DEVELOPMENT OF A NEW COLD BINDER COURSE EMULSION ASPHALT

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A thesis submitted in partial fulfilment of the

requirements of Liverpool John Moores University

for the degree of Doctor of Philosophy

February 2017

DECLARATION

The research reported in this thesis was conducted at Liverpool John Moores University, Civil Engineering Department, between October 2013 and February 2017. I declare that the work is my own and has not been submitted for a degree at another university.

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ABSTRACT

Hot Mix Asphalt (HMA) is the most commonly used material in the construction of asphalt pavements. Approximately 650 million tonnes of asphalts for road pavements were produced, worldwide, in 2014. However, the HMA industry is responsible for a substantial consumption of energy, the creation of health and safety issues and has a negative impact on the environment. These shortcomings initiated substantial discussion within the industry with the aim to develop more environmental friendly, sustainable and economic pavement materials. These have resulted in the development of cold bitumen emulsion mixtures (CBEMs). However, to date, low early life stiffness, a slower rate of curing, the length of time necessary to achieve full strength, high air void contents and the presence of moisture in these mixtures have prevented them from being fully embraced by pavement authorities. This led to them being considered inferior to HMA because of a lack of essential mechanical properties. Currently, the use of CBEMs in pavement construction is limited to low traffic road surface course, reinstatement works and footways. Because of this, the development of CBEMs with high early strength and minimal time delay requirements before structural loading, would be considered as a breakthrough in CBEM research.

This research aims to develop a novel, fast-curing and environmentally friendly, cold binder course emulsion asphalt (CBCEA) for heavily trafficked roads. The new CBCEA mixture comprises the same gradation as conventional dense bitumen macadam (DBM) mixtures which are normally used as a binder course and base in road pavements in the UK. The new CBCEA incorporates a new cementitious material, alkali activated binary blended cement filler (ABBCF), made from Paper Making Sludge Ash (PMSA) and a Fluid Catalytic Cracking Catalysts Residue (FC3R) activated by a waste NaOH solution (W-NaOH). Incorporation of the PMSA and FC3R was achieved through the replacement

of conventional limestone filler (LF), while W-NaOH replaced the pre-water necessary to wet the aggregate in the CBCEA. It was found that the glass phases of the new filler particles were broken and reacted with $Ca(OH)_2$ creating C-S-H gel through the hydration process. This results in a very high early strength and improved mechanical properties. Balanced oxide compositions, within the new filler, were identified as responsible for an enhanced hydration reaction.

A laboratory programme of testing measured the stiffness modulus, conducted at 1, 3, 7, 14, 28, 90 and 180 days. Susceptibility to temperature, wheel track testing to establish rutting resistance, fatigue resistance measured by a four-point beam bending test, fracture resistance testing via semi-circular bending tests, moisture damage resistance and ageing tests were successfully performed. Advanced techniques for microstructure assessment, i.e. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD), were used to provide scientific data to provide a deeper understanding of the microstructure and internal composition. An environmental investigation was performed using a Toxicity Characteristic Leaching Procedure (TCLP) test.

The new ABBCF mixture offers a significant improvement in stiffness modulus compared to HMA and the reference cold binder course mixture containing conventional limestone filler (LF). Target stiffness, according to British and European standards, can be surpassed after less than one day of curing. The new ABBCF mixture offers a stiffness modulus which is 27 times better than the LF mixture after 3 days. This will overcome restrictions caused by the length of time required to achieve acceptable stiffness by traditional CBEMs. More remarkably, the new ABBCF mixture is 78% better than mixtures treated with Ordinary Portland Cement (OPC) in terms of ITSM after 3 days. Furthermore, the impact of a rise in temperature on stiffness modulus from 5 to 45°C, was much larger in LF and both HMA mixtures in comparison to ABBCF, revealing the

potential to use these mixes in severe conditions, both hot and cold weathers. ABBCF mixtures displayed considerably reduced susceptibility to permanent deformation, demonstrating the potential advantage of using this material on heavily trafficked roads. Fatigue resistance was noticeably improved by the use of ABBCF in comparison to the reference LF and HMAs. Improved water sensitivity for progressive hydration with the new ABBCF was also established resulting in an enhanced long ageing performance meaning that these mixtures can be considered durable. SEM observation and XRD analysis confirmed the formation of hydration products at various curing times. The concentration of heavy metals in the samples incorporating ABBCF was observed to be less than the regulatory levels determined for hazardous materials. Microwave treatment has proven to be an effective technique to reduce the air void contents of the ABBCF mixture and achieve acceptable levels of porosity. Finally, achieving the aim of the current research will theoretically increase the application of such mixtures and allow them to be used as structural pavement materials. On a further positive note, the inclusion of waste and by-product materials in CBEMs results in more sustainable practice and eliminates disposal problems.

ACKNOWLEDGEMENTS

DEDICATION

This thesis is dedicated specially to:

Allah, the most Gracious and the most Merciful.

Prophet Mohammed (May Allah bless him) and his household.

My Mother, the most precious person in my life. Your death when I was in the final stages of my PhD was the biggest loss. You have sacrificed so much for us and I hope that this work will be of benefit for humanity; the reward will be for you. I hope you are proud of me.

In loving memory of my Father, whose death prevented him from seeing this work.

My beloved wife for her endless love, patience, encouragement and support.

My beloved children for their smiles and love that motivates me.

My brothers and sisters for their support and encouragement.

My parents-in-law for their continuous support.

My country, Iraq, martyrs who have sacrificed for the homeland and all heroes defending it.

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ACRONYMS AND ABBREVIATIONS

Alkali activated binary blended cement filler (ABBCF)

Asphalt concrete (AC)

Asphalt Emulsion Manufacturers Association (AEMA)

Binary blended cement filler (BBCF)

Calcium aluminium silicate hydrate (C-A-S)

Calcium hydroxide (C-H)

Calcium silicate hydrate (C-S-H)

Cement kiln dust (CKD)

Cement-asphalt emulsion composite (CAEC)

Coarse paper making sludge ash (PMSA-C)

Cold binder course emulsion asphalt (CBCEA)

Cold asphalt emulsion mixtures (CAEMs)

Cold bituminous emulsion mixture (CBEM)

Cold mix asphalt (CMA)

Cold-rolled asphalt (CRA)

Degrees Celsius (^{o}C)

Dense bitumen macadam (DBM)

Energy dispersive X-ray fluorescence (EDARF)

Ethylene Vinyl Acetate (EVA)

European Asphalt Pavement Association (EAPA)

Fine paper making sludge ash (PMSA-F)

Fluid catalytic cracking catalysts residue (FC3R)

Ground granulated blast furnace slag (GGBS)

Half warm foam (HWF)

Half-warm mix asphalt (HWMA)

Heavy vehicle simulator (HVS)

Highway Authority and Utility Committee (HAUC)

Hot mix asphalt (HMA)

Incinerated sewage sludge ash (SSA)

Indirect tensile stiffness modulus (ITSM)

Indirect tensile stiffness modulus ratio (SMR)

Initial emulsion content (IEC)

Initial residual bitumen content (IRBC)

Limestone filler (LF)

Liverpool Centre for Material Technology (LCMT)

Mega Pascal (MPa)

Optimum pre-wetting water content (OPWwc)

Optimum residual bitumen content (ORBC)

Optimum total liquid amount at compaction (OTLC)

Ordinary Portland cement (OPC)

Palm oil fuel ash (POFA)

Paper making sludge ash (PMSA)

Particle size distribution (PSD)

Permanent cold lay surfacing materials (PCSMs)

Polyvinyl acetate emulsion (PVA-E)

Proportional rut depth (PRD$_{AIR}$)

Pulverised fuel ash (PFA)

Rapid setting cement (RSC)

Scanning electron microscopy (SEM)

Styrene-butadiene-styrene (SBS)

Supplementary cementitious materials (SCMs)

Ternary blended filler (TBF)

Toxicity characteristic leaching procedure (TCLP)

U.S. Environmental Protection Agency (EPA)

Warm mix asphalt (WMA)

Waste fly ash (WFA)

Waste NaOH solution (W-NaOH)

Wheel-tracking slope (WTS$_{AIR}$)

X-Ray diffraction (XRD)

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CHAPTER 1

INTRODUCTION

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1.1 General background

Roads are built to withstand traffic loading safely, conveniently and economically during their service life. They play a substantial role in the transportation system and are essential for the economy of any nation. The main structural load-carrying elements of roads are pavements which, in general, are comprised of asphalt mixtures. These mixtures are well-established paving materials, this based on over 100 years of satisfactory performance. Approximately 650 million tonnes of asphalts were produced in 2014 (EAPA, 2014a).

Asphalt mixtures can be categorised by means of the temperature used to generate them as follows: 1) cold mix asphalt (CMA) made at a temperature below 60°C; 2) half-warm mix asphalt (HWMA) produced lower than 100°C, usually at 70-95°C; 3) warm mix asphalt (WMA) manufactured at a temperature range of 110-140°C (Rubio et al., 2013), and 4) hot mix asphalt (HMA) prepared, laid and compacted at high temperatures ranging between 110-170°C.

HMA is the most universally utilized material for manufacturing of asphalt pavement (Su et al., 2009) but despite its excellent performance, HMA production consumes a substantial proportion of energy and emits pollutant gases generated from drying huge quantities of mineral aggregates in combination with heating bitumen at high temperatures (Capitão et al., 2012). Rubio et al. (2012) stated that one of the major causes of pollution stemming from road construction lies in the production, spreading and conservation of HMAs, this creating a harmful environmental impact which contributes to global warming (Rubio et al., 2013). This aside, another restriction associated with HMA is the difficulty in maintaining its temperature when hauling long distances. In

summary, HMA manufacture is a high energy and emissions intensive process with harmful environmental impacts. Because of this, the pavement industry has been looking for more environmentally friendly and sustainable asphalt pavement construction practices (Yang et al., 2015).

The relatively high demand for bituminous products, combined with the high ecological footprint and energy consumption of such materials, has paved the way for the development of environmentally sustainable methods and practices to meet the demands of ever increasing roadway infrastructures while decreasing environmental costs. Utilizing cold bituminous emulsion mixtures (CBEMs) is a step in that direction and has the potential to be accepted as one of the more commonly used sustainable strategies for asphalt pavements as they can be considered environmentally friendly mixtures having social, environmental and economic benefits with reference to their production and application.

1.2 Cold Bituminous Emulsion Mixture (CBEM)

Cold mix asphalt (CMA) is a technology that allows asphalt mixes to be manufactured and laid at ambient temperatures (Thanaya et al., 2014; Gómez-Meijide et al., 2016). Cold bitumen emulsion mixtures (CBEMs) are one of the more popular types of CMAs (Al-Busaltan et al., 2012; Nassar et al., 2016b) defined as asphalts comprising of aggregate, asphalt emulsion and water which can be mixed at ambient temperature and applied on the road (Gómez-Meijide and Pérez, 2015).

CBEM technology has been widely used in various countries, including the USA and France, since the 1970s. However, the use of bitumen emulsion is generally limited to surface treatment, for example slurry surfacing, surface dressing and reinstatement work on low trafficked highways and footways (Highway Authority and Utility Committee

(HAUC), 1992; Read and Whiteoak, 2003; James, 2006), its use as a structural layer in the UK attracting relatively little attention (Brown and Needham, 2000a; Oruc et al., 2007a). This has arisen because of problems associated with inadequate performance, time taken for full strength to be achieved after paving, early life damage/sensitivity to rainfall and to UK weather conditions which do not facilitate the curing process for these emulsion mixtures.

1.3 The advantages of using Cold Bituminous Emulsion Mixtures

CBEMs have several benefits over HMA, but the main difference lies in the fact that CBEMs do not need heat to produce or be successfully laid. In addition, CBEMs can offer the following advantages:

1. Elimination of the need to heat both the aggregate and binder which will lower energy costs regarding production, leading to a reduction in paving costs. These mixtures need around 13% of the total energy needed to produce HMA (Bouteiller, 2010) as only bitumen is heated in the emulsification process to produce a liquid called a bitumen emulsion.

2. CBEMs may allow pavement construction in colder weather because there is no longer the threat of a critical loss of temperature thereby extending the paving season.

3. It is an environmentally friendly material because it is produced without heating processes that create fumes, greenhouse gas emissions, fire hazards and other chemical pollutants which affect air quality. The CO_2 emissions generated are approximately 14% of those of HMA (Kennedy, 1998). Therefore, they have a lower environmental impact compared to HMA. In addition, the use of CBEMs in places such as tunnels, where there is no open air circulation, represents an excellent solution to safety concerns of workers. In these circumstances, HMA

workers are usually exposed to 0.1 to 2 mg/m^3 of bitumen fumes which include 10 to 200 ng/m^3 of benzo(a)pyrene toxic gas (Chauhan et al., 2010).

4. Lower plant emission and fumes will improve working conditions, workers' health and general safety at the job site by decreasing the risk of burns and exposure to fuel emissions.

5. CBEM technology strengthens the philosophy of a sustainable transportation system by meeting the principle conditions for sustainable pavements defined as eco-friendliness, increased safety, energy efficient and economical viability.

6. It is suitable for road construction in remote and isolated areas because mixes can be hauled over longer distances.

7. It has logistical benefits as it can be stockpiled or, as mentioned above, can be hauled longer distances without taking special precautions.

8. It avoids problems such as binder hardening through oxidation and other negative effects caused by the heating process.

9. It can utilize both recycled and virgin aggregate, as well as waste and by-product materials which will reduce construction costs. In addition, latex polymers can be incorporated in comparison to HMA.

10. CBEM can be produced in mixing plants without a drier, chimney or dust filters, thus simplifying manufacturing plants.

11. Production reduces construction waste, in comparison to HMA, due to the elimination of heating.

1.4 Drawbacks of CBEMs and Statement of Problem

CBEMs are usually used for the preventative maintenance of pavements as micro-surfacing and slurry seal. Due to its inferior performance in comparison to HMA, it has not been used as a structural layer (Leech, 1994; Thanaya, 2003; Oruc et al., 2007b; Al

Nageim et al., 2012). The factors which represent barriers to wider utilization in the road industry can be summarized as follows:

1. Weak strength at early ages as a result of high porosity due to a high air void content.

2. Long curing periods which are required to achieve maximum performance where the development of strength is dictated by moisture loss and setting of the emulsion. The Chevron Research Company carried out both laboratory and field studies in order to evaluate the performance of CBEMs in California, reporting that full curing in the field of such mixtures may take between 2 and 24 months (Leech, 1994).

3. To enhance the performance of CBEMs, additives have been used such as cement which substantially increases the cost of production.

4. A lack of standards and specifications. There are no universally accepted mix designs, manufacturing or construction specifications procedures.

5. Under adverse climatic conditions, i.e. wet and cold weather, there will be a slow rate of increase in strength.

6. If water invades the mixture before curing is complete, there is a risk of re-emulsification or erosion.

7. Production requires more binder compared to other asphalt.

8. Drainage of the binder can occur when in storage as a result of the low viscosity of the emulsion.

9. Poor coating occurs because of incompatibility between the emulsion and aggregates.

10. There is low binder film thickness on coarse aggregates because the emulsion is more attracted to finer particles.

Ordinary Portland cement (OPC) has been utilized as a filler substitute to overcome some of these shortfalls in CBEMs (Brown and Needham, 2000a; Oruc et al., 2007b; Fang et al., 2014). However, the production of Portland cement is an energy intensive process. releasing a substantial quantity of greenhouse gases representing approximately 5% of greenhouse gas annual emissions, in addition to the comparatively high prices of cement and environmental pollution control (Setyawan et al., 2015; Fouchal et al., 2015).

1.5 Aim and Objectives of the Research

Sustainability, economy and safety are important factors in road pavement construction and constitute the main driving forces impacting on the incentives to further develop CBEMs. As mentioned in section 1.4, a review of the literature revealed three main shortfalls associated with CBEMs in binder course asphalts, namely:

i)   Low early strength.

ii)   Long curing times as it can take between 2 months to 2 years to develop ultimate strength.

iii)   High air void content after compaction which has forced road engineers to restrict the use of CMA to footways, reinstatement works and pavements carrying low traffic levels.

The aim of the current research originates from previous and ongoing studies at the Liverpool Centre for Material Technology (LCMT), in collaboration with an industrial partner namely Colas Ltd. The author, working with his supervisory team, decided to develop a new, fast curing, cold binder course emulsion asphalt (CBCEA) with continuous grading similar to traditional asphalt concrete gradation which is appropriate for use as a binder course in heavily trafficked pavements. These mixtures will meet current traditional hot binder course requirements detailed in BS and EU specifications

by replacing conventional limestone filler with new, novel cementitious filler from waste materials and by products thus removing the said restrictions imposed by the use of such mixtures. This is a challenge as the work entails:

i)   Creating a new cementitious filler.

ii)   Providing a cold binder course mixture with mechanical and durability properties better than or equivalent to the same course produced from HMA.

iii)   Application of the scientific knowledge that can explain improvements in both the mechanical and durability aspects of the new products. Fulfilling these objectives requires the development of a new cement-like filler. A number of waste materials and industrial by-products have been chosen as candidates to replace traditional limestone filler. Their selection was based on their preliminary chemical properties, availability in the UK and worldwide, and their environmental impact.

The novelty of this research is two fold:

i)   The transformation of waste materials into a high value, cementitious material using new activation method techniques.

ii)   Application of this cementitious material to develop a new, fast-curing, cold emulsion asphalt for use in heavily trafficked roads as a binder course.

Based on their chemical and physical properties and safe use in asphalt pavements, the following waste materials and industrial by-products have been used: paper making sludge ash (PMSA), Fluid Catalytic Cracking Catalysts Residue (FC3R), Cement Kiln Dust (CKD), Sewage Sludge Ash (SSA), Ground Granulated Blast Furnace Slag (GGBS), Palm Oil Fuel Ash (POFA) and Waste NaOH solution (W-NaOH).

The proposed research aims to address the following objectives:

1. Carry out a detailed literature review of:

   i)   Asphalts in general and the technology of CBEMs.

   ii)   The properties, testing and design procedures associated with the current use of CBEMs.

   iii)   The techniques used to improve CBEMs by adding OPC and/or other materials which provide various enhancing properties.

2. To examine prospective candidate waste materials and by-products such as PMSA, FC3R, CKD, POFA, SSA, GGBS and W-NaOH in terms of their physical, chemical, mineralogical and morphology properties. This will involve carrying out a comparative study in terms of the physico-chemical properties of these candidate waste materials including a critical analysis of their potential use as pozzolanic and/or hydraulic activators as a substitute for traditional mineral limestone filler, individually or collectively.

3. The development of a new, fast-curing, cold binder course emulsion asphalt (CBCEA) at ambient temperature which needs no heat. This includes:

   i)   Carrying out comparisons by substituting traditional limestone mineral filler with OPC and also with a candidate filler from 2 above, in terms of the indirect tensile stiffness modulus (ITSM) test. The stiffness of asphalts is a significant factor in flexible pavements, and is directly associated with the capacity of the material to distribute load (Pasetto and Baldo, 2010).

   ii)   Applying optimization, in addition to the use of different activations, for the generation of the new CBCEA by incorporation of the newly developed pozzolanic/cementitious materials from the candidate waste materials.

iii)   Conducting a laboratory testing programme by applying different mixing and curing regimes, and heating techniques for the mechanical improvement of the new fast-curing CBCEA properties in terms of achieving the target ITSM.

4. An assessment of the improvements of different fundamental mechanical and durability properties of CBCEA by using current European and British Standards such as:

   i)   Permanent deformation under repeated loading using wheel tracking test facilities under different environmental conditions.

   ii)   Fatigue cracking in terms of four-point load fatigue tests using Cooper testing apparatus under different loading conditions.

   iii)   Water sensitivity by studying the Indirect Tensile Stiffness Modulus Ratio (SMR).

   iv)   Temperature susceptibility by measuring the ITSM at various temperatures.

5. Explanation of the results achieved utilizing scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis to examine the microstructure of dry powders and pastes at different curing stages (3, 7, 14 and 28 days).

6. An investigation of environmental issues by performing a toxicity characteristic leaching procedure (TCLP) test to analyse the leachate obtained from the specimens for heavy metal concentrations to ensure cleaner and environmentally-friendly products.

7. Application of microwave conditioning to samples in order to improve the mechanical and volumetric properties including air void content, bulk specific gravity, percentage of voids filled with bitumen and percentage of voids in mineral aggregate.

8. Writing PhD thesis.

9. Publishing journal and conference papers.

1.6 Research Benefits

Many benefits can be realised, based on the results of this research, both now and in the future. Current benefits are derived from the use of waste materials and by-products in road construction. Future benefits include pavements that perform better, more environmental friendly construction practices, more cost effective solutions, enhanced sustainability and ultimately, a better service to society.

1.7 Thesis Organisation

This thesis is organised into twelve chapters.

Chapter 1: the introduction which includes general background information about CBEMs, the advantages and drawbacks of such mixtures, the project aim and objectives, and the research benefits.

Chapter 2: an overview of the previous research on asphalt classification, types of cold asphalts, CBEMs, practices regarding CBEMs and CBEM design procedures.

Chapter 3: a review of the literature concerning bitumen emulsion including the different types available, their composition and characteristics.

Chapter 4: a comprehensive review of previous research on CBEMs.

Chapter 5: details of the research methodology, materials characterization and the test methods chosen for CBCEA characterisation.

Chapter 6: elements of the development of new CBCEAs. This includes determining the stiffness modulus using sequential optimisation to generate novel CBCEA mixtures taking into account the effect of different curing times and testing temperatures.

Chapter 7: findings of the mechanical and performance properties of CBCEA including rutting, fatigue and fracture toughness.

Chapter 8: specifics of the durability properties of the CBCEA mixtures in terms of water sensitivity and ageing.

Chapter 9: evaluation of the microstructural characterisation of the new cementitious material in terms of SEM observation and XRD analysis. This will help explain improvements in both the mechanical and durability properties of the new binder course.

Chapter 10: particulars about the CBCEA environmental investigation, specifically the leaching of heavy metals into water re the application of waste materials into CBCEA mixtures.

Chapter 11: information about microwave applications used to improve the volumetric properties of CBCEA mixtures.

Chapter 12: main findings and conclusions derived from this study and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW I- BITUMINOUS EMULSION MIXTURES

2.1 Introduction

This chapter provides a general overview of CBEMs as well as an introduction into the existing state of associated technologies in the pavement industry. Asphalts consist of graded aggregates bonded together with bitumen and are ideal for the upper courses of pavement structures. Various kinds of asphalts are used all over the world. In 1990, there were over 350 recipes for mixtures currently in use in the UK alone (Venton, 1990). These have been developed to meet certain requirements for example, load bearing capacity, resistance to permanent deformation, fatigue resistance, durability, surface texture and permeability. Various technologies have been involved in their manufacture, there being major differences in preparation and compaction temperatures.

2.2 Pavement Structure

The structure of a road pavement comprises several layers of different materials necessary to support traffic loads. These layers together with the foundation upgrade the soil subgrade which does not usually have the capacity to support traffic directly. A typical flexible pavement structural layer in the UK is shown schematically in Figure 2-1 where the asphaltic layers are indicated as surface course, binder course and base, respectively (Read and Whiteoak, 2003). Generally, pavement structures comprise the following four main components:

- ➢ The foundation is the platform upon which more expensive layers are placed and constitutes the basis of the load bearing layers of the pavement.

- ➢ The base represents the major structural layer, its main purpose to spread traffic load to the layers beneath and to avoid them becoming overloaded. It must be able to withstand the stresses and strains produced by traffic loads without excessive or quick deterioration of any type.

- ➢ The binder course can be defined as the pavement structural platform (O'Flaherty, 2007b). The binder course, together with the base, constitute the main structural layers, their chief purpose to spread traffic loading to the layers beneath as well as to protect them from excessive stress (Sutanto, 2009a). Said binder course allows asphalt contractors to achieve the very high standards of surface uniformity stipulated by current asphalt specifications. The main properties of asphalt mixtures used in the binder layer are high stiffness to spread the traffic load to lower layers, resistance to permanent deformation, resistance to fatigue cracking, durability, workability and impermeability (Taherkhani, 2006). O'Flaherty (2007b) demonstrated that if the surface course is impervious, the binder course can be composed of a more permeable material.

- ➢ The surface course provides a safe and smooth surface with suitable skid resistance and resistance to water penetration. It can vary from a very thin surface dressing to a 50 mm dense bituminous mixture (Taherkhani, 2006).
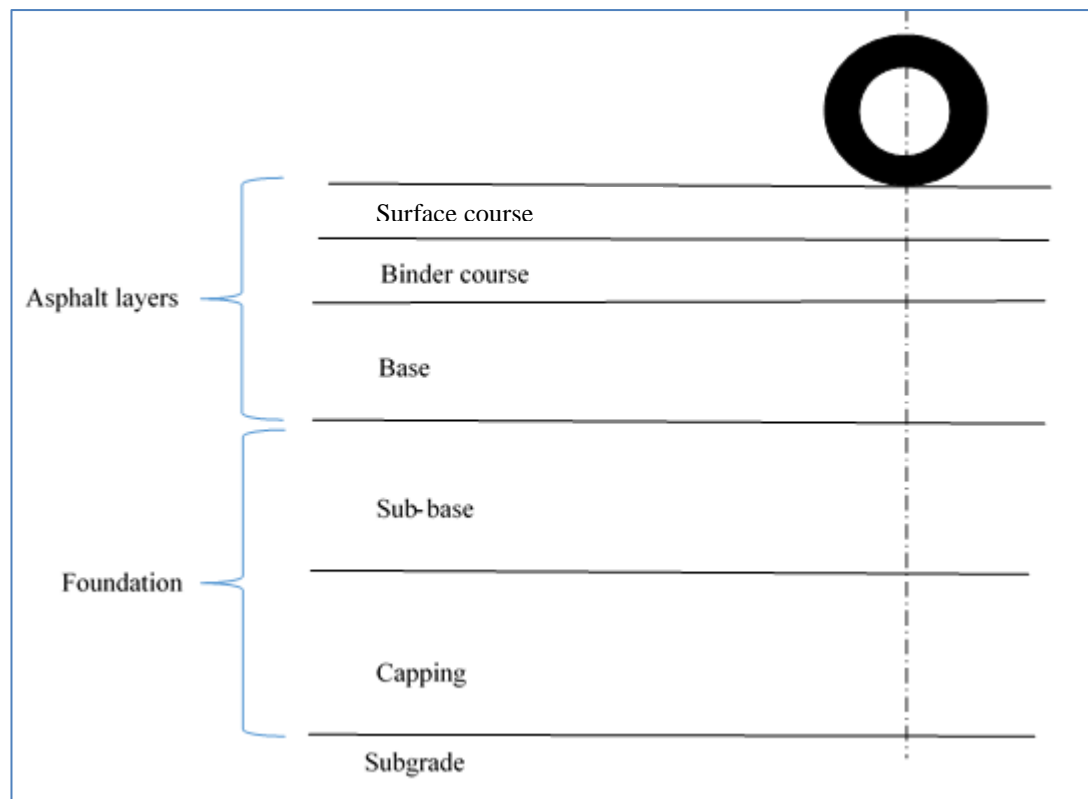
Figure 2.1. A typical flexible pavement in the UK

2.3 Classifications of Asphalt Mixtures

Asphalt mixtures are divided into two major classifications according to their proportion and particle size distribution known as continuously graded and gap graded mixtures (Figure 2-2). In continuously graded mixtures, there are various size fractions of aggregate, the assumption being that the voids generated by the bigger particles will be filled up by the smaller particles (Roberts et al., 1991). Therefore, the interlock between aggregate particles is responsible for the strength of the aggregate skeleton. Asphalt concrete based on BS EN 13108-1 (European Committee for Standardization, 2006), is the continuously graded mixture classification which depends on the gradation of aggregate and binder content. Taherkhani (2006) stated that Dense Bitumen Macadam (DBM), an example of a continuously graded mixture, is typically utilized for lower layers such as the binder course and base in major roads. Acceptable compaction is

required to attain a durable material which is suitable as a surface course for high speed roads.

Conversely, the grading in gap graded asphalts is not continuous; creates a high void content to be filled with sand, filler and bitumen. The structural strength of gap graded mixtures is based on the mortar of sand, bitumen and filler. In consequence, continuous graded mixtures offer better deformation resistance than gap graded mixtures, however, the fatigue resistance of continuously graded mixtures is less than that of gap-graded because less binder content is used in the mix (Read, 1996).
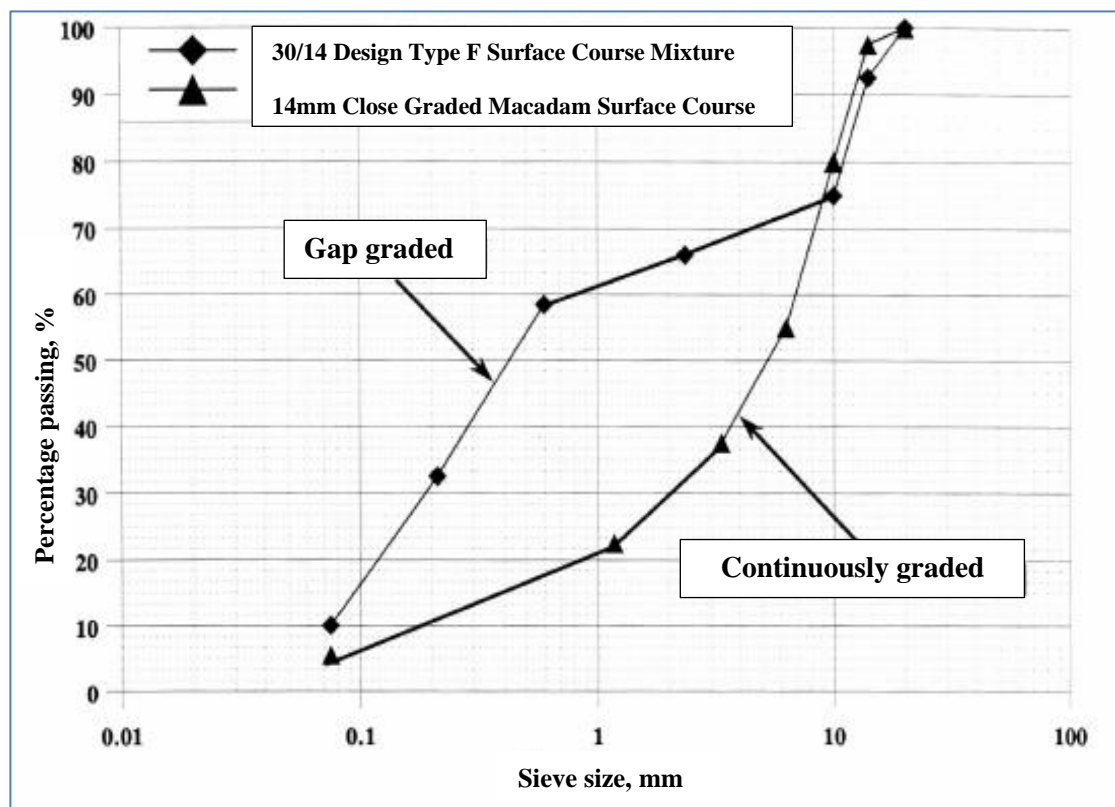
Figure 2.2. Comparison of continuous-graded and gap-graded mixtures (Read, 1996), permission to reproduce this figure has been granted by Professor John Read

Asphalt mixtures, according to their temperature during mixing and the energy consumed in the process of heating, are divided into different types described below (Vaitkus et al., 2009).

2.3.1 Hot Mix Asphalt (HMA)

HMA is generally used in the production of highway pavement layers, airfields, parking areas and pedestrian streets. It is manufactured between 150°C and 190°C, depending on the hardness grade of the bitumen, by heating the asphalt binder to reduce its viscosity and by removing the moisture in the aggregate through drying prior to mixing. This ensures that the aggregates will be coated with the bitumen binder and that the mixture is workable during application. The main three mix design methods for HMA are Marshall, Hveem and Superpave methods.

For all designs, paving and compaction must be undertaken while the mixture is hot (Needham, 1996). In several countries, HMA application is limited to the summer months because HMA cools too quickly in winter meaning that optimum density by compaction cannot be achieved. The temperatures required are however, dependent on the grade of bitumen; hard bitumen needs high temperatures while soft bitumen requires lower temperatures. The choice of bitumen grade is governed by the ambient temperature in the construction area; hard bitumen is appropriate for hot weather regions while soft bitumen is suitable for cold areas. Unfortunately, the production of HMA is a major source of carbon emissions which have a significant environmental impact (U.S. Environmental Protection Agency (EPA), 2013). The Environmental Protection Agency (EPA) estimate the annual emissions of a drum mix asphalt plant which generates around 200,000 tonnes of asphalt mix, is around 13 tons of carbon monoxide (CO), 5 tons of volatile organic compounds, 2.9 tons of nitrogen oxides, 0.65 tons of total hazardous air pollutants and 0.4 tons of sulphur oxides (United States Environmental Protection Agency, 2000).

2.3.2 Warm Mix Asphalt (WMA) and Half-Warm Mix Asphalt (HWMA)

Lower mixing and compaction temperatures reduce fumes and odour emissions from plants as well as reducing the energy needed to produce the mixes. This, in turn, improves safety conditions and comfort during application (Aziz et al., 2014; EAPA, 2014b; Vaitkus et al., 2016). A number of techniques have been developed since the mid-1990s to decrease mixing and application temperatures and to reduce the energy required to produce HMAs (EAPA, 2014b).

WMA technologies have gained acceptance in recent years due to the fact that they allow a decrease in mixing and compaction temperatures of HMA mixtures without harming the mix quality. The application of WMA is simple requiring little modifications to the processes used in the production of HMA. The European Asphalt Pavement Association (EAPA) (2014) and Rubio et al. (2012) have reported that WMAs are normally fabricated at temperatures ranging from 100 to 140°C this about 20-40°C lower than that for HMA. Figure 2-3 illustrates how WMA fits into the full range of techniques from cold mixing through to HMA.
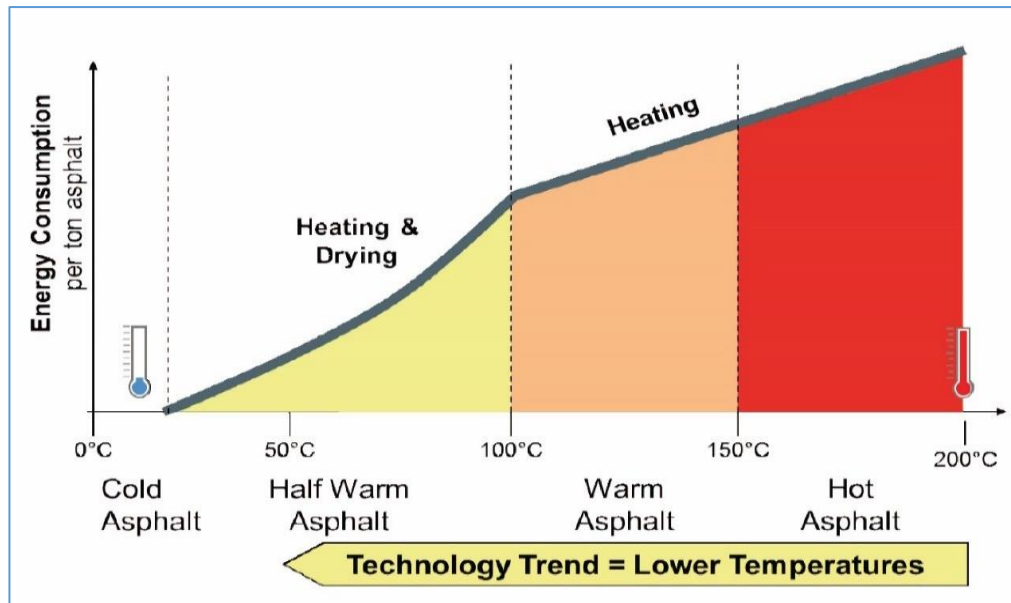
Figure 2.3. Classification by temperature range (EAPA, 2014), permission to reproduce this figure has been granted by Ammann Group

WMA technology also has advantages over CMA and can be considered a better in-service material because firstly, there is no time needed for the curing process before opening up to traffic and secondly, there is no need for a sealing layer as required by some CMA applications. The placement and compaction processes, as well as the process of aggregate coating by the binder, are considered better than those for CMA (Button et al., 2007).

Despite the advantages mentioned above, the production of WMA involves some challenges. There are some worries linked to the cost of WMA because its technologies increase early stage manufacturing costs (Button et al., 2007). The widespread use of WMA technologies also faces some resistance as, to date, there is not sufficient understanding of long-term performance (Kristjansdottir et al., 2007) on top of concerns that the production of additives could create carbon emissions (Zaumanis, 2010). The most common WMA technologies utilized to decrease the viscosity of the binder to allow

better coating and subsequent compactability at lower temperatures are explained below (Capitão et al., 2012; Oliveira et al., 2012; Dinis-Almeida et al., 2016):

➢ Organic additives

These additives, usually waxes or fatty amides, can be added to the mixture or to the bitumen. The additive type must be chosen carefully to guarantee its melting point is above expected in-service temperatures otherwise rutting may occur. Asphalt embrittlement also decreases at low temperatures. Organic additives normally decrease temperatures by 20-40°C in addition to developing resistance to deformation (European Asphalt Pavement Association (EAPA), 2014). Sasobit is the most commonly commercial product manufactured from natural gas utilizing the Fisher-Tropsch (FT) process (Sasol, 2016).

➢ Chemical additives

There is no change in bitumen viscosity when using chemical additives. They normally comprise groups of surfactants, emulsification agents, polymers and additives to enhance coating, the workability of the mixture and compaction as well as promoting adhesion (anti-stripping agents) (Rubio et al., 2012). They decrease frictional forces at the microscopic interface of the aggregates and bitumen at a range of temperatures between 85°C and 140°C. As a result, the working temperature can be reduced by 20-40°C. Rediset^{TM} WMX and Cecabase$^{®}$ RT are examples of chemical additives.

➢ Foaming technology

In order to reduce the viscosity of bitumen, a range of foaming techniques is applied whereby small quantities of water are injected into hot bitumen by different means. The water converts into steam resulting in increased bitumen volume and decreased viscosity for a short period. This expansion of the bitumen allows aggregates to be coated at lower

temperatures while residual moisture supports compaction of the asphalt on site. Foamed bitumen can either be mixed together with aggregates at an ambient temperature or the aggregate can be heated earlier to a moderate temperature (under 100°C) then mixed with foamed bitumen. A number of factors govern the degree of expansion including the amount of water added and binder temperature (Jenkins, 2000).

Half-warm mix asphalt (HWMA) allows the production of asphalt mixtures between 70°C and 100°C representing a decrease in temperature in comparison to hot mixes, of approximately 80°C (European Asphalt Pavement Association (EAPA), 2014). Jenkins et al. (1999) introduced this process which includes applying foamed bitumen to aggregate which has been heated to less than 100°C. Van de Ven et al. (2007) stated that CO_2 emissions during the manufacture of HWMA are 33% lower than in the manufacture of the equivalent HMA while Jenkins (2000) reported that enhanced aggregate coating represents the main benefit of using HWMA. Figure 2-4 presents the relationship between aggregate temperature and coating using various particles sizes of continuously graded aggregate. Three coating aggregate percentages are standard comprising practically no coating (20% or less particle coating); partial coating ranging between 21% and 99% and complete coating (100%).
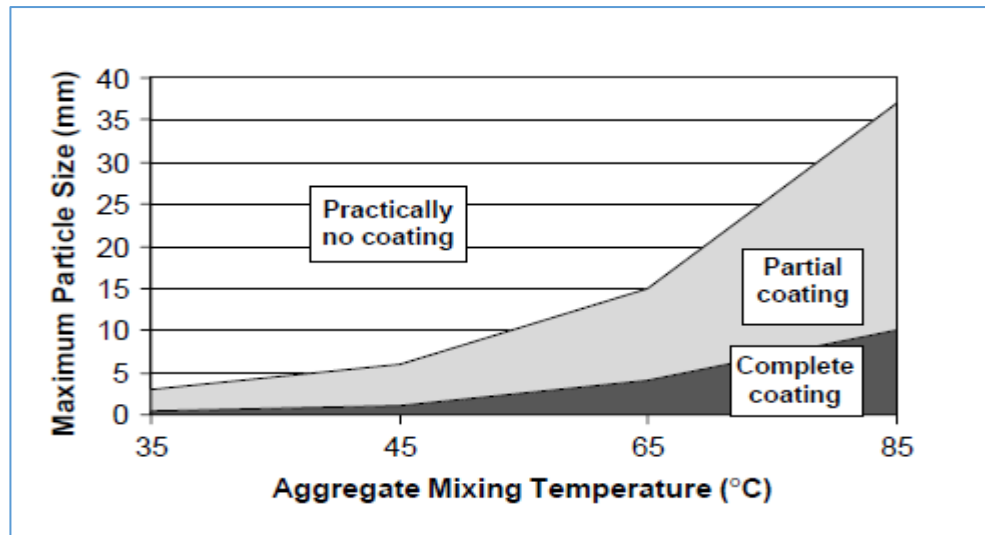
Figure 2.4. Influence of aggregate temperature on particle coating for a continuously graded hornfels mixed with foamed bitumen (Jenkins et al., 1999), permission to reproduce this figure has been granted by Professor Kim Jenkins

2.3.3 Cold Mix Asphalt (CMA)

CMA can be defined as a blend of aggregate with reduced viscosity bitumen binder, prepared and compacted at ambient temperature (Jenkins, 2000). Three methods are employed to produce pre-reduced bitumen; emulsification, cut back and foaming. Although CMAs are safe, environmentally friendly and energy saving (Needham, 1996; Oruc et al., 2006; Mellat et al., 2015), their properties are poor due to the presence of water in the mix and the fact that they needs curing time before opening to traffic, meaning that they are not used for roads which have a high volume of traffic. That said, Needham (1996) suggested that the aggregate in CMA can be used without drying, although the water content must be measured as it has a major influence on the mixture nature. With reference to production, aggregate mixtures are fed into a mixture device such as a pug mill or a rolling drum mixer. Pre-water is added to wet the surface of the aggregate to avoid an early break of the emulsion. Bitumen emulsion is then incorporated until it achieves maximum coating of said aggregates. Over-mixing will cause the

emulsion to break as a result of the input of mechanical energy so care must be taken otherwise a stripped or unworkable mixture will occur. Figures 2-5 and 2-6 illustrate the typical layout for batch and continuous cold mix plants. It is worth noting that the main difference between hot mix plants and cold mix plants is the absence of facilities that are responsible for heating and drying in the latter.

2.4 Types of Cold Bituminous Mixtures

The most common categories of cold bituminous mixtures used are: cold lay macadams, grave emulsions, foamed bituminous mixtures and cold bituminous emulsion mixtures (CBEMs) (Thanaya, 2003).

