing of the Stone Mastic Asphalt surface demonstrated that the main chemical transfer mechanism on the surface is due to the passage of chemicals through the bitumen mastic due to the atmospheric conditions and relative humidity. The very limited interconnecting air voids in the pavement surface course would appear to limit the transfer of chemicals to the upper 15-20mm of the pavement surface course.

The increase in air void content of the surface course is likely to increase the amount of chemical transferred. However, increasing the air void content of the surface course may increase the durability concerns related to moisture absorption and water sensitivity.

It is recommended that further studies are conducted to optimise the air void content in terms of allowing for the chemical particles to be easily transferred without restricting the durability of the pavement surface course and anti-icing performance.

It is recommended that this is achieved by undertaking a number of performance tests at air void contents ranging from dense material at 2.0% air voids to air void contents in excess of 8.0% where permeability and interconnectivity is achieved. The following performance tests are considered suitable for each parameter:-

- Chemical Transfer – Permeability (6.6.1.2) and leachate testing (6.6.1.3)
- Anti-icing performance – Freezing point of measurements of chemical modified asphalt (6.6.2.3)
- Durability – Water sensitivity tests (6.4.11.3 – 6.4.11.5) and Moisture absorption (6.5.2 and 6.5.3).

It is recommended that in conjunction with the findings of this report, a relationship between the air void content and the key parameters outlined above is undertaken, with the view of determining the optimum air void content for chemically modified anti-icing surface courses.

4). Anti-Icing Performance – Longevity and Influencing Factors

This report has assessed the initial anti-icing performance in terms of freezing point depression and ice bond reduction. The analysis of the submerged wheeltracking solutions has indicated that over time the chemical leaches from the pavement surface.

It seems logical that the leaching of chemicals will reduce the anti-icing performance over time and at some point the modified pavement surface course may fail to provide any anti-icing benefits.

It is recommended that future work is conducted to assess the factors affecting the longevity of the anti-icing performance and rate of leaching. These may include the role of:

- Air void content
- Climatic conditions such as relative humidity and precipitation
- Trafficking
- De-icing chemical
- Concentration of the chemical modification

The overall objective of future work should be to establish the relationship between these parameters and the anti-icing performance with time, and to predict the service life of de-icing chemical formulations. This will enable winter service providers to conduct an informed whole life costing evaluation of such products and to create a risk based matrix, which sets out when traditional winter weather events should be applied to the pavement surface.

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