2.4.1 Cold lay Macadam

This is a mixture of aggregate with a low viscosity bitumen created by the addition of a solvent or flux oil to the bitumen (cutback emulsion). Flux oil is a non-volatile fraction of petroleum used as a diluent to soften bitumen to a more useful consistency. The evaporation of flux oil governs the performance of the cutback emulsion which, in turn, relies on flux volatility and weather conditions. These mixtures are normally used for surface dressings, macadam mixtures and temporary fill material in reinstatement work which has suffered from low stiffness as a result of the presence of flux (Robinson, 1997). The downside is that the solvents used in this are considered to be environmental pollutants, flammable and usually expensive. The use of cold lay macadams as temporary fill materials is uneconomical, this led to the introduction of specifications as far back as 1992 by road authorities in the UK to permit the use of permanent, cold lay surfacing materials (Thanaya, 2003). Nichollas (2004) stated that different solvents could be used individually or collectively including white spirt, kerosene and gas oil.
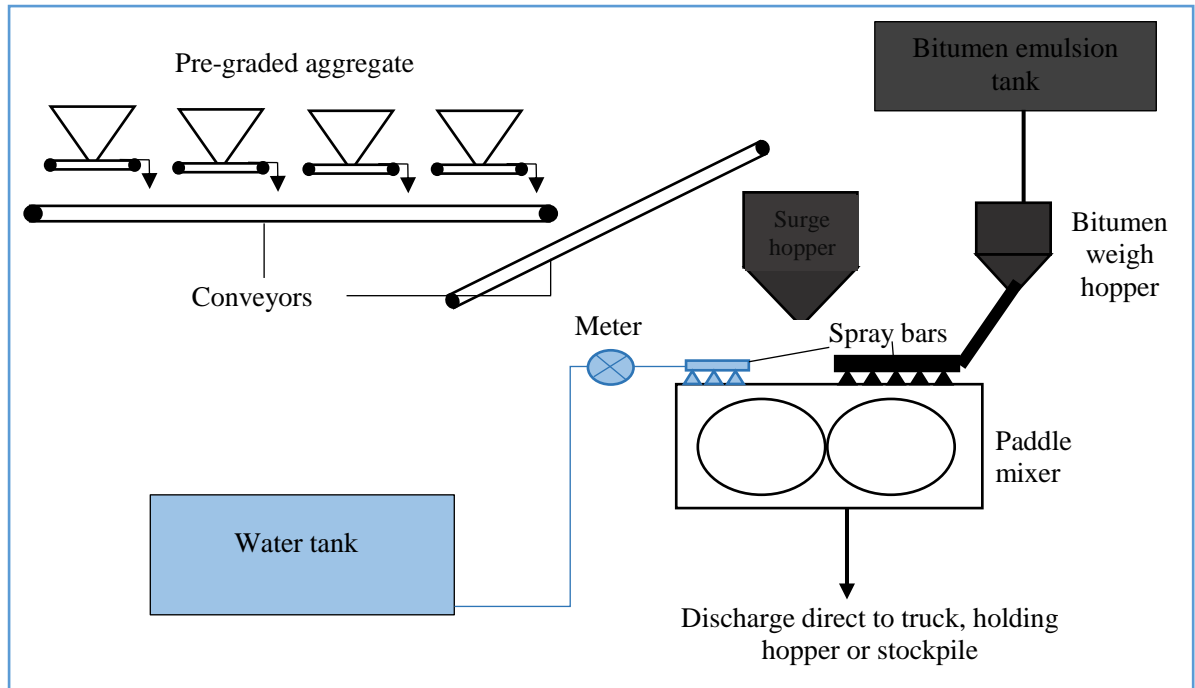
Figure 2.5. Batch cold mix plant, permission to reproduce this figure has been granted by Dr David Needham
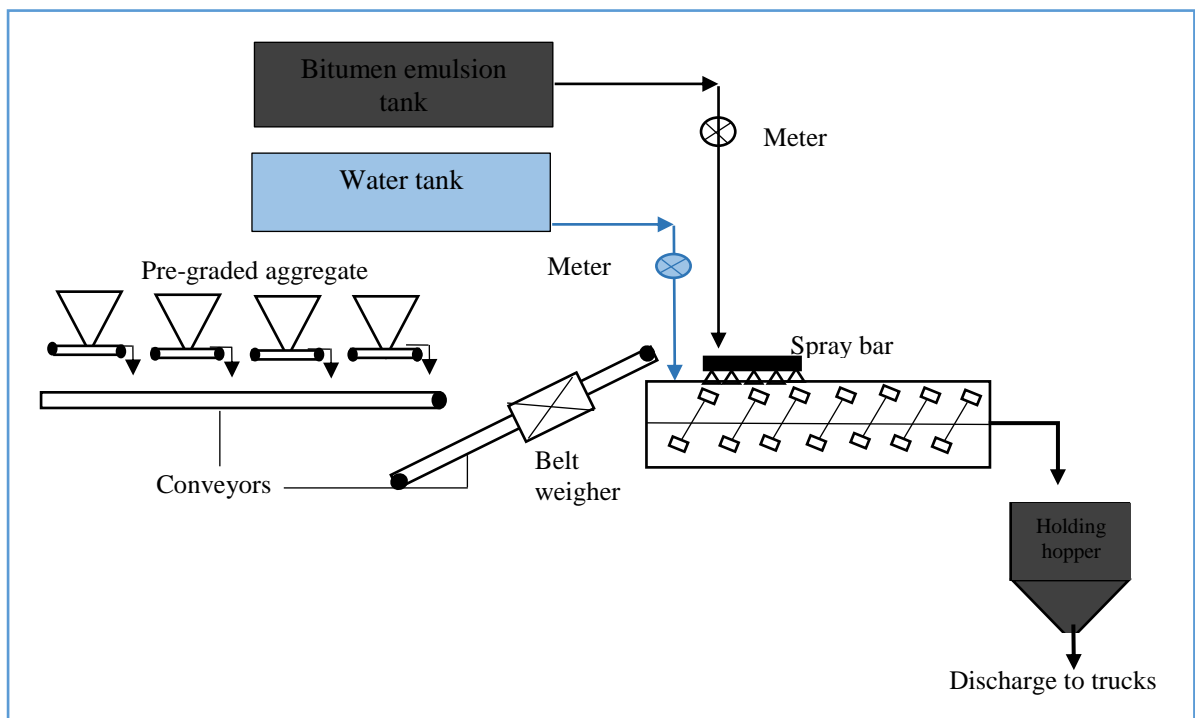
Figure 2.6. Continuous cold mix plant, permission to reproduce this figure has been granted by Dr David Needham

2.4.2 Grave Emulsion

Grave emulsion was firstly launched in France and subject of a specification in 1974 (Needham, 1996). Medium setting bitumen emulsions are designed to be used as a binder mixed with pre-wetted aggregate. Because of the water sensitivity of the mixture, it was used in the southern regions of France where it is warmer and drier. Grave emulsion can be a cost effective substitute to traditional hot asphalts, particularly in remote areas where the nearest hot mix plant is too far away. These mixtures are appropriate for base and surface courses (Thanaya, 2003).

Ojum (2015) reported that grave emulsion has also been used for the construction of low trafficked roads and to overlay cement bound bases to avoid crack propagation. Aggregates with a nominal size of either 20mm or 14mm can be crushed rock or gravel as long as they satisfy French standards on durability, angularity and cleanliness for use in continuously graded virgin aggregate mixtures.

Grave emulsion usually has a lower binder content (3-3.5%) which provides partial coating of the aggregate compared with other types of cold mixtures, this increases rutting resistance by promoting higher aggregate contact. However, recently, higher binder contents of 4% or more are being used making the mixtures less sensitive to water ingress (Ojum, 2015). Emulsification coats the fine aggregate with bitumen before partial coalescence happens, the fine coated mastic then acts as a discontinuous cement binding the larger aggregate matrix together. This claims to address underlying cracks from propagation up through the layer of grave emulsion (Needham, 1996). The mixture is kept uncovered for many months, subject to the weather conditions, to permit satisfactory curing before an overlay is utilized. A simple mobile variety plant, as shown in Figure 2-6, is used to blend grave mixtures as they are often employed in fairly remote regions.

2.4.3 Foamed Asphalts

This technique was first promoted by Prof. Ladis H. Csanyi at Iowa State University, USA in 1956. Initially, foamed bitumen was manufactured by injecting water into hot bitumen; the ensuing steam is trapped in thousands of tiny bitumen bubbles which increase the volume of the bitumen and decrease its viscosity for a short period. Thereafter, the foam disperses in under one minute, the bitumen resuming its original characteristics. Due to the increase in volume, this bitumen will coat aggregates at lower temperatures when it is in its foamed state. In 1968, Mobile Oil Australia introduced enhancements to the production method by adding cold water as a substitute for steam, creating a more economical and simpler production method (Muthen, 1998; Ebels, 2008). Figure 2-7 gives a schematic of foamed bitumen manufacture where flowing water and hot bitumen are combined in a mixing chamber, the resulting mixture discharged through a spray head onto aggregates in the pug mill. This technology gained popularity, the mix broadly accepted as potential material for pavements in many countries such as France, New Zealand, United Kingdom, South Africa, Norway and Germany (Sunarjono, 2008). In the mid-1990s, a system was developed by Wirtgen injecting both water and air into the hot bitumen in an expansion chamber as shown in Figure 2-8. Water in the range of 1% to 5% by mass of bitumen in combination with compressed air was injected into hot bitumen (140°C to 180°C) leading the water to convert into vapour, generating tiny bitumen bubbles (Kuna, 2014).

Foaming increases the bitumen surface area and substantially decreases its viscosity making it appropriate to mix with both cold and wet aggregates. When the air escapes, the foam collapses leaving a bitumen residue, with similar properties to the original bitumen, to coat the aggregate. The main benefit of using foamed bitumen is that it makes use of a standard penetration grade bitumen utilising only a small ratio of water, normally

about 2%, by bitumen mass meaning that foamed bitumen can be laid, compacted and opened to traffic almost immediately, remaining workable for longer and can also be stockpiled for later use (Wirtgen, 2004).
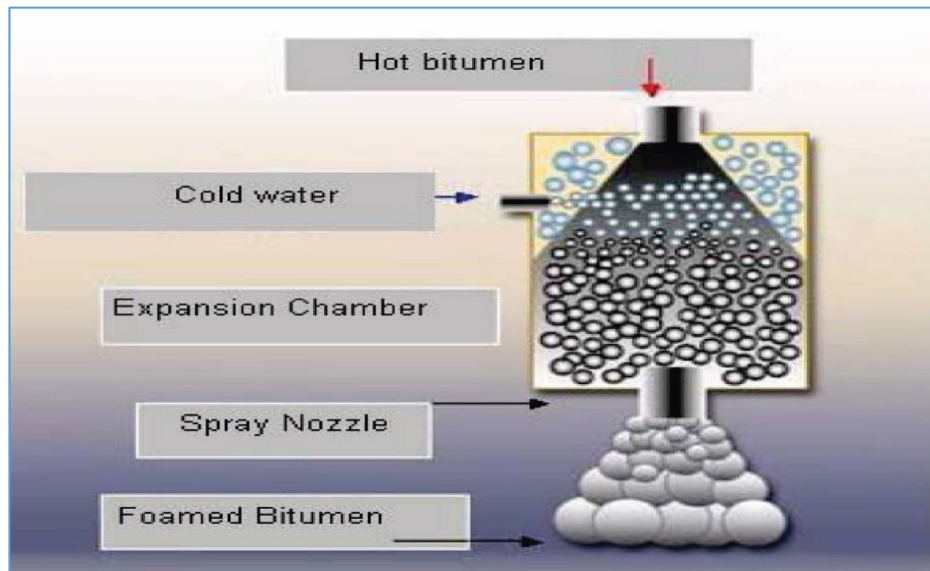
Figure 2.7. Schematic of foamed bitumen by Mobil Oil organisation technique (Jenkins, 2000), permission to reproduce this figure has been granted by Professor Kim Jenkins
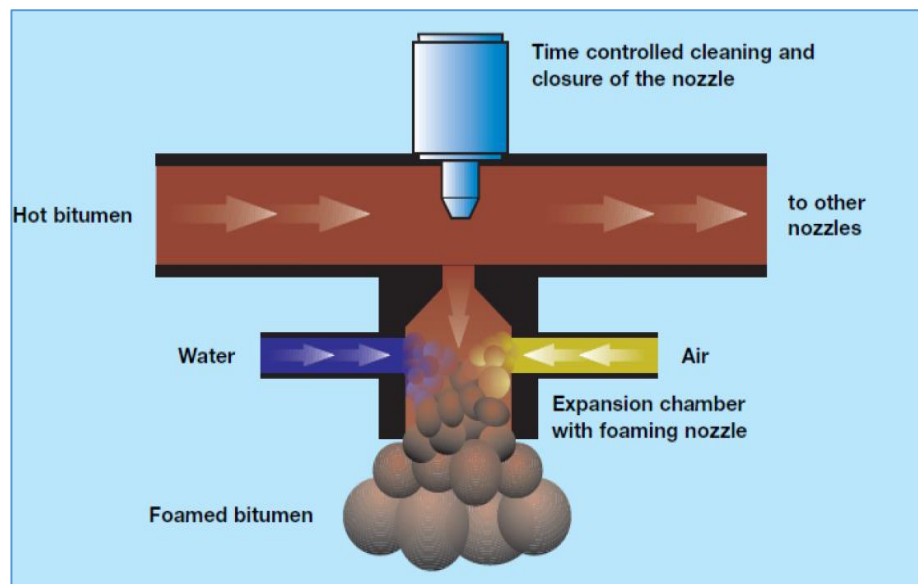
Figure 2.8. Schematic of foamed bitumen by Wirtgen, permission to reproduce this figure has been granted by Wirtgen GmbH

2.4.4 Cold Bituminous Emulsion Mixtures (CBEMs)

CBEMs are well known types of CMAs that use bitumen emulsion as a binder (Thanaya, 2003). A multi-part material, CBEMs comprise no less than four major constituents: bitumen, graded mineral aggregate, water and air. In contrast to HMAs, CBEMs may take from a few months to a few years to develop their ultimate strength and associated properties (Nikolaides, 1983). That aside, and in response to growing concerns over global warming and rising greenhouse gas emissions, the asphalt industry is looking for alternatives to HMA (Vaitkus et al., 2016; Dinis-Almeida et al., 2016). A reasonable solution is the use of CBEMs technologies which allow mixing, laying and compaction of mixtures with no heating.

However, there are shortcomings associated with CBEMs such as their low early life strength, the long curing time necessary to achieve maximum performance and high air void content which results in limited application in, for example, low/medium low trafficked roads, footways and reinstatements (Leech, 1994; Read and Whiteoak, 2003; Thanaya, 2003; Gómez-Meijide and Pérez, 2014b; Ojum, 2015). Using CBEM as a structural layer is very restricted; it has rarely been used for heavy duty pavement layers (Doyle et al., 2013), because of the long period required to reach full strength after paving, especially in the UK, as well as higher sensitivity to rainfall at early stages of installation (Oruc et al., 2007b). Serfass et al. (2004b) demonstrated that there were evolutional characteristics exhibited by such mixtures, especially during their early life, where the initial cohesion is low and builds up progressively. CBEMs also exhibit unusual behaviour, particularly during their early life. A combination of factors leads to this unusual behaviour: water presence; reactivity resulting from aggregate emulsion; binder film coalescence and the build-up of cohesion.

After several research studies by the Chevron Research Company in California, Leech (1994) reported that full curing of cold asphalts may take anywhere between 2-24 months. However, the story is different in the UK where climatic conditions, cold, humid and wet, do not help to reduce curing time. Previously, CBEMs were only produced with open or semi-dense graded mixtures permitting better air flow due to greater air voids. However, CBEMs can now be used with dense gradations due to the enhancements in emulsion technology and mixing techniques (Thanaya, 2003). Gap graded mixture can also be applied especially if an active filler is incorporated (Al-Hdabi et al., 2013a).

2.5 Hot Mix Asphalt and Cold Mix Asphalt: A Brief Appraisal

Hot mix technology is the most commonly used approach for the preparation of asphalts around the world, accounting for around 90% of the total mixes produced. It is the principal material used for structural and surfacing layers from the base through to binder course to surface course, reaching its full properties in a short period of time. Nevertheless, the emissions of gases, which have unpleasant odours associated with the heating process, the risk of fire and melting bitumen create health hazards. Reductions in fumes and emissions will provide a better working environment for those who are involved in the manufacture and placement process of asphalts as it has been found that workers can be exposed to 0.1 to 2 mg/m^3 of bitumen fumes containing 10 to 200 ng/m^3 of benzo(a)pyrene toxic gas (Chauhan et al., 2010). Applying asphalts in places such as tunnels where there is no open air represents a huge challenge to the safety of workers in these conditions due to toxic air emission.

In addition to the above mentioned safety issues, eco-friendliness, energy efficiency and cost effectiveness are also driving the development of CBEMs. With respect to energy saving, it is obvious that cold mixtures are significantly less expensive than hot mixtures. Kennedy (1998) reported that approximately 30 million tonnes of hot mix coated

[roadstone] is used in the UK per annum, this consuming 6 to 7 million MWhs of energy, equivalent to the generation of 1 million tonnes of CO_2. The total energy consumption using cold mix technology equates to around 40% to 60% of that of traditional hot mixtures, a figure that Dinnen (1998) also found with CMA technologies. Bouteiller (2010) stated that the energy required to produce one tonne of CMA equals 13% of that needed to produce a similar quantity of HMA. In addition, the emissions of CO_2 in the case of CMA, is approximately 14% that of HMA as can be seen in Table 2-1 below. According to Bahia et al. (2011), CO_2 emissions per tonne of CMA mix, may be up to 40 % less than that for HMA manufacture.

The paving season, defined by weather constraints, and haulage distance also have an impact on energy consumption. In cold weather, there is a substantial difference between hot mixtures and the ambient temperature meaning that heating is needed to maintain the mix at the required temperature. Hauling long distances also results in a drop in temperature which in turn, represents cost. These points were also identified by Leech (1994) who reported that the main reasons for an increase in the challenges for CBEM technology in the UK are climatic, specifically wet and cold conditions, which do not encourage higher curing rates and the fact that there are less HMA plants available and more remote areas.

Table 2-1. Comparison between CMA and HMA in terms of CO_2 emission and energy consumption (Bouteiller, 2010)

Process of production	CO_2 (kg/MT)	Energy (MJ/MT)
HMA	21	277
CMA	3	36

A comparison between cold and hot mixtures is shown in Table 2-2 by Taylor (1997) illustrating the differences between the two technologies in the manufacture and placement process.

Table 2-2. General comparison between cold mixture and hot mixture (Taylor, 1997)

Cold mixture	Hot mixture
Storage of binder at refinery in cold state	Storage of binder at refinery in hot state
No special transport required for either binder or mixture	Special tankers required with heating for binder. Lagged and sheet lorries necessary for transport of mixture
Simple storage plant	Heated and lagged storage and pipes at plant
Mixed cold with damp aggregates	Mixed hot with pre-dried aggregates
Easy to store mixed materials	Storage needs care
Placement and compaction have wide time and temperature ranges	Laying and compaction have a narrow time and temperature window
Minimal effect of temperature variation	Hot weather creates the danger of wheel tracking and over embedment of chippings. Cold weather can result in poor compaction

2.6 Stages of CBEMs Process

Taylor (1997) described three stages in the preparation of CBEM during which the emulsion is expected to accomplish various functions:

➢ Mixing stage: the first stage where the emulsion is mixed with the aggregates. The emulsion must remain stable and coat coarse and fine aggregate particles uniformly.

➢ Storage and laying stage: in this stage the emulsion must remain workable and partly broken as this allows resistance to moisture and rain. The mixture must also not be drained after mixing with the aggregates.

➢ Compaction stage: this stage requires a quick break by the emulsion in order to revert back to its original base bitumen.

Most emulsions need comparatively long curing times to allow evaporation of the volatiles that lead to a complete break thus achieving maximum strength.

2.7 Worldwide Practices for CBEM Mixtures

CBEM technology has been widely utilised by the pavement industry in several countries such as the USA and France where it has been used since the 1970s (Leech, 1994). Annual manufacturing levels reached 1.5 million tonnes in France alone (EAPA, 2014a). Such usage has also enabled the development of a clear understanding of the performance of these mixtures. Due to the weather conditions in the UK, which do not facilitate the curing process of emulsion mixtures, this technology has only lately came to the fore. Acknowledgement of CBEM technologies was partly due to the publication in 1992 of 'Specification for Reinstatement of Opening in Highways' by the Highway Authority and United Committee (HAUC), allowing the use of Permanent Cold Lay Surfacing Materials (PCSMs) as a substitute to hot mixture materials for reinstatement works in low volume roads and footpaths.

CBEMs are used in other countries European countries as well as South Africa, Australia, New Zealand and the USA (Ojum, 2015). A brief discussion follows on the different approaches used in France, Sweden, Spain, South Africa and the USA.

2.7.1 USA

In the USA, CBEMs are termed Emulsified Asphalt Materials (EAMs). The design of EAMs are detailed in the Manual Series (MS-19) 3rd Edition 1997, issued by the Asphalt Institute. The Asphalt Institute Design Manual (MS-1,1991), classifies EAMs into three categories as listed below (Thanaya, 2003):

➢ EAMs Type 1: EAMs made with processed, dense graded aggregate.

➢ EAMs Type 2: EAMs made with semi-processed, crusher run, pit run or bank run aggregates.

➢ EAMs Type 3: EAMs made with sand or silt.

The grade of base bitumen depends on an acceptable coating; the percentage of coating necessary for surfacing materials is 75% and 50% for bases. Type I EAM's do not need complete coating of aggregate but the aggregate particles should have 65% of crushed faces for a good interlock. Slow setting emulsions are often used with 0.5% to 2% Ordinary Portland Cement (OPC) added to enhance strength at early life.

EAMs Type I are considered to have a strength equal to that of asphalt concrete. It is recommended that the thickness of the layer should not exceed 50 to 75 mm to speed up curing which may take between 2 months to 2 years. If necessary, any additional upper layers of EAM should be placed after early curing of the lower EAM layer is complete as they require a good level of compaction.

Thanaya (2003) reported that two main methods of design have been developed; the Hveem Method and the Marshall Method, development including recent modifications.

2.7.2 France

In France, grave emulsion is used extensively as a base material to re-profile, overlay and strengthen deteriorated pavements as mentioned before in section (2.4.2). Vivier and

Brule (1991) developed a novel gap graded, cold asphalt concrete which offers enhanced skid resistance, durability and wearing resistance by using a gap graded aggregate in addition to bitumen emulsion. In manufacture, two types of additives are applied, namely polyacrylonitrile fibres and a polymer, EVA (ethyl vinyl acetate). Fibre addition is 0.1-0.2% dosage by total dry aggregate weight with 4 mm length. The aim of this fibre addition is to decrease chip loss, reduce mixture segregation and improve shear strength after curing while EVA is added to the binder to improve cohesion, temperature sensitivity, rheological behaviour and adhesion properties.

2.7.3 Sweden

Cold recycled asphalt materials are usually used in Sweden for flexible pavements because of the high volume of old pavements which are recycled, approximately 1 million tonnes each year (Jacobson, 2002). It is applied in the form of surface courses, binder courses or bases to roads with low traffic volume (Average Daily Traffic (ADT) less than 1500 vehicles per day). Regarding binder courses, the maximum RAP aggregate size is restricted to a sieve size of 22 mm. This process can be considered a cost effective and environmentally friendly practice since there is no heating involved. Recently, Mellat et al. (2015) developed image-based models of CMA to investigate the morphology effect on mechanical performance. A parametric study of the interface properties is achieved connected to the aggregate bitumen interface strength because of the process of coalescence.

2.7.4 Spain

Emulsion mixtures have been used in Spain since the late 1950s (Needham, 1996), comprised of either gravel or open graded mixtures. High viscosity, medium setting, cationic or anionic emulsions are used in open graded mixtures to ensure a thick coating of bitumen on the aggregate. These mixtures normally have around 20% voids which

provides mixtures that are resistant to fatigue cracking, have good resistance to skidding due to the surface friction and satisfactory drainage of the mixture, and also have more deformation resistance due to the interlocking of large aggregate. In addition, thick binder films used in these mixtures are resistant to aging. It was found that these mixtures are more stable when in storage but still cure faster once placed. Needham (1996) reported that polymer modification of the binder has been employed in such mixtures to further improve their properties.

2.7.5 South Africa

The use of bitumen emulsion for base construction in South Africa is driven by Sabita (South African Bitumen Association). Realising the potential of this approach, Sabita published different design instructions and standards in 1993 and 1999. Using a Heavy Vehicle Simulator (HVS), considered to be an ideal tool for accelerating the testing and assessment of the performance of emulsion based mixtures, test results revealed that the material was a reasonable choice and that the addition of cement or lime improved strength and durability as well as improving the resistance to cracking of the mixtures (Needham (1996).

 Curing methods for bitumen emulsion treated materials specify firstly curing the samples at ambient temperatures for 24 hours, followed by 48 hours at 40°C (if the optimum moisture content is lower than 8%), or 45 hours at 60°C (if the optimum moisture content is more than 8%). Another curing method is to keep the samples in the mould for 7 days at ambient temperature when cement is included, or in the case where no cement has been included, for 28 days at ambient temperature (Ojum, 2015).

2.8 Curing of CBEMs

In contrast to traditional asphalts, appropriate curing is required for CMAs so that mixtures can achieve full strength as the water content evaporates (Thom, 2009). Jenkins (2000) described the curing process of cold bituminous mixes as where the mixture discharges water over evaporation, repulsion of particle charge or pore pressure induced flow paths. The consequent decrease in moisture content results in an increase in the strength of the mix (both tensile and compressive).

Serfass et al. (2004a) recounted that cold emulsion mixes show peculiar behaviours, particularly in their early life, due to the combination of factors such as the presence of water, reactions of the aggregate emulsion, binder film coalescence and development of cohesion. He recommended an accelerated curing of 14 days at 35°C. Adding to the discussion, Oke (2010) found that cold mixes seldom become fully dry in field conditions; moisture contents have frequently been found to be between 0.5% and 1.5% in road bases in temperate climates.

Ruckel et al. (1983) suggested that to produce mature cold mixtures that represent field conditions, specimens should be cured for 1 day at 40°C, this simulating intermediate curing, and at 40°C for 3 days to simulate long term curing. He also recommended curing at temperatures higher than 60°C to stiffen the binder and thus change the properties of mixtures. Bocci et al. (2002) observed that when both curing time and curing temperature rise, the performance of mixtures is significantly enhanced; curing for 14 days at 20°C is almost comparable to 7 days at 40°C.

Another curing regime proposed by the UK Highways Agency's Manual of Contract Documents for Highway Works (MCHW) Volume 1 Series 900 Clause 948, suggests either 40±2°C or 20+2°C for 28 days depending on the mix bond; cementitious, hydraulic

or bituminous binders individually or in combination. This approach also recommends keeping moisture in the specimens by sealing them. These curing regimes simulate field conditions over the first year of life of the road.

2.9 Design Procedure for Cold Bituminous Emulsion Mixtures (CBEMs)

At present, there is no universal design procedure for CBEMs, however several design procedures have been suggested by different road authorities and research organizations. The majority of these procedures are based on American design procedures, e.g. the Asphalt Institute or AASHTO, with some amendments. The following sections provides a brief description of the four main design procedures for CBEMs, namely: Asphalt Institute design procedures, the design procedure of the Ministry of Public Work, Republic of Indonesia, Nikolaides' design procedure and the Nynas test procedures.

2.9.1 Asphalt Institute Design Procedures

Two design methods for emulsified asphalt aggregate cold mixtures are given in the Asphalt Institute Manual Series No.14 (MS-14); the modified Haveem method and the Marshall method. The former requires specific equipment which is less widely available while the latter uses Marshall testing equipment. The Marshall Method for emulsified asphalt aggregate cold mixture design was established through research carried out at Illinois University. The detailed design procedure is described in manual series MS-14 and has been largely adopted by the current author in this investigation.

The design procedure (Asphalt Institute, 1989) comprises:

- ➢ Selection of suitable aggregate grading.
- ➢ Obtaining an Initial Emulsion Content (IEC) and Initial Residual Bitumen Content (IRBC) based on empirical formula.

➢ Carrying out a coating test to appraise the ability of the emulsion to coat the aggregate particles and decide the Optimum Pre-Wetting water content (OPWwc).

➢ Determination of Optimum Total liquid amount at Compaction (OTLC) based on the maximum dry density of CBEMs.

➢ Indication of the Optimum Residual Bitumen Content (ORBC) for the selected grading.

In 1997, the Asphalt Institute in association with the Asphalt Emulsion Manufacturers Association (AEMA), published their latest manual on asphalt emulsions; Manual Series (MS-19) 'Basic Asphalt Emulsion Manual', 3rd edition (Asphalt Institute and Asphalt Emulsion Manufacturers Association, 1997). In this version, some changes were made to the MS-14 manual which can be summarized as follows:

➢ Bitumen emulsion can only be used if the degree of coating of aggregate particles after a specific adhesion test, remains within an acceptable range.

➢ There are no requirements for OTLC in comparison to MS-14, but mixtures should be air dried until neither too wet nor too dry for compaction.

➢ The specimens are cured by keeping them in the compaction mould in an oven at 60°C for 48 hours, after which a static load is applied, 178 kN load for 1 minute, whilst the samples are still at 60°C, with the aid of a double plunger at each side of the sample.

2.9.2 Design Procedure of the Ministry of Public Work Republic of Indonesia, 1990

Thanaya (2003) described this design procedure as covering two main types of mixtures; open and dense graded emulsion mixtures. The design procedure itself is principally dependant on AASHTO and is comparable to the Marshall design procedure explained in the Asphalt Institute MS-14 (1989), albeit with some modifications which take regional and national conditions in Indonesia into account. Described as a modified Marshall test

procedure, a Marshall testing frame is used to test specimens at ambient temperature. Pre-conditioning the samples in water at 60°C for 30 minutes is not recommended for this test.

2.9.3 Nikolaides Design Procedure

Nikolaides combined both the American Standard and the Ministry of Public Work Republic of Indonesia procedures to create a hybrid design. He also introduced a method to characterise permanent deformation performance which is governed by controlling the maximum allowable bitumen content. The relationship between the residual bitumen content (RBC) and the creep stiffness coefficient (CSC) is important as it indicates the maximum residual bitumen value (Thanaya, 2003). Nikolaids (1994) stated that the CSC is obtained from the results of creep strain as measured by the 1 hour static creep test, normally performed at 40°C under 100 kPa vertical applied static stress. The mixture stiffness (S_{mix}) for a specific test of any bitumen content, can be determined at any time of loading. The stiffness of bitumen (S_{bit}) can also be calculated individually using the Van der Poel nomograph.

2.9.4 Nynas Test Procedures

Nynas tests are only used on loose mixtures during storage or before laying and are known as runoff, washoff and workability tests.

In the runoff test, 500g of loose bitumen emulsion mixture is poured into a funnel with a mesh (< 2 mm) at the bottom. The quantity of bitumen that runs off in 30 minutes is measured. This is followed by the washoff test which is performed while the mixture in the funnel; 200 ml of water is poured over the mix. Both the wash water and any wash-off bitumen is collected and measured. Finally, the workability test is carried out using a Nynas workability tester. This identifies the maximum force required to shear off the top

of the uncompacted CBEM during storage or just before placing, performed by scraping a small amount of the surface layer off the mixture.

Table 2-3 below presents a comparison in terms of sample preparation and testing procedures, for these mixture designs.

Table 2-3. Summary of procedures for samples preparation and treating

Description	The Asphalt Institute, MS-14	Nikolaides	MPW Indonesia
Degree of coating (%), for: Binder course Surface course	 50 75	 85 85	 75 75
Compaction (Marshall hammer)	2 x 50 blows	2 x 50 blows	2 x 50 blows
Curing in mould	24 hours at room temperature	24 hours at room temperature	24 hours at room temperature (28 ± 1°C for tropical climate)
Curing in oven	24 hours at 38°C	24 hours at 40°C	24 hours at 40°C
Sample testing temperature	22.2°C	Room temperature	28 ± 1°C
Soaking procedures	Submerge the sample in water and vacuum saturated at 100 mm of Hg for 1 hour, followed by submersion in water (no vacuum) for an additional 1 hour at 22.2°C	Capillary soaking: half the depth of each compacted sample is soaked in water at room temperature for 24 hours. The sample is then inverted and the other half soaked for 24 hours	Capillary soaking: half the depth of each compacted sample is soaked in water at room temperature (28 ± 1°C) for 24 hours. The sample is then inverted and the other half soaked for a further 24 hours

CHAPTER 3

LITERATURE REVIEW II- BITUMEN EMULSIONS

3.1 Introduction

Bitumen is a thermoplastic material used as a binder in road construction. A highly viscous semi-solid material at room temperature, it is heated to between 100-200°C until it reaches sufficient fluidity to mix with aggregate. This process is costly - ecologically, socially and financially - resulting in research to develop alternative road pavement techniques including improvements to mixtures manufactured at lower temperatures. There are several processes available to decrease bitumen viscosity and facilitate mixing with mineral aggregates such as raising the temperature by heating (hot mixtures), dissolving it in a petroleum solvent (cutback bitumen), emulsification in water to form bitumen emulsion and foaming the bitumen (Read and Whiteoak, 2003; Thanaya, 2003).
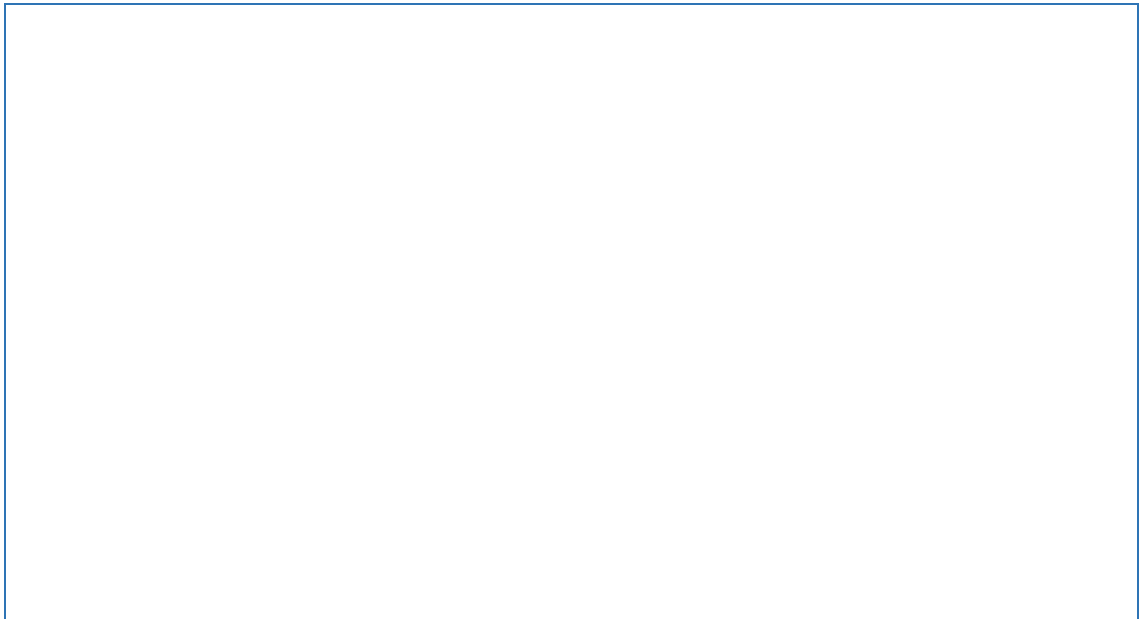
3.2 Bitumen Emulsion Technology

James (2006) and Akzo Nobel (2008) define emulsion as the dispersion of small droplets of one liquid into another. In contrast to creating a solution, the two liquids are co-existent rather than mutually mixed (Needham, 1996). Bitumen emulsion can further be defined as a two phase system involving bitumen and water and one or more additives to support formation and stabilisation, and to modify the properties of the emulsion (Read and Whiteoak, 2003).

Bitumen emulsions were initially developed in the early 1900s, coming into common use as pavement applications in the 1920s (James, 2006). Le Coroller (1999) described how, at that time, they were mainly used in spray sealing applications to stop dust from the ever increasing traffic on roads. Currently, emulsion usage has grown for reasons connected with the environment, cost and technical preparation, becoming an attractive

choice in the industry; they are non-flammable, can penetrate porous materials and can have good coating capabilities of damp aggregate surfaces (Thanaya, 2003; Asphalt Emulsion Manufacturers Association (AEMA), 2009). Le Coroller (2002) detailed the world consumption level of bitumen emulsions as seen in Table 3-1.

Table 3-1. Bitumen emulsion usage (Le Coroller, 2002)

The diagram originally presented here cannot be made freely available via LJMU Digital Collections because of 'copyright'. The diagram was sourced from Le Coroller (2002)

Currently, one of the main objectives of using bitumen emulsion is to develop a product that does not require heating (Asphalt Emulsion Manufacturers Association (AEMA), 2009). This will decrease emissions and the consumption of energy, avoid oxidation of asphalt and be less hazardous (James, 2006).

Emulsions can be classified into three general groups (Akzo Nobel, 2008; James, 2006): oil-in-water (O/W), water-in-oil (W/O) and multiple phase emulsions. The first are those in which the continuous phase is water with oily liquid dispersed in it while water-in-oil (W/O) emulsions are those in which oil is the continuous phase and water the dispersed phase. Water-in-oil emulsions are occasionally termed inverted emulsions. More complex

multiple phase emulsions can be created by which the dispersed droplets themselves contain droplets of a smaller size, usually comprising the same liquid as in the continuous phase (Akzo Nobel, 2008). Figure 3-1 illustrates the three emulsions types. Standard bitumen emulsion is normally oil in water consisting of base bitumen (40% to 75%), water (25% to 60%), emulsifier (0.1% 2.5%) and other minor components (James, 2006).
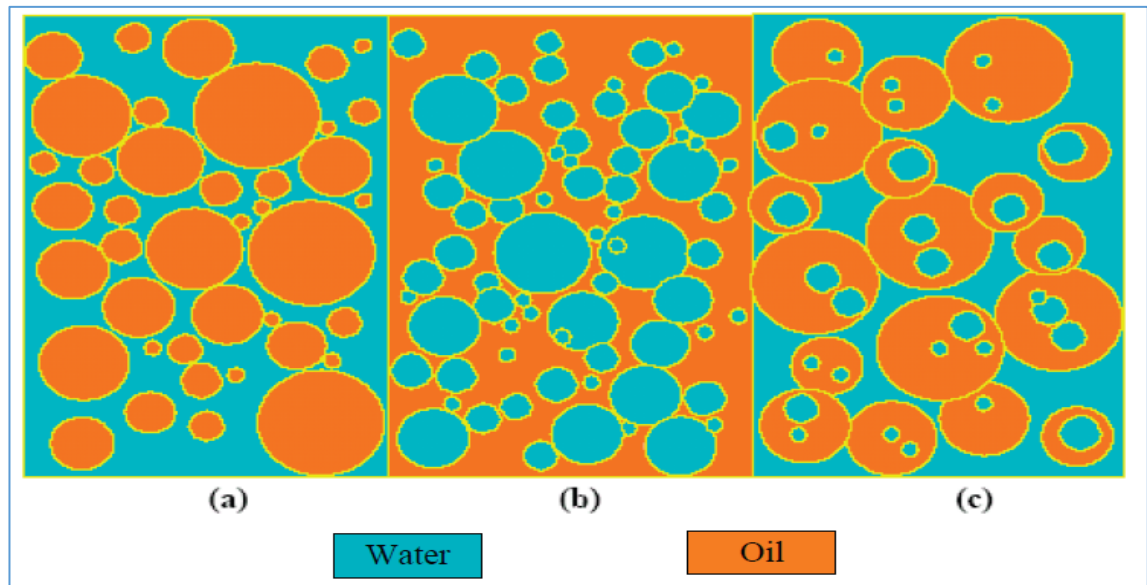
Figure 3.1. The three groups of emulsion, (a) oil-in-water emulsion (b) water-in-oil emulsion (c) multiple emulsion (James, 2006), permission to reproduce this figure has been granted by the Transportation Research Board

3.3 Bitumen Emulsion Composition

> **Bitumen and water**

The main constituent part of bitumen emulsion is bitumen, in most cases comprising 40 to 75% of the emulsion depending on the intended application. It is a mixture of organic liquids that are highly viscous, black, sticky, completely soluble in carbon disulphide and which consist mainly of highly condensed, polycyclic aromatic hydrocarbons (Bonner, 2001). Bitumen is produced from the distillation of crude petroleum and is manufactured in a wide range of grades whose characteristics differ from hard and brittle to soft and

viscous at service temperatures. Most emulsions are produced with bitumens in the 60-250 penetration range where the choice of grade for use is governed by the climate and conditions of end use; low viscous base bitumen is appropriate for colder climates and vice versa (James, 2006). Bitumen is a non-polar, complex material in that there is a uniform distribution of electrons in the constituent molecules across the structure, there being no regions of charge concentration or deficiency. That said, it does contain some polar constituents.

The second component used in the production of bitumen emulsions is water which makes up between 25% to 60% of the emulsion (James, 2006). Water, in contrast to bitumen, is a polar medium comprising of different ionic species, for example H_3O, OH^- and H^+, and the polar water molecule itself. The polarity of the H_2O molecule is attributed to oxygen, an electronegative atom, and hydrogen which is electropositive. If polar and non-polar composites are mixed under normal circumstances, the two constituents will separate as the molecules in the polar medium strive to be in contact with each other in order to cancel out positive and negative regions of charge (Needham, 1996).

> **Emulsifiers or surfactants**

Emulsifiers are responsible for providing globule surfaces with electrical charges which simplify the dispersion of bitumen keeping the bitumen globules in permanent suspension; as a result, a homogenous emulsion can be achieved (Thanaya, 2003) comprising 0.1% to 2.5% emulsifier. The bitumen droplets in the emulsion are either positively (cationic) or negatively (anionic) charged. The emulsifier which is active on the surface of the bitumen droplet is responsible for this electrostatic charge. This means that the emulsifier is a surface active agent, also known as surfactant (Asphalt Institute and Asphalt Emulsion Manufacturers Association, 1997; James, 2006; Akzo Nobel,

2008). According to Read and Whiteoak (2003), several functions are performed by the emulsifier within a bitumen emulsion as follows:

- Creates a decrease in the interfacial tension between bitumen and water to make emulsification easier.

- Dictates whether the emulsion is water-in-oil or oil-in-water.

- Stabilizes the emulsion by avoiding droplet coalescence.

- Dictates the performance characteristics of the emulsion such as setting rate and adhesion.

Read and Whiteoak (2003) also stated that surfactants must be water soluble in order to be effective. The ionic part of the emulsifier is situated on the surface of the bitumen droplet in the emulsion whereas the hydrocarbon chain positions itself on the surface of the bitumen and is firmly bound to it as illustrated in Figure 3-2. Emulsifiers molecules have hydrophobic (oil-loving) and hydrophilic (water-loving) portions (Thanaya, 2003), Figure 3-3.

Figure 3.2. Schematic diagram of charges on bitumen droplets (Read and Whiteoak, 2003), permission to reproduce this figure has been granted by Shell International Petroleum Company Limited
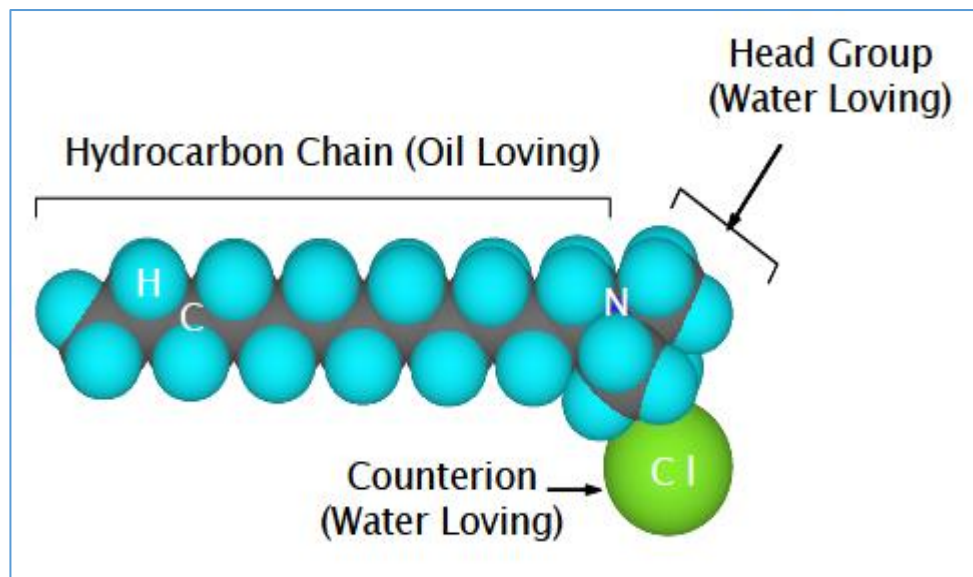
Figure 3.3. Emulsifier structure (James, 2006), permission to reproduce this figure has been granted by the Transportation Research Board

Emulsifiers can be categorised into anionic, cationic and nonionic according to the charge their head groups adopt in water (James, 2006). Cationic emulsifiers are principally acidic

solutions, characterized by large cation organic fractions. Cetyl trimethyl-ammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$) is a typical example of this kind of emulsifier. This type of emulsifier dissociates in water into the positive cetyl trimethyl-ammonium cation ($C_{16}H_{33}(CH_3)N^+$) and the negative anion bromine (Br^-) (Thanaya, 2003). An example of a cationic emulsion system is shown in Figure 3-4.

Anionic emulsifiers are usually stabilized with fatty acids or sulphonate emulsifiers (Read and Whiteoak, 2003). Thanaya (2003) explained how anionic emulsifiers have a pH more than 7 and that they comprise large anionic ions, an example being sodium stearate ($CH_3(CH_2)_{16}COONa$). This emulsifier dissociates in water into (negative) stearate anions ($CH_3(CH_2)_{16}COO^-$) and (positive) sodium cations (Na^+). Stearate anion is soluble in bitumen within the carboxylic group (COO^-) that carries a negative charge, the least soluble part, producing bitumen globules with negative charges on the surface. Positively charged ions are then attracted to the negatively charged ions to create electrical double layers (Figure 3-5). These charges on the globules repel each other and form the emulsion system.

Non-ionic emulsifiers are seldom used for road emulsions. They can be used to make ethers and esters that are required for producing fatty acids and alcohol. Similarly, colloidal emulsifiers are commonly used for industrial purposes and not for road emulsions.

> **Stabilizers**

Bitumen may include salt remains because of insufficient desalting of the crude oil source. This results in swelling of the bitumen droplets through osmosis as water is drawn into the droplets giving increased emulsion viscosity, also creating an effect on stability. In cationic emulsions, calcium chloride or other soluble salts are added at 0.05% - 0.2% during the water phase of the emulsion to decrease water osmosis into the bitumen, this

minimizing changes in viscosity (Thanaya, 2003). Trisodium polyphosphate is used for the same reason in anionic emulsions.

➢ **Solvents**

Solvents can be added to emulsions to enhance emulsification, decrease settlement, enhance the rate of curing at low temperatures or to produce the correct binder viscosity after curing (James, 2006). Thanaya et al. (2006) also found that solvents such as white spirit will improve coating ability.
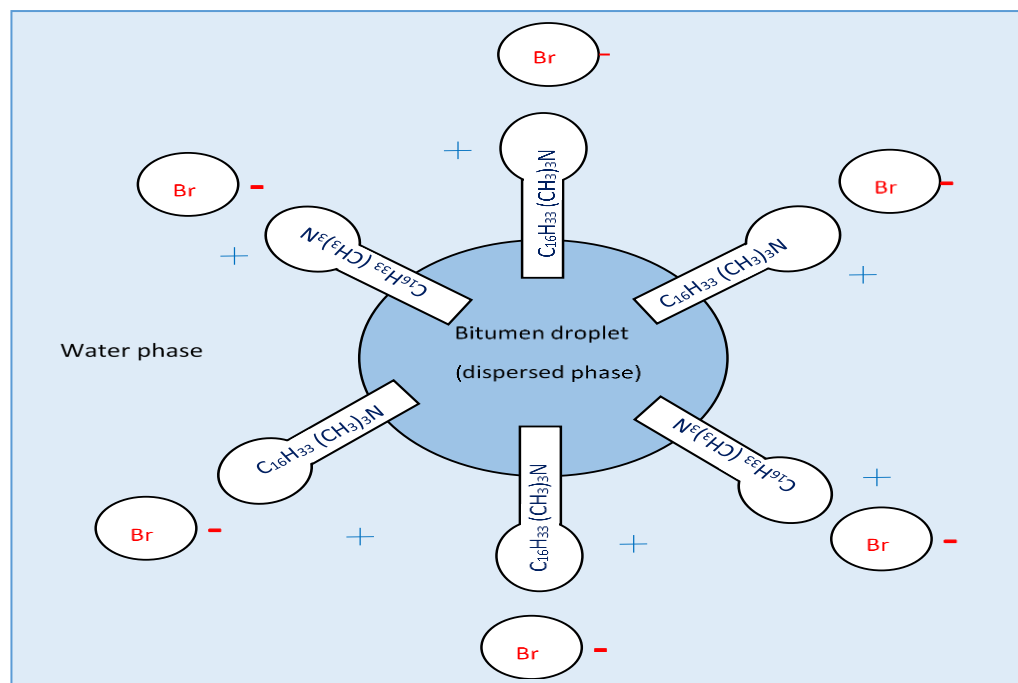
Cetyl trimethly-Ammonium Bromide: $C_{16}H_{33}(CH_3)_3NBr$, dissociates in water to become: i) Bromide Anion, Br^- (in water/ continuous phase). ii) Cetyl Trimethylammonium Cation, (large portion), $C_{16}H_{33}(CH_3)N^+$, (in the bitumen globules/ discontinuous phase).

Figure 3.4. Diagrammatic illustration of the arrangement of cationic emulsifier around dispersed bitumen globules in typical emulsion (Thanaya, 2003), permission to reproduce this figure has been granted by Dr Arya Thanaya
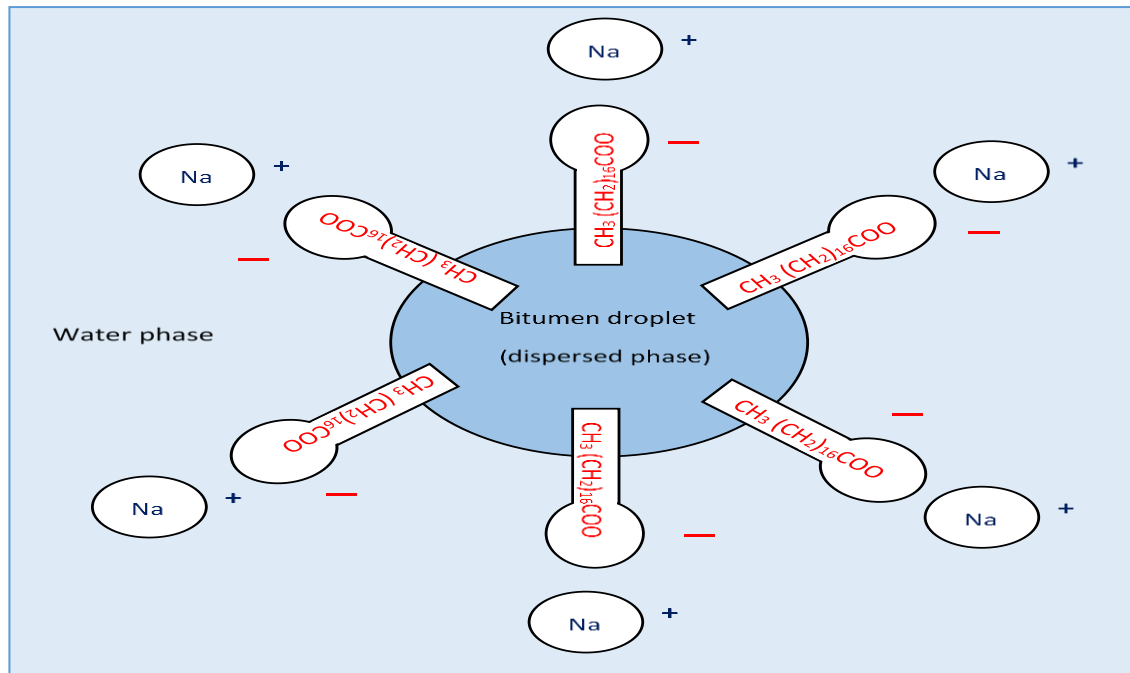
Sodium stearate: CH3(CH2)16COONa dissociates in water becomes: i) Sodium Cation, Na+ ,(in water/continous phase). ii) Strearate Anion (large portion), CH3(CH2)16 COO-, (in the bitumen globles/discontinous phase).

Figure 3.5. Diagrammatic illustration of the arrangement of anionic emulsifier around dispersed bitumen globules in typical emulsion (Thanaya, 2003), permission to reproduce this figure has been granted by Dr Arya Thanaya

> **Sodium Tripolyphosphate**

Sodium tripolyphosphate acts as a water softener and is used at 0.1% in anionic emulsions which are sensitive to hard water, to improve emulsion quality (Akzo Nobel, 2008).

> **Thickeners**

Including thickeners which are water soluble in the emulsion, can increase the viscosity of the emulsion and decrease emulsion run-off in open graded mixes. They can be included at the water phase or added to the finished emulsion at quantities of around 0.02–0.20%. Breaking and adhesion of emulsions are influenced by these thickeners meaning that they must be chosen with care (Akzo Nobel, 2008).

> ➢ **Adhesion Promoters**

These materials can increase the adhesion of bitumen to aggregates therefore decreasing the risk of stripping. They can be included in the asphalt or added to the finished emulsion. These adhesion promoters are usually surface active amine compounds (James, 2006).

> ➢ **Asphalt Peptizer**

Treating the bitumen with an asphalt peptizer produces enhanced emulsion quality by improving emulsifiability, leading to the creation of smaller droplets. In addition, it can decrease settlement, increase viscosity and improve adhesion (Thanaya, 2003).

> ➢ **Latex**

Including a polymer can enhance the properties of bitumen with regard to cohesion, crack resistance at low temperatures and resistance to flow at high temperatures. Latex, which is a water based dispersion of polymer, is suitable for the modification of emulsions; however, it is essential that the type of latex should be harmonious with the emulsion. Latex comes in cationic, non-ionic and anionic forms (Akzo Nobel, 2008). Regarding paving grade emulsions, the most common are styrene butadiene rubber, polychloroprene and natural rubber latex (James, 2006).

3.4 Classification of Bitumen Emulsions

Read and Whiteoak (2003) describe four categories of bitumen emulsions, the first two commonly used in road construction:

> ➢ **Cationic**
>
> ➢ **Anionic**
>
> ➢ **Non-ionic**
>
> ➢ **Clay-stabilised emulsions**

Electronic charges on bitumen globules are responsible for emulsion classification, both positive and negative. Cationic emulsion refers to the emulsion system that has positive

charges, while anionic is the system of bitumen droplets which have negative charges. Cationic emulsions are acid emulsions with pH < 7, whereas anionic emulsions are commonly alkaline with pH > 7. An emulsion consisting of bitumen particles with neutral charges is a non-ionic emulsion. Clay-stabilised emulsions include fine powders which are natural or processed clays or bentonites.

Cationic emulsions constitute the largest volume of emulsions manufactured universally (Read and Whiteoak, 2003). These emulsions are known to be more effective than anionic ones for coating aggregates across all weather conditions. With granite for instance, the positively charged cationic emulsifier attracted to the globules is drawn to the opposite charge on the aggregate surface; there is no attraction between negatively charged anionic emulsifiers and the negatively charged surface of idealized granite (O'Flaherty, 2007a). Non-ionic emulsion is seldom used in highways application while clay-stabilised emulsions are used for industrial applications.

3.5 Properties of Bitumen Emulsions

The perfect emulsion should be stable under storage, delivery and application conditions. In addition, it should break quickly and soon after application, forming a binder which has the properties of the original bitumen with strong adhesion (Read and Whiteoak, 2003). The main properties of bitumen emulsion are described below.

3.5.1 Emulsion Stability

Emulsions can be said to be stable in storage when there is no sign of settlement (Thanaya, 2003). The main two factors that impede or accelerate settlement are gravity and repulse repulsion/attraction forces between bitumen droplets produced by the layers of emulsifier on the droplets. Emulsions with a low bitumen content as well as low viscosity, are susceptible to settlement. Grades of bitumen at ambient temperatures have a density that

is a little greater than that of the water phase of the emulsion. Accordingly, particles of bitumen tend to settle through the aqueous phase, leading to high bitumen concentrations in the lower layer and low bitumen concentrations in the upper layer (Read and Whiteoak, 2003).

3.5.2 Emulsion Viscosity

The objective of bitumen emulsification is to decrease the viscosity of the binder thereby enabling coating of the aggregates at ambient temperatures and during spray applications; the bitumen content of the emulsion is mainly controlled by emulsion viscosity (Thanaya, 2003). Emulsions which have a high concentration at the disperse phase (bitumen), seldom have Newtonian viscosity characteristics, i.e. apparent viscosity changes with the shear rate at which the viscosity is measured. Emulsion viscosity is almost independent of the viscosity of the disperse phase (bitumen). Consequently, it is possible to manufacture emulsions of hard bitumen (< 10 pen) which are easily poured at 10°C (Read and Whiteoak, 2003). Differences in viscosity of the emulsion are affected by:

➢ **Bitumen Content**

  The effect on viscosity is small at low bitumen content, however a small increase in concentration can induce a dramatic change in viscosity which may be uncontrollable at high bitumen content.

➢ **Modification of the Aqueous Phase**

  Aqueous phase composition is greatly influenced by the viscosity of the bitumen emulsion. For instance, viscosity can be increased in traditional cationic road emulsions by reducing the acid content or increasing the emulsifier content. Additives specifically prepared as viscosity modifiers can also be used.

➢ **Flow Rate Through the Mill**

The particle size distribution of the emulsion is dependent on the flow rate through the mill, particularly where bitumen content is higher than 65%. Globules of bitumen are packed relatively closely together, resulting in a change in particle size distribution and viscosity.

3.6 Breaking Mechanisms of Bitumen Emulsions

Bitumen emulsions must remain stable so that they can be transported, stored and handled. Eventually, they must break so that the bitumen can coat particles of aggregate or pavement surfaces. It is very important that the breaking process should be accomplished as soon as possible after the application of the bitumen emulsion. The water in the emulsion must separate from the bitumen phase and evaporate, this separation referred to as breaking or setting, generally distinguished by a change in colour from brown to black. There are six factors responsible for the breaking properties of emulsions (Read and Whiteoak, 2003):

➢ **Bitumen Content**

By increasing the bitumen content, particles are more likely to be in contact with each other leading to a rise in the rate of breaking.

➢ **Aqueous Phase Composition (pH Changes)**

By reducing the acid content as well as increasing the emulsifier content, the rate of breaking will be improved. Reducing the ratio between acid and emulsifier contents will have the same effect. In some types of aggregate such as limestone or filler like cement, lime filler can neutralise the acid in cationic emulsion and increase the pH resulting in destabilisation of the bitumen emulsion. In other cases, a smaller rise in pH results from the adsorption of hydrogen ions by aggregates; this is still enough to destabilise the emulsion. Some soluble

aggregates, for example limestone, can supply calcium or magnesium ions to the solution which tends to neutralise the charge on an anionic emulsion.

> **Particle Size Distribution**

When bitumen particles are small, dispersion will be finer and as a result, the rate of breaking will be slower. The surface area at the binder/water interface will increase because of a reduction in emulsion particle size. The size of emulsion droplets and their distribution rely on the process of emulsification because of, for example, mechanical tools, developed energy, physical-chemical aspects (such as phase inversion) and other emulsification parameters. Smaller droplets and narrow distributions can be achieved by increasing agitation speed (Nagata, 1975).

> **Environmental Conditions**

Water evaporation from the emulsion system is affected by environmental conditions such as temperature, humidity and wind velocity. Bitumen emulsion application through the night is challenging as low temperatures, in addition to relatively high humidity, will stop water evaporation. Conversely, bitumen particles in the emulsion system are more mobile at higher temperatures. These particles tend to come into contact with each other leading to coalescence.

> **Adsorption of Emulsifier on the Surface of Aggregate**

Emulsion comprises emulsifier molecules in both the water and on the surface of bitumen droplets. Some emulsifier ions within the water form micelles. However, in a stable emulsion system, there is equilibrium as shown in Figure 3-6.
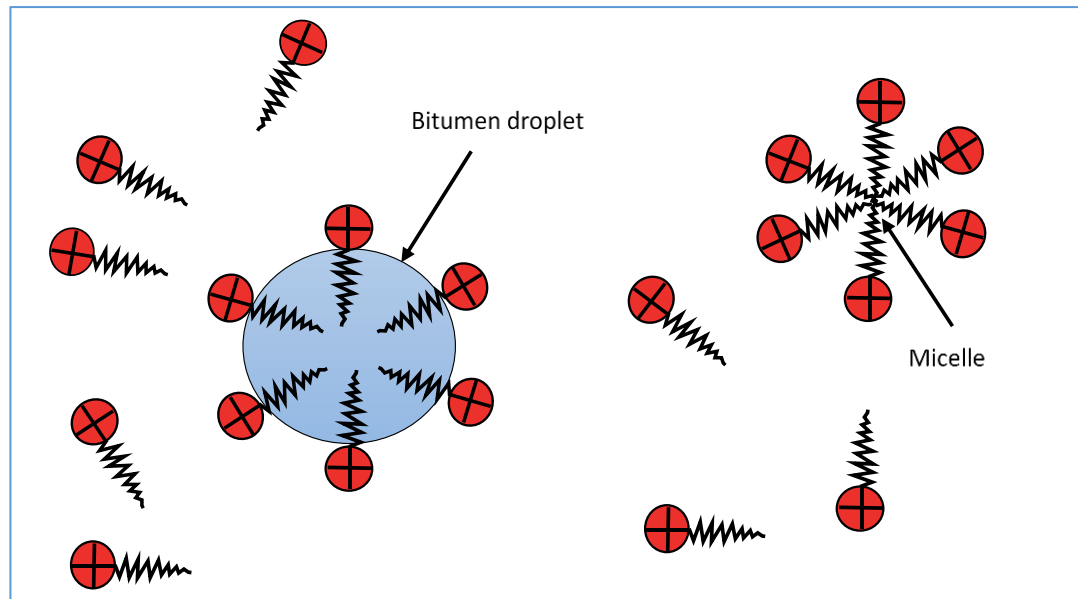
Figure 3.6. Emulsion ions forming micelles in a stable emulsion (Read and Whiteoak, 2003), permission to reproduce this figure has been granted by Shell International Petroleum Company Limited

If emulsifier ions are removed from the solution, equilibrium is restored by ions from the micelles and the droplets' surface. This happens when an emulsion comes into contact with a mineral aggregate. An aggregate surface with a negative charge quickly absorbs some of the ions from the solution resulting in a weakening of the charge on the droplets' surface; this will begin the process of breaking as shown in Figure 3-7. A point is reached where the charge on the surface of the globules is so depleted that fast coalescence occurs and the aggregate is covered in hydrocarbon chains. This is when adhesion occurs between the liberated bitumen and aggregate surface.

➢ **The Use of Breaking Agents**

Das (2008) stated that the type and concentration of emulsifying agent highly influences the speed of break of the emulsion. These chemical breaking agents can be sprayed together with the emulsion or just after emulsion application. Much attention is required when using these agents as too little will have no effect; too much will break the emulsion and adversely affect its adhesively.
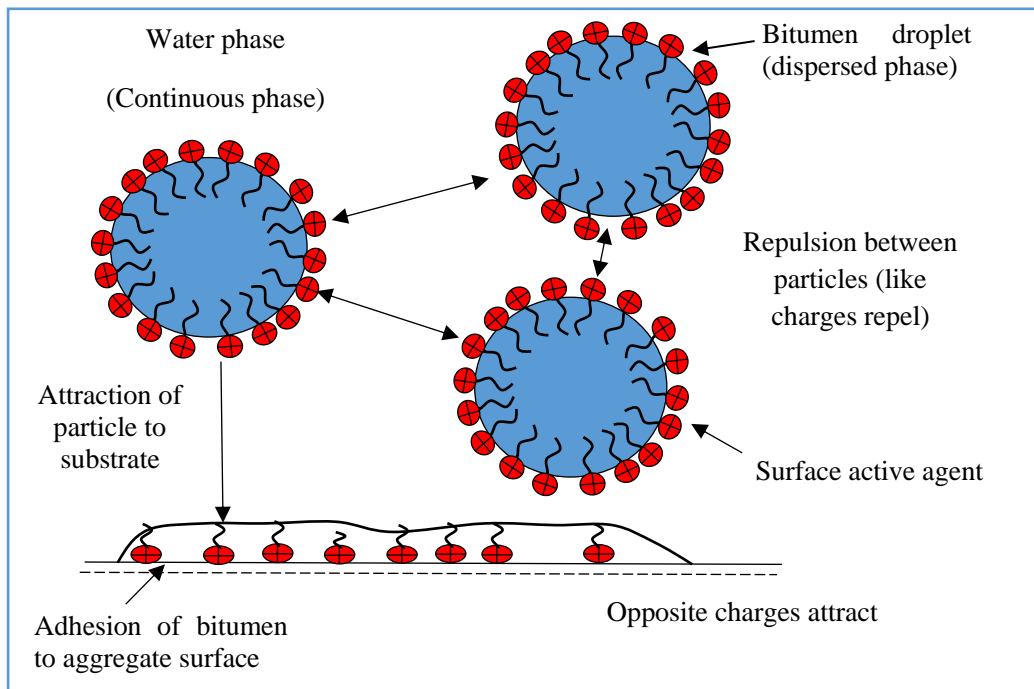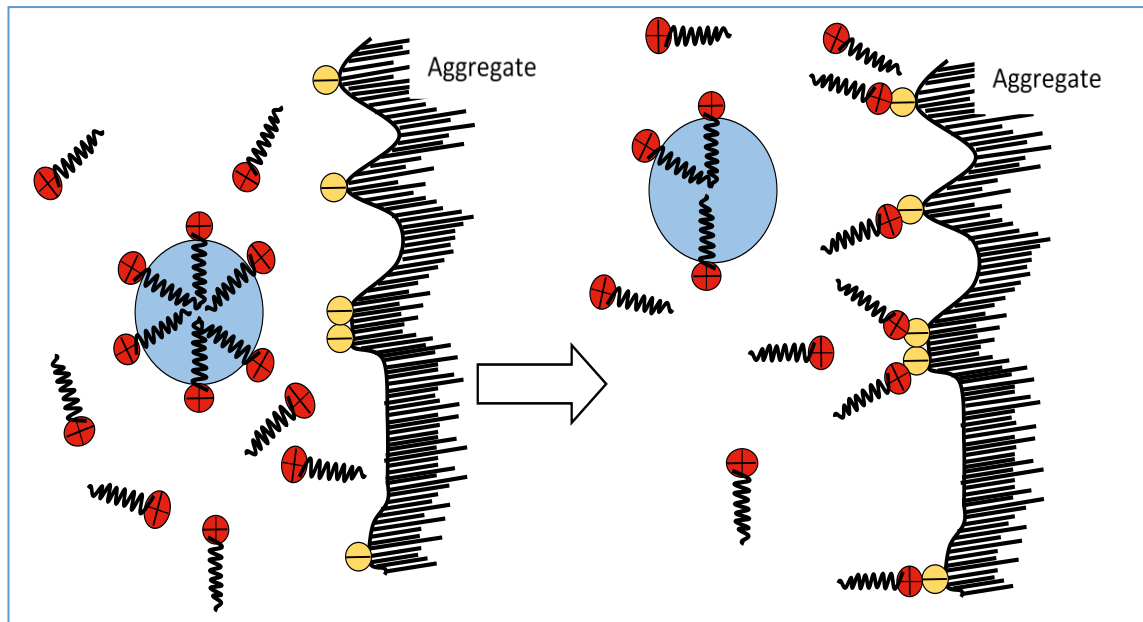
Figure 3.7. Schematic diagram of breaking mechanism (Read and Whiteoak, 2003), permission to reproduce this figure has been granted by Shell International Petroleum Company Limited

3.6.1 Breaking Mechanism of Cationic Emulsion

There are several ways to explain the complicated process of bitumen emulsion breakage. Three methods were introduced by Wates and James (1993) to describe how cationic emulsions break onto negative aggregates, e.g. granite.

➢ **Emulsion Abstraction**

Here the emulsifier is withdrawn from the bitumen/water interface by the surface aggregate. The emulsion then becomes unstable because of the loss of emulsifier, causing the bitumen droplets to coalesce as shown in Figure 3-8.

➢ **Emulsifier Deprotonation**

In this situation, the acidified emulsifiers are deprotonated by which the protons are adsorbed onto the surfaces of the aggregate, deactivating the emulsifier, producing emulsion breaking as shown in Figure 3-9.
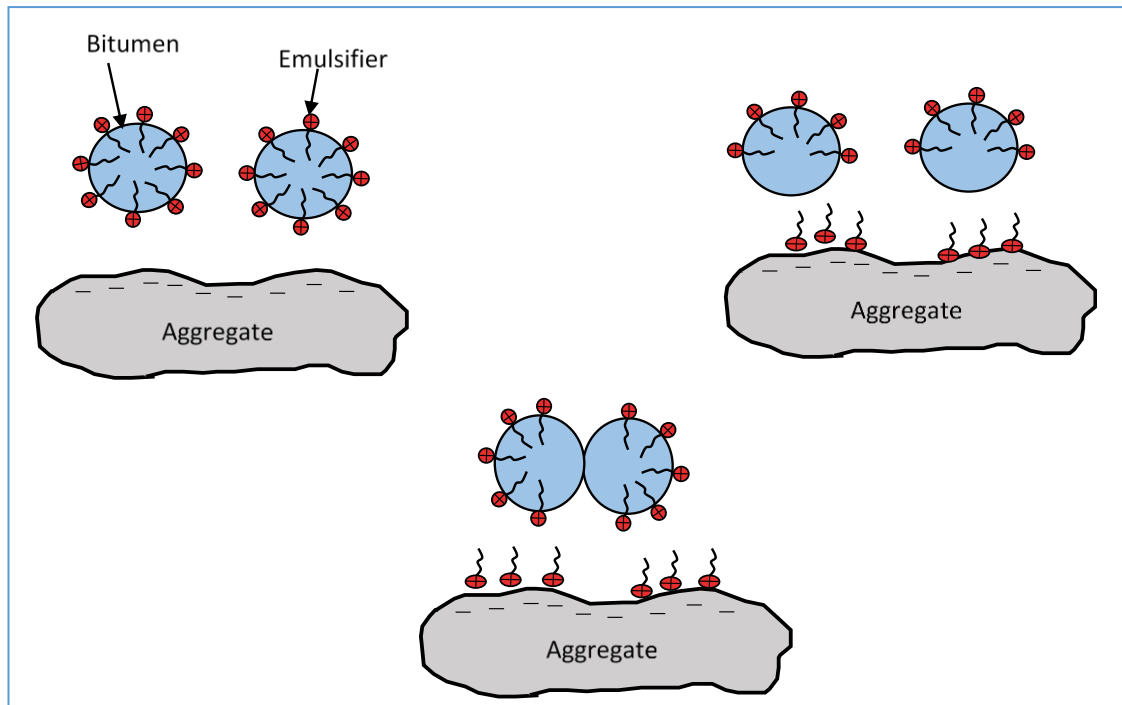
Figure 3.8. Breaking mechanism of cationic emulsion by emulsifier abstraction, permission to reproduce this figure has been granted by Dr David Needham
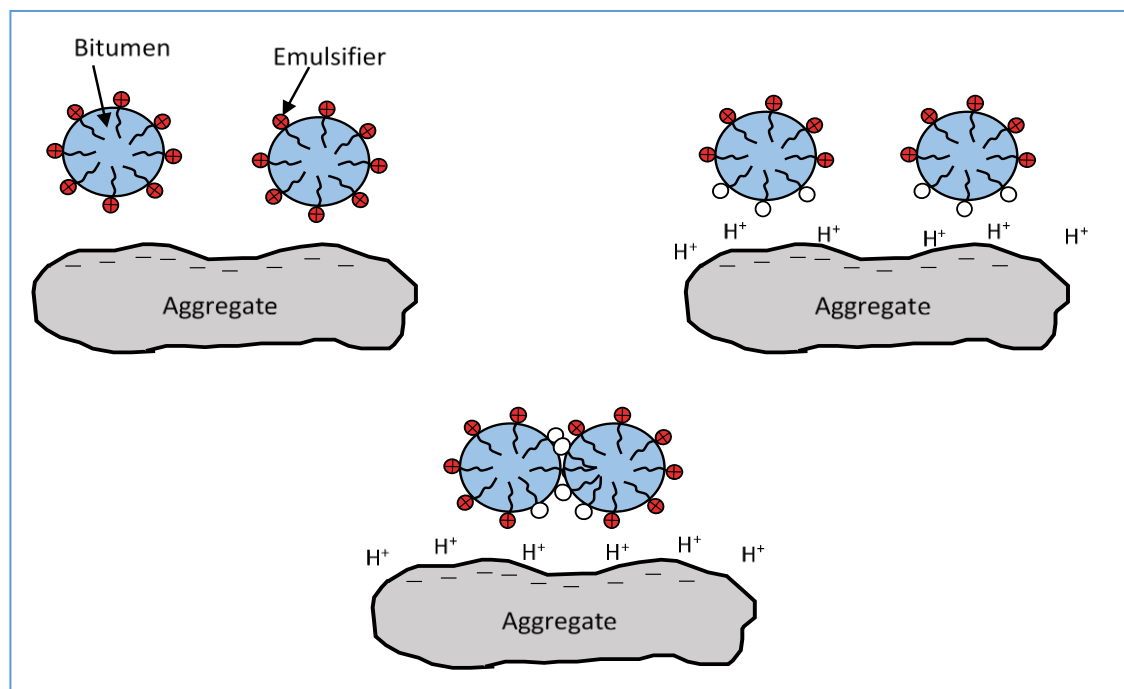
Figure 3.9. Breaking mechanism of cationic emulsion by emulsifier deprotonation, permission to reproduce this figure has been granted by Dr David Needham

➢ **Droplets Migration**

This approach is considered to be the most acceptable as evidenced by its extensive use. Positively charged bitumen droplets are drawn to the negatively charge aggregates surfaces. Assisted by the surfactant, the droplets spread over the aggregate surfaces as shown in Figure 3-10. The surfactant molecules act as adhesion or anti-stripping agents, resulting in binding of the bitumen to the surface of the aggregate. This is the major reason that cationic emulsifiers have become more commonly used in comparison to anionic emulsifiers for road applications. Plotnikova (1993) presented another theory on the breaking mechanism of cationic emulsion on siliceous aggregates (granite). He claimed that free emulsifiers are firstly adsorbed onto the aggregate surfaces. After that, the emulsifiers are taken away or withdrawn from the bitumen droplets and adsorbed onto the aggregate surfaces which become hydrophobic because of the adsorption of emulsifiers, as illustrated in Figure 3-11. The rate of breaking of the emulsion can be influenced by the rate of adsorption of the emulsifier onto the aggregate, which in turn is governed by the surface area and chemical nature of the aggregate and bitumen emulsion.
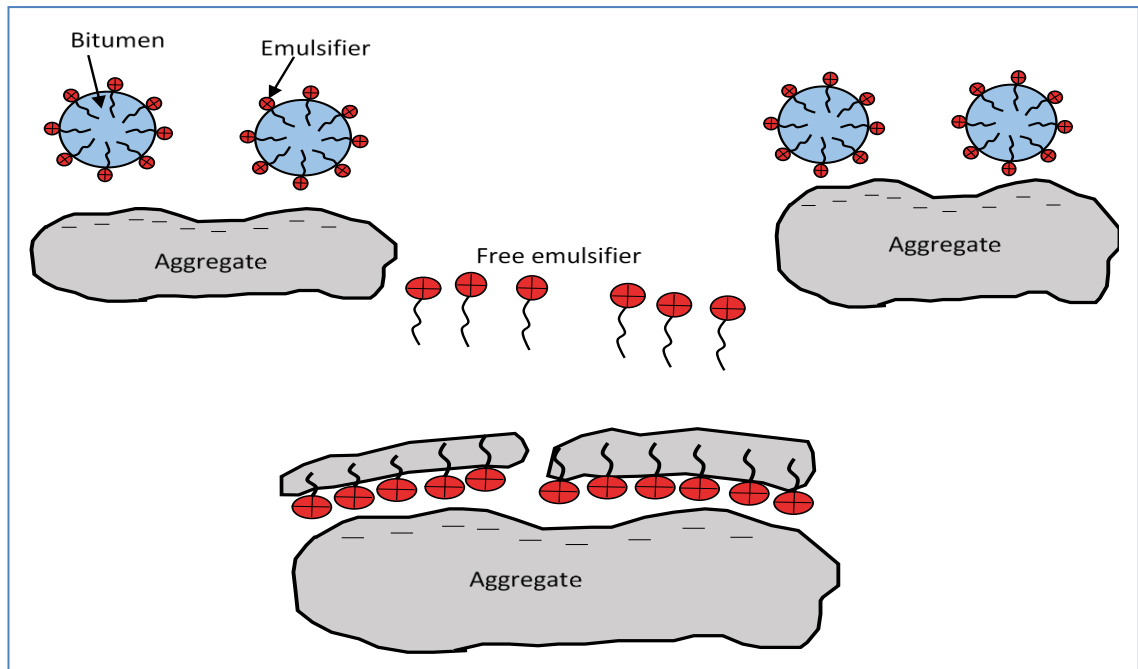
Figure 3.10. Breaking mechanism of cationic emulsion by droplets migration, permission to reproduce this figure has been granted by Dr David Needham
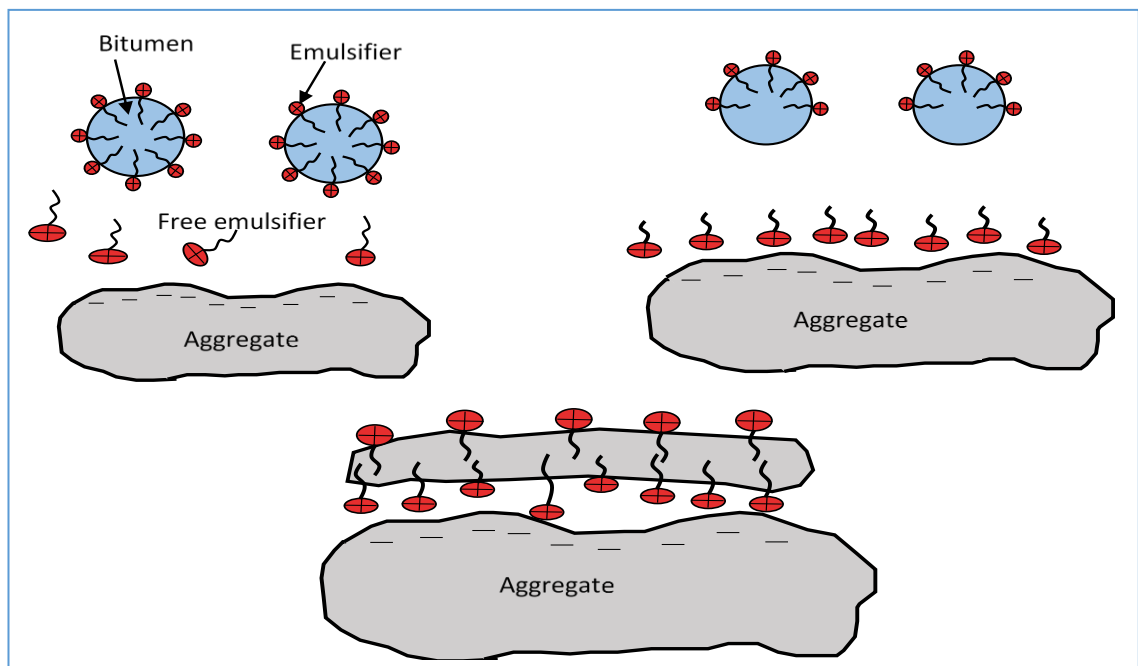
Figure 3.11. Breaking mechanism of bitumen emulsion by emulsifier adsorption, permission to reproduce this figure has been granted by Dr David Needham

3.7 Bitumen Emulsion Adhesively

The amount of adhesion between bitumen emulsion and aggregates is influenced by how much surface area is coated by the emulsion. In all applications, it is very important that the aggregate surface is slightly damp to ensure easy spreading of the emulsion over the aggregate surface. The adhesion or bonding quality between emulsion and aggregate are affected by a number of factors such as:

  ➢ the type and amount of emulsifier

  ➢ the grade of bitumen and components

  ➢ the pH of the emulsifier solution

  ➢ the particle size distribution of the bitumen particles in the emulsion, and

  ➢ the aggregate type (Read and Whiteoak, 2003)

Theoretically, the best adherence occurs when the aggregates and the emulsion have opposite charges meaning that anionic emulsions are more suitable for positively charged aggregates, for instance limestone or basalt, whereas cationic emulsions should be used with negatively charged aggregates, for example, granite or quartzite. That said, experience shows that cationic emulsions have a good affinity with all aggregates types. Furthermore, an emulsifier of this category can actively provide an anti-stripping actions which means that it is less affected by weather conditions and will be more durable than anionic emulsifiers (Leech, 1994).

3.8 Naming of Bitumen Emulsion

The designation of cationic emulsions comprises five components in accordance with the BS EN 13808: 2013 (European Committee for Standardization, 2013). The first component indicates the emulsion type, e.g. 'C' for cationic. The second indicates the binder content, followed by 'B', the third added if there is polymer included, represented by the letter 'P'. If the emulsion content flux is more than 2%, this is the fourth component

indicated by the letter 'F'. Finally, the breaking rate is added which ranges from 1 to 7 where the higher the number, the slower the break rate, lower numbers referring to rapid setting. For instance, C 55 BPF 7 indicates cationic, binder content of 55%, manufactured from bitumen which contains polymers and more than 2% flux with a Class 7 breaking value.

Conversely, anionic bitumen emulsions are categorised according to the BS EN 434-1 (European Committee for Standardization, 2011) using a three element designation. The first part indicates emulsion type e.g. 'A' for anionic emulsion. The second component indicates the breaking rate or stability ranging from 1 to 4, where 1 indicates rapid setting and 4 indicates slow setting. The third part of the code represents the percentage bitumen in the emulsion. For instance, A1-60 is an anionic emulsion with rapid breaking and a bitumen emulsion of 60%.

3.9 Application of Bitumen Emulsion

The consumption of bitumen emulsion rises from time to time as a result of the development of CBEM technology and demand on bitumen emulsions for different applications. The USA and France top the list of production using bitumen emulsion in road applications because of their mainly secondary and rural networks with medium to low traffic as well as success in application (Corroler, 2010). Table 3-2 summarises typical applications of emulsions with various breaking rates. Bitumen emulsions have been utilised in areas such as cold mix asphalt, slurry seals, slip layers, soil stabilization, protective coats and fog seal.

Table 3-2. Typical applications for emulsions with different breaking rates (James, 2006)

Application	Breaking or setting rate		
	Rapid	Medium	Slow
Plant mixes			
Open graded		√	
Dense graded			√
RAP mixes		√	√
Stockpile mix		√	
Pre-coated chips		√	√
Mix paving			
Open graded		√	
Slurry seal			√
Slurry for Cape seal			√
Microsurfacing			√
In-place mixes			
RAP mixes		√	√
Dense graded			√
Soil stabilisation			√
Spray applications			
Chipseal	√		
Fog seal	√	√	
Tack coat		√	√
Prime coat			√
Dust palliative			√
Penetration macadam	√		

CHAPTER 4

LITERATURE REVIEW III- CBEM ENHANCEMENT

4.1 Introduction

It is generally accepted that an asphalt should reach its full design strength in a short period of time, thus enabling its characteristics to be measured almost immediately after manufacture. For a number of reasons, the same measurements cannot be made with CMAs (Serfass et al., 2004b). CBEMs are known to have low early strength, long curing times and end mixtures which have relatively high porosities (Thanaya et al., 2009). When comparing CBEM mixtures to asphalts, CBEMs tend to be of relatively low quality as demonstrated by Ibrahim and Thom (1997). In consequence, the use of CBEMs is limited to reinstatement works and to pavement layers on low volume roads. This chapter investigates and assesses the methods and approaches that have been used by previous researchers to improve the poor performance of CBEMs.

4.2 Previous Attempts to Enhance CBEMs

4.2.1 Enhancement by Compaction

The mechanical and performance characteristics of CBEMs are directly influenced by compaction as satisfactory compaction is necessary for optimal performance. Brown and Needham (2000b) for example, found that increases in compaction efforts lead to an increase in the degree of emulsion coalescence when using granite aggregate with a 20 mm Dense Bitumen Macadam (DBM) specification.

Thanaya (2003) reported that the upper limits of porosity could be reached by adopting heavy compaction (120 revolution, 240 kPa, 2° angle of gyration) rather than medium compaction (80 revolution, 240 kPa, 2° angle of gyration). He also established that compaction of 240 gyrations is needed to attain a target air void content of between 5-

10%, this categorised as extra heavy compaction. This is of note because for cold mixes, a heavy compaction application is necessary to confirm breaking of the emulsion and ensure that mixtures strengthen properly (Thanaya, 2007). The amount of excessive fluids in CBEMs decrease the effect of compaction and prevents mixtures from reaching their optimal density leading, in turn, to decreased stiffness and strength properties. Figure 4-1 describes the relationship between compaction efforts and stiffness modulus on CMAs as reported by Serfass et al. (2004b). Here it is noted that an increase in the level of compaction results in an improvement in stiffness modulus of the mixtures.
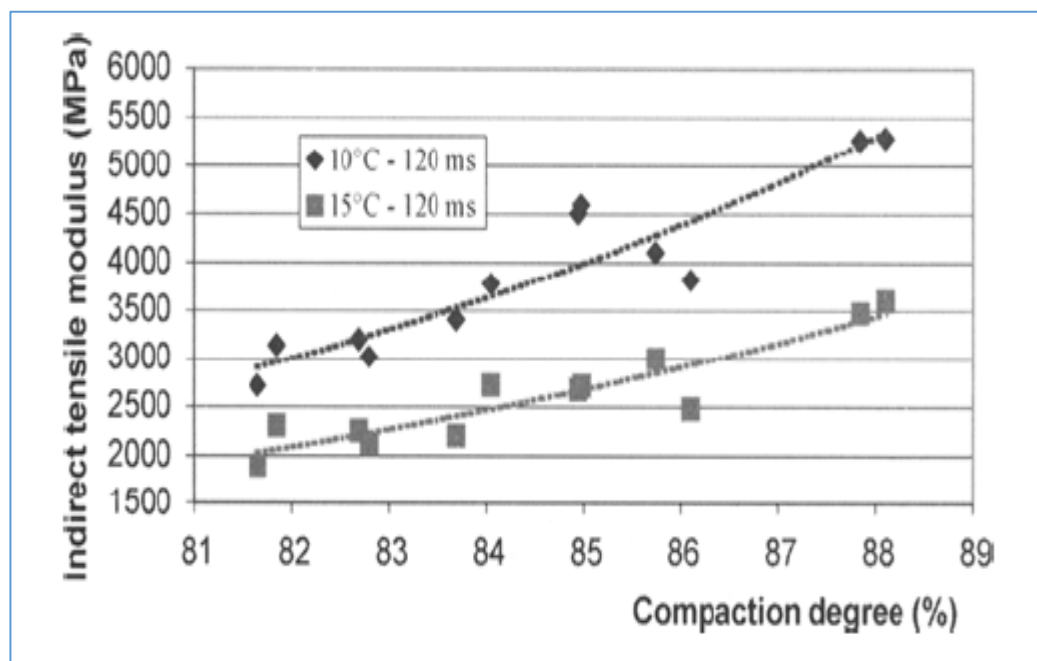
Figure 4.1. Influence of compaction on stiffness (Serfass et al., 2004b), permission to reproduce this figure has been granted by Springer Science+Business Media

4.2.2. Improvement by the Inclusion of Fibres

In the case of asphalts, strength and bonding can be enhanced by the addition of fibres (Wu et al., 2006; Ye et al., 2009). Fibre type and content, diameter, length, and surface texture have a considerable impact on the performance of fibre-reinforced mixtures. The use of fibre reinforcement to improve the mechanical properties of cold emulsion, densely

graded, emulsified asphalt mixes has been addressed by Bueno et al. (2003). Staple polypropylene fibres (10 mm, 20 mm and 40 mm) were added to mixtures in three percentages; 0.10%, 0.25% and 0.50%. This addition of fibre was found to be accountable for a reduction in dry density, Marshall Stability and mixture resilient moduli in comparison to mixtures with no fibres. Another study implemented by Ferrotti et al. (2014), investigated the experimental characterization of a high performance CMA mixture reinforced by three types of fibres (cellulose, glass-cellulose, nylon-polyester-cellulose) with two different contents (0.15% and 0.30%) by aggregate weight. The materials were examined at different curing times (1, 7, 14, 28 days) and conditions (dry and wet). The results indicated that the mix with 0.15% cellulose fibres offered a comparable (for 14 and 28 days curing times) or even better performance (for curing times within 7 days) than the standard mixture (without fibres).

4.2.3 Improvement by Utilization of Polymers

Khalid and Eta (1997) conducted experiments on the effect of polymer modified emulsions (PMEs) on the characteristics of emulsified bitumen macadams (EBMs). They used different aggregate gradings, a close graded surface course and a dense graded binder course or base with a cationic emulsion containing 65% base bitumen. The base bitumen grade was 100 pen with Ethylene Vinyl Acetate (EVA) and Styrene-Butadiene-Styrene (SBS) admixtures. They found that polymer positively modified bitumen emulsions enhanced stiffness and permanent deformation of the mixtures compared to unmodified bitumen emulsion mixtures. In addition, the fatigue lives of the 4% SBS and 6% EVA modified EBMs were approximately 45 to 35 times greater, respectively, compared to the fatigue life of the unmodified EBMs. Further research implemented by Chávez-Valencia et al. (2007) used polyvinyl acetate to enhance the compressive strength of CMA. Polyvinyl acetate emulsion (PVA-E) was added to a rapid-set emulsified

asphalt. Two CMA types were prepared: the aggregates were coated in the first type by a film of asphalt-polyvinyl acetate (A-PVAC) binder, while in the second, the aggregate was mixed with a diluted PVAC-E to cover it with the polymer, the A-PVAC binder then layered. They found that the second type achieved a 31% improvement in compressive strength as a result of the improvement in void content. Recently, Xu et al. (2015) added a specially developed polymer modified emulsifier to an AC-13 asphalt mixture. They concluded that in terms of moisture susceptibility, high temperature and resistance to low-temperature crack, the mixture met performance specification requirements in addition to an improvement in rutting resistance performance.

4.2.4 Incorporation of Recycled Aggregate

The incorporation of milled, old road pavement in cold emulsion mixtures was carried out by Thanaya et al. (2014) mixing them with virgin aggregate, rice husk ash and cement. The specimens were subjected to a compaction delay of up 24 hours, thereafter cured at ambient temperature. They found that such mixtures can include a high percentage of RAP (72.73%) while the lowest stability achieved was 3 kN. In addition, it was reported that an increased early strength was attained when aged at tropical room temperatures as a result of the evaporation of water in comparison to cement content. Gómez-Meijide and Pérez (2014a) conducted experiments using 100% recycled aggregates from construction and demolition waste on CMA. They revealed that the indirect tensile strength, stiffness modulus, unconfined compression strength and moisture sensitivity were acceptable in comparison to 100% natural aggregates (control mix) and in line with values agreed by various standards and recommendations. In addition, these mixtures normally displayed higher stiffness compared with the control mixes. However to achieve this, substantially more bitumen and water was required (Gómez-Meijide et al., 2015).

4.2.5 Enhancement by the Incorporation of Active Fillers

Fillers can play an important role in governing the engineering properties of asphalt concretes in terms of stiffness, permanent deformation resistance, fracture resistance and moisture sensitivity (Kim et al., 2003; Kim et al., 2008).

Mineral filler includes materials passing through a 63 µm sieve. In CBEMs, fillers can be either reactive or non-reactive (inert) materials (Zizi et al., 1997). The former is a filler type that reacts when it comes into contact with emulsion and/or any additional water in the mixture, resulting in a hydration process e.g. cement. The latter, for example silica fillers, will not react with emulsions. The quantity of the filler in asphalt depends on grading and the type of mixture.

Supplementary cementitious materials (SCMs) represent an alternative for the industry to achieve sustainability by reducing cement content without significantly compromising mechanical properties while at the same time enhancing durability. A cementitious or hydraulic material is finely ground and contains adequate calcium to form compounds which react directly with water to form cementitious compounds (Thanaya, 2003). Cement and high calcium fly ash belong to this category. However, pozzolanic materials react chemically in water with calcium hydroxide (C-H), the compounds formed having cementitious properties. Pozzolanic materials are siliceous or silico-aluminous or a combination of both, having no binding properties when mixed with water but when in a finely ground state, will react with dissolved hydroxide $Ca(OH)_2$ and produce calcium silicate and calcium aluminates which facilitate the development of strength (Hewlett, 2006). Mineral admixtures such as pozzolanic and cementitious materials, have been used extensively in concrete construction. The properties of both materials are controlled by their mineralogical content in addition to their particle properties such as particle size, surface area, shape and texture (Thanaya, 2003).

4.2.5.1 Improvement by Cement Incorporation

From a technical point of view, a cement can be defined as any material which, if added in an appropriate procedure to an accumulation of particles with a non-cohesive nature, will later harden by physical or chemical means, the particles binding into a coherent mass. Cements such as Portland, slag, pozzolanic and high alumina cements, are all finely ground powders which undergo hydration processes to generate a binding material with very strong and durable properties (O'Flaherty, 2007a).

Cement production requires balanced quantities of the raw materials to be ground and mixed, after which the mix is usually fed over a coal-fired, high temperature kiln. Incipient fusion happens when the temperature of the material is around 1450°C, leading to the constituent lime and clay to combine and generate clinkers consisting of tricalcium silicate ($3CaO.SiO_2$, abbreviated C_3S), tricalcium aluminate ($3CaO.Al_2O_3$ or C_3A), dicalcium silicate ($2CaO.SiO_2$, or C_2S), and calcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$ or C_4AF). Burnt clinkers are taken to ball-and-tube mills, allowed to cool then ground to generate a fine powder. Gypsum is added (normally 1%-5%) to the mix during the grinding process.

The use of cold emulsified asphalt as structural layers is very restricted as a result of the long period required for such materials to reach their full strength after paving (particularly in the UK), as well as because of its high sensitivity to rainfall in the early stages of installation (Oruc et al., 2007b). To enhance the weak properties of CBEMs, several studies have been implemented examining the addition of OPC.

The use of cement in asphalt is not a new idea; Portland cement has been used as a filler in warm mixed asphalts to avoid binder stripping from dried aggregate. It has also been used to improve wet aggregate coating with bitumen or tar (Transport and Road Research

Laboratory (TRRL), 1969). One of the first studies which incorporated cement into emulsion-treated mixes was conducted by Terrel and Wang (1971). They established that the rate of development of the resilient modulus could be accelerated by using cement as a catalyst to increase the rate of curing of asphalt emulsion mixtures. They suggested that Ca^{2+} ions from cement neutralizes the anionic emulsifier allowing emulsion droplets to coalesce and adhere to the aggregate. This helps the emulsion to break faster as well as absorb water in the mixture thus reducing curing times. In addition, Schmidt et al. (1973) investigated the role of cement in emulsion-treated mixes as a means of speeding up the development of their strength. They found that when cement was added to the aggregate at the same time as the asphalt emulsion, mixes cured quicker, had a more resilient modulus (Mr), developed at a quicker rate and had more resistance to water damage.

Head (1974) aimed to improve the Marshall stability of modified cold asphalt mixes. He saw that the incorporation of 1% OPC increased the Marshal stability of modified CMA by around three times compared with untreated mixes. However, ravelling of the surface occurred as a result of the brittle nature of the resultant mixtures. Dardak (1993) suggested that thickness of the treated unbound layer, which formerly needed to be 22 cm, can be reduced to 12 cm by using OPC treated emulsion mixtures as a result of the increase in stability (200%-300%) of a sand emulsion treated mixture by incorporating cement. Li et al. (1998) investigated the mechanical properties of three phase Cement-Asphalt Emulsion Composite (CAEC). Their findings revealed that most of the features of both cement and asphalt were possessed by CAEC; they have a longer fatigue life and lower susceptibility to temperature, like that of cement concrete, and a higher toughness and flexibility in common with asphalt concrete. Cement works as an adhesion agent and can assist the enhancement of the short term properties of compacted mixtures implying that

its use may be a foregone conclusion to act as either as the main binder or as a supplementary binder (Milton and Earland, 1999).

Brown and Needham (2000b) examined cement modified emulsion mixtures where the prime aim was the evaluation of the positive influence of adding OPC to such mixtures. They used a granite aggregate grading in the middle of 20mm Dense Bitumen Macadam (DBM) with a single slow-setting emulsion. They concluded that the addition of OPC enhanced the mechanical properties namely, stiffness modulus (Figure 4-2), resistance to permanent deformation and the fatigue strength. OPC caused an increase in pH which led to an increase in the tendency of the emulsion to break. Scanning Electron Microscopy (SEM) provides evidence of the cement hydration and where said cement becomes part of the binder (Figure 4-3).
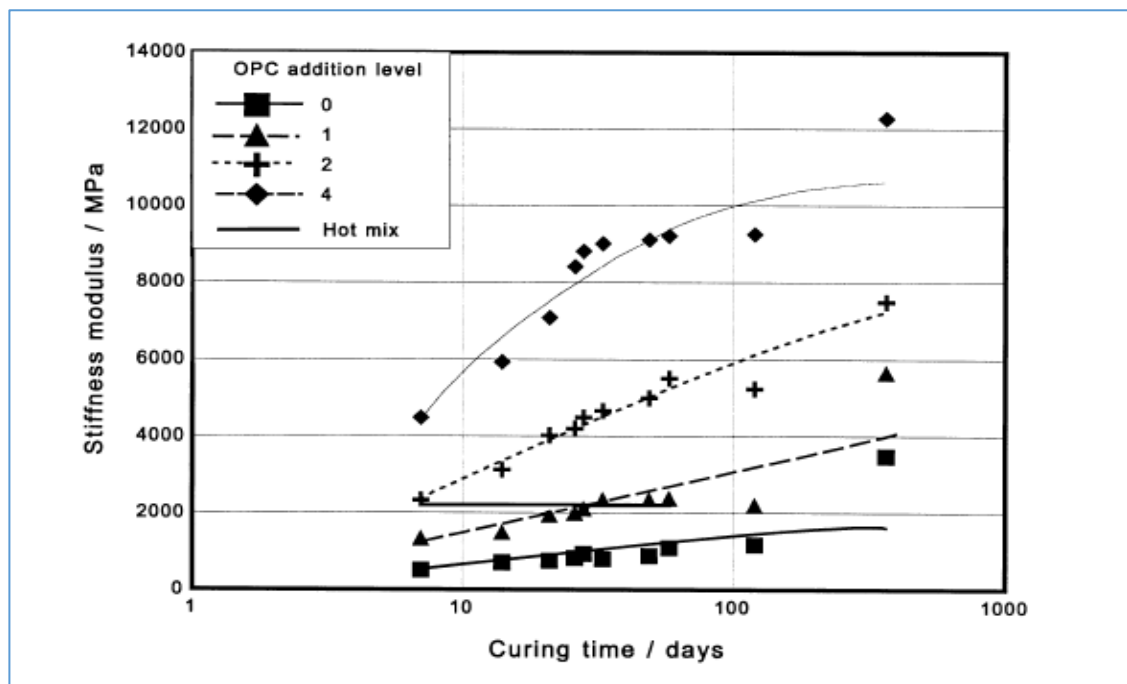
Figure 4.2. Influence of OPC on stiffness modulus (Brown and Needham, 2000), permission to reproduce this figure has been granted by Association of Asphalt Paving Technologists
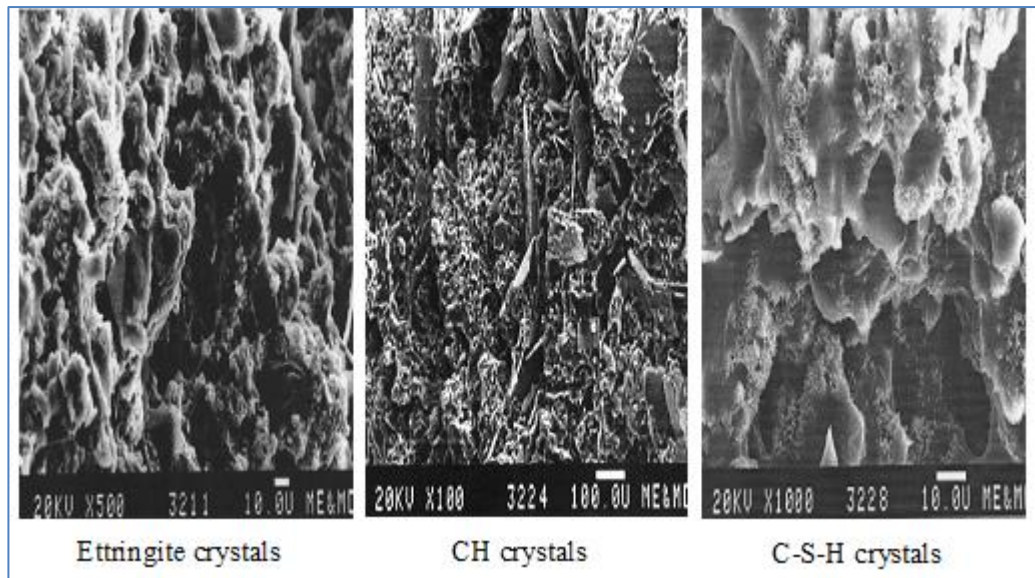
Figure 4.3. Hydration products of OPC (Brown and Needham, 2000), permission to reproduce this figure has been granted by Association of Asphalt Paving Technologists

The type of cement used affects the rate of increase in strength of CBEMs (Thanaya, 2003). Thanaya reported that Rapid Setting Cement (RSC) provides a better rate of increase in strength in comparison to OPC. He described how a stiffness of 2000-2500 MPa can be achieved in just a few weeks by incorporating 2% RSC, rather than the 16 weeks needed for mixes without RSC. This is because the cement behaves as an active filler in CBEMs resulting in an increase in pH. Subsequently, if a cationic emulsion is used (the system is acidic with pH values of less than 7), the inclusion of cement results in a rise in pH meaning that the emulsion becomes unstable and sets faster. Thanaya (2007) stated that the performance enhancement of the CAEMs can simply be achieved by including up to 2% OPC by aggregates mass.

Taking this further, Oruc et al. (2006) and Oruc et al. (2007b) conducted investigations to evaluate the mechanical properties of emulsified asphalt which included 0% to 6% OPC substituted for mineral filler. Significant improvements were realised with higher percentages of OPC as can be seen in Figure 4-4. This led them to suggest that cement

modified asphalt emulsion mixtures might be utilized as a structural layer. They also established that without cement incorporation, CMAs have poor mechanical performance and a high susceptibility to moisture. More recently, Oruc et al. (2013) examined the effect of Portland cement as a substitution for mineral filler in cement modified emulsified asphalt. They used three asphalt emulsion mixtures with various residual asphalt contents of 4.2%, 5.2% and 6.2% by dry aggregate mass, finding that the cement acted as a secondary binder in the emulsion mixtures, responsible for improvement in creep and resistance to permanent deformation. The increase in residual asphalt content caused a reduction in creep deformation resistance in emulsion mixtures.
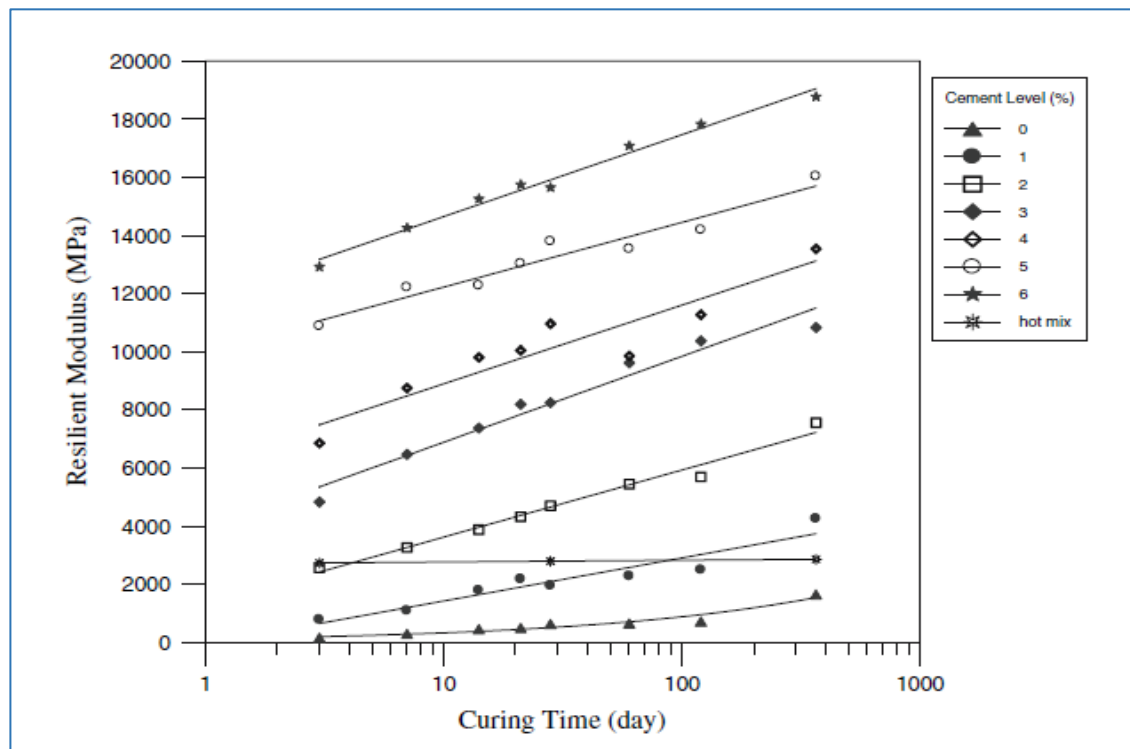
Figure 4.4. Influence of cement on resilient modulus (Oruc et al., 2007), permission to reproduce this figure has been granted by Springer Science+Business Media

Recently, there has been much more research on using cement in emulsion mixtures. Wang and Sha (2010) investigated the interfacial characteristics of cement asphalt emulsion mastics and aggregate finding that a finer cement and mineral filler enhances

the micro hardness of the interface, but care has to be taken not to use mineral filler which is too fine. García et al. (2012) tested CMAs with various cement quantities in terms of the Marshall stability test. Mixtures were cured at various environmental humidity levels (35, 70 and 90% RH). They demonstrated that combining asphalt emulsions and cementitious material results in a material possessing beneficial properties for both asphalt and concrete. The incorporation of cement causes changes in the pH of the emulsion leading to it break, as shown in Figure 4-5. This suggests that composites of asphalt and cement may be appropriate for use as a road material.
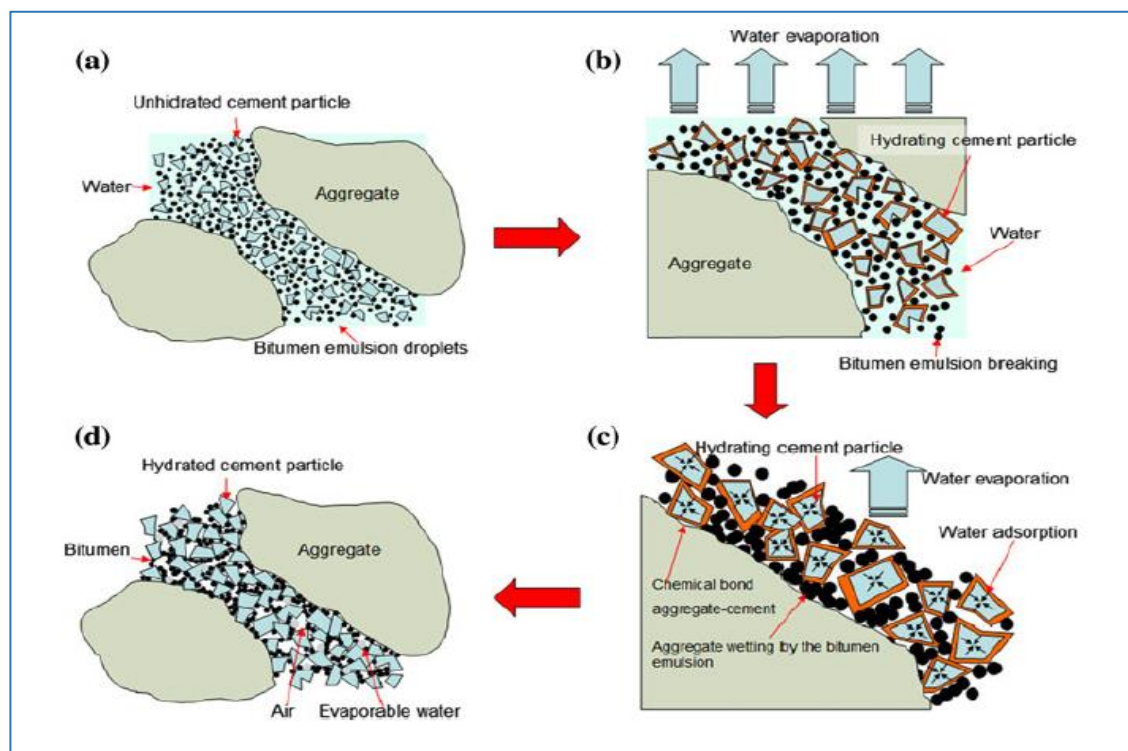
Figure 4.5. Schematic representation of the hardening process of an asphalt-emulsion composite (García et al., 2012), permission to reproduce this figure has been granted by Springer Science+Business Media

Wang et al. (2013) studied the influence of pH and water loss induced on emulsion stability by the hydration of cement. They concluded that the increase in pH value significantly influenced the chemical stability of cationic emulsions. A droplet

flocculation evident at upper pH levels, was revealed in the optical photos of cationic

emulsions as presented in Figure 4-6. The charge and cationic emulsifier on the cationic

emulsion droplets are rapidly broken down, leading the emulsion to speedily flocculate

and coalesce. Increasing the pH a little, gives some enhancement to the anionic emulsion

stability.
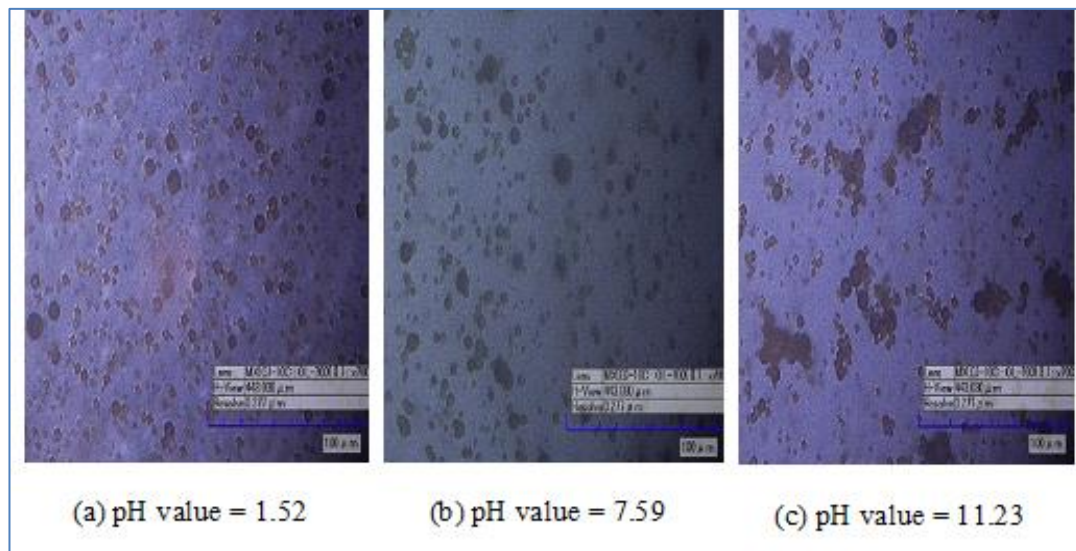
Figure 4.6. Optical image of cationic emulsion at different pH value (Wang et al., 2013), permission to reproduce this figure has been granted by Elsevier

Al-Hdabi et al. (2014b) investigated the use of OPC as a full substitution for traditional

mineral filler, focussing on mechanical properties and water damage resistance, in order

to develop a new cement treated CBEM made with gap grading. Their results indicated

that gap-graded, cold rolled asphalt mixtures gained significant enhancements in

mechanical properties, resistance to water damage and temperature susceptibility.

Fang et al. (2014) reported that the benefits of Cement Asphalt Emulsion Composites

(CAEC) are lower susceptibility to temperature in comparison to asphalt concrete and

higher flexibility compared with cement concrete. They studied the influence of cement

hydration on mechanical properties using two types of emulsions (cationic and anionic).

CAEC mixtures were examined by isothermal calorimetry as well as Marshall tests by incorporating OPC in three percentages; 0%, 3% and 6% by dry mass of aggregates. They revealed that the emulsion had no substantial influence on the degree of cement hydration. A higher amount of cement added to the mixture did however, lead to more bonds being formed.

The use of rapid hardening cements in Cement Bitumen Emulsion Asphalt (CBEA) was also investigated by Fang et al. (2016a), their aim to accelerate the improvement of mechanical properties of such mixtures and achieve a better understanding of the role of cement in CBEA. The mechanical properties after one day of curing by the incorporation of calcium sulfoaluminate and calcium aluminate cement are comparable to those achieved by using Portland cement after one week of curing.

In summary, from the previous studies it can be seen that cement has been widely used in CBEMs to enhance the properties of the mixtures. However, cement manufacture is a very energy intensive process leading to harmful environmental effects during production (Schneider et al., 2011). The manufacture of 1 tonne of OPC involves the consumption of 1.5 tonnes of quarry material, an energy consumption of 5.6 Gj/tonne and emissions of approximately 0.9 tonne of CO_2. The cement industry is responsible for the production of 5% of total global carbon dioxide CO_2 emissions (O'Rourke et al., 2009). Ravikumar et al. (2010) reported that the recent drive to increase the consumption of waste and by-product materials has resulted from a growing awareness about the ecological impact of Portland cement as a construction material.

Most of the above research work has concentrated on road surfacing pavement mixtures with OPC added as a filler; no similar studies have been done on the performance of binder courses using alternative fillers made from waste fly ash and waste materials as is

the case in this research work. Developments addressing the challenges in this area have focused on the exploration and utilization of waste and by-product materials to reduce the cement content in CBEM mixtures for the enhancement of the mechanical properties and durability of these mixtures.

4.2.5.2 Incorporating Waste and By-Products Materials as A Filler Replacement

The utilization of by-product and waste materials as filler in the pavement industry, specifically in the manufacture of CBEMs, is one way to address issues around the removal or treatment of such materials, something which is becoming a serious challenge. The increase of by-product and waste materials is unavoidable, but new and useful recycling opportunities which are economically sound and environmentally friendly, can be established and applied. By using these materials, two advantages can be achieved; they have a slight or no manufacture cost and the re-use of such material will eliminate the need for expensive disposal.

Previous studies have established that the mechanical properties of CBEMs can be enhanced by using cementitious materials, for example Portland cement and rapid setting cement. Unfortunately, these materials have two main disadvantages; their environmental impact and cost. Therefore, the re-use of industrial by-products and waste materials in CBEMs production is justifiable for technical, economic and ecological reasons as explained earlier. In addition, the greater thickness of binder courses will allow the quantity of the waste materials to be maximized which, in turn, will produce environmental advantages. The pavement sector is a great consumer of materials, so there is huge potential for the utilization of substantial amounts of waste materials in this field.

Thanaya (2003) has carried out research applying different waste materials to CBEMs to enhance their mechanical properties. He found that red porphyryn sand, synthetic

aggregates made from sintering quarry fines and crushed glass, can easily be incorporated into CBEMs and still allow satisfactory stiffness values. Examining other materials, Thanaya (2003) found that steel slag was risky as it leads to an expansion in volume in wet conditions while crumb rubber causes cracks at early stages of compaction. Conducting experiments using pulverized fly ash (PFA) as a filler in CBEMs at full curing conditions Thanaya et al. (2006) also established that CBEMs stiffness was comparable to hot mixes thus confirming its suitability for use.

Research work performed by Ellis et al. (2004) considered a variety of storage grade macadams consisting of recycled aggregates from various sources bound by bitumen emulsion and Ground Granulated Blastfurnace Slag (GGBS). The results here showed that the stiffness and strength can development when GGBS is added in high humidity conditions.

Recently, Al Nageim et al. (2012) conducted experiments using waste materials and industrial by-products to develop a new close-graded CBEM that has superior mechanical properties compared to traditional HMA surface courses. Waste domestic fly ash, namely LJMU-FA1, was substituted for traditional mineral filler and as a result, another binder was produced from the process of hydration between LJMU-FA1 and the trapped water.

Al-Hdabi et al. (2014a) performed experiments on the mechanical properties and water sensitivity of cold-rolled asphalt (CRA) by using a Waste Fly Ash (WFA) as a substitution for traditional mineral filler. A silica fume, a by-product, was also incorporated as an additive to improve the mechanical properties and durability of CRA. The results confirmed a substantial enhancement in stiffness modulus and uniaxial creep tests, in addition to water damage resistance.

More recently, Nassar et al. (2016a) examined the improvement of CAEMs using binary and ternary blended fillers (BBF and TBF). OPC, fly ash and GGBS were used for the BBF while silica fume (SF) was added to the BBF to achieve TBF. He concluded that TBFs are more suitable than BBFs based on the mechanical and durability results, suggesting that TBFs would be active in road pavements subjected to severe conditions both in hot and cold climates.

Dulaimi et al. (2016b) developed a new cold asphalt concrete binder course mixture by replacing limestone filler with a new binary blended filler material produced from high calcium fly ash and a fluid catalytic cracking catalyst (FC3R). It proved to be very effective in providing microstructural integrity having a very high early strength and showing a significant improvement in permanent deformation and fatigue resistance. Adding a waste alkaline NaOH solution to the this binary blended filler (Dulaimi et al., 2017) resulted in the development of a new fast curing and environmentally friendly cold asphalt concrete for binder courses mixture. Dulaimi et al. (2017) concluded that incorporating an alkali activated binary blended cementitious filler (ABBCF) considerably improved its mechanical properties and water susceptibility. This high performance ABBCF mixture also has a substantially lower thermal sensitivity than traditional hot asphalt concrete binder course mixtures. SEM analysis revealed that the main crystallisation had taken place at an early stage and more significantly, the new mixture had a comparable stiffness modulus with the traditional asphalt concrete binder course after a very short curing time (less than one day).

4.3 Summary

This chapter has focused on the previous attempts to improve the performance of CBEMs. Different techniques have been used to enhance the mechanical properties of such mixtures to make them environmentally friendly, economical and sustainable alternatives to traditional asphalts because they can be mixed with aggregates without the need to heat the stone and the bitumen in contrast to traditional asphalts. However, weak early strength, long curing times to achieve full strength and high porosity of compacted CBEMs have been cited as the main barriers to wide utilisation. The inclusion of OPC in CBEMs has an advantage in that satisfactory strength can be reached in a short period of time. However, OPC is not a green material and has a negative impact on the environment. The re-use of waste materials in CBEMs is commonly promoted for two reasons; environmental sustainability and economic advantages. Accordingly, several candidate waste materials have the potential for inclusion in CBCEA mixtures to generate new cementitious materials to overcome the shortfalls of CBCEA mixtures.

CHAPTER 5

RESEARCH METHODOLOGY AND CHARACTERIZATION OF CANDIDATE MATERIALS

5.1 Introduction

To meet the overall research aim, this chapter provides information on the research methodology adopted for the work, together with the characterizations of the materials used to develop new CBCEA mixtures. A number of industrial waste materials were collected, their mineralogical, chemical and morphological properties explored to assess their potential for further research. This is important as such characteristics have a significant influence on the properties of CBCEA mixtures. The characteristics of OPC and LF are also defined.

5.2 Research Methodology

A laboratory study approach has been selected to explore techniques which can be used to develop new, fast-curing CBCEA mixtures using different waste materials. Potential activation techniques were proposed based on the initial properties of candidate waste materials. The methodology adopted for this study has been detailed below, a schematic diagram of the entire method summarized in Figure 5-1. Concentrations of calcium, silicon and aluminium in waste materials had to be considered when choosing replacements for conventional limestone filler as a balanced oxide composition and an alkaline environment was necessary in the new cement material.

Literature review

Cold mix asphalt, hot mix asphalt, definitions, benefits, disadvantages, CMA with OPC as a filler

Waste candidates to replace LF as a filler, new cementitious filler

Identify candidate waste materials for filler replacement by applying XRF, XRD, PSD and SEM analysis and compare with OPC

Mix design of the new cold binder course emulsion asphalt

Production of cold binder course with OPC replacement for the limestone filler

Determine the ITSM of the new CBCEA mixture by optimizing the cementitious/pozzolanic candidate/s PMSA filler and applying mechanical activation by grinding

Develop and optimize a new CBCEA by applying FC3R as an activator to produce a binary blended cement filler from FC3R and PMSA

Develop the new fast-curing CBCEA using waste NaOH alkali activation with the BBCF

Evaluate the performance of the new CBCEA mixture/s in terms of mechanical and durability properties

Assess the environmental impact of using waste materials in CBCEA by utilizing a toxicity characteristic leaching procedure (TCLP)

Explain the reasons for improvements in properties using SEM and XRD technologies

Apply microwave curing techniques for further enhancement

Publish journal and conference papers

WRITE UP PhD THESIS

Figure 5.1. Schematic diagram of the proposed research methodology

5.3 Experimental Techniques for the Characterisation of Candidate Filler Materials

The following analytical techniques were implemented in order to explore the physical and chemical characterisations of the candidate waste materials and assess their incorporation, individually or collectively, in this research. The main aim was to determine and explain the relationship between the physico-chemical structure of the selected waste materials and hence produce a new cementitious filler for use in CBCEA mixtures.

> ➢ **Energy Dispersive X-ray Fluorescence (EDXRF)**

An X-ray fluorescence technique (XRF) was applied to explore the chemical composition (major oxide and trace elements) of the selected waste materials using a Shimadzn EDX 720, energy dispersive, X-ray fluorescence spectrometer (Figure 5-2). Qualitative and quantitative element analyses were performed as it is ideal for non-destructive application. The analysis is accomplished by applying X-rays to the specimens and analysing the re-emitted characteristic fluorescent X-ray.

Figure 5.2. Energy dispersive X-ray fluorescence (EDXRF) spectrometer

➢ **X-Ray Diffraction (XRD)**

X-ray diffraction is a method where a focused X-ray beam is targeted at a sample in a powder state, the pattern of diffracted rays recorded. This technique involves analyses of the intensity and the angle of the diffracted X-ray beam after encountering a plane of atoms in a material (Alizadeh, 2009b). Patterns identified using this technique, each material composed of a unique fingerprint, can be utilized to classify the mineralogy of crystal particles in the powder and is usually used for the characterization of crystalline materials and the detection of different chemicals. In this research, XRD testing was performed by using a Rigaku Miniflex diffractometer, as shown in Figure 5-3. The phase composition of the materials was determined using CuK X-Ray radiation, 30 kV voltage, current 15 mA at a scanning speed of 2.0 deg./min. in continuous scan mode with an aluminium specimen holder. The samples tested in a dry state.

Figure 5.3. Rigaku Miniflex diffractometer

➢ **Laser Diffraction Particle Size Analyser**

Particle shape and size play a substantial role in the improvement and application of sustainable CBEMs technology. A Beckman Coulter Laser Diffraction Particle Size Analyser LS 13 320 (Figure 5-4), was used to determine the Particle Size Distribution (PSD) of the filler materials while in liquid mode. It uses reverse Fourier optics incorporated in a patented fibre optic spatial filter system and a binocular lens system. This allows the LS 13 320 to optimize light scattering measurements across the widest dynamic range, from 40 mm to 2000 µm, in a single scan in aqueous liquid mode (ALM) (Beckman, 2016). The average from five consecutive runs was taken for each measurement of particle size.

Figure 5.4. Laser diffraction particle size analyser

➢ **Scanning Electron Microscopy (SEM)**

SEM is a method for high resolution imaging of sample surfaces by scanning with a high energy beam of electrons across a surface. It is a technique used to illustrate the microstructure morphology of particles and the surface characterization of materials.

SEM images were collected using both Inspect S and Quanta 200 scanning electron microscopes as shown in Figure 5-5. The specimens were coated with palladium, using an auto fine sputter coater, to increase conductivity. SEM applies a focused beam of high energy electrons to produce a diversity of signals at the surface of solid samples. The signals arising from electron sample interactions reveal information about the specimen, comprising external morphology (texture), chemical composition, crystalline structure and the orientation of materials (Swapp, 2016). Test conditions comprised an SEM resolution of 3-4 nm, high vacuum and a test voltage of 5-25 kV.

Figure 5.5. SEM apparatus

> **pH Measurement**

The pH, or hydrogen activity, is a measure of the acidity or alkalinity of a solution. Cement hydration and pozzolanic materials, are pH dependent and as such, the pH value determination test is a significant test to identify different reactions which may occur. By using a pH meter (a Corning model 240 as shown in Figure 5-6), the pH of selected

materials was measured, a Buffer solution used for calibration prior to the test. A suspension of water with filler was prepared and the pH measured at lab temperature.

Figure 5.6. pH meter

➢ **Concentrations of Heavy Metals**

The environmental impact of including waste materials in pavement layers is a significant issue that must be considered for a number of reasons. These layers are in continuous direct contact with the surface and also with underground water, this increasing the hazard of water pollution because of leaching of harmful materials, such as heavy metals, into underground water resources (Modarres et al., 2015a). It was reported by Halim et al. (2003) that small quantities of heavy metals are essential for health, but excessive amounts can cause serious or chronic toxicity. In this research, a Toxicity Characteristic Leaching Procedure (TCLP) test was used to determine the leached concentrations of cadmium (Cd), chromium (Cr), lead (Pb), barium (Ba), copper (Cu), arsenic (As), nickel (Ni) and zinc (Zn) from the new CBCEA following the procedure adopted by Xue et al. (2009) and Modarres and Ayar (2016) to analyse the possibility of heavy metals leaching

from the CBCEA mixtures. The concentration of heavy metals was measured using an atomic adsorption spectrophotometer (type: Thermo, Model: ICE 3300) as shown in Figure 5-7.

Figure 5.7. Atomic adsorption spectrophotometer

➤ **Density**

Density is required for volumetric analysis performed according to the standard BS EN 1097-7 (European Committee for Standardization, 2008) using a pyknometer. Density is measured as the volume of irregularly shaped samples determined by substituting a certain quantity of liquid of identified density with the test portion over known mass sample.

5.4 Selected Fillers Characterizations

5.4.1 Limestone Filler (LF)

Commercial limestone filler (LF) was supplied by Francis Flower Ltd at BS EN 13043 grade, fulfilling the following parameters: a $CaCO_3$ content greater than 70%; loose bulk density in kerosene between 0.5-0.9 g/ml; a particle size with more than 70% passing

63µm, and a moisture content of less than 0.1%. The measured pH was 9.39 and the measured density 2.57 Mg/ m^3. From the SEM seen in Figure 5-8, it can be observed that the particles are irregular with sharp angles. Figure 5-9 shows the powder XRD pattern of LF which is composed of calcite and quartz. The PSD of LF in Figure 5-10 shows that is composed of 24.22µm and 96.48µm d$_{50}$ and d$_{90}$, respectively. Most of LF particles are between 3µm and 130µm in size. The chemical composition under XRF analysis is shown in Table 5-1 where it can be seen that the LF was mainly composed of CaO and SiO$_2$.
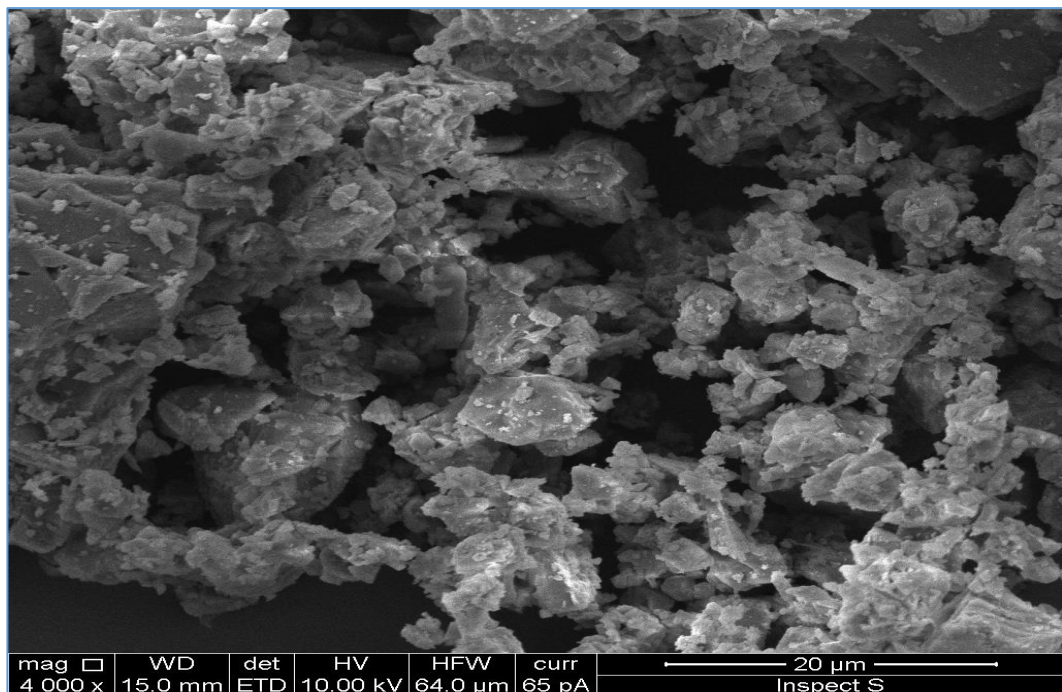
Figure 5.8. SEM view of limestone filler particles

(calcite-C, quartz-Q)
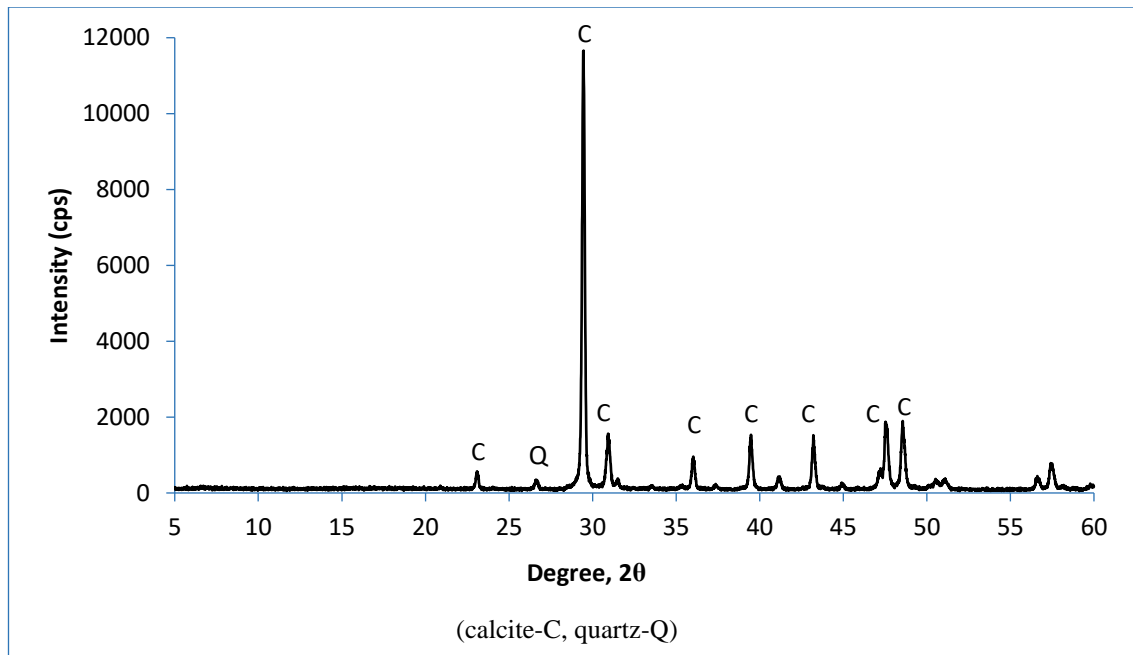
Figure 5.9. Powder XRD pattern for limestone filler
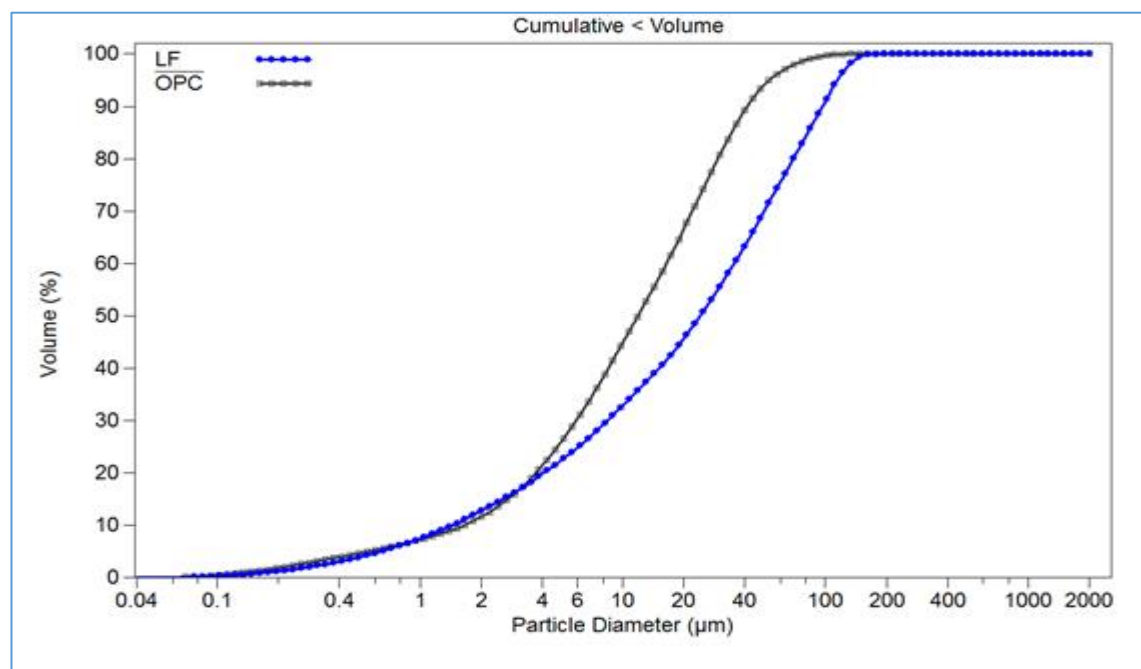
Figure 5.10. Comparative PSD of LF and OPC

Table 5-1. Comparative chemical properties of LF and OPC

Properties	LF	OPC
CaO, %	76.36	62.379
SiO$_2$, %	16.703	26.639
Al$_2$O$_3$, %	0	2.435
MgO, %	0.981	1.572
Fe$_2$O$_3$, %	0	1.745
SO$_3$, %	0.096	2.588
K$_2$O, %	0.348	0.724
TiO$_2$, %	0.185	0.385
Na$_2$O, %	2.258	1.533
pH	9.39	12.92

5.4.2 Ordinary Portland Cement (OPC)

A commercially available cement type CEM-II/A/LL 42.5-N, manufactured by Hanson UK, has been used throughout this work. OPC has a density of 2.913 Mg/m^3; the pH of the aqueous solution was found to be 12.92. It can be observed from the PSD of OPC shown in Figure 5-10 that d$_{50}$ and d$_{90}$ were measured as 11.90μm and 41.10μm respectively, with the majority of particles falling in the range of 4μm to 60μm. The small d$_{90}$ value of OPC makes the particles finer than those in LF. This allows a higher level reactivity through hydration reactions producing higher strength. Table 5-1 above details the prime oxides identified in EDXRF, namely Ca, Si, Al, Mg and Fe with a 2.588% SO$_3$ content. The high Ca and Si content and significant content of Al, Mg and Fe oxide constitute the major chemical strength behind their pozzolanicity. These results are consistent with those obtained by Corinaldesi and Moriconi (2009); Sadique et al. (2012b); Sadique et al. (2012a) on the same type of cement. In the SEM view as shown in Figure 5.11, OPC particles show as irregular shapes produced after grinding clinker. The powder XRD pattern of the reference cement as shown in Figure 5.12, reveals that it

was composed of alite ($3CaOSiO_2$), belite ($2CaOSiO_2$), ferrite ($4CaOAl_2O_3.fe_2O_3$), calcite ($CaCO_3$) and periclase (MgO). Cement has conventionally been used to speed up the breaking of bitumen emulsion in CMA and the consumption of water by cement hydration (Fang et al., 2016b).
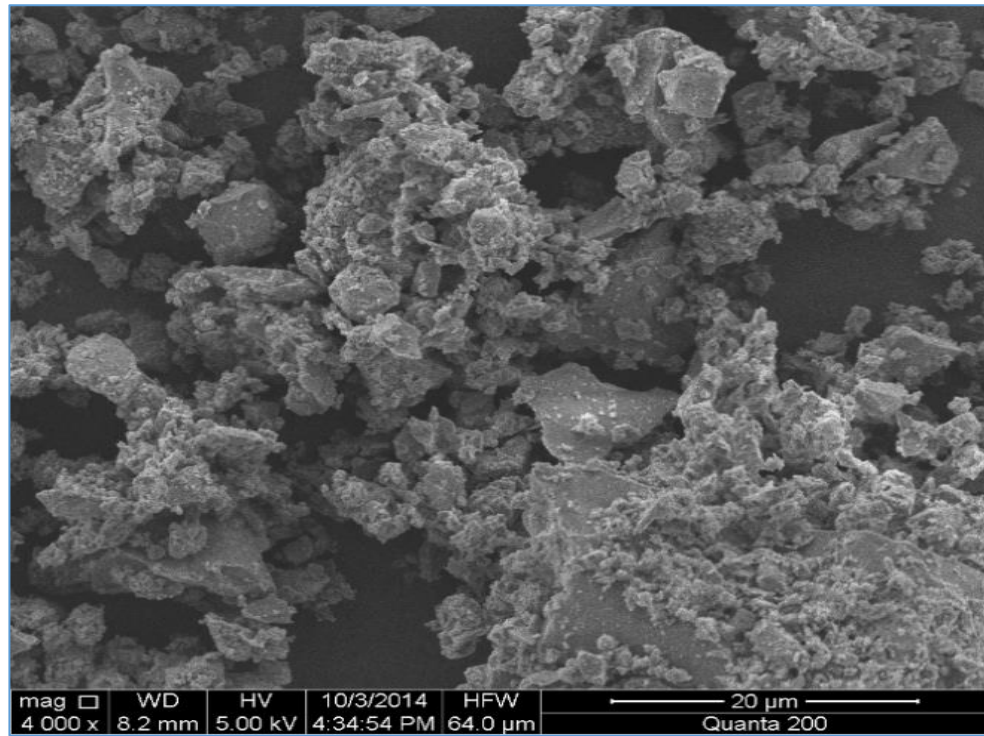
Figure 5.11. SEM view of OPC particles

(alite-A, belite-B, calcite-C, ferrite-F, periclase-Pc)
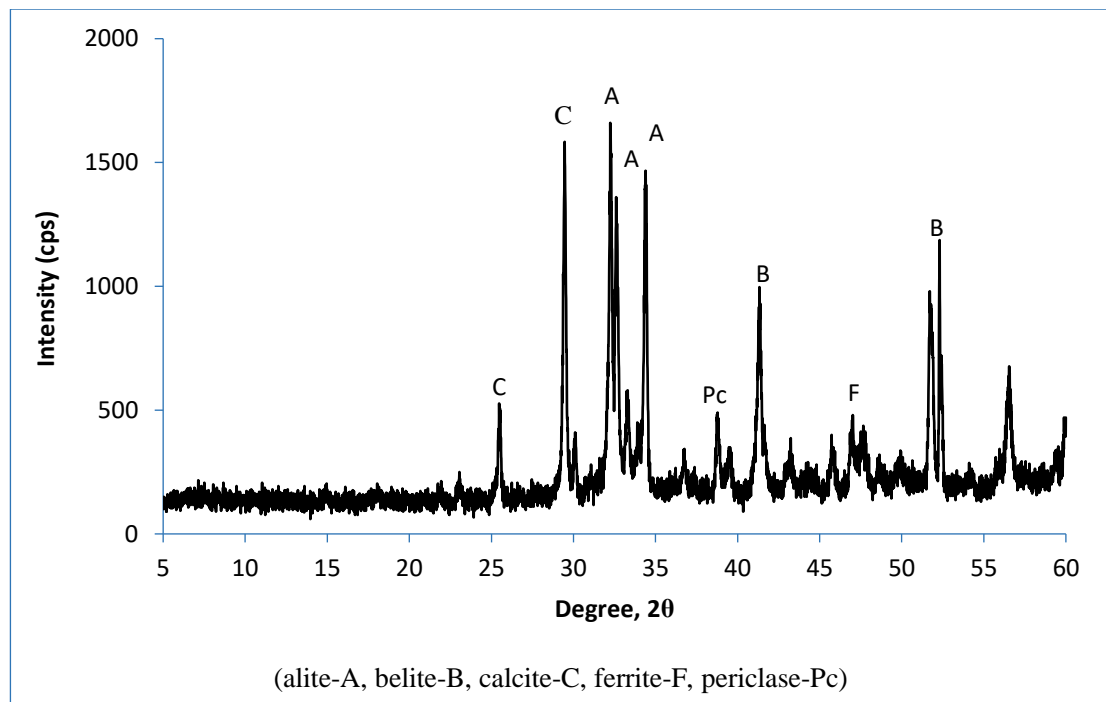
Figure 5.12. Powder XRD pattern for OPC

5.4.3 Paper Making Sludge Ash (PMSA)

PMSA is produced by the paper recycling industry from the combustion of waste paper and is classified as unsuitable for recycling. These wastes are burned to decrease their volume and generate energy. PMSA is rich in hydraulic minerals such as lime (CaO), mayenite and gehlenite and can be categorised as a hydraulic mineral admixture (Segui et al., 2012). Free lime in the mix reacts with water providing a highly alkaline solution leading to the release of more reactive phases such as Al_2O_3 and SiO_2 into the system (Mozaffari et al., 2009).

PMSA is a dry white ash residue and was obtained from Aylesford Newsprint Mill Limited Ltd (ANL), Europe's principal wastepaper recycling company for the production of newsprint, manufacturing 400,000 tonnes annually of recycled newsprint from 500,000 tonnes of waste paper fibre. This produces around 125,000 tonnes of PMSA annually in the UK (WRAP, 2007). In the EU, the process of combustion is controlled and usually utilizes fluidised bed combustion at 850°C to 1100°C (Wong et al., 2015).

In this research, two grades of PMSA have been collected, sourced from the same manufacturer namely: Fine Paper Making Sludge Ash (PMSA-F) and Coarse Paper Making Sludge Ash (PMSA-C). It can be seen from Figure 5-13 that PMSA-F has finer grain size distribution than PMSA-C but they have the same coarse particles in the range 0-1 µm. Most of the PMSA-F particles are in the region of 30 µm to 160 µm having d_{50} and d_{90} equal to 41.24 µm and 119.0 µm respectively. Conversely, most of the PMSA-C particles fall in the region of 30µm to 400µm having d_{50} and d_{90} equal to 97.58µm and 323.1µm respectively.

The PMSA samples are generally calcium aluminosilicate, seen in Table 5-2, as identified by X-ray fluorescence spectroscopy. The major oxides for both grades are Ca, Si, Al, Mg and Fe with some trace elements. No major variation has been identified in the chemical structure of either grade of PMSA. The presence of Ca, Al and Si in fly ash is significant for the development of a new cementitious material from waste and by-product materials (Sadique et al., 2013). Sadique and Al-Nageim (2012) reported a lower CaO content (57%) in their investigation with a higher proportion of SiO_2 (28%). The pH value for PMSA-F and PMSA-C are 12.74 and 12.72, respectively. The benefit of this higher pH with high calcium and silicon oxide contents will be discussed as this is deemed necessary to explain the mechanical properties of the new CBCEA mixtures.

The SEM view of both PMSA samples particles in Figures 5-14 and 5-15, shows both grades to be flaky, thin and agglomerated. However, these photos confirm the PSD results which identified PMSA-F particles as finer than PMSA-C particles. The d_{50} equal was to 41.24 µm for the PMSA-F sample while it was equal to 97.58µm for the PMSA-C sample.
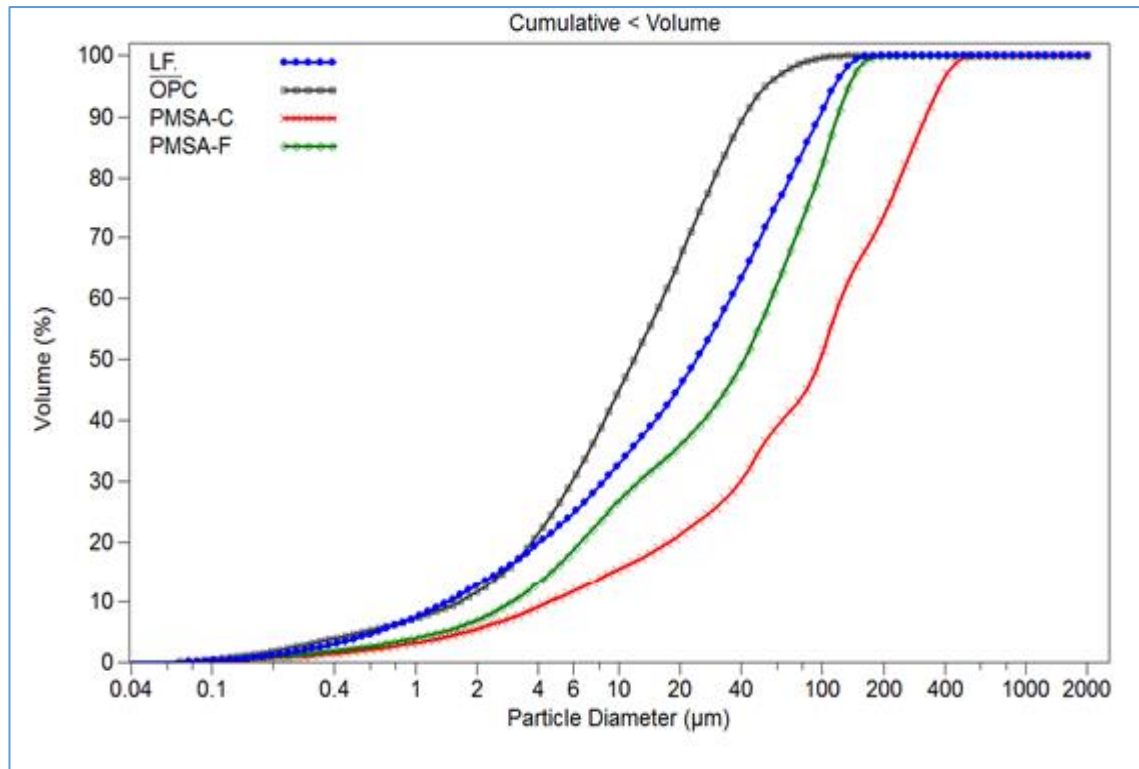
Figure 5.13. Comparative PSD of PMSA-F, PMSA-C, LF and OPC

Table 5-2. Comparative chemical properties of PMSA-F and PMSA-C fillers

Properties	PMSA-F	PMSA-C
CaO, %	67.057	66.964
SiO_2, %	24.762	24.662
Al_2O_3, %	2.430	2.347
MgO, %	2.845	2.744
Fe_2O_3, %	0	0
SO_3, %	0.340	0.332
K_2O, %	0.266	0.326
TiO_2, %	0.473	0.519
Na_2O, %	1.826	1.760
pH	12.74	12.72
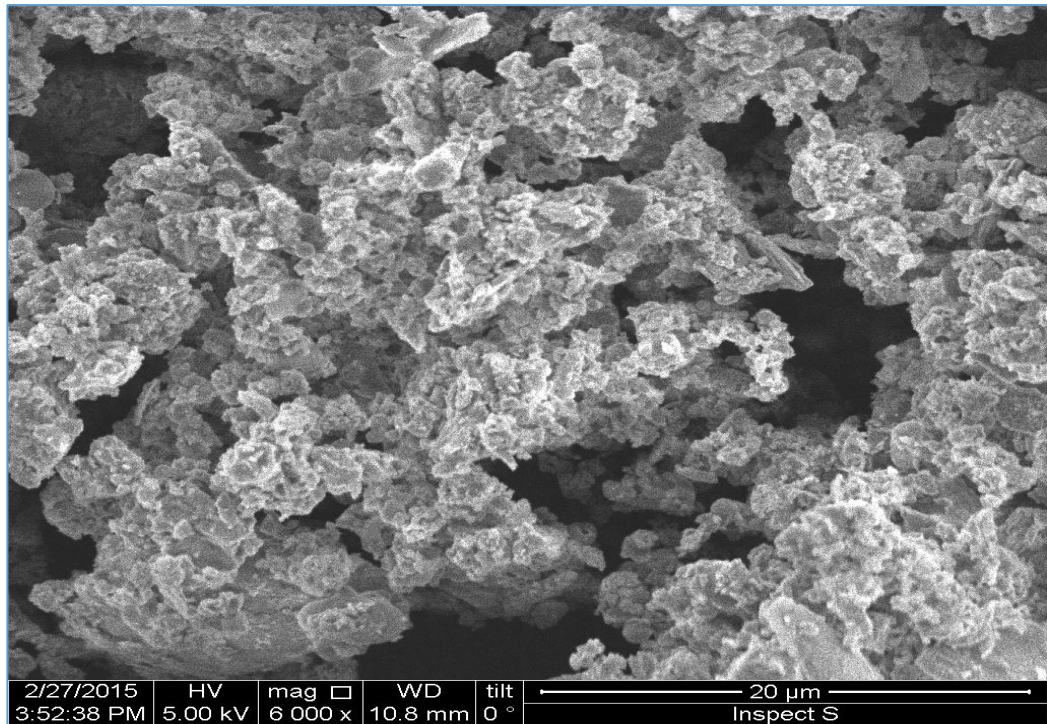
Figure 5.14. SEM view of PMSA-Fine particles
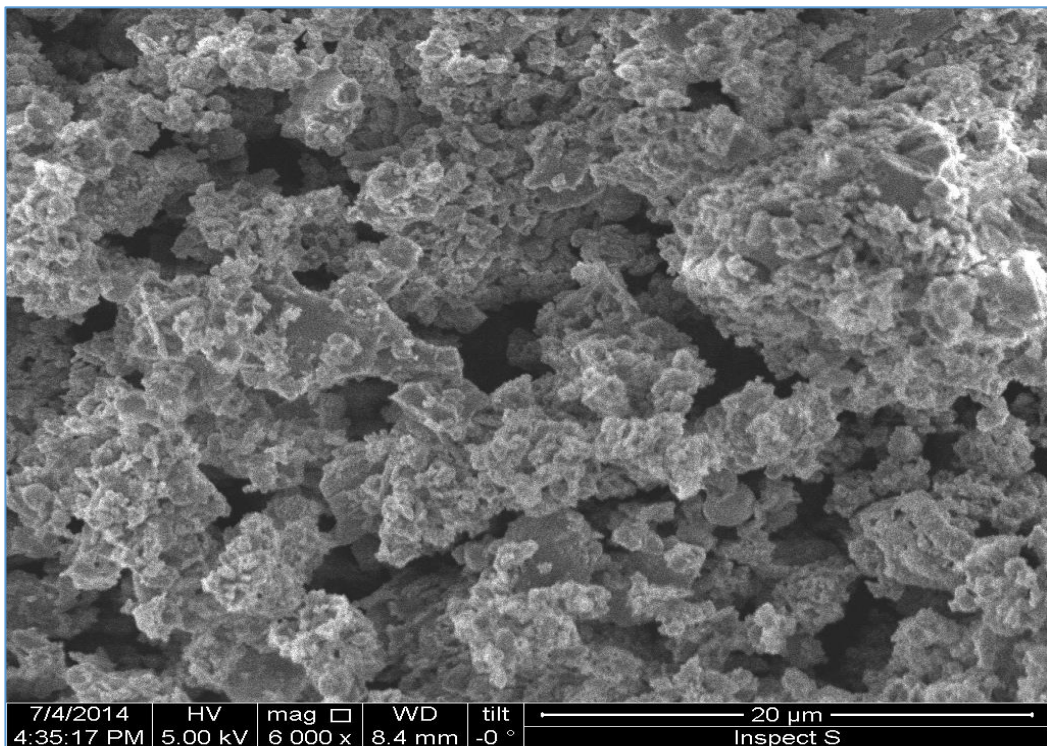
Figure 5.15. SEM view of PMSA-Coarse particles

It was found that both PMSA powder samples had the same XRD pattern, as shown in Figure 5-16, the samples observed to be crystalline, containing sharp peaks without

significant noise in the background. The major crystalline phases determined by XRD are: calcite ($CaCO_3$), lime (CaO), mayenite ($Ca_{12}Al_{14}O_{33}$), merwinite ($Ca_3Mg[SiO_4]$) and gehlenite ($CaAl[Al,SiO_7]$). A similar mineralogy was reported by Sadique and Al-Nageim (2012) and Sadique et al. (2012a), however no merwinite was detected in the latter.

(lime-L, calcite-C, gehlenite-G, belite-B, mayenite-M, merwinite-Mr)
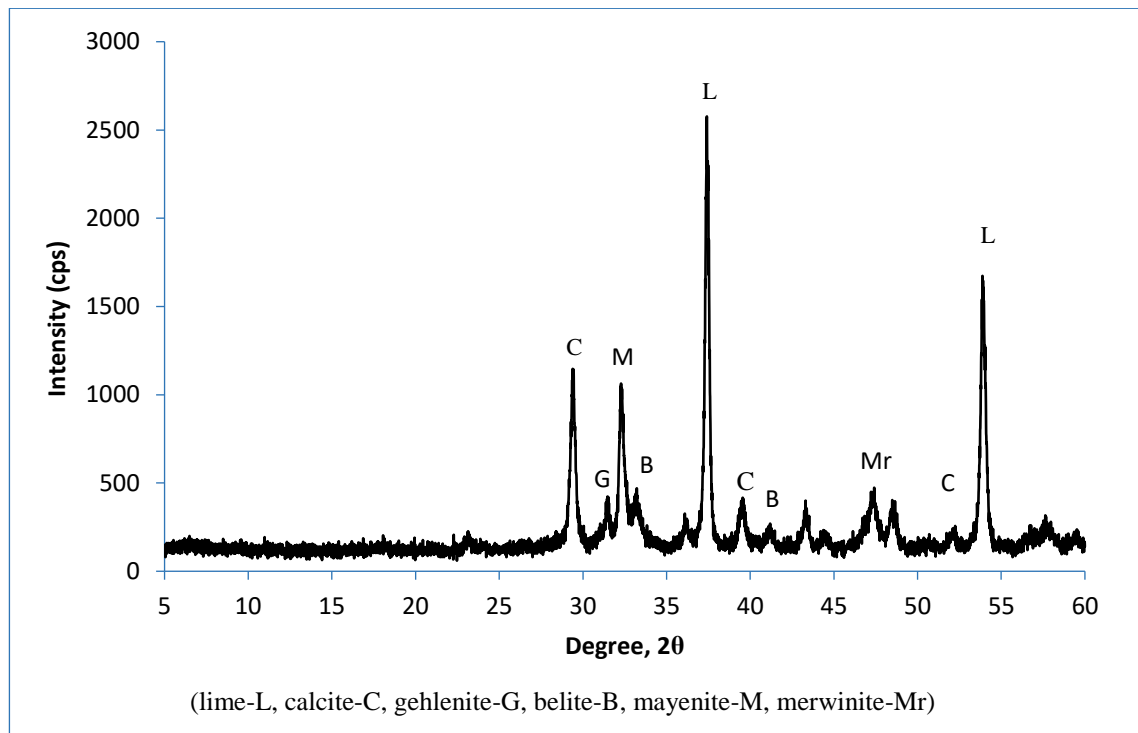
Figure 5.16. Powder XRD pattern of PMSA

5.4.4 Fluid Catalytic Cracking Catalyst Residue (FC3R)

FC3R is white or very slightly grey, created as a petroleum waste product from the fluid catalytic cracking (FCC) units of oil cracking refineries and has a specific or certain molecular weight. It is composed chiefly of inorganic silica and alumina with an open zeolitic structure and shows pozzolanic activity (Mejía de Gutiérrez et al., 2015). These products have a short life with regard to catalytic activity and old inactive catalysts may be substituted by a new, active catalyst. Consequently, substantial amounts of FC3R are generated, about 400,000 tonnes every year (Furimsky, 1996; Pacewska et al., 2002), resulting in significant waste disposal problems (Payá et al., 1999). Pacewska et al. (1998)

have studied the pozzolanic nature of this catalyst using thermal and spectroscopic techniques and have suggested that the ability of FC3R to react with Ca(OH)$_2$ is comparable to microsilica. It has been proved that FC3R is an excellent by-product pozzolanic material enhancing the early strength of cement mixtures and improving pozzolanic reaction (Payá et al., 2001; Mármol et al., 2015). For the current research, FC3R was collected from OMYA CLARIANA, originally generated by a BP oil refinery in Castellón (Spain). The main oxides in this FC3R (Table 5-3) are Al$_2$O$_3$ and SiO$_2$, consistent with those found by Mármol et al. (2015); Mas et al. (2015). The measured pH of this FC3R was 6.09.

From the PSD shown in Figure 5-17, it can be seen that most of the particles of FC3R are in the region of 0.8µm to 60µm having d$_{50}$ and d$_{90}$ equal to 9.16µm and 40.52µm respectively. Microstructural studies in SEM, seen in Figure 5-18, show that FC3R particles are not irregular shapes but agglomerated. The powder diffraction in XRD (Figure 5-19) reveals that FC3R has very low crystalline peaks comprising kyanite (Al$_2$O$_5$Si), quartz (SiO$_2$), mullite (Al6Si$_2$O$_{13}$), and dehydrated Ca-A zeolite (Al$_{96}$Ca$_{48}$O$_{38}$4Si$_{96}$), of an amorphous nature meaning that it will show high reactivity during the hydration process and can be used as an activator material. Mármol et al. (2015) investigated the pozzolanic activity of FC3R comparing its reactivity to Metakaolin, a synthetic pozzolan. They found that FC3R has a comparable chemical structure and high pozzolanic activity. Pacewska et al. (1998) revealed that both spent catalyst and microsilica have the same potential to be combined with Ca(OH)$_2$, as the hydration process is highly exothermic, resulting in rapid setting of the cement paste. Therefore, FC3R has the potential   be used as a supplementary cementitious material (SCM) which can replace cement in CBEMs offering a way to manage sustainability by eliminating the need for cement in CMAs.

The soluble SiO_2 and Al_2O_3 present in the glass phase of the pozzolanic materials, reacts with $Ca(OH)_2$ released through the hydration of cement to make an extra calcium silicate hydrate (C-S-H) gel that improves the mechanical strength of the hardened concrete structure (Lea, 1970).

Table 5-3. Comparative chemical properties of FC3R

Properties	FC3R
CaO, %	0.047
SiO_2, %	35.452
Al_2O_3, %	44.167
MgO, %	0.684
Fe_2O_3, %	0.368
SO_3, %	0
K_2O, %	0.049
TiO_2, %	0
Na_2O, %	0
pH	6.09
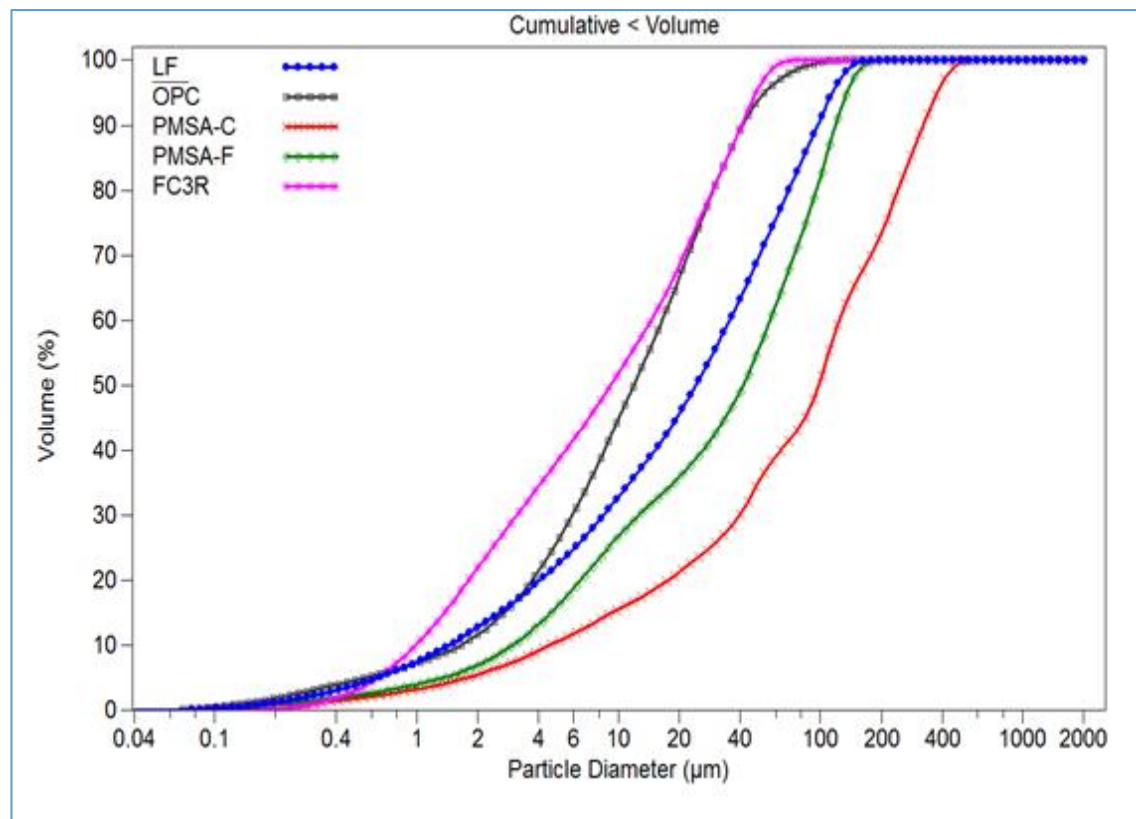
Figure 5.17. Comparative PSD of candidate materials
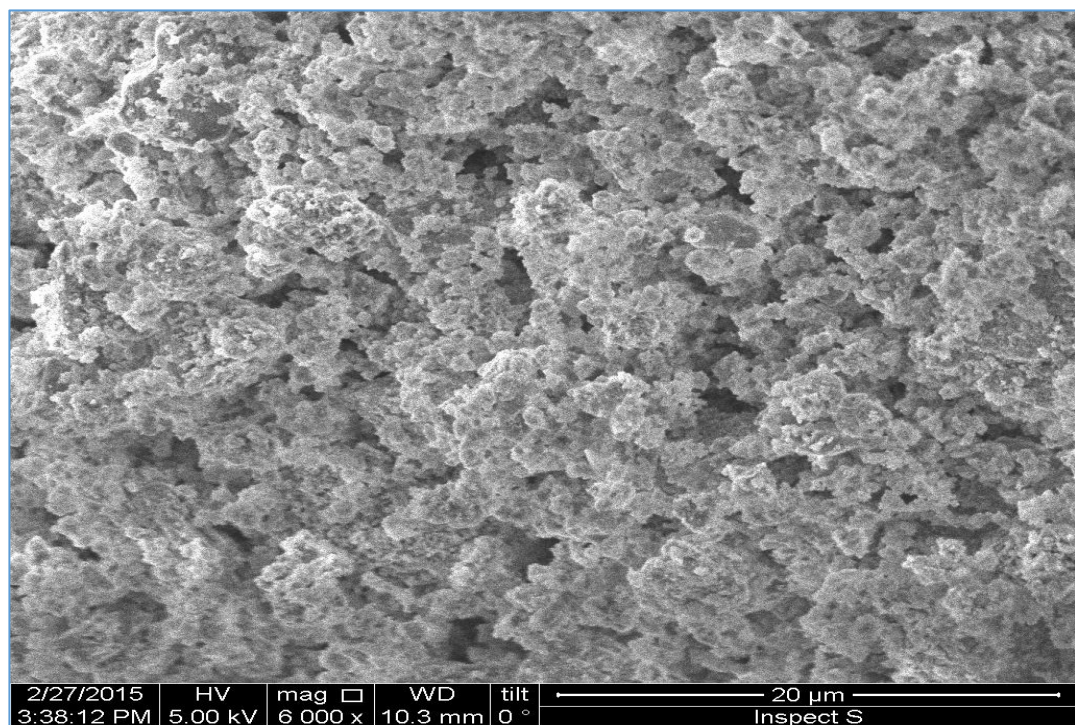
Figure 5.18. SEM view of FC3R particles

(K- kyanite (Al2O5Si), Q- quartz (SiO2), M- mullite (Al6Si2O13) andZ- dehydrated
Ca-A zeolite (Al96Ca48O384Si96))
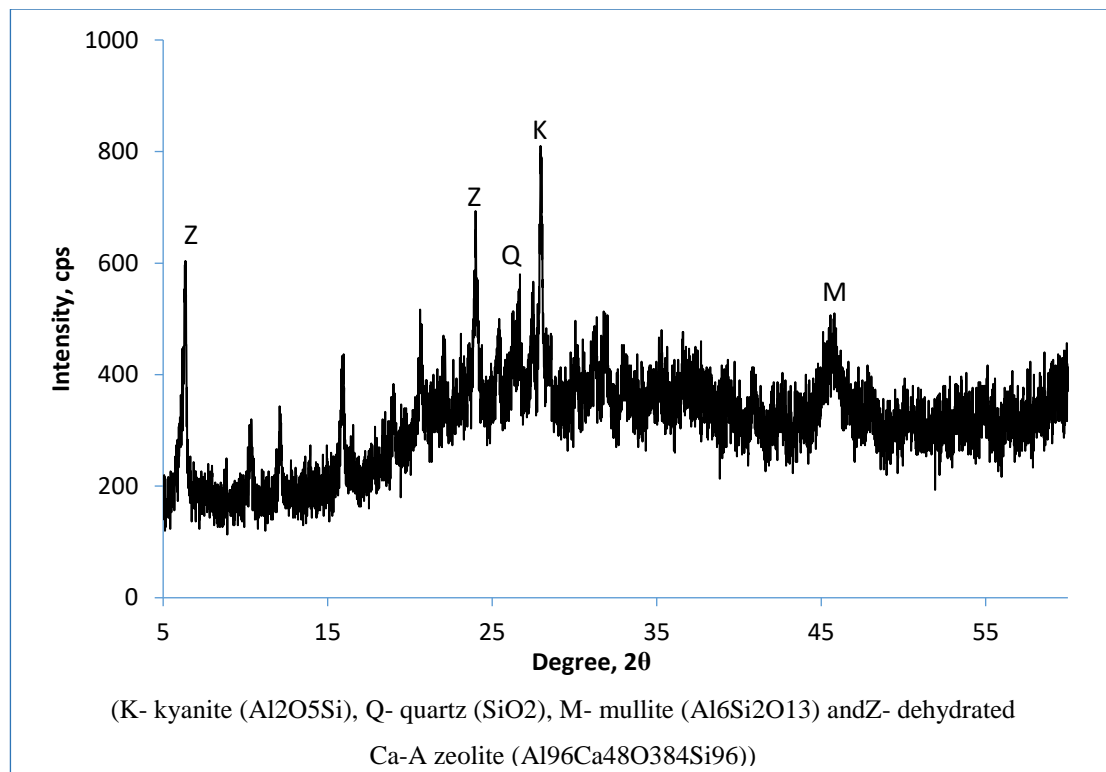
Figure 5.19. Powder XRD pattern of FC3R

5.4.5   Sodium Hydroxide (NaOH) Alkali Waste

Sajedi and Razak (2011) discuss a range of chemicals that can be used to activate reactivity in cementitious components, for example, sodium hydroxide (NaOH) which is usually used as the alkaline activating agent for fly ash and other waste materials (Ravikumar et al., 2010; Bui et al., 2015). In this research, sodium hydroxide (NaOH) alkali waste has been used as the alkali activator, the first time as a replacement for the pre-water content. The W-NaOH alkali waste solution was produced by an acid neutralisation plant (Lambson Limited, West Yorkshire) and contains $\leq$ 8% NaOH in water.

The glassy component of fly ash powdered material is changed through alkaline activation into very well compacted cement (Fernández-Jiménez and Palomo, 2005). Palankar et al. (2015) reported that Alkali-Activated Slag Fly Ash Concrete (AASFC) mixes have an acceptable enough performance for use in pavement quality concrete when

using steel slag aggregates, arguing that alkali-activated binders have the potential to replace traditional OPC binders. Many materials such as Ground-Granulated Blast Furnace Slag (GGBFS), Fly Ash (FA), Rice Husk Ash (RHA), FC3R and Metakaolin, can be used to produce alkali-activated binders through alkali activation. Morsy et al. (2008) found that alkali-activated cementitious binders display greater mechanical properties in comparison to OPC binders so, the alkali activation of fly ash offers potential financial and environmental savings when used as a cement replacement (Davies, 2011).

Xu and Van Deventer (2000); Sofi et al. (2007) reported that the alkali activation of aluminosilicate materials such as GGBFS or FA as binder systems are being investigated for use in concretes. For example, during alkali activation of aluminosilicates, the dissolution stage was found to be similar to Portland cement hydration at early ages (Xu and Van Deventer, 2000; Fernández-Jiménez et al., 2005). Al-Hdabi et al. (2014c) reported that the incorporation of high alkali waste material as a filler replacement in CBEMs provides an ambient environment to activate the hydration process of the incorporated cementitious constituents.

5.5 Mechanical and Durability Laboratory Testing

Thanaya (2003) stated that the properties of asphalts must be assessed by suitable testing methods. An extensive range of tests and configurations exist to evaluate relevant properties. The Marshall stability test and the Indirect Tensile Strength test (ITS) are tests modes which do not take into consideration the elastic properties of asphalts. In other testing modes, in particular in the Indirect Tensile Stiffness Modulus (ITSM) test, the elastic properties of asphalts play a significant role.

In general, there are three properties to consider in order to classify the performance of an asphalt namely mechanical properties, durability and volumetric properties. At present, there are no CBEM design procedures, testing protocols or specifications similar to asphalt. Consequently, researchers have usually adopted asphalt testing methods to characterize CBEMs. Some amendments have been made to cover the compatibility of the properties of CBEMs under related testing temperatures, curing and condition times. Fundamental tests, i.e. ITSM on cylindrical samples, wheel track test on slab samples, four-point load tests on prismatic samples and semi-circular bending tests, were implemented to investigate the mechanical properties for the new product/s. Table 5.4 shows a summary of the tests carried out to establish CBCEA properties for this research. With reference to ecological issues, a toxicity characteristic leaching procedure (TCLP) test was performed to analyse the leachate from the specimens for concentrations of heavy metal.

5.5.1 Mechanical properties

A laboratory testing programme was set up to investigate the mechanical properties and behaviour of the CBCEAs and to evaluate the effect of replacing traditional limestone filler with new cementitious material. Four tests were performed to investigate the mechanical properties as seen in Table 5-4.

Table 5-4. Tests used to identify the properties of CBCEA mixtures

Properties	Test	Specification
Mechanical properties	Indirect Tensile Stiffness Modulus (ITSM) on cylindrical specimens	BS EN 12697-26: 2012
	Wheel track test on slab sample at 45°C and 60°C	BS EN 12697-22: 2003
	Fatigue test (four-point bending test) on prismatic samples	BS EN 12697-24, Annex D: 2012
	Semi-circular bending test (SCB)	BS EN 12697-44:2010
Durability	Water sensitivity	BS EN 12697-12: 2008
	Ageing test	SHRP A-003A
Volumetric properties	Bulk density	BS EN 12697-6: 2012
	Air voids, Voids in Mineral Aggregate(VMA) and Voids Filled with Bitumen(VFB)	BS EN 12697-8: 2003

5.5.1.1 Indirect Tensile Stiffness Modulus (ITSM) test

The stiffness of an asphalt is defined as the proportion of uniaxial stress and corresponding strain. With a high stiffness modulus, the structural layers of a road will distribute wheel loading over a large area, protecting the underlying layers of the pavement. The ITSM test is designed to test the capacity of individual layers of pavements to spread traffic loads to the layer underneath. An ITSM test with diametric pulsed loads on a cylindrical specimen has been selected because it is relatively fast, non-destructive and widely used throughout the world to assess the stiffness modulus of asphalts. It can also be considered as a synthetic index of the structural properties of mixes. The test is conducted to measure small strains on asphalts by applying impulse loading on a vertical diameter of a cylindrical sample (Ojum, 2015).

Currently, stiffness modulus is generally accepted as a highly significant performance property of asphalts, used as an indication of their load distribution capability. Stiffness modulus is one of the most significant properties which affects the critical strains produced in both base and subgrade layers (Read and Whiteoak, 2003). O'Flaherty (2007a) also stated that the stiffness modulus is a significant performance property of both base and binder course, defined as the load spreading ability of asphalt layers. Sunarjono (2008) suggested that measurements of stiffness may also be used as an indicator of the quality of mixtures in terms of susceptibility to temperature, sensitivity to water and ageing. This test has often been used by researchers as an indicative test for ranking CBEMs (Thanaya, 2003; Oke, 2010; Al Nageim et al., 2012; Al-Busaltan et al., 2012; Al-Hdabi et al., 2013a; Dulaimi et al., 2016b). At minimum of five samples have been used for each mixture type.

In this test, five load pulses were applied to the sample to determine stiffness. An indirect deformation on the horizontal diameter will be caused and because the specimens' diameter is known, the strain can be determined. The applied stress can also be calculated since the cross sectional area is known, meaning that the force utilized can be calculated (Read and Whiteoak, 2003). The stiffness modulus of asphalts can be determined, after calculating the stress and strain, by using the equation below:

$$S_\mathrm{m} = \frac{L}{D \times t} \times (v + 0.27) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5\text{-}1)$$

Where:

S_m = indirect tensile stiffness modulus (MPa)

L = the peak value of the applied vertical load (N)

D = the peak horizontal diametric deformation resulting from the applied load (mm)

t = the mean thickness of the test specimen (mm)

v = the value of Poisson's ratio for the asphalt at the temperature of test.

A measurement of the stiffness of the mixture is obtained by the application of predetermined, repeated loads to each sample under test, and by deciding the particular recorded passing deformations through two Linear Variable Displacement Transducer (LVDT) sensors. The test was conducted at 20°C according to the standard BS EN 12697-26 (European Committee for Standardization, 2012c). Figure 5-20 depicts the test configuration of the ITSM test using the Cooper Research Technology HYD 25 testing apparatus with a pneumatic close loop control system, while Table 5-5 comprises a summary of the test parameters for the ITSM test.

Table 5-5. ITSM Test Conditions

Parameter	Range
Specimen diameter, (mm)	100 ± 3
Rise time, (ms)	124 ± 4
No. of conditioning pulses	5
Loading time, (s)	3–300
Transient peak horizontal deformation, (μm)	5
Poisson's ratio	0.35
No. of test pulses	5
Test temperature, (°C)	20 ± 0.5
Specimen thickness, (mm)	63 ± 3
Compaction	Marshall 50 blows/face
Specimen temperature conditioning	4 hours before testing
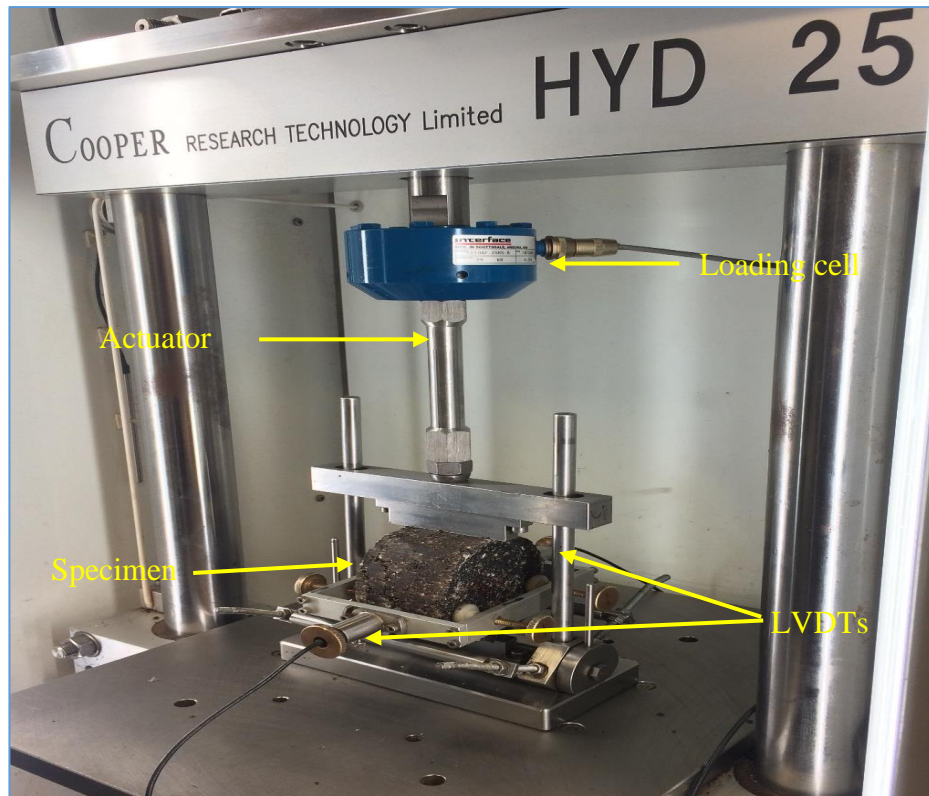
Figure 5.20. ITSM Test Configuration

5.5.1.2 Resistance to Permanent Deformation

Permanent deformation is one of the major issues for bound and unbound layers in asphalt pavements defined as an accumulation of the minor, irrecoverable part of the deformation produced by each wheel load. It develops slowly with an increase in number of load applications, appearing as a longitudinal depression taking place in the wheel path of the vehicle. It is affected by mixture properties, i.e. material properties and volumetric composition. The resistance of asphalt to permanent deformation has been assessed using the wheel tracking test by several researchers Bodin et al. (2009); Ma et al. (2015); Dulaimi et al. (2016b). Wheel tracking tests have been applied to investigate the permanent deformation resistance in this research to establish CBCEAs susceptibility for failure under loading. These tests are widely accepted as a reproduction of the effects of traffic on the surface of asphalt. The test was performed to recreate, as closely as possible,

conditions on the road in order to identify and appraise the mechanisms of failure of CBEMs under controlled conditions (Ojum, 2015).

The test was conducted at two temperatures, 45°C and 60°C, in a temperature controlled chamber using a small, model HYCZ-5, wheel tracking device as presented in Figure 5-21. This device is used by the Liverpool Centre for Material Technology (LCMT) lab to assess rutting resistance at moderate to heavily stressed sites and very heavily stressed sites respectively, according to BS EN 13108 (European Committee for Standardization, 2015). The tests were carried in accordance with BS EN 12697-22 instructions (European Committee for Standardization, 2003a), Table 5-6 illustrating the test conditions. In the wheel track test, a rubber tyre moving at a speed of 42 passes/minute, is acting on the sample in a forwards and backwards mode in the centre of the slab sample with a contact width of 50 mm. A Linear Variable Differential Transformer (LVDT) was employed to measure the vertical displacement of the slab sample along the path of wheel. The final vertical deformation was used as an indicator of rutting resistance. The tests were performed with five specimens per mix type.

A slab specimen of length 400 mm, width 305 mm and thickness 50 mm was compacted in a steel mould using a Cooper Technology Roller Compactor device following the standard BS EN 12697-33 (European Committee for Standardization, 2003b), which is shown in Figure 5-22.

The parameters for both the Wheel Tracking Slope (WTS_{AIR}) and Proportional Rut Depth (PRD_{AIR}) were determined according to the standard BS EN 12697-22 (European Committee for Standardization, 2003a) to assess the mixtures' resistance to permanent deformation where:

➢ PRD_{AIR} is the proportional depth of the rut after 10000 cycles (%)

 ➢ WTS$_{AIR}$ is the tangent of the angle of slope of the rut depth increase (mm/ cycles),

 determined from:

WTS$_{AIR}$ = $\dfrac{d\ 10000 - d\ 5000}{5}$ …………………………………………….. (5-2)

where: d5000, d10000: the depth of the rut after 5000 and 10000 loading cycles (mm).
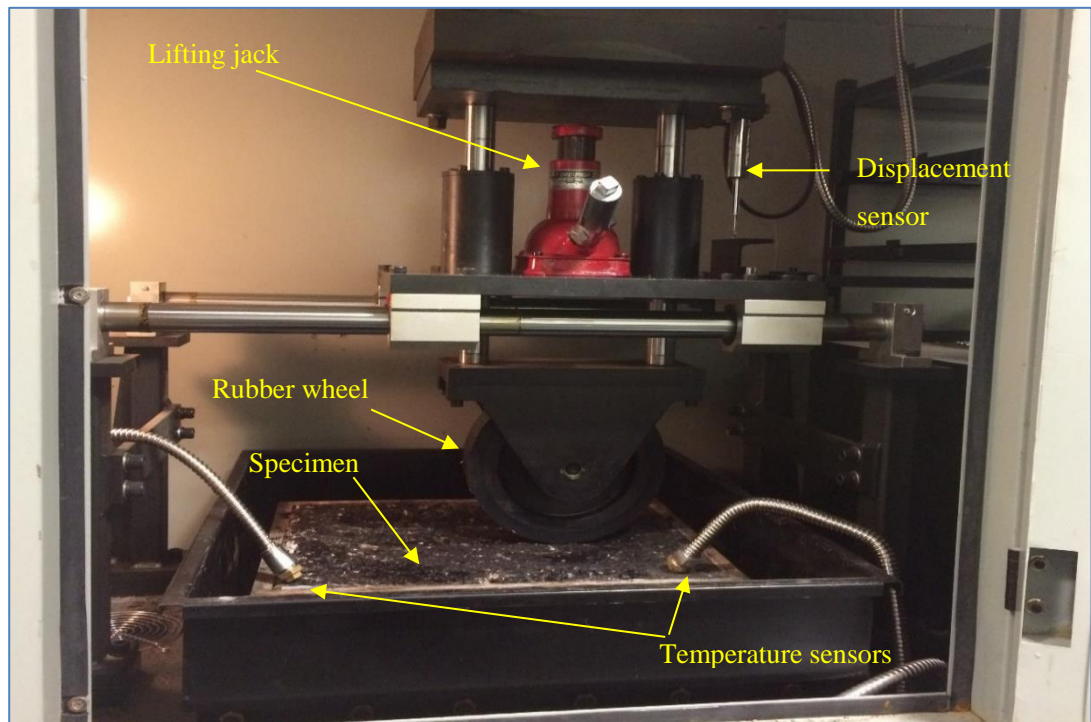
Figure 5.21. Wheel-tracking equipment used by LCMT lab

Figure 5.22. Roller compactor machine

Table 5-6. Wheel-tracking test conditions

Parameter	Range
Tyre of outside diameter, (mm)	200-205
Tyre width, (mm)	50 ± 5
Trolley travel distance, (mm)	230 ± 10
Trolley travel speed, (time/min)	42 ± 1
Contact pressure, (MPa)	0.7 ± 0.05
Poisson's ratio	0.35
No. of conditioning cycles	5
No. of test cycles	10000
Test temperature, (°C)	45, 60
Compaction	Roller compactor
Specimen temperature conditioning	Four hours before testing

5.5.1.3 Resistance to Fatigue Cracking

Fatigue cracking is fracturing which occurs under repeated loading, having a maximum

value usually less than that of the material tensile strength (Read, 1996). It is one of the

primary sources of distress resulting from cumulative damage under repeated loads, variations in temperature and construction practices which induce stress less the tensile strength of asphalt. Fatigue resistance is an important mechanical property in asphalts as fatigue is one of the most common mechanisms of pavement degradation. It comprises two main stages; crack initiation which can be described as the coalescence of micro-cracks to generate a macro-crack under repeated application of tensile strains, and crack propagation which constitutes the growing of the macro-crack through the material under the additional application of tensile strains (Read and Whiteoak, 2003).

In this research, fatigue cracking resistance has been carried out at 20°C at a frequency of 10 Hz in strain control mode by means of four-point bending beam tests on shaped prismatic samples according to the standard BS EN 12697-24:2012 (European Committee for Standardization, 2012b). The compaction of slab samples was carried out using a roller compactor, the prismatic samples then generated from these slabs. These prismatic specimens measured 400 x 50 x 50 mm with a swan face (Figure 5-23). The tests were carried out with five samples per mix type.

The prismatic beams were subjected to four-point, periodic bending with free rotation and translation at all load and reaction points. Bending is effected by loading the two inner load points (inner clamps), in a vertical direction, vertical to the longitudinal beam axis. The perpendicular position of the end bearings (outer clamps), is fixed. This load configuration will create a constant moment and therefore a constant strain between the two inner clamps. During the test, a sinusoidal waveform load was applied. The four-point beam fatigue set up is depicted in Figure 5-24 while Table 5-7 provides a summary of the test conditions. In this study, fatigue life is defined as the number of cycles (N_f) required to achieve a 50% decrease in material stiffness modulus. The relationship between fatigue life and range of strain levels, i.e. 100, 125 and 150 microstrains, have

been examined for the new fast curing CBCEA mixtures and compared to asphalts with

binder grade 100/150 pen and 40/60 pen. The fatigue line can be plotted according to the

results representing the length of life (N_f) for the chosen fatigue criteria by forming a

linear regression between the natural logarithms of N_f and the natural logarithms of the

initial strain amplitude (ε). The equation below determines the fatigue line shape:

$$In\ N_f = A_0 + A_1\ In\ (\varepsilon) \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\ (5\text{-}3)$$

where:

A_0 represents intercept with y-axis

A_1 represents the slope of the fatigue line

Figure 5.23. Four Point Load Prismatic Specimens
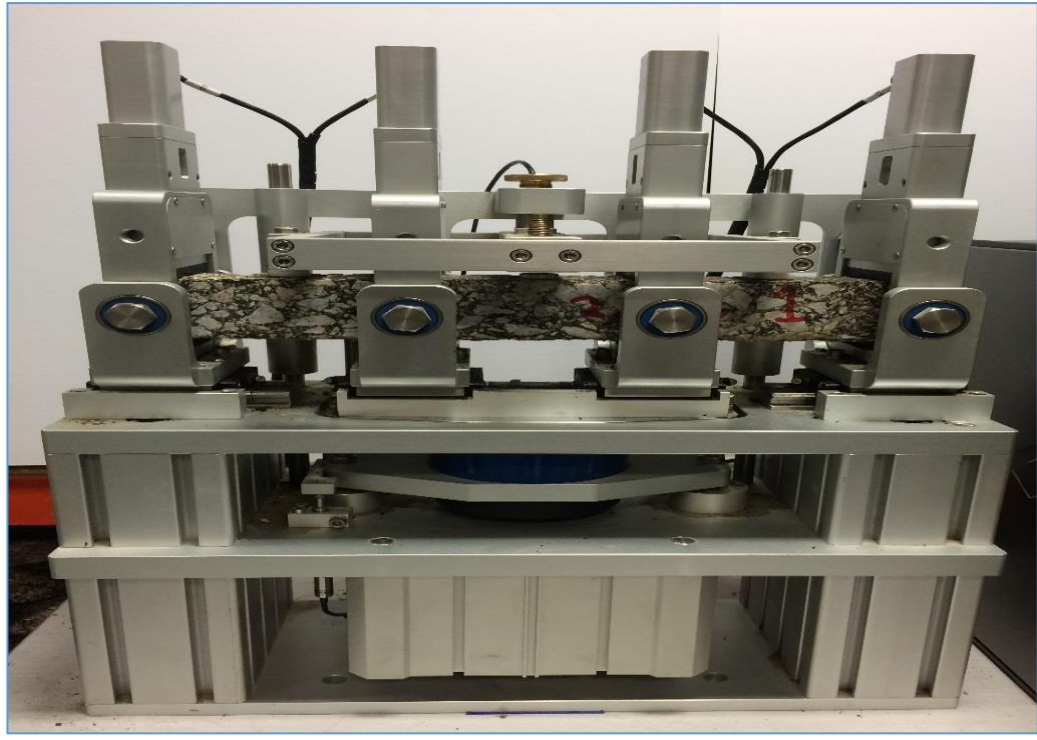
Figure 5.24. Test Set Up for Four-Point Bending

Table 5-7. Four Point Bending Fatigue Test Conditions

Parameter	Range
Control method	Constant strain
Test temperature, (°C)	20±1
Sample dimension, (mm)	400 x 50 x 50
Frequency, (Hz)	10
Microstrain	100-150
Initial stiffness end value, (%)	50

5.5.1.4 Semi-Circular Bending (SCB) Test

Semi-circular bending (SCB) tests have been used to assess the potential for crack propagation by determining the tensile strength or fracture toughness of asphalts. The test was performed at 5°C, according to BS EN 12697-44 (European Committee for Standardization, 2010a), using a Universal Testing Machine type (H25KS) as shown in Figure 5-25. A vertical load is applied until the semi-circular specimens (150 mm

diameter) are fractured, this providing flexural strength and fracture toughness readings. The laboratory compacted slabs, prepared by using a roller compactor, were cored using the core machine. Three specimens were obtained from each slab, measuring 150 mm in diameter, each then sliced down the middle to produce two duplicate samples (Figure 5-26). A notch of depth 10 mm was made on each sample before the third-point flexural test was performed, following the specification BS EN 12697-44 (European Committee for Standardization, 2010a), on the semi-circular specimen. Loading was carried out on the centre of the semi-circular specimen under a constant displacement rate of 5 mm/minute, until the sample was damaged. Loading sensors and LVDT were used to record the applied load and the corresponding vertical deflection at the centre of the semi-circular samples.

In accordance with the European Committee for Standardization (2010a), the maximum stress at failure, (σ_{max}), and the toughness, (K_{Ic}), of each sample was calculated, according to Equation (5-6) and (5-7) respectively.

$$\sigma_{max} = \frac{4.263 \; x \; F\text{max}}{D \; X \; t} \; Nmm^{-2} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \quad (5\text{-}4)$$

where:

D = is the specimen diameter, mm

t = is the specimen thickness, mm

F_{max} = is the maximum force of specimen, N

$$K_{Ic} = \sigma_{max} . f\left(\frac{a}{w}\right) \; N/mm^{3/2} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. \quad (5\text{-}5)$$

where:

w = specimen height, mm

a = notch depth of specimen, mm

σ_{max} = stress at failure of specimen, Nmm^{-2}.

f (a/W) = geometric factor of specimen, for 9 < a < 11 mm and 70 <W< 75 mm, then f

(a/W) = 5.956.
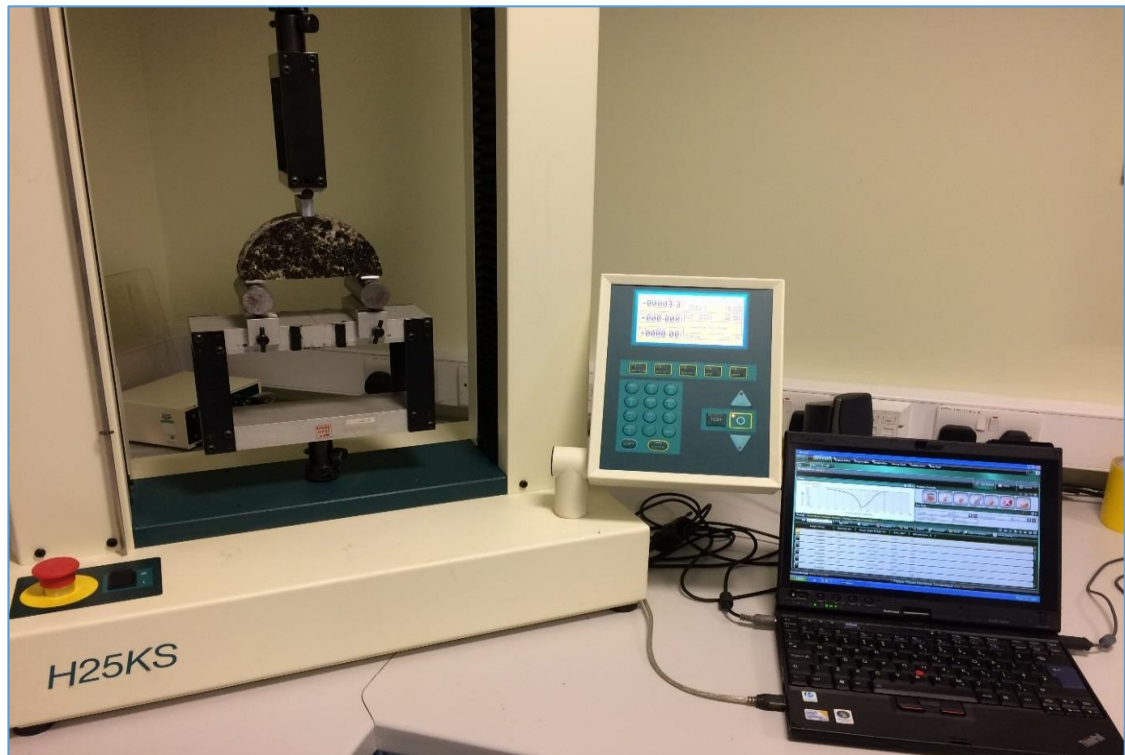
Figure 5.25. SCB Universal Testing Machine
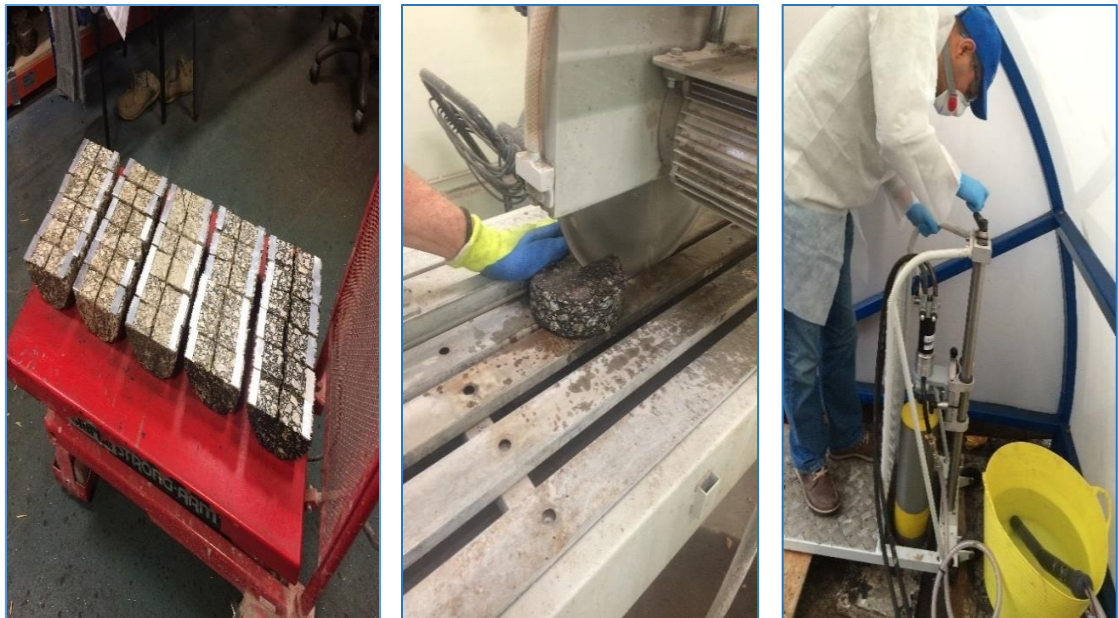
Figure 5.26. SCB samples preparation

5.5.2 Durability Tests

Durability can be conceptualised as the capacity of materials in an asphalt pavement, to withstand environmental effects such as temperature variation, water and ageing without any substantial weakening over a period of time for a given level of traffic loading. It is generally accepted that water sensitivity and ageing are the most sensitive parameters that affect the durability of asphalts. In this research, the durability of the mixtures has been tested in terms of water damage resistance and age hardening failure.

5.5.2.1 Water Sensitivity Test

Moisture damage in asphalt is connected with the loss of adhesion and/or cohesion in the material which leads to a decrease in stiffness, durability and strength (Breakah et al., 2009). Water sensitivity is therefore an index of evaluation of the performance of asphalt in a pavement. The existence of water in the layers of the pavement will cause initial failures in asphalt pavements in two ways: stripping distress as a consequence of debonding of the bitumen film from the aggregate surface and/or premature rutting/fatigue distress resulting from a reduction in the strength of the mix.

In this research, water sensitivity tests were performed according to BS EN 12697-12 (European Committee for Standardization, 2008) where the Stiffness Modulus Ratio (SMR) was used to examine sensitivity. Two sets of specimens with three parallel samples in each set were prepared using a Marshall hammer. The first set was assigned as the unconditional test (dry), the samples kept in their moulds for 24 hours after which they were extruded and placed in the lab at 20°C for 7 days. Following this, they were subjected to ITSM at 20°C. The second set was prepared for the conditional test (wet), left in the moulds for 24 hours before extrusion and cured at 20°C for 4 days. They were then conditioned as follows:

- Immersed in water, making sure they were completely covered with water, thereafter subject to a vacuum (6.7 kPa pressure) as shown in Figure 5-27 for 30 minutes at 20°C.

- Left submerged for the next 30 minutes after gradually letting atmospheric pressure into the vacuum desiccator. The pressure was decreased slowly to avert damage to the samples from expansion.

- Immersed in a water bath for 3 days at 40°C.

After conditioning, all samples were tested for ITSM test at 20°C where the water sensitivity was evaluated by determining SMR as the percentage of wet to dry samples' stiffness modulus, according to the standard BS EN 12697-12 (European Committee for Standardization, 2008).
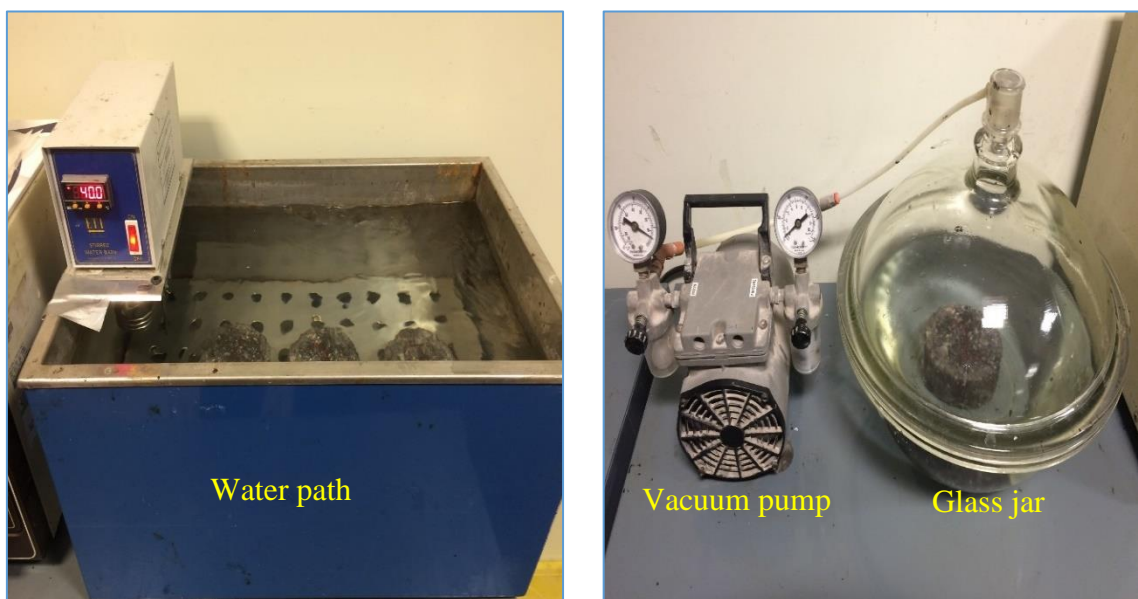
Figure 5.27. Water sensitivity apparatus

5.5.2.2 Ageing Test

It is generally agreed that short term oven ageing, which simulates the ageing of mixtures during the production stage, may not be applicable for CBEMs because of heat elimination through the process of production. A more appropriate method may be long

term oven aging which simulates the ageing of mixtures on the road when in use. The method recommended by the Strategy Highway Research Program (SHRP) A003A was adopted in order to simulate long term ageing. Kliewer et al. (1995) describe this procedure as curing compacted samples in an oven at 85°C for 2 or 5 days to simulate 5 or 10 years ageing of bitumen in the field.

Two groups of samples were prepared and divided to two sets. The first set was unconditioned where the samples were kept for normal curing and not exposed to oven curing. Regarding the second set, specimens were prepared and placed in an oven at 85°C for five days to simulate 10 years of the age-hardening effects. Both groups of samples were subjected to ITSM following the BS EN 12697-26 (European Committee for Standardization, 2012c) to measure the Stiffness Modulus Ratio (SMR).

5.5.3 Volumetric Properties

Air voids percentage, dry bulk density, Voids in Mineral Aggregate (VMA) and Voids Filled with Bitumen (VFB) were determined following MS-14 (Asphalt Institute, 1989). Volumetric properties can be calculated as follows:

$$Wet\ density = \frac{weight\ in\ air}{SSD\ weight - weight\ in\ water} \quad \text{..} \quad (5\text{-}6)$$

$$Dry\ density = \frac{(100+RBC)}{(100+RBC+W)}\ \text{x wet density} \quad \text{..} \quad (5\text{-}7)$$

$$SG_{max} = \frac{100}{\frac{GA}{SG\ GA} + \frac{FA}{SG\ FA} + \frac{F}{SG\ F} + \frac{B}{SG\ B}} \quad \text{..} \quad (5\text{-}8)$$

$$Air\ voids = (1 - \frac{dry\ density}{SG\ max})\ \text{x }100\% \quad \text{..} \quad (5\text{-}9)$$

$$VMA = air\ voids + \frac{bitumen\ content}{SGB} \quad \text{..} \quad (5\text{-}10)$$

$$VFB = \frac{(VMA - air\ voids)}{VMA} \times 100\%$$ ....……………………………… (5-11)

where:

SSD: weight: saturated surface dry condition by towel drying the soaked samples,

RBC: residual bitumen content,

W: water content at the testing time.

SG $_{max}$: is the maximum specific gravity for the mixture.

CA: percentages of coarse aggregate.

FA: percentages of fine aggregate.

F: percentages of filler.

B: percentages of bitumen.

5.6 Mix Design Procedure

5.6.1 Mix Design

Until now, there has been no universally accepted, design mixture for CBEMs. Some mix design procedures have been proposed by various authorities and researchers, e.g. the Asphalt Institute (1989); Jenkins (2000); Thanaya (2003). The majority of these procedures are based on the Asphalt Institute procedure but with some modifications. In this research, the design procedure for the CBCEA mixtures was based on the method adopted by the Asphalt Institute (1989), namely the Marshall Method for Emulsified Asphalt Aggregate Cold Mixture Design (MS-14). The Marshall test in this method was replaced by the indirect tensile stiffness modulus test. The following steps represent the design method for the preparation of the samples.

➢ **Determining Aggregate Grading**

Grading and the properties of the aggregate play an important role and exert an influence on the performance of CBEMs (OJUM, 2015). The Marshall Method for Emulsified Asphalt Aggregate Cold Mixture Design (MS-14) requires the maximum size of aggregate to be 25 mm or less. In this research, a crushed granite aggregate for both coarse and fine aggregate obtained from Carnsew Quarry at Mabe, Penryn, UK (operated by Colas) was used. These materials are normally used to produce asphalts.

Asphalt concrete is a continuous graded mixture providing good aggregate interlock. This means that it has very good load spreading properties as well as a high resistance to permanent deformation, making them the choice for use in places with slow moving traffic, e.g. uphill, and at locations exposed to stationary traffic, e.g. car parks and aircraft stands (Read and Whiteoak, 2003; O'Flaherty, 2007a; Defence Estates, 2008). Read and Whiteoak (2003) describe how these mixtures are produced with comparatively low bitumen contents. O'Flaherty (2007b) reported that dense bitumen macadam (DBM) is the predominant asphalt utilized in the binder courses and bases of trunk roads (including motorways) in the UK. A number of factors associated with the chosen aggregate affect final mix properties such as filler type and its percentage, shape and the type of aggregate and the specific gravity of different aggregate portions.

Following a healthy discussion with the Liverpool Centre for Material Technology's (LCMT) industrial partner, the author with his supervisory team decided to use the same aggregate grading as the current binder course made for asphalts. Therefore, an AC 20 dense binder course was selected with grading as shown in Figure 5-28 and according to the standard BS EN 13108-1 (European Committee for Standardization, 2006). The physical properties of the aggregate with traditional limestone mineral filler are presented in Table 5-8. This represents a traditional dense asphalt concrete which is the most

common mixture in use as a binder course and base in road pavements in the UK. The

aggregate was completely dried in an oven at 110°C, the materials then riffled and subject

to sieve analysis in accordance with BS EN 933-1 (European Committee for

Standardization, 2012a). The fractions were recombined to give the desired grading for

the manufacture of the mixtures.

Table 5-8. Physical characteristics of the granite aggregate

Material	Property	Value
Coarse aggregate	Bulk particle density, Mg/m^3	2.62
	Apparent particle density, Mg/m^3	2.67
	Water absorption, %	0.8
Fine aggregate	Bulk particle density, Mg/m^3	2.54
	Apparent particle density, Mg/m^3	2.65
	Water absorption, %	1.7
Conventional mineral filler	Particle density, Mg/m^3	2.57
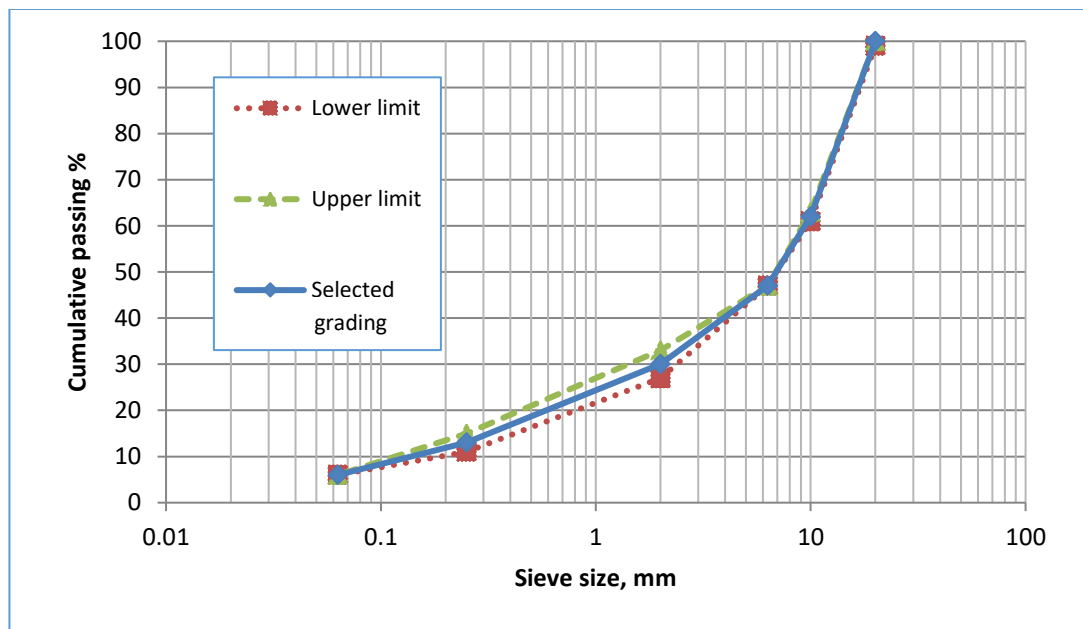
Figure 5.28. AC 20mm dense binder course aggregate grading

➢ **Bitumen Emulsion Selection**

The choice of bitumen emulsion is highly dependent on the type of aggregate and grading, environmental conditions and preparation in addition to the laying equipment. The Marshall Method for Emulsified Asphalt Aggregate Cold Mixture Design (MS-14) specifies that slow setting emulsion is appropriate for well graded aggregate whereas for open graded mixtures, fast setting emulsion is suggested, in accordance with the Asphalt Institute (1989) guidelines.

A slow setting cationic emulsion (C60B5), containing 60% residual bitumen designed for use in road pavement and common maintenance applications, was used throughout this research. The emulsion has to supply a bituminous binder for bonding the mix ingredients and water for the hydration of cementitious materials used to replace conventional filler, and at the same time, retain the flexibility of the mixtures. The high adhesion and high stability of such emulsion i.e. cationic emulsions, make them the preferred choice for use in CBEMs, as recommended by Nikolaides (1994); Thanaya (2003). The emulsion was supplied by Jobling Purser, Newcastle, UK, its main properties presented in Table 5-9.

Regarding the production of hot asphalt concrete binder course mixtures, two bitumen grades of 100/150 pen and 40/60 pen have been used for comparison purposes. Table 5-10 shows the properties of both bitumens.

Table 5-9. Properties of (C60B5) bitumen emulsion

Description	(C60B5) bitumen emulsion
Type	Cationic
Appearance	Black to dark brown liquid
Base bitumen, 1/10 mm	147 pen
Bitumen content, %	60
Boiling point, °C	100
Relative density at 15 °C, g/ml	1.05

Table 5-10. Characteristics of 40/60 and 100/150 penetration grade bitumens

Bituminous binder 40/60		Bituminous binder 100/150	
Property	Value	Property	Value
Appearance	Black	Appearance	Black
Penetration at 25°C	49	Penetration at 25°C	131
Softening point, °C	51.5	Softening point, °C	43.5
Density at 25°C	1.02	Density at 25°C	1.05

➢ **Determination of Initial Emulsion Content (IEC)**

Applying the Asphalt Institute empirical formula given below (Asphalt Institute, 1989), the Initial Residual Bitumen Content (IRBC), designated as P, can be calculated as shown below:

P = (0.05 A + 0.1 B + 0.5 C) x (0.7) ………………………….……… (5-12)

where:

P = per cent by weight of emulsified asphalt, based on weight of dry aggregate,

A = per cent of aggregate retained on sieve 2.36 mm,

B = per cent of aggregate passing sieve 2.36 mm and retained on 0.075 mm,

C = per cent of aggregate passing 0.075 mm.

A value of P = 6.23% was obtained for the mixture gradings Some modifications were made in line with common practice in the UK whereby a sieve size of 2mm was used rather than 2.36mm and also a sieve size 0.063mm used instead of sieve size 0.075mm. The initial emulsion content (IEC) value can be determined by dividing P by the percentage of bitumen in the emulsion as shown below:

$$\text{IEC (\%)} = \frac{P}{X}$$ …………………………………………………(5-13)

where:

X is the bitumen content of the emulsion which is 60%.

IEC = 6.23 / 0.6 = 10.38 (rounded up to 10.5%)

> **Determination of Pre-Wetting Water Content**

Thom (2009) reported that aggregates need to be pre-wetted to make an acceptable binder coating. The ability of bitumen emulsion to aggregate coating is sensitive to the pre-wet water content of aggregate. Inadequate pre-wet water results in balling of the asphalt with the fines leading to unsatisfactory coating (Thanaya, 2003). He also stated that this pre-wetting water content will facilitate uniform distribution of the emulsion onto the aggregate surface allowing for better binder coating. Ojum (2015) described how pre-wetting with water lubricates aggregates as well as activating the surface charges on the aggregate particles prior to the addition of the bitumen emulsion. The optimum pre-water content depends on aggregate grading and the physical properties of the aggregates. The Asphalt Institute (1989) recommended testing various percentages of pre-mixing water with the determined initial emulsion content (IEC) to establish the lowest pre-mixing water content needed to create the maximum coating percentage. This test was carried out on a range of pre-wetting water content. Two and a half of total aggregate weight was

used as starting point with 60 seconds of mixing. Pre-wetting water was added to the aggregate, followed by the emulsion and mixed for 60 seconds. In addition, four, 0.5% additional increments were prepared as shown in Figure 5-29. The optimum pre-wetting water content giving the best bitumen coating on the mineral aggregate, where the mixture is neither too sloppy nor too stiff, was 3.5%, this the lowest percentage that gives the highest coating percentage by visible judgment.
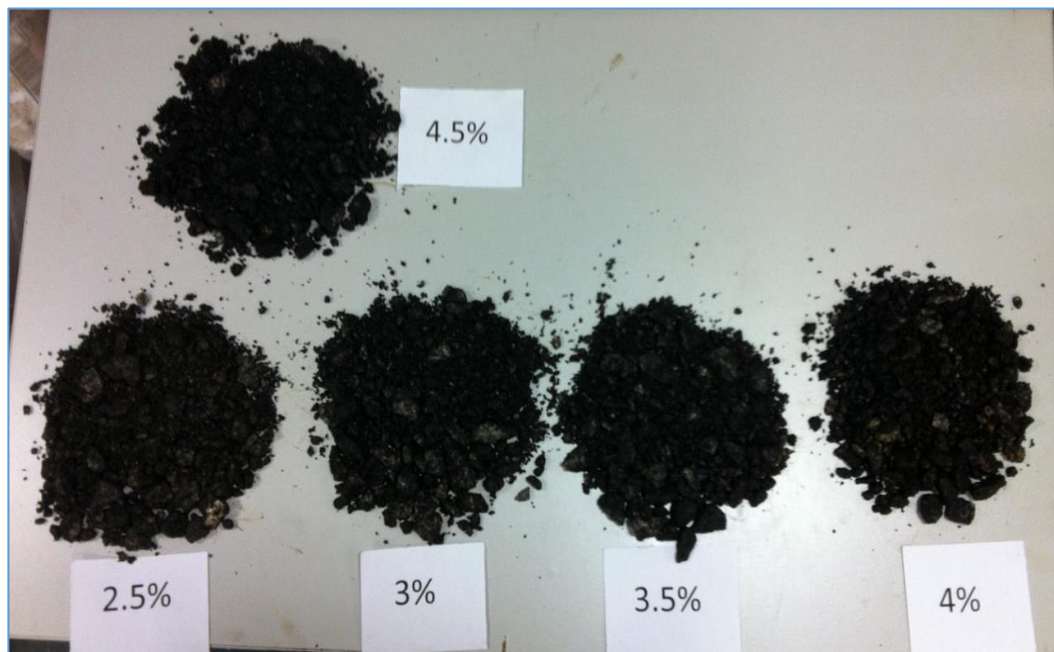
Figure 5.29. Pre-wetting water content test

> **Obtaining the Optimum Residual Bitumen Content (OREC)**

Using the optimum pre-mixing, a sequence of tests was carried out with various residual bitumen contents to optimize the residual bitumen content. The indirect tensile stiffness modulus (ITSM) test was applied according to the standard BS EN 12697-26:2012 (European Committee for Standardization, 2012c) to decide the optimum emulsion content. According to the chosen material's characteristics, the optimum residual bitumen was found to be 6.3% of total aggregate weight for soaked specimens. 10.5% emulsion content was adopted as the optimum emulsion content.

> ➢ **Optimum Total Liquid Content at Compaction (OTLC)**

During this research, all the cold mixtures were compacted directly after mixing. Consequently, the OTLC was 14% by aggregate mass. High performance CBCEAs, which are suitable for use as a binder course, can be produced without any delay between mixing and compaction leading to fast manufacture of high density CBCEA mixtures for binder course.

5.6.2 Preparation of Samples

5.6.2.1 Cold Binder Course Emulsion Asphalt (CBCEA)

These mixtures were prepared according the method outlined by the Asphalt Institute (Asphalt Institute, 1989). Using a Hobart mixer (Figure 5.30a), aggregate materials were placed into a mixing bowl and mixed with the specified 3.5% pre-wetting water for 60 seconds at a low speed. This was followed by the gradual addition of the bitumen emulsion (10.5%) over 30 seconds and mixed for the next one and a half minutes at the same speed. The samples were subject to impact compaction, using a Marshall hammer, of 100 blows, 50 blows per face (Figure 5.30 b). It was reported by Nassar et al. (2016a) that Marshall compaction is an accepted procedure used to create a suitably dense material. Finally, the 100 mm diameter samples were left inside their moulds for 24 hours then extruded using a hydraulic de-moulding apparatus.
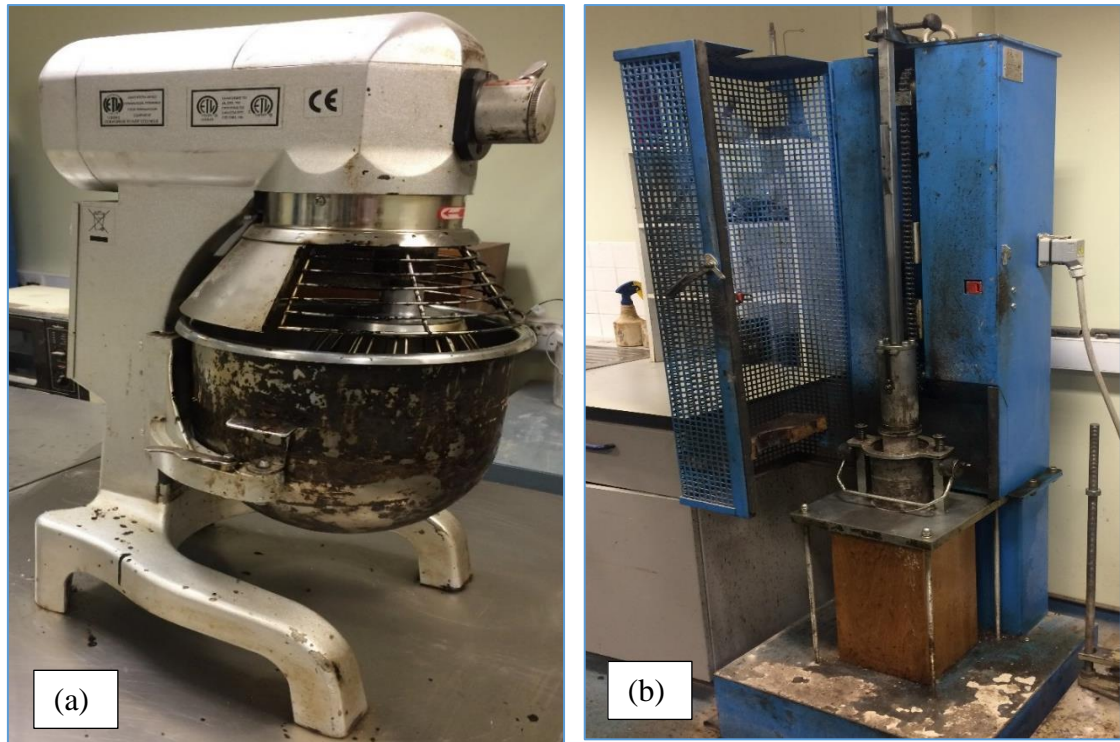
Figure 5.30. Mixing and compaction apparatuses

5.6.2.2 Hot Asphalt Concrete Binder Course Mixtures

Appropriate comparisons can be made by measuring the mechanical properties of CBCEA in relation to those of standard, AC 20 mm dense binder course mixtures. To do this, two asphalt concrete binder course mixtures were fabricated, namely an AC 20 mm dense binder course (100/150) and an AC 20 mm (40/60) dense binder course using the same aggregate type and gradation as the CBCEA mixtures with two different bitumen grades. 4.6% optimum binder content by weight of aggregate was added according to PD 6691 (European Committee for Standardization, 2010b) for the AC 20 dense binder course. The two grades of AC 20 binder course were mixed at temperatures of 150-160°C and 160-170°C for the 100/150 pen and 40/60 pen bitumens, respectively.

5.7 Summary

This chapter has examined and investigated the candidate waste materials that have the potential to be used in new cementitious material to produce a novel CBCEA mixture.

The research methodology adopted has been described to give guidelines on the procedure used to achieve the research aim by accomplishing the research objects. The selection of tests used to evaluate the novel CBCEA mixture in terms of mechanical and durability properties based on the fundamental tests that are used successfully for asphalts, have also been discussed.

Characterisation of the candidate waste materials revealed that the PMSA samples had a high lime concentration with sharp peaks; the existence of Al and Si were expected to have a substantial effect in the development of the new cementitious material. The high silica-aluminous concentration of FC3R, similar to metakaolin, makes this material promising with reference to the activation of PMSA. The amorphous nature of FC3R means that it will demonstrate high reactivity during the hydration process. Furthermore, the inclusion of W-NaOH will provide an alkaline environment which is expected to break the glass phases of fly ash particles and react with $Ca(OH)_2$ creating C-S-H gel. The results discussed in the next chapters will substantiate the above claims.

CHAPTER 6

THE DEVELOPMENT OF FAST-CURING COLD BINDER COURSE MIXTURE/S

6.1 Introduction

This study aims to produce a fast curing, cold binder course emulsion asphalt mixture/s (CBCEA) using a continuous aggregate grading. In this chapter, the process of adding different types of fillers generated from waste materials and appropriate activation for the filler will be discussed and analysed. The development of a new CBCEA will overcome the problems associated with the use of conventional CBEMs; low early strength and a lengthy curing time ranging from 2 to 24 months as stated by Leech (1994). The first step was to produce a cold binder course using traditional limestone mineral filler. This filler was replaced by Ordinary Portland Cement (OPC) which has been used extensively by the pavement industry and researchers in the production of CBEMs in order to enhance their mechanical properties. To overcome the disadvantages of OPC filler, high energy consumption and environmental impact, candidate cementitious and pozzolanic materials were used both individually and collectively. The results are reported and discussed in this chapter, demonstrating the suitability for use in new CBCEA mixture/s.

6.2 Curing of New CBCEA Samples

A room temperature of 20°C was adopted as the normal curing environment for all the mixtures in this research work. Doyle et al. (2013) reported that curing regimes at ambient temperature have been adopted lately to overcome the difficulties relating accelerated laboratory testing to in situ conditions.

The specimens were kept inside their moulds for 24 hours before being extruded, this representing the first stage of curing. Samples were then left in the lab and tested for ITSM at various ages, i.e. 1, 3, 7, 14, 28, 90, and 180 days. In the past, many researchers used higher temperatures such as 40°C in their curing regimes such as Thanaya (2003); Al Nageim et al. (2012); Al-Busaltan et al. (2012); Al-Hdabi et al. (2013b). Adopting a normal curing temperature in this research will simulate the production, compaction and placing of such mixtures in field conditions and will also avoid any premature ageing of the binder (Serfass et al., 2004b; Khalid and Monney, 2009; Ojum et al., 2014).

6.3 CBCEA Mixtures Production

6.3.1 Production of the Control CBCEA Mixtures

The first CBCEA control mixture was made using commercial limestone mineral filler (LF). The preparation process for these mixtures was explained in section 5.6.2.1. All samples were subject to ITSM testing at 1, 3, 7, 14, 28, 90 and 180 days to measure their stiffness modulus. ITSM is a non-destructive test used primarily to assess the stiffness modulus of asphalts, this associated to the materials' capacity to distribute traffic loads.

Both grades of 20mm asphalt concrete binder course mixtures (the second control mixtures) were stored at 20°C and tested at the same ages, i.e. 1, 3, 7, 14 and 28, 90 and 180 days.

The presence of water in the LF mixture makes it behave in a more complex manner in comparison to the control AC mixtures. Figure 6-1 illustrates the behaviour of these mixtures, in terms of ITSM at different curing times, where it can be seen that the LF specimens failed the ITSM test and could not withstand test loads after 1 day of curing. However, the samples gained some strength after curing for three days, showing an increase in the stiffness modulus. Increases in ITSM were observed mainly during the

first 28 days curing; there was only a further 37% increase at age 180 days compared to 28 days. These results were very low in comparison to the ITSM of a traditional asphalt concrete binder course 100/150 pen with a value of 2152 MPa. The ITSM for the LF-mixture was around 9% of the AC 100/150 after 3 days, while at 28 days this value increased to about 17%. After 6 months, the ITSM of the LF was around 24% of that of the AC 100/150. The main reason for low early strength is trapped water in the LF-mixture; the evaporation of this water governs gains in strength. It should be noted that five samples were prepared and tested for each specific curing time for the LF mixtures because some damage was noticed for these reference samples especially at early ages. There was no noticeable change in the ITSM for both types of AC binder course.
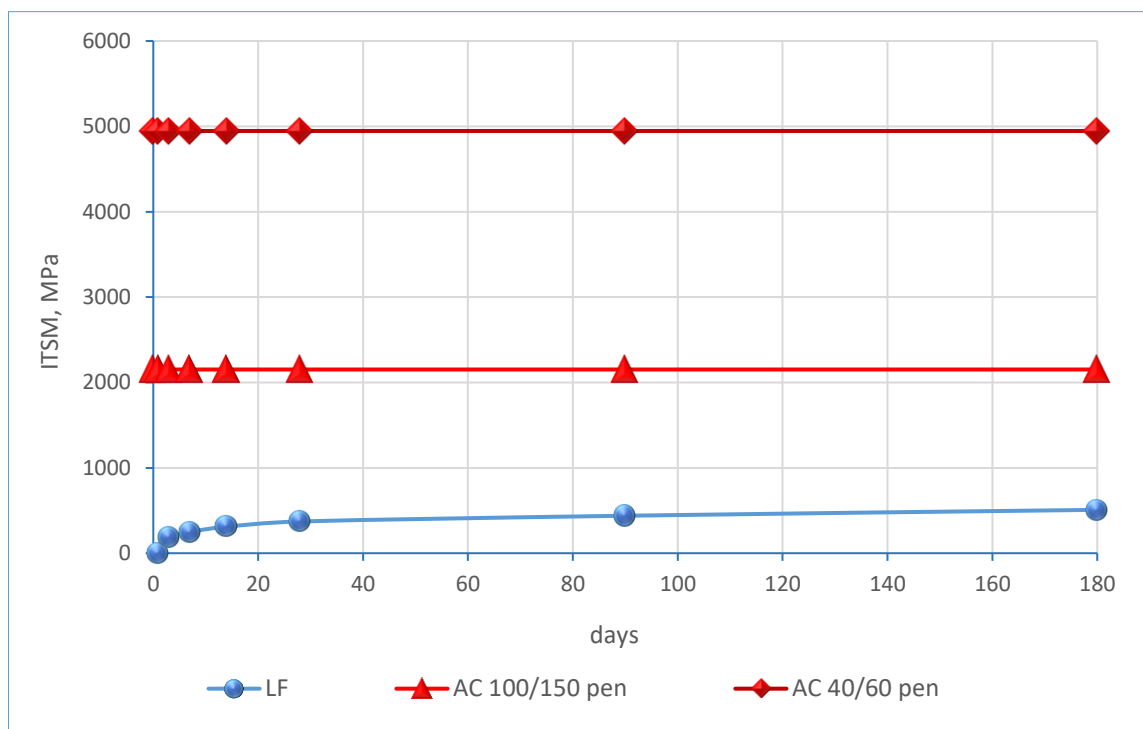
Figure 6.1. ITSM development of the control CBCEA with LF

6.3.2 CBCEA Mixtures Treated with OPC

Needham (1996) reported that the addition of OPC to 20 mm Dense Bitumen Macadam (DBM) results in an increase in the stiffness values of such mixtures, as well as

improvements in other mechanical properties. The effect of adding OPC to CBEMs and the associated positive effect of this, has been examined in some detail as described in Chapter 5.

In the current research where the aim is to produce a new, fast-curing CBCEA treated with OPC, OPC has been used as a replacement to traditional limestone mineral filler in the following percentages: 0%, 1.5%, 3%, 4.5% and 6% by total dry aggregate weight. It can be observed from Figure 6-2 that the incorporation of OPC significantly improved the stiffness modulus of the samples reaching its maximum value when all the limestone filler was replaced by OPC. The CBCEA mixtures treated with OPC have a stiffness modulus around 19 times more than the reference CBCEA with LF after 3 days. In addition, incorporating OPC in CBCEA mixtures enhanced the rate of increase and strength values for these mixtures in the early days (up to 7 days) of curing. After 7 days, the rate of increase was comparatively low (Figure 6-3).

This enhancement in the ITSM will overcome the major shortcomings of CBCEAs that contain LF; low early stiffness and a long curing time. After one day, the ITSM for the OPC treated mixtures was 1763 MPa which is not far from the target ITSM (2152 MPa). In addition, OPC treated mixtures surpass AC 100/150 within the first three days and achieve about a 60% increase in ITSM after 3 days compared to the AC 100/150. This result satisfies the first aim of the current research work, to decrease the curing time in the field for such cold mixtures. The formation of cementitious bonds is the main reason behind this improvement, as well as the consumption of trapped water induced by the hydration process of OPC, which leads to a loss in moisture from the mixtures. In addition, the alkaline nature of the cement paste (see section 4.2.5.1 of Chapter 4) neutralizes acids in cationic emulsions leading to an increase in pH. This increases the

rate of destruction of the charge and cationic emulsifier on the cationic emulsion droplets

allowing the emulsion to flocculate rapidly as described by Wang et al. (2013).
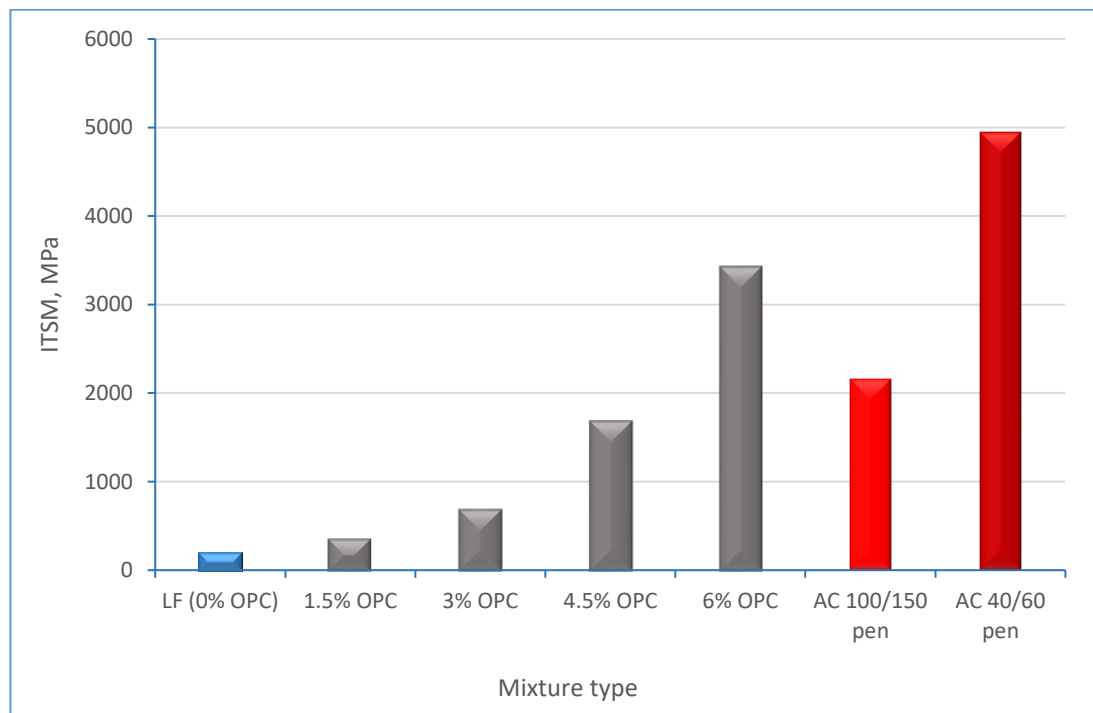
Figure 6.2. ITSM results for OPC incorporation after 3 days
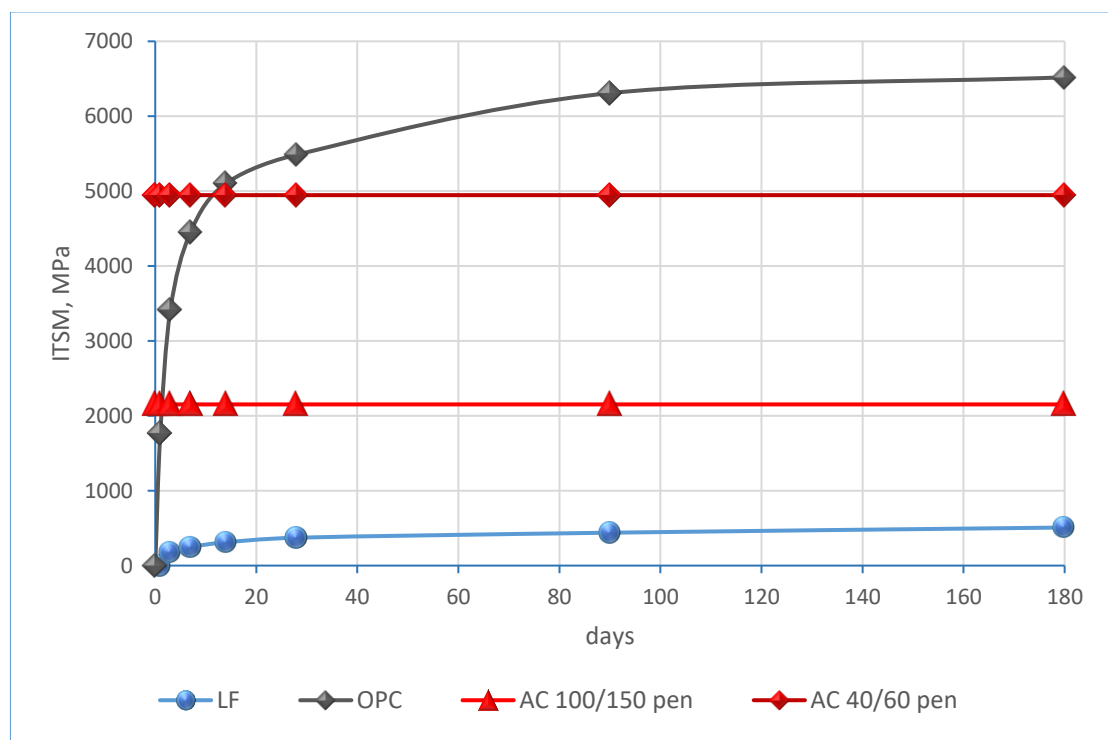
Figure 6.3. ITSM results for different curing times of OPC mixtures

6.3.3 CBCEA Mixtures Treated with PMSA

One of the main aims of this research work is the substitution of OPC filler in CBCEAs with filler made from waste materials which have cementitious or pozzolanic activity properties in order to produce fast-curing CBCEA mixtures. From the previous section, the importance of replacing limestone filler with OPC has been established, enhancing the weak early stiffness modulus of CBCEA mixes. However, cement manufacture requires extensive quarrying and energy intensive procedures, causing ecological impacts at all stages (Sadique and Al-Nageim, 2012). 3.8 million tonnes of CO_2 were released by the cement industry in the UK in 2010 alone (Department for Energy and Climate Change, 2012).

Because of this, many waste and by-product materials (PMSA, FC3R, CKD, SSA, GGBS) have been analysed, both physically and chemically, to explore their cementitious and pozzolanic properties. It was concluded that the existence of silicate bearing minerals (e.g. ghelinite), calcium bearing hydraulic minerals (e.g. merwinite, lime) and other pozzolanic calcium-alumino-silicate phase in PMSA (Figure 5-14) allow materials to have a degree of pozzolanic and hydraulic properties. Two grades of PMSA have been used as limestone filler replacement in this research, as described earlier in Chapter 5. Both have been incorporated in 0%, 1.5%, 3%, 4.5% and 6% by dry aggregate weight. Figure 6-4 illustrates the ITSM results of both PMSA grades at 3 days. Both grades show a significant improvement in ITSM especially at full PMSA replacement thus demonstrating the positive effect of the addition of PMSA.

The addition of PMSA-F lead to a marked increase in ITSM at a curing time of 3 days as compared to the PMSA-C specimens and LF samples. The ITSM of the former, with full filler substitution, was approximately 13 times higher than the control LF mixture after 3

days, while the latter displayed an ITSM approximately 11 times better than the reference LF (with 6% filler replacement) at the same age.

These enhancements are due to the generation of a new binder from the hydration process of the PMSA in addition to the residual bitumen binder. The absorption of trapped free water during this process is also of note as this water is mainly responsible for low early strength. The alkaline nature of both PMSA grades caused the emulsion to flocculate very quickly and perform in a similar way to OPC as explained in section 6.3.2. However, finer PMSA-F particles (see Figure 5-10) speed up the pozzolanic reaction, something which is usually a slow process. The ITSM of PMSA-C was lower than that of PMSA-F as the larger particles in this material did not permit full hydration leading to a weakness in the core of the particle, resulting in low stiffness modulus. Unfortunately, the ITSM for both PMSA grades were still lower than the OPC treated mixtures by 31% and 40% for PMSA-F and PMSA-C, respectively.
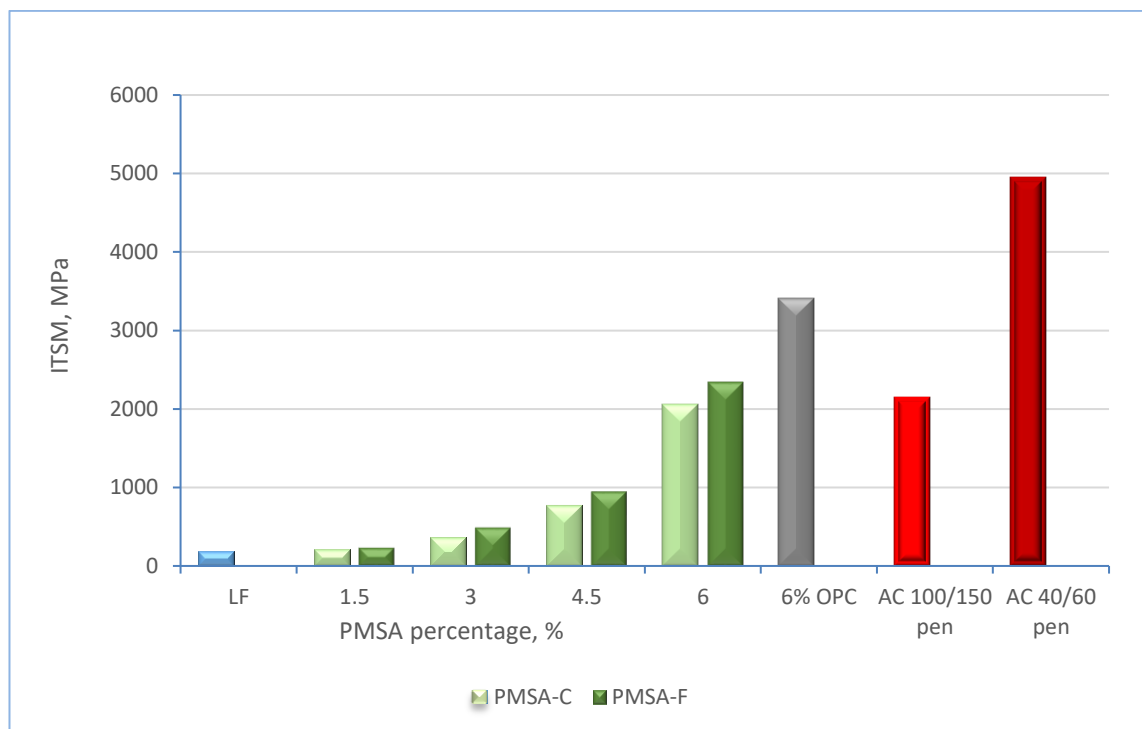
Figure 6.4. ITSM results for PMSA-C and PMSA-F treated mixtures after 3 days

6.3.4 PMSA-F Activation: the Effect of PMSA-F Grinding on ITSM

PMSA-F powder was subject to grinding, via low energy intensive dry agitation, using a pestle and mortar as detailed in Figure 6-5 (1 horsepower motor with 2.5 litre bowl capacity). The powder was ground for a short period of time (12 and a half minutes) taking sustainability into account and to prevent particle agglomeration which is harmful for the quality and activity of the ground product (Juhasz and Opoczky, 1990). Although grinding produces a larger surface area, the agglomeration phenomena that is generally associated with extended grinding time, negatively affects pozzolanic action (Rodrigues et al., 1999).

It was decided to grind the PMSA-F to make the PSD of this material similar to the OPC to explore the effect of its fineness on the mixes' mechanical properties in terms of ITSM improvement. After various tests, it was established that grinding PMSA-F for $12\frac{1}{2}$ minutes produced identical PDS to OPC (see Figure 6-6). It can be seen from Figure 6-6 that the particle size of ground PMSA-F has been improved compared with untreated PMSA-F. The fineness of the ground PMSA-F is more or less the same as OPC except in the range 14-47 µm where it is a little finer. OPC has more fine particles than ground PMSA-F in the range of 1.5 to 0 µm.
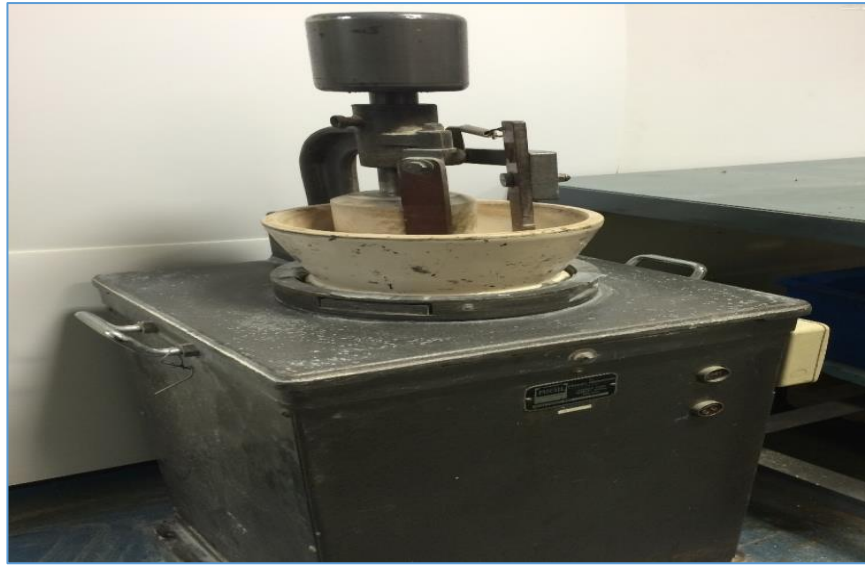
Figure 6.5. Pestle and mortar
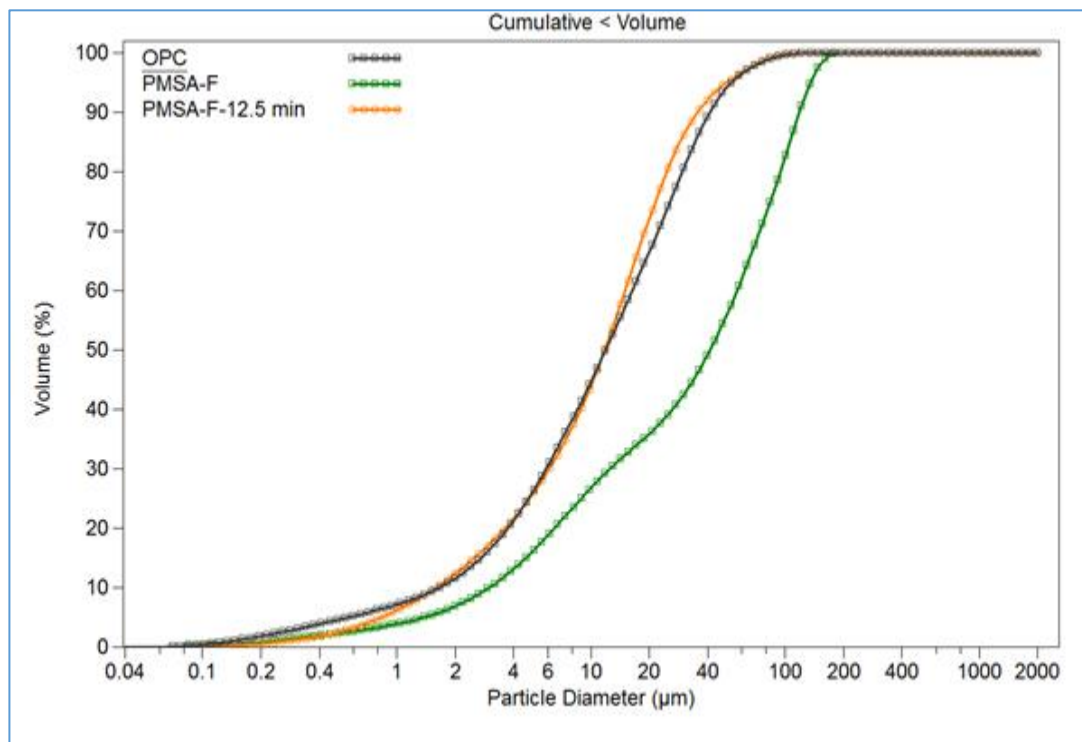
Figure 6.6. Comparative PSD

Ground PMSA-F was incorporated in 0%, 1.5%, 3%, 4.5% and 6% by aggregate dry weight, percentages which represent 25%, 50%, 75% and 100% filler replacement. Figure 6-7 illustrates the ITSM test results of ground PMSA-F and the control mixtures where it can be seen that a substantial increase in ITSM was achieved for the mixtures

incorporating ground PMSA-F. ITSM increased significantly when the percentage of ground PMSA-F was increased reaching ultimate strength value (3181 MPa) when all the traditional LF was replaced. This improvement is around 36% greater than mixtures with PMSA-F. The early stiffness of the ground PMSA-F mixtures (at 3 days), is more than 17 times the control LF mixtures, this helping to minimize curing times in the field. The ITSM for the ground PMSA-F mixtures under normal curing process conditions, is higher than the control AC 100/150 by around 48%. This is due to the extra fineness of the ground PMSA-F facilitating sound cementitious characteristics and packing effects. Furthermore, these fine particles accelerate the pozzolanic reaction as they react better than coarser particles. Peris Mora et al. (1993) reported that increasing the fineness of fly ash can reduce the interior friction in fresh mortar. According to this phenomenon, called a 'lubricant effect', the workability of ground PMSA-F mixtures in this research has been improved.

It can be observed from Figure 6-8 that the increase in ITSM for ground PMSA was dramatic in the first 7 days, the increment rate decreasing thereafter. This pattern of behaviour is similar to that of the OPC mixtures, providing evidence of the cementitious action of the ground PMSA-F. The results also established that neither AC binder course mixtures showed ITSM development during the curing period.
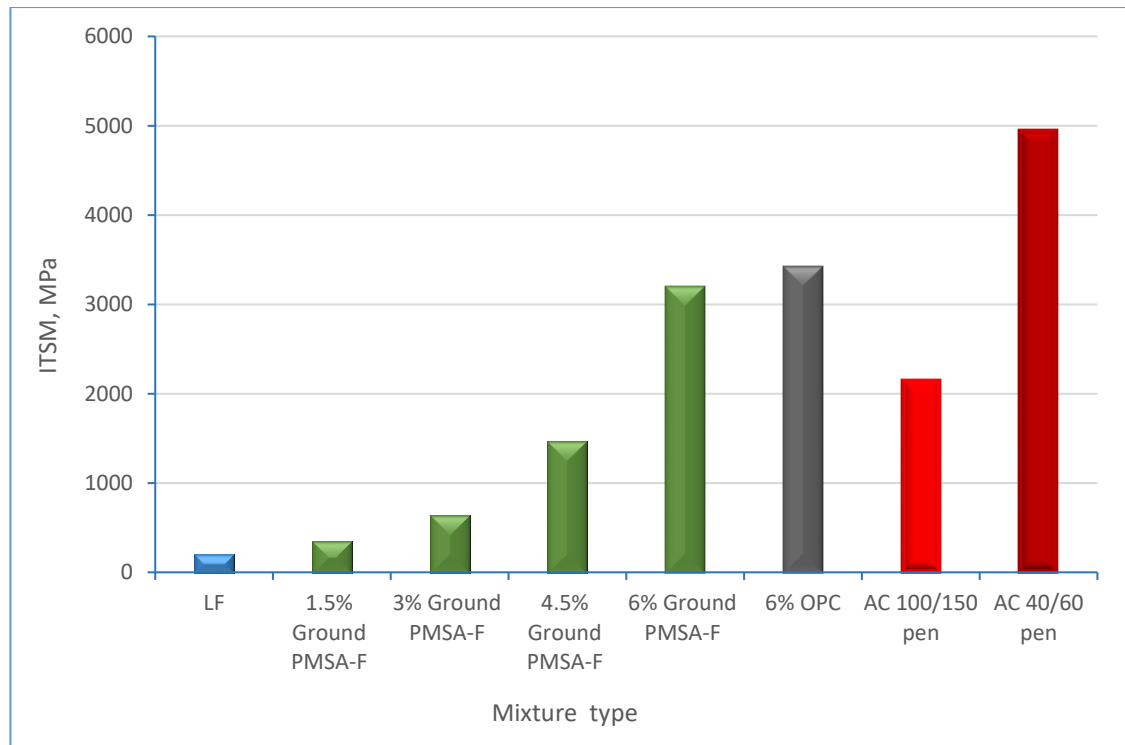
Figure 6.7. ITSM results for ground PMSA-F
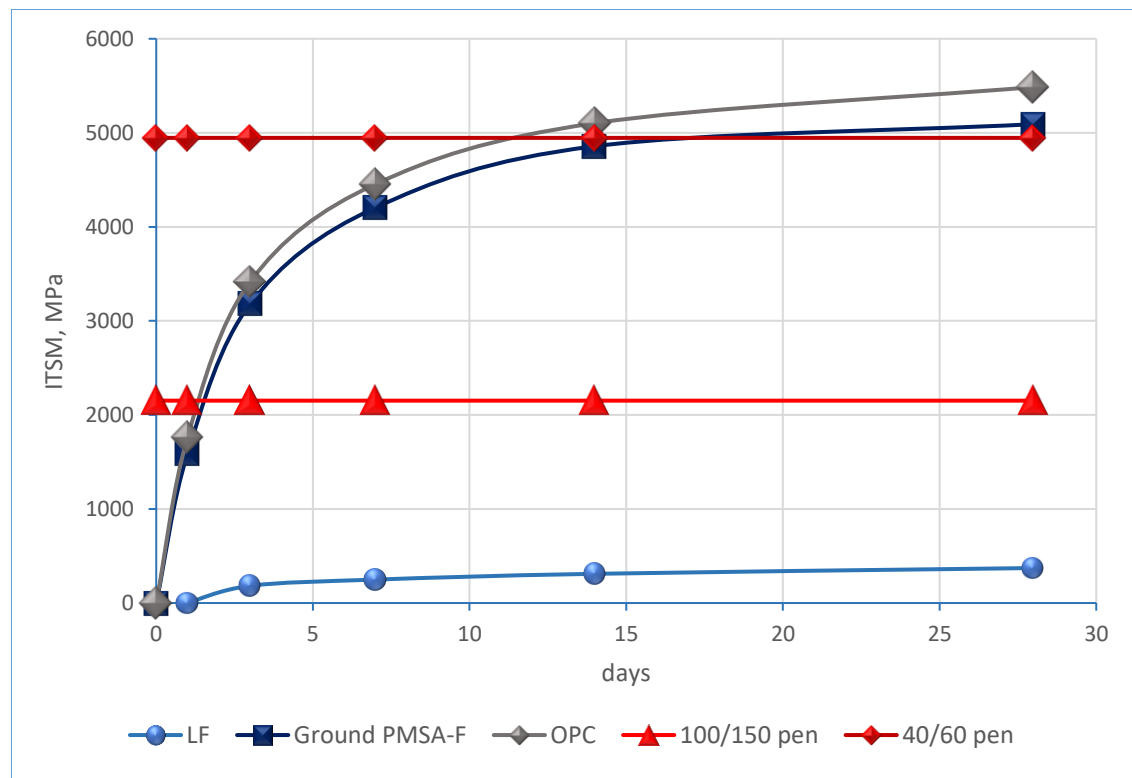
Figure 6.8. The ITSM development of mixtures

6.3.5 CBCEA Mixtures Treated with a Novel Binary Blended Cement Filler (BBCF)

Metakaolin has been identified as an effective material to activate PMSA. Dulaimi et al. (2015) demonstrated that a relatively small amount of Metakaolin facilitated a substantial improvement in the strength of sustainable cold asphalt concrete binder course mixtures. The fluid catalytic cracking catalyst residue (FC3R) is aluminosilicate waste material which is similar to Metakaolin with reference to its chemical components, the main oxides being AL_2O_3 and Si_2O_3. The powder diffraction in XRD, as seen in Figure 5-16, shows that FC3R has very low crystalline peaks which are amorphous in nature. In consequence, high reactivity will occur during the hydration process meaning that this material can be used as an activator. It is expected that it will convert the soluble calcium hydroxide (C-H) produced by the hydration process of ground PMSA-F into a dense calcium silicate hydrate (C-S-H)/ calcium aluminum silicate hydrate (C-A-S) gel by pozzolanic reaction.

It was therefore decided to use this material to activate ground PMSA-F filler and produce a new Binary Blended Cement Filler (BBCF) to use as a filler replacement to generate a new fast-curing cold binder course mixture based on continuous aggregate grading. FC3R was used as a substitute for the ground PMSA-F and introduced in four percentages, 1%, 2%, 3% and 4% by aggregate dry weight to specify the optimum composition which provides the maximum ITSM after 3 days (Figure 6-9). A considerable enhancement in the ITSM was achieved when 1.5% of FC3R replaced the ground PMSA-F. A new BBCF was generated at this point (1.5% FC3R + 4.5% ground PMSA-F) which lead to an increase in ITSM by around 17% compared to the ground PMSA-F mixture. A balanced oxide composition was expected to be formed within the BBCF. This improvement illustrates the positive role of FC3R in the new CBCEA mixtures. The improved stiffness of the new BBCF mixtures after 3 days, are approximately 20 times higher than the LF mixture, surpassing OPC treated mixtures by about 9%.

It can be observed from Figure 6-10 that the addition of FC3R to ground PMSA-F results in the significant development of early strength as well as long term strength. The rate of stiffness modulus improvement was also higher up to the seven day point when a reduction in this rate was detected. The ITSM of the BBCF mixtures was comparable to the AC 100/150 mixture after just one day, leading to a decrease in curing time in the field. This FC3R reaction reflects its pozzolanic activity as reported by Payá et al. (1999). FC3R is rich in pozzolanic particles, helping to accelerate the hydration of ground PMSA-F particles, generating more hydrated products. These pozzolanic particles reacted with $Ca(OH)_2$ released during the hydration process generating C-S-H/C-A-S gel which is responsible for the development of strength.
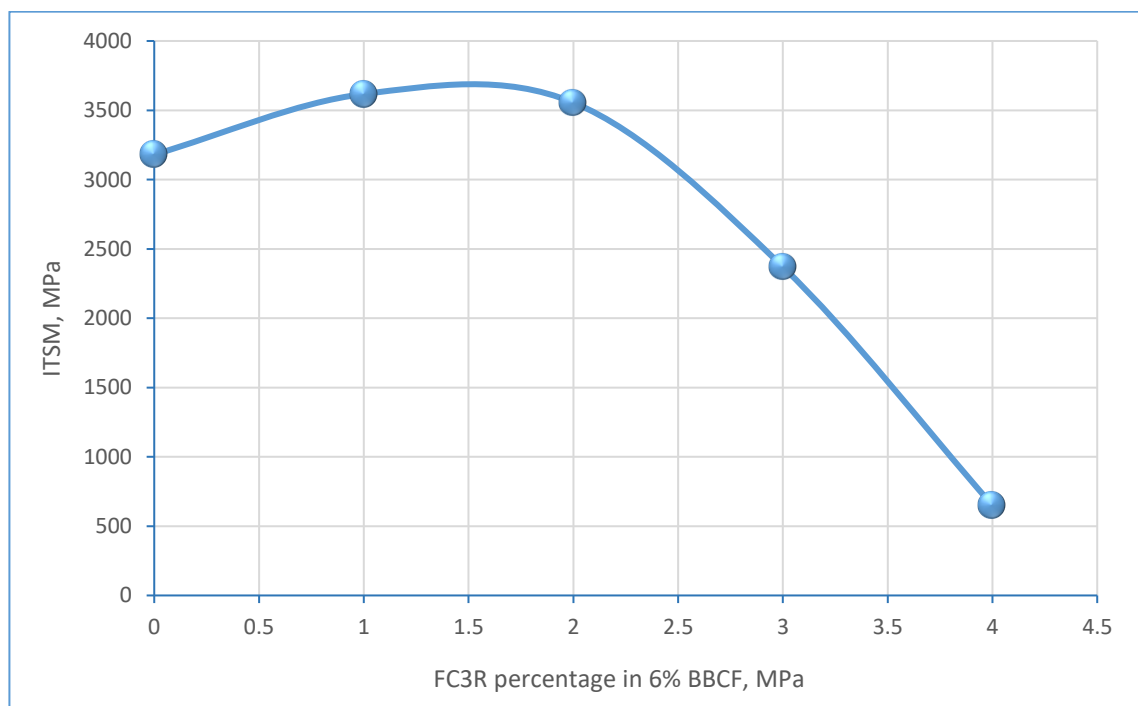
Figure 6.9. Influence of ground PMSA-F replacement with FC3R after 3 days on ITSM
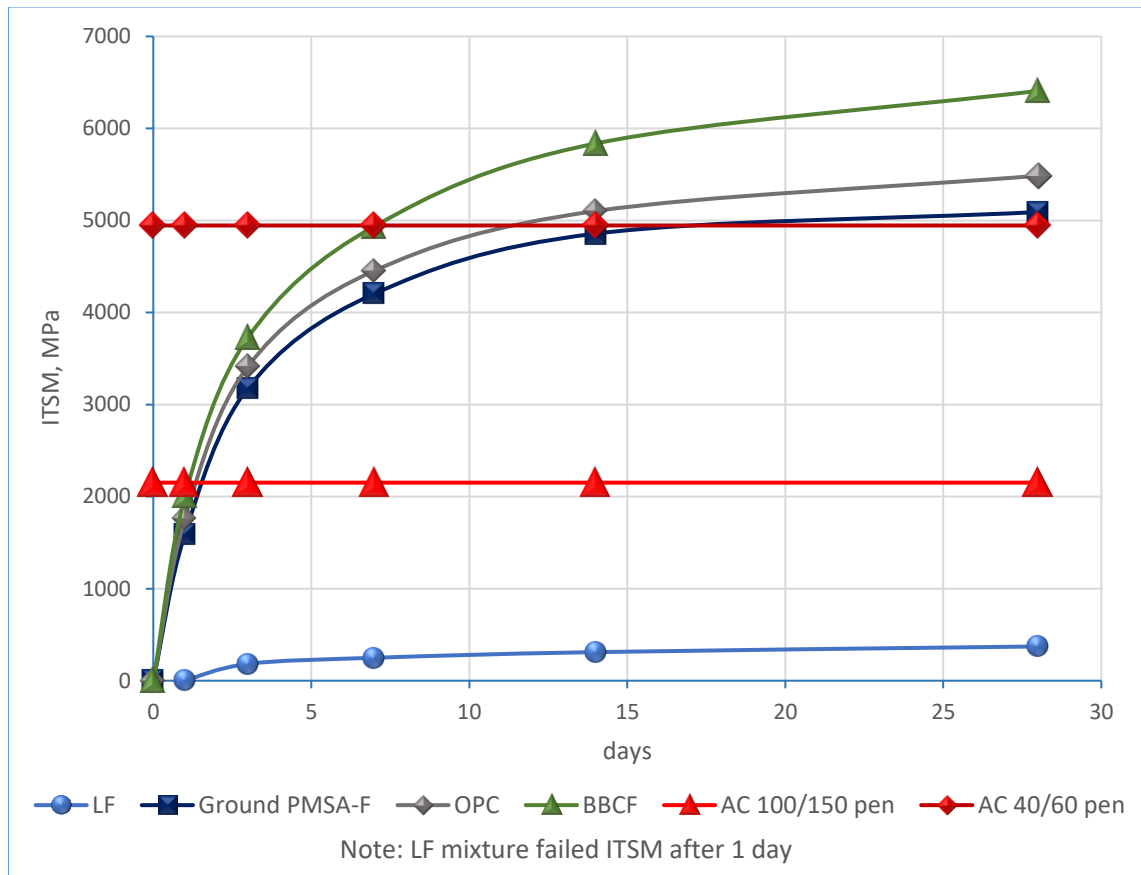
Figure 6.10. Effect of curing time of BBCF mixtures on ITSM

6.3.6 CBCEA Mixtures Treated with Alkali Activated BBCF

Alkaline activated materials have been found to have better mechanical characteristics than cement (Davies, 2011). The inclusion of alkali-activators increases the pH of hydration mediums which in turn will improve breaking and dissolution in the glassy phase of the pozzolanic material (Bakharev et al., 1999; Shi and Day, 2000). Li et al. (2000) reported that adding a NaOH solution is a common method of increasing alkalinity.

This stage in the process involves the use of alkali activation to facilitate further improvement of the BBCF by generating more activation in the hydration process. In the current study, waste alkali sodium hydroxide (W-(NaOH)) will be used as a replacement for 3.5% of the pre-wetting water content. New fast-curing, alkali activated binary

blended cement mixtures for binder course (ABBCF) have been produced by replacing the pre-wetting water content with W-NaOH in three percentages; 33%, 66% and 100%.

The samples were tested after three days to gauge ITSM improvements. Figure 6-11 shows that maximum ITSM values were achieved by replacing all the pre-wetting water content with the W-NaOH solution. In comparison to the BBCF mixture, increments in ITSM by percentage of W-NaOH solution added (33%, 66% and 100%), were 6%, 22% and 33%, respectively. This increase in alkalinity facilitates a breaking down in the glass phase of particles in the alkaline environment which react with $Ca(OH)_2$ creating C-S-H gel and a denser structure.
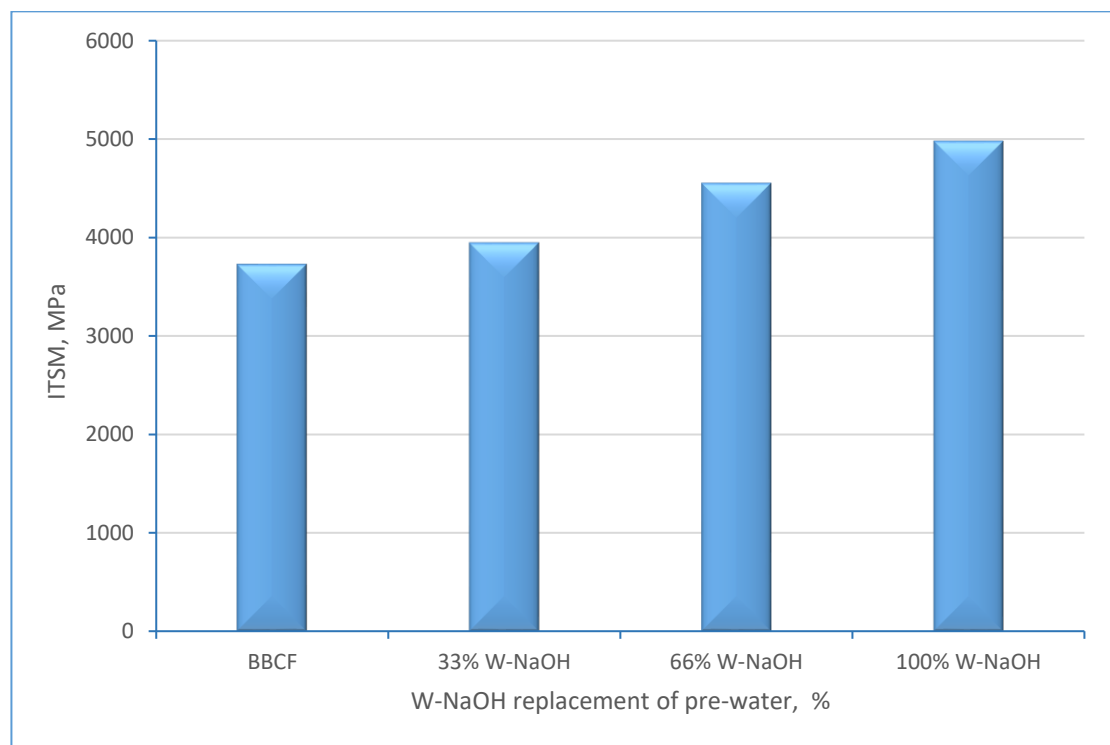
Figure 6.11. Stiffness development using alkali activation after 3 days

The ITSM tests, carried out at different curing times for the alkali activated binary blended cement filler mixtures (ABBCF), are seen in Figure 6-12. It is important to observe the properties of such mixtures over different curing periods in order to understand performance.

A substantial increase in the ITSM was found when all the pre-wetting water content was substituted by a W-NaOH solution. Under these conditions, the ABBCF mixture produced a higher stiffness modulus than control LF, OPC, ground-PMSA-F, BBCF and AC 100/150 mixtures over all curing times. The ITSM increment rate was very high in the first three days, increment rates decreasing after this. The stiffness modulus of the ABBCF mixture after one day and at normal curing, was more than the control AC 100/150 by 46% and achieved the British and European requirements in terms of ITSM. This new, fast-curing ABBCF mixture, overcame the OPC mixture, in terms of stiffness modulus, after one day by 78% at normal curing. This represents a substantial environmental and economic advantage because of the use of waste materials as a replacement for OPC. Accordingly, a new binder generated completely from different waste and by-product materials has been produced as a new cementitious material which has the opportunity to be employed in OPC fields.

Increasing the stiffness modulus of ABBCF mixtures means that this is now an appropriate material for use as a binder course layer for major heavy trafficked motorways, as it significantly decreases the loads transferred by traffic to the foundation. ABBCF mixtures permit early and temporary trafficking where site restrictions prevent the placement of a surface course prior to the elimination of traffic management. This mixture also eliminates restrictions imposed by road engineers on traditional cold binder course by decreasing the curing time to less than one day, because according to Leech (1994), traditional cold mixtures only achieve their required strength somewhere between 2 and 24 months.
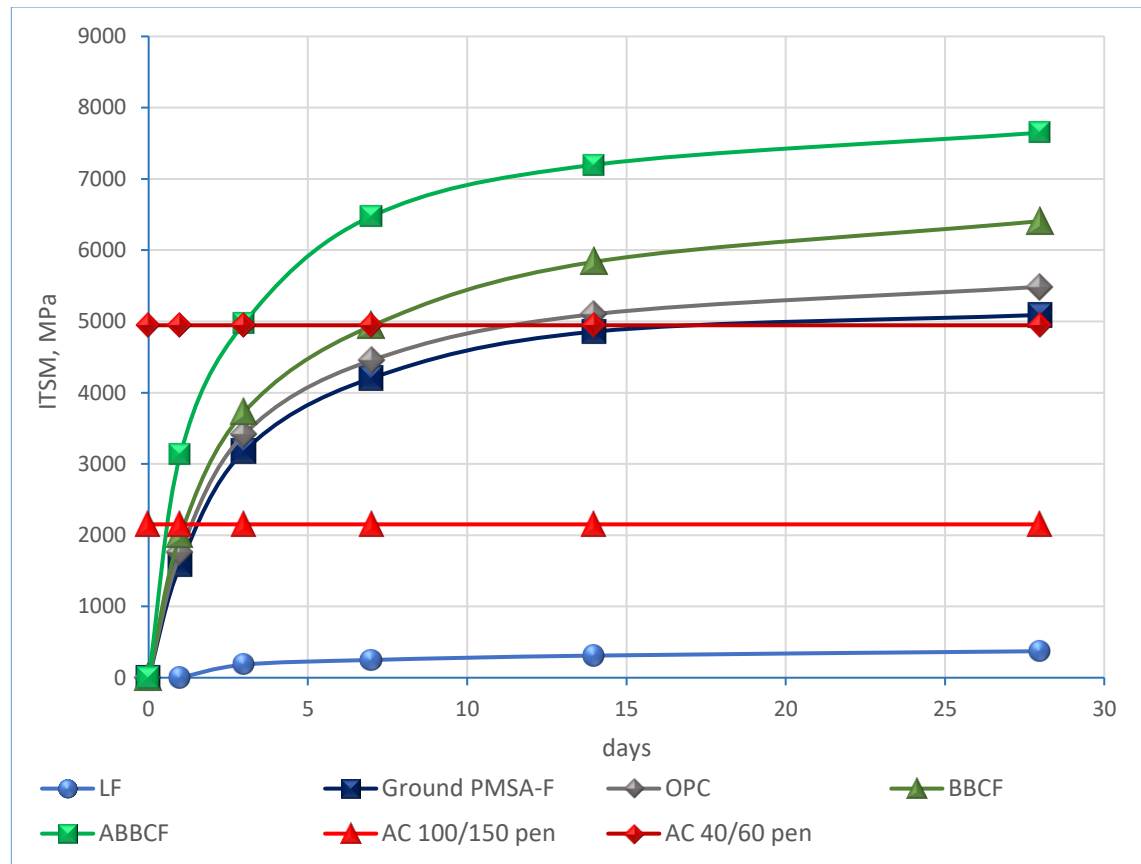
Figure 6.12. Influence of curing time on stiffness modulus

6.4 Water Loss in the CBCEA Mixtures

Moisture loss gives an indication about the gains in strength of CBCEA mixtures and the hydration process. Water loss was measured at 1, 2, 3, 7, 14, 21 and 28 days by weighing them, the average loss percentages noted at different curing times. After compaction, all the samples were left in their moulds for 24 hours before extrusion then placed in the lab at 20°C for curing throughout the period of the investigation.

In Figure 6-13, it can be observed that the main water loss occurred during the first three days, the rate of the water loss during these three curing days higher than at later ages. This rate also decreases with the inclusion of active fillers i.e. OPC, ground PMSA-F, BBCF and the incorporation of W-NaOH. CBCEA with LF had the highest loss of water over the testing ages. However, CBCEA mixtures with cementitious additives lost less water as some of the trapped water was absorbed by the active filler and used during the

hydration process. ABBCF mixtures had the lowest percentage of water loss as most of the water was consumed during the hydration process.
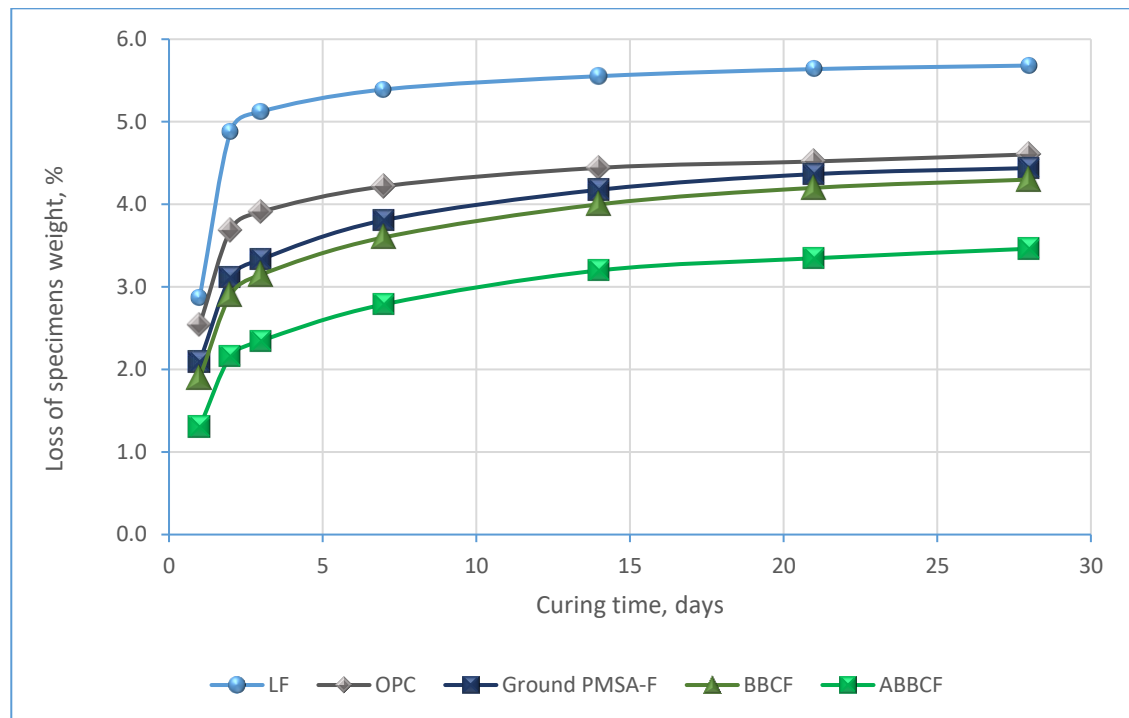
Figure 6.13. Water loss at different curing times

6.5 Temperature Susceptibility of CBCEA Mixtures

To assess the thermal sensitivity of mixtures, ITSM tests were performed at different temperatures. All the CBCEA mixtures, as well as the two reference AC mixtures, were tested for ITSM after 28 days of curing at three different temperatures; 5°C, 20°C and 45°C. The stiffness modulus decreased with an increase in testing temperature as seen in Figure 6-14. The curve of the slope in a semi-logarithmic plane can indicate temperature sensitivity where the higher rate of change of the mixture represents higher sensitivity to temperature.

Regarding ITSM, the CBCEA with LF exhibited a very strong trend to decrease in common with the two AC mixtures. It was not possible to test the ITSM for the LF samples at 45°C as all the samples failed which confirmed the thermo-dependence of such mixtures. Both the AC 100/150 and AC 40/60 lost around 97% of their stiffness when

heating from 5°C to 45°C. In contrast, a reduction in stiffness for the other CBCEA mixtures i.e. ground PMSA-F, OPC, BBCF and ABBCF indicates that they are less susceptible to temperature change, specifically hot temperatures. They are more thermally stable, this of huge benefit in terms of pavement performance in hot weather, reducing their tendency to high temperature rutting. In addition, these mixtures are also less likely to suffer from low temperature cracking. The presence of strong bonds as a result of the binding of cementitious materials, the interlocking of aggregates within the mass of the mixtures and paste cohesion between aggregate particles, ensures high stiffness properties at high temperatures. These results are consistent with those obtained in previous research (Bocci et al., 2002; Al-Hdabi et al., 2014b).
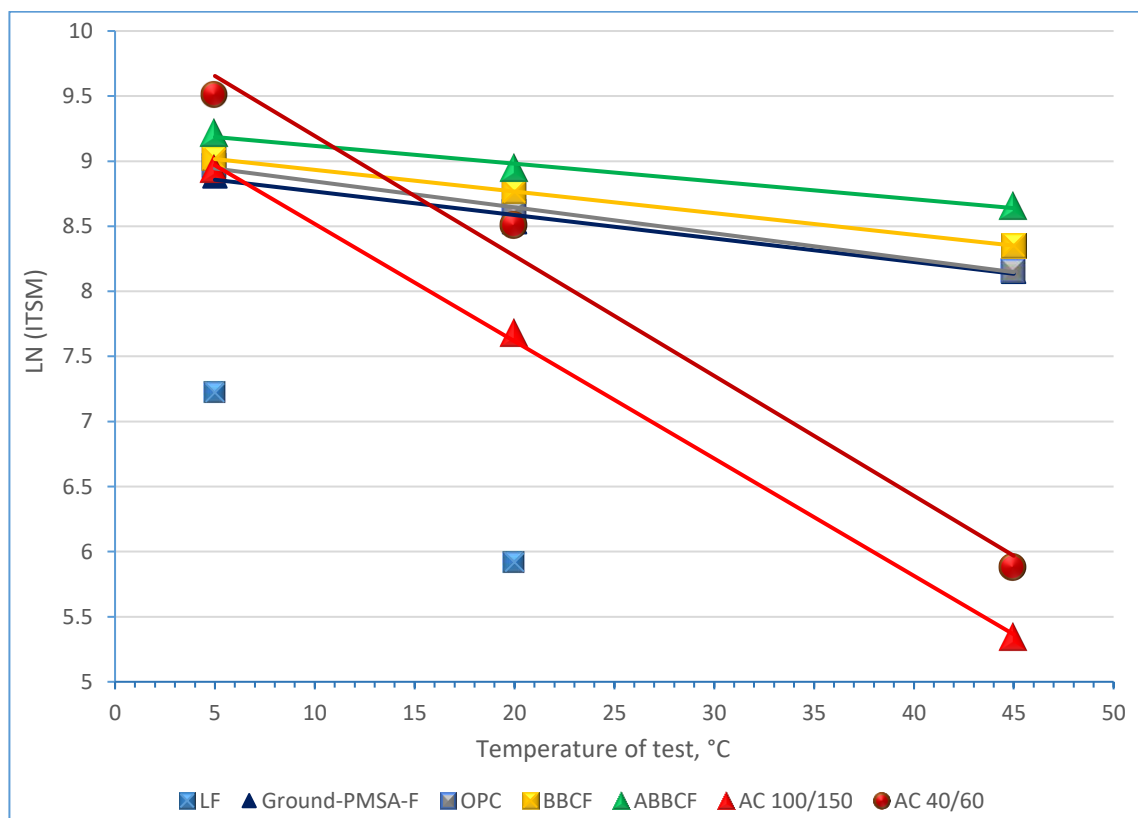
Figure 6.14. Stiffness modulus results at various testing temperatures

6.6 The Performance of Outdoor Samples

Specimens of all the cold mixtures; LF, OPC, ground PMSA-F, BBCF and ABBCF were fabricated and cured in outdoor exposure conditions, the aim being to better simulate site conditions and assess the rate of strength gain of the mixtures at normal climate conditions with rain and real temperature profiles. After compaction, the samples were left inside their mould for 24 hours before extrusion. The sides of the samples were sealed with plastic adhesive tape to simulate site conditions where, according to Thanaya (2003), the evaporation of volatiles will mainly happen through the mixture surface. The specimens were then placed outdoors on a flat surface in the car park area of the Henry Cotton Building, Department of Civil Engineering, Liverpool John Moores University as shown in Figure 6-15. The mean monthly temperatures in 2015 in Liverpool, UK are illustrated in Figure 6-16, the average weather by month in Liverpool detailed in Table 6-1.

Two sets of samples were prepared, the first fabricated on 1 June, 2015 when the average monthly outdoor temperature is 14.5°C (Tutiempo, 2016) to represent the summer condition. The second set was made on 7 December, 2015 when the average outdoor temperature is 8.9°C representing the winter condition. The samples were tested at ages 1, 3, 7, 14, 28, 90 and 180 days. Figure 6-18 and 6-19 illustrate the rate of strength gain in terms of ITSM at 20°C for the two outdoor specimens as well as the indoor samples cured at ambient temperature.

It can be observed in Figure 6-17 that after 28 days, the results for the summer set of outdoor CBCEA mixtures are close, in terms of ITSM, to the samples subjected to normal curing. The summer set is better in ITSM performance than the winter set, where high humidity and a low temperature in winter lead to a decrease in ITSM. That said, both sets still have a much improved performance in comparison to the reference AC 100/150 pen.

The higher temperature in summer months encouraged the hydration process and evaporation. Figure 6-18 shows that the improvements in strength over time for both sets of ABBCF outdoors samples is similar to normal lab curing. Both summer and winter ABBCF samples achieved the target ITSM for AC 100/150 pen within 1 day. The strength gain, in terms of ITSM for the ABBCF, occurred significantly faster than the LF mixture. This constitutes a considerable enhancement to curing in comparison with some CBEM site trials where much longer curing times (2 to 24 months) were required (Leech, 1994). The improved early strength seen in the new treated CBCEA mixtures, especially the ABBCF mixture, confirms the positive contribution of such mixtures under the real weather conditions with rain and real temperature profiles.

Figure 6.15. Curing of outdoor sample

Table 6-1. Average weather by month for 2015 in Liverpool (Tutiempo, 2016)

Month	Average temperature		Total days of rained	Mean humidity %	Average snow days	Average fog days
	Max	**Min**				
January	8.3	2.7	25	82.1	4	3
February	7.5	2.6	15	82.4	0	1
March	10	3.4	18	79	2	2
April	13.5	5.2	13	76.4	1	4
May	13.8	8.3	76.1	27	0	1
June	18.4	10.6	75	15	0	0
July	19.1	12.3	77	26	0	0
August	20	12.6	77.6	17	0	0
September	16.8	9.6	82	13	0	4
October	14.7	8.3	86	13	0	3
November	12.7	7.7	87.2	26	0	3
December	10.2	7.6	86.6	27	0	0
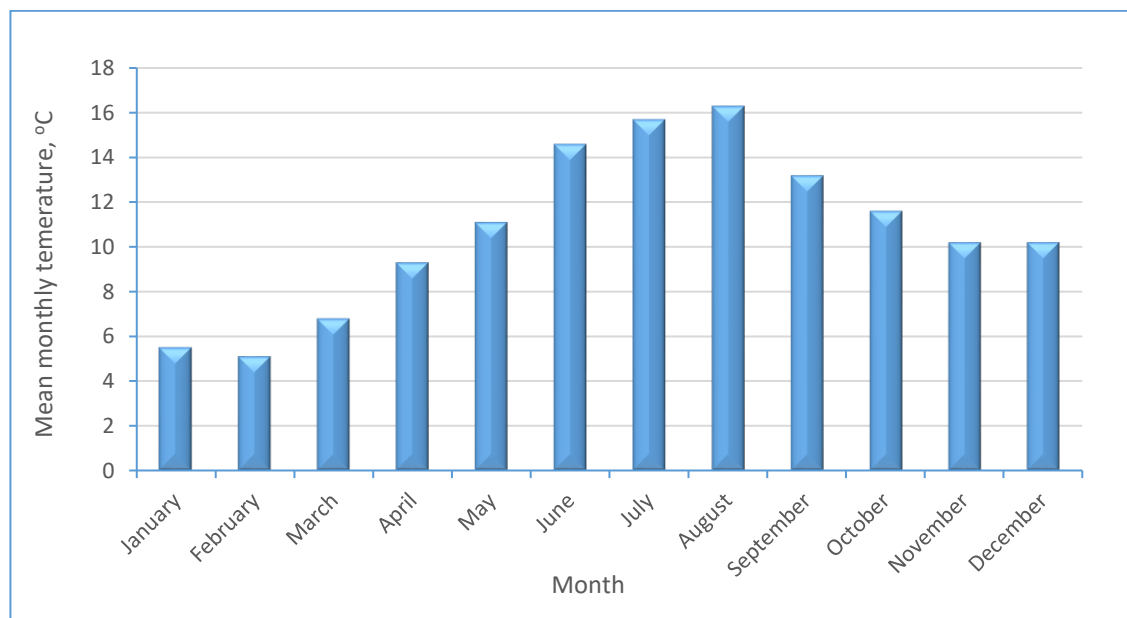
Figure 6.16. Average monthly temperature in Liverpool, UK for 2015 in °C (Tutiempo, 2016)
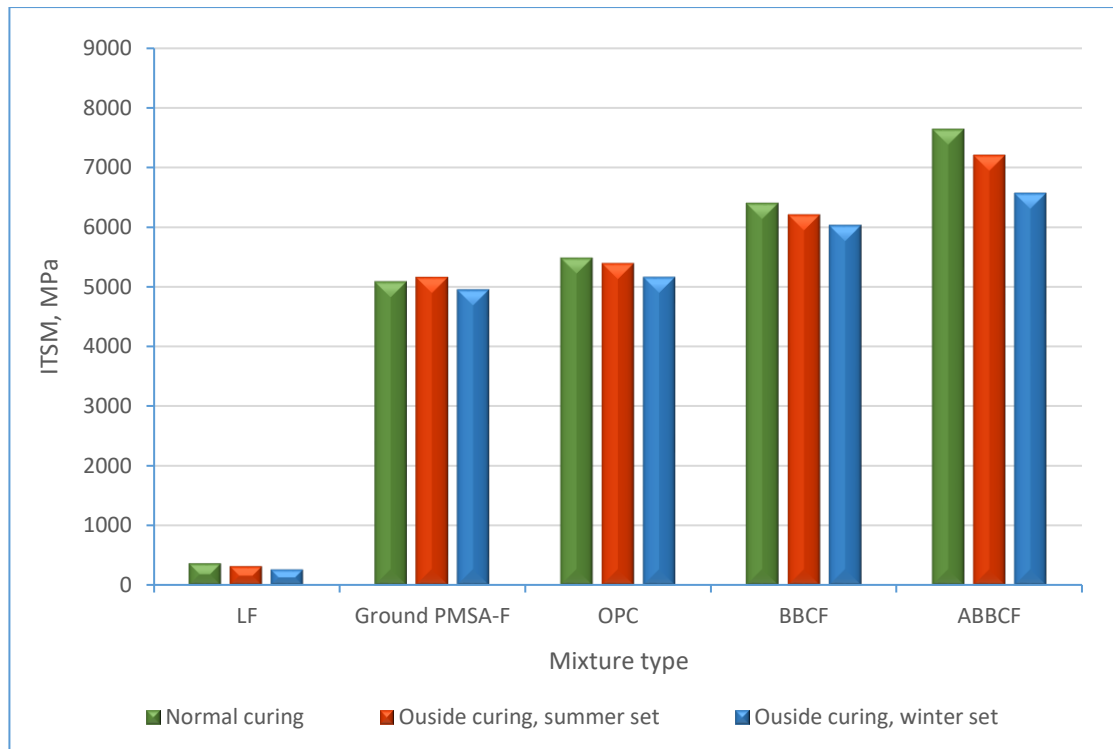
Figure 6.17. ITSM results for indoor and outdoor CBCEA mixtures after 28 days
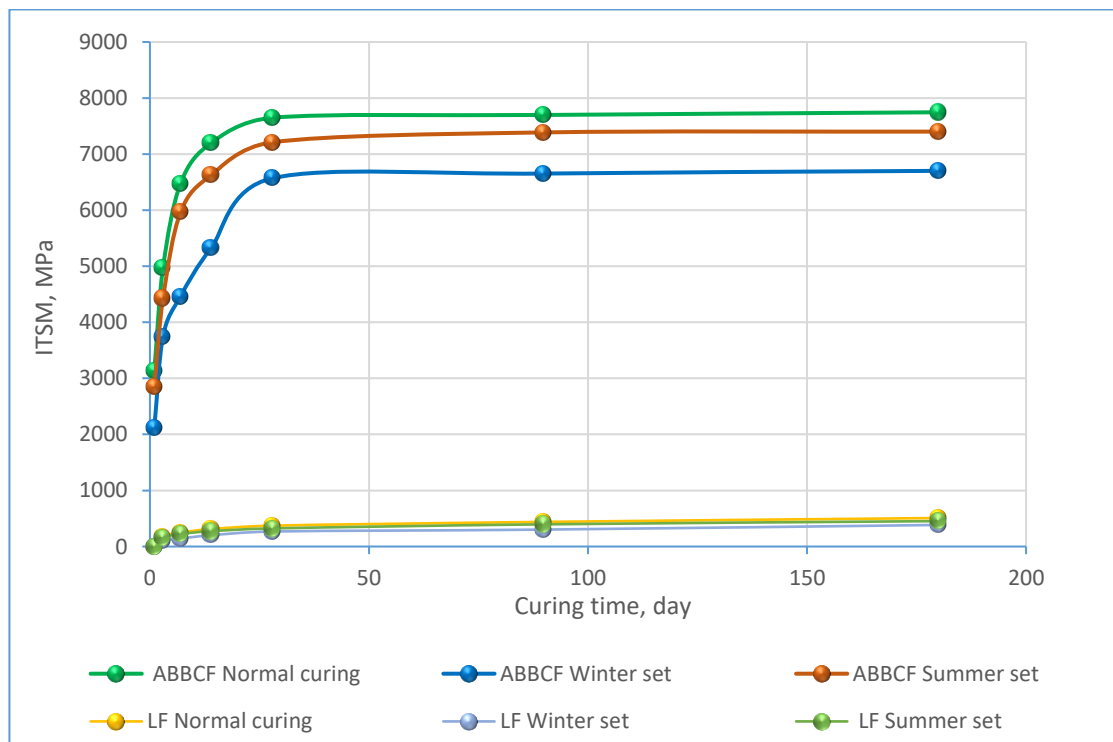
Figure 6.18. Rate of stiffness modulus gain of outdoor LF and ABBCF specimens

6.7 The Effect of Early Stage Curing Temperature on ITSM Performance

In the case where an inert filler is used in CBEMs, early stage curing temperature plays a major role in the development of strength by facilitating chemical reactions and thus water removal from the mixtures. However, a high early temperature, as in the case of active fillers, will also activate the hydration process. Curing temperature not only plays a substantial role in the development of hydrated phases but also impacts on the amount of hydrated phases generated (Rojas and Cabrera, 2002). All the samples in this research were cured at ambient temperature. Therefore, in order to examine the effect of high early temperature curing, a curing procedure was carried out adopted from Jenkins (2000) who suggested that 1 day at 20°C plus 1 day at 40°C represents 7-14 days in the field. Samples from each mixture type were prepared and compacted and allowed to cure under Jenkins curing procedure conditions, the samples were then tested for ITSM at 20°C at day 1 and day 28 of curing. Comparisons were made with the relevant specimens at normal curing. A 40°C early curing temperature was also adopted to represent the summer temperature of the authors' country as well as this has been trialed in previous studies (Ruckel et al., 1983).

Figure 6-19 shows the results of the ITSM after 1 day for the tested samples. It can be observed that the reference LF gained stiffness under the high early curing temperature while the same samples failed when using normal curing. This shows the impact of trapped water on the weak early strength of such mixtures. Increasing the temperature results in an increase in water evaporation leading to gains in strength. For the other mixtures i.e. ground PMSA-F, OPC, BBCF and ABBCF, it was found that a substantial development in the ITSM was achieved after just one day of curing at 40°C revealing the importance of increased temperatures for the hydration process this resulting in the development of more hydration products at early ages. Increments, in terms of ITSM for

the ground PMSA-F, OPC, BBCF and ABBCF mixtures, were 192%, 181%, 170% and 117% when compared to normal curing results. These outstanding results substantiate the use of such mixtures in summer and also in areas with high temperatures. The target ITSM of 2152 MPa can easily be surpassed in 1 day for all CBCEA mixtures.

Figure 6-20 illustrates the ITSM improvement after 28 days for both cured specimens. It can be observed that the samples with high early temperature curing were still better in ITSM than the relevant normal curing specimens. However, the differences between the two groups was less than the 1-day ITSM results as the early high curing mixtures developed more hydration products which were responsible for the ITSM at early ages. The ground PMSA-F, OPC, BBCF and ABBCF mixtures increased by 26%, 22%, 8% and 5% after 28 days when compared to the normal curing results. The hydration process was accelerated under high early curing temperature conditions, leading to an increase in the influence of the secondary binder.
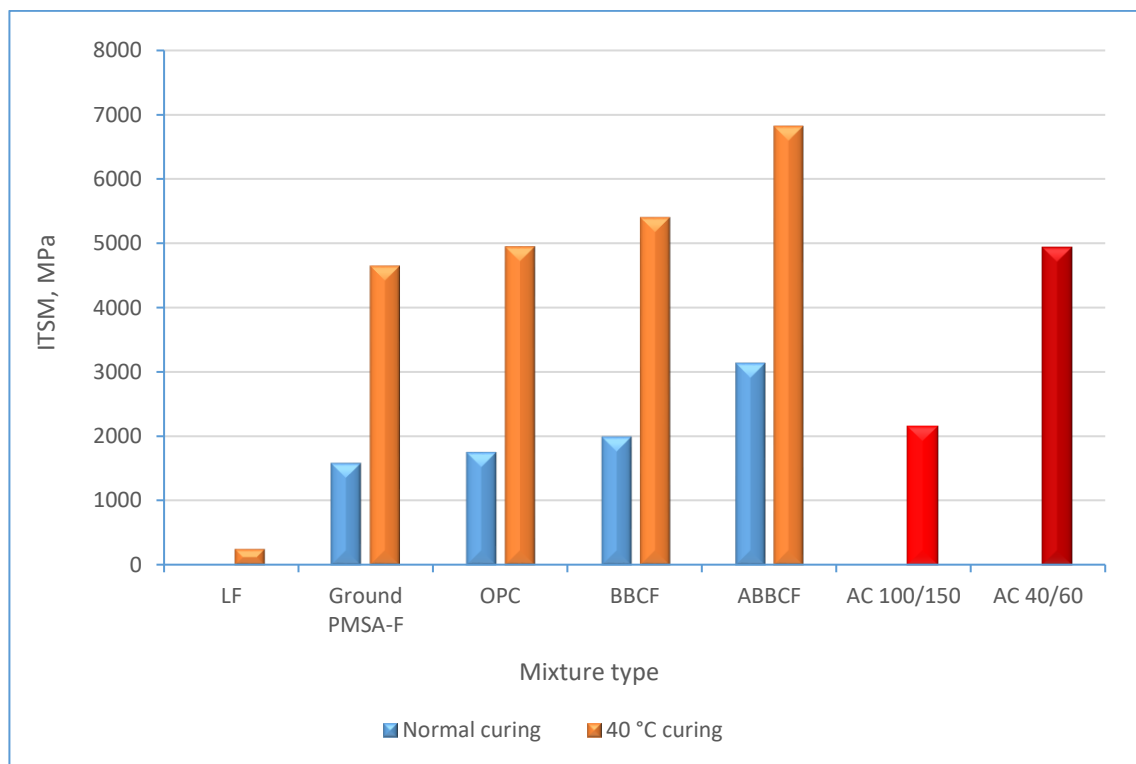
Figure 6.19. Influence of early curing on ITSM after 1 day
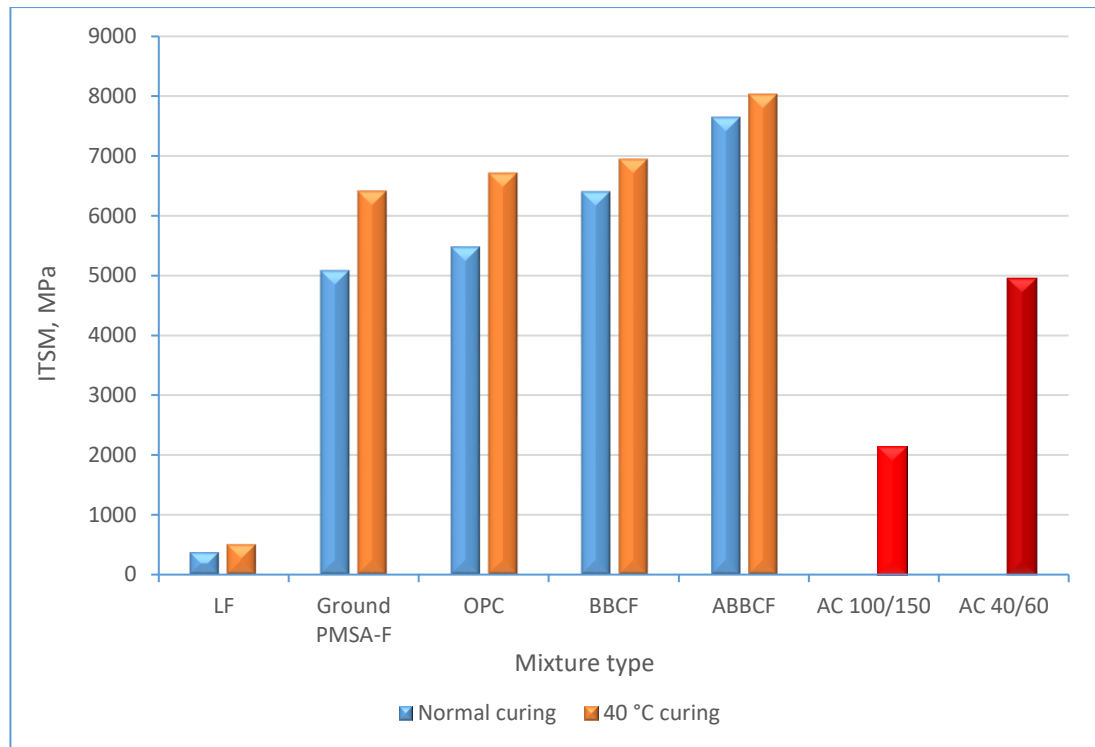
Figure 6.20. Influence of early curing on ITSM after 28 days

6-8 Summary of the Development of Novel CBCEA mixture/s

To summarize, tests carried out on the CBCEA mixtures have resulted in several remarkable conclusions, namely:

➢ Replacing LF with OPC resulted in a significant improvement in the ITSM. This proves that filler made from cementitious waste materials can be used to produce environmentally friendly CMAs similar to those produced using OPC as limestone filler replacement.

➢ The PMSA-F revealed its superiority in comparison to the PMSA-C mixture in that the greater surface area and finer particles play important roles in the hydration process.

➢ Low grinding time for PMSA-F is essential. This gives a considerable improvement in the fineness of the material, increases the specific surface area, reduces grain size, increases density, and increases particle packing compared

with untreated PMSA-F. Said ground PMSA-F mixture creates a considerable improvement in the ITSM test results and as such, grinding can be considered a cheap and suitable means of improving the properties of the mixture at early life.

➢ A new, novel CBCEA mixture has been produced by incorporating FC3R, which is categorised as a waste material, to generate BBCF containing 4.5:1.5 ground PMSA-F: FC3R.

➢ Further improvements were gained by generating a novel CBCEA mixture through the addition of W-NaOH to the binary cement to manufacture an ABBCF mixture. This mix has fast-curing properties leading to improvements in ITSM values by ensuring advanced activation through the alkaline solution. The stiffness results after 1-day are promising, illustrating no damage danger due to early trafficking.

➢ The new CBCEA mixtures, i.e. OPC, ground PMSA-F, BBCF and ABBCF have lower thermal sensitivity compared to the LF mixture and the two AC mixtures.

The next chapter will investigate other mechanical properties of the new CBCEA mixtures in terms of wheel track, fatigue and fracture tests.

CHAPTER 7

MECHANICAL PROPERTIES OF CBCEA MIXTURES

7.1 Introduction

The previous chapter dealt with the improvement of the CBCEA mixtures in terms of ITSM. In this chapter, the results of tests carried out on all the optimized mixtures i.e. LF, OPC, ground PMSA-F, BBCF and ABBCF, for permanent deformation resistance, resistance to fatigue and fracture toughness, will be discussed.

7.2 Permanent Deformation Resistance by Wheel Track

One of the major modes of failure in pavement structures is permanent deformation. This usually leads to deterioration of the pavement resulting in a reduction in ride quality. Permanent deformation manifests itself as rutting in the wheel path resulting from accumulated deformation (strain) as a result of repeated traffic loading (Elnasri, 2014). This deformation, which takes place within the asphalts, develops through shear displacement and densification under traffic (Taherkhani, 2006). Perraton et al. (2011) stated that mechanical loading from traffic and climate impact as a result of thermal differences in the pavement, are the two main kinds of loading that affect pavements. As a result of traffic load on asphalt pavement layers, stresses are induced. These stress pulses generate strains which are very small in comparison to the strength of said mixtures and mostly recoverable. Any irrecoverable strain induced by a single application of load, is small but under repeated load conditions, the real case in pavements, these small, irrecoverable strains accumulate creating permanent deformations in pavement layers (Kuna, 2014).

Taherkhani (2006) reported that magnitude of pavement deformation is influenced by the properties of the materials, temperature, load level and loading time. Some deformation

is recoverable after removing the load but there will be some permanent deformation linked to the plastic and viscous properties of the material.

Many factors influence permanent deformation resistance in asphalts such as bitumen and aggregate properties, their ratios in the mixture, compaction level and climatic conditions where temperature has a significant influence. From these factors, the main characteristic of bitumen which protects against permanent deformation is its grade or hardness. The aggregate properties considered protective against the generation of permanent deformation resistance are grading, surface texture, shape and size. Brown and Cooper (1984) found that continuously graded mixtures had more permanent deformation resistance in comparison to gap graded mixtures at 30°C. Taherkhani (2006) reported that aggregates with angular crushed rock and rough surface textures are more effective than smooth surface textures and round shaped aggregates at resisting permanent deformation.

Wheel track tests are employed as a simulator of in situ conditions for pavement materials. These tests are popular as they are simple and simulate traffic loading (Gibb, 1996). The aim here is to examine the permanent deformation characteristics for the CBCEA mixtures, namely LF, OPC, ground PMSA-F, BBCF and ABBCF, using wheel tracking tests in accordance with the standard BS EN 12697-22 (European Committee for Standardization, 2003a). The implications of using ground PMSA-F, FC3R and W-NaOH in CBCEA mixtures can be quantified and explained with these tests, at the same time comparing their performance with two types of conventional AC binder courses.

7.2.1 Test Procedure and Sample Preparation

The tests were performed on all mixtures at test temperatures of 45°C and 60°C, for a duration of 10000 load cycles (approximately 460 minutes), as reported in the experimental plan in Table 5-5. The wheel track test was performed in a temperature controlled chamber to examine the effect of temperature. A schematic of the wheel track apparatus is depicted in Figure 7-1.

The CBCEA slab sample (Figure 7-2) was compacted by means of a roller compactor at ambient temperature. The specimens for the test comprised of fabrication slabs of dimensions 400mm x 305mm x 50mm. After compaction, the slab samples were kept in their moulds at lab temperature (20°C) for 24 hours before extraction, this representing the first curing stage. Following this, the samples were cured at 40°C for 14 days before being removed from the oven and allowed to cool; only then were they subject to the wheel track test. This curing protocol was recommended by Thanaya (2003) to guarantee that a completely cured condition was realised. All tests were therefore performed on the CBCEA mixtures at full curing conditions.

The slabs were conditioned at test temperatures for at least 4 hours prior to testing after which the specimens were wheel tracked with a wheel of diameter 200 mm and width 50 mm. To record the development of rutting in the slab sample as the test progresses, the vertical position of the wheel is mounted by means of an LVDT. The wheel tracker moves with a forwards and backwards motion at a frequency of 0.8Hz under a loaded wheel with a travel length of ($230 \pm 10mm$), passing over the top of the sample. The load applied was 0.7 MPa based on BS EN 12697-22 instructions (European Committee for Standardization, 2003a).
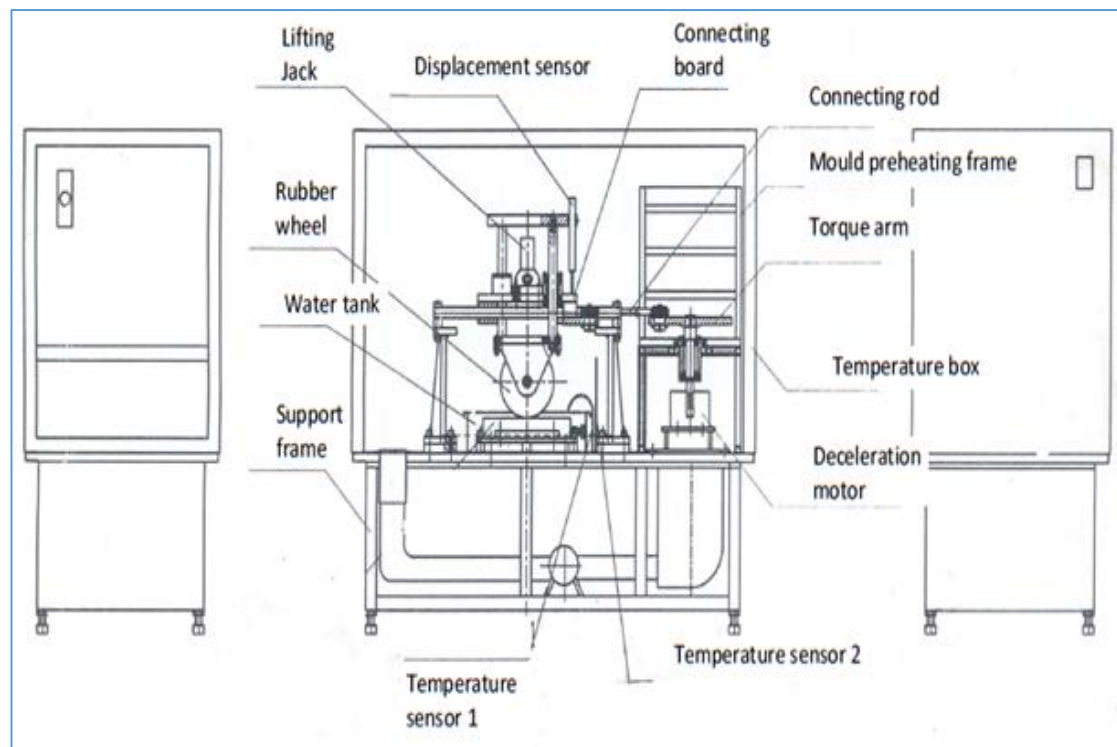
Figure 7.1. Schematic of the wheel-tracking test

Figure 7.2. CBCEA slab sample materials before being subjected to the roller compactor

7.2.2 Wheel Track Test Results

7.2.2.1 Wheel Track Test Results at 45°C

The first stage in the wheel track test consists of tracking the slab samples at 45°C to represent moderate to heavily stressed sites which require high rutting resistance according to PD 6691 (European Committee for Standardization, 2015). These test results are displayed in Figure 7-3 where rutting depth has been plotted against the number of cycles. The LF mixture shows a substantial increase in permanent deformation leading to a significant deterioration of the slab sample, making this type of mixture unsuitable for pavement application. The inferior performance of the LF mixture is due to the low early stiffness and high air void content in comparison to the two control hot mixtures, AC 100/150 and AC 40/60, as shown in Table 7-1. Figure 7-4 shows the LF slab sample after testing where substantial rutting can be seen. AC 100/150 and AC 40/60 show more rutting resistance in comparison to the LF mixture. The rut depth after 10000 cycles for the LF mixture was 11.8 mm while it was 3.349 mm and 2.666 for the AC 100/150 and AC 40/60 mixtures, respectively.

Table 7-1. Comparison between LF and both AC mixtures

Mixture type	ITSM after 3 days, MPa	Air voids, %
LF	183	10.93
AC 100/150	2152	5.63
AC 40/60	4946	6.06
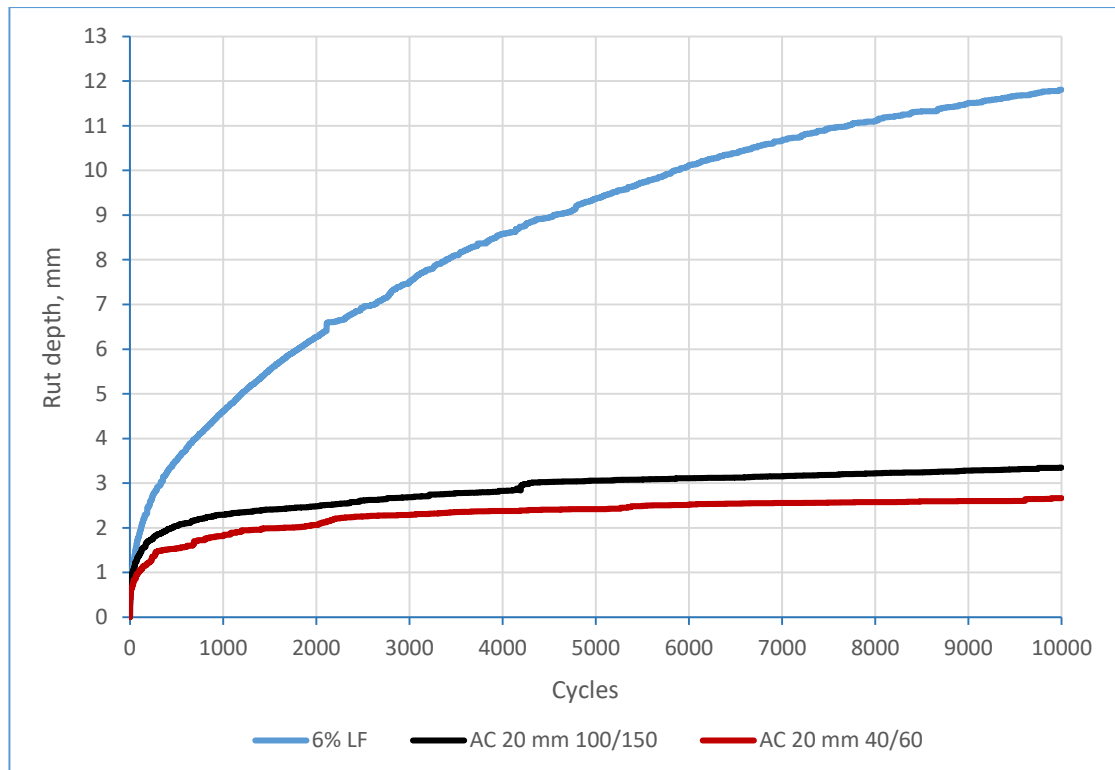
Figure 7.3. Wheel track results for LF, AC 100/150 and AC 40/60 at 45°C

Figure 7.4. Deformation of the LF slab after the wheel track test at 45°C

The effect of incorporating OPC was investigated by producing CBCEA mixtures with 6% OPC content as a replacement for limestone filler. The results presented in Figure 7-5 indicate the positive effect of OPC inclusion in CBCEA, substantially increasing its resistance to permanent deformation in comparison to the control LF and both asphalts. A cementitious bond is responsible for this improvement, the rut depth for the OPC mixture measuring 0.745 mm after 10000 cycles, which is around 16 times less than that of LF. It is also less than that of the AC 100/150 (4.5 times) and AC 40/60 (3.6 times) mixtures, substantiating the suitability of the OPC mixture for heavily trafficked pavement in terms of permanent deformation resistance.

OPC was replaced by ground PMSA-F, BBCF and ABBCF as shown in Figure 7-6, where it is seen that the inclusion of ground PMSA-F resulted in an increase in permanent deformation resistance approximately 15 times greater in comparison to the LF mixture in the wheel track test. The incorporation of BBCF in the mixtures resulted in a significant decrease in permanent deformation of around 16.5 times relative to the LF mixture. This was also better than the OPC mixture. This is attributed to the characteristics of FC3R which produce improvements in the hydration of BBCF as explained in Chapter 6, Section 6.3.5.

Interestingly, the best resistance to permanent deformation was seen in the ABBCF mixture. Here, rutting depth was approximately 20 times less than that for the LF mixture. The permanent deformation resistance for the ABBCF mixture is quite high in comparison to the mixture treated with OPC. This is also connected to the role of W-NaOH as it generates a dense microstructure by improving the hydration process.
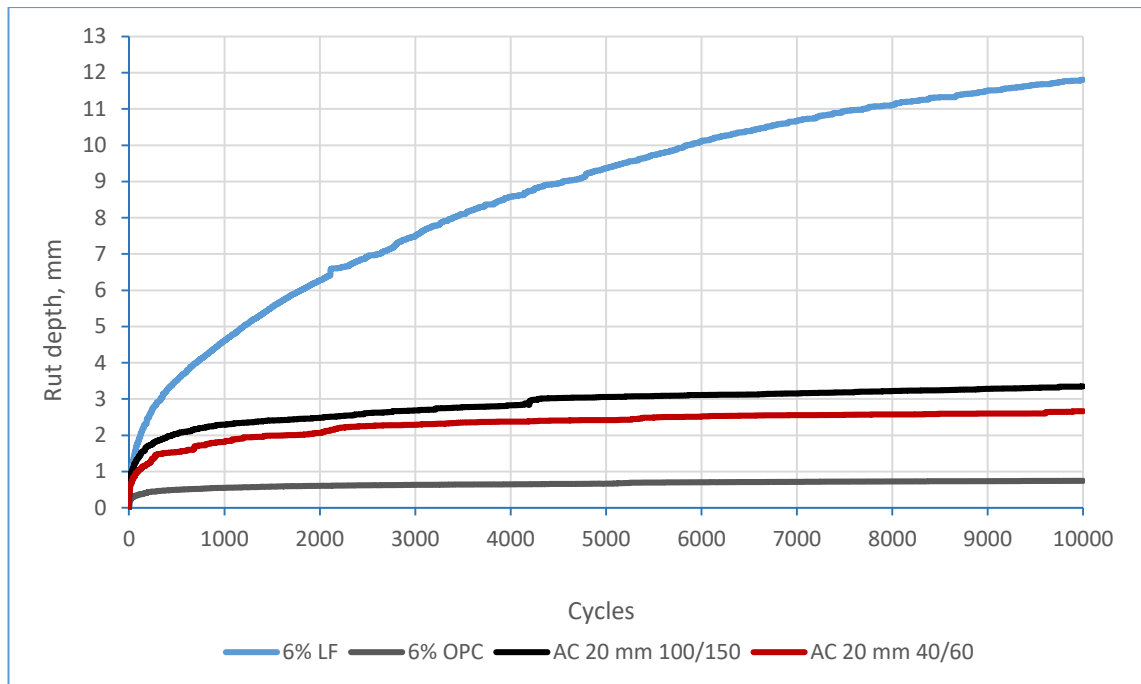
Figure 7.5. Wheel track results for LF, OPC, AC 100/150 and AC 40/60 at 45°C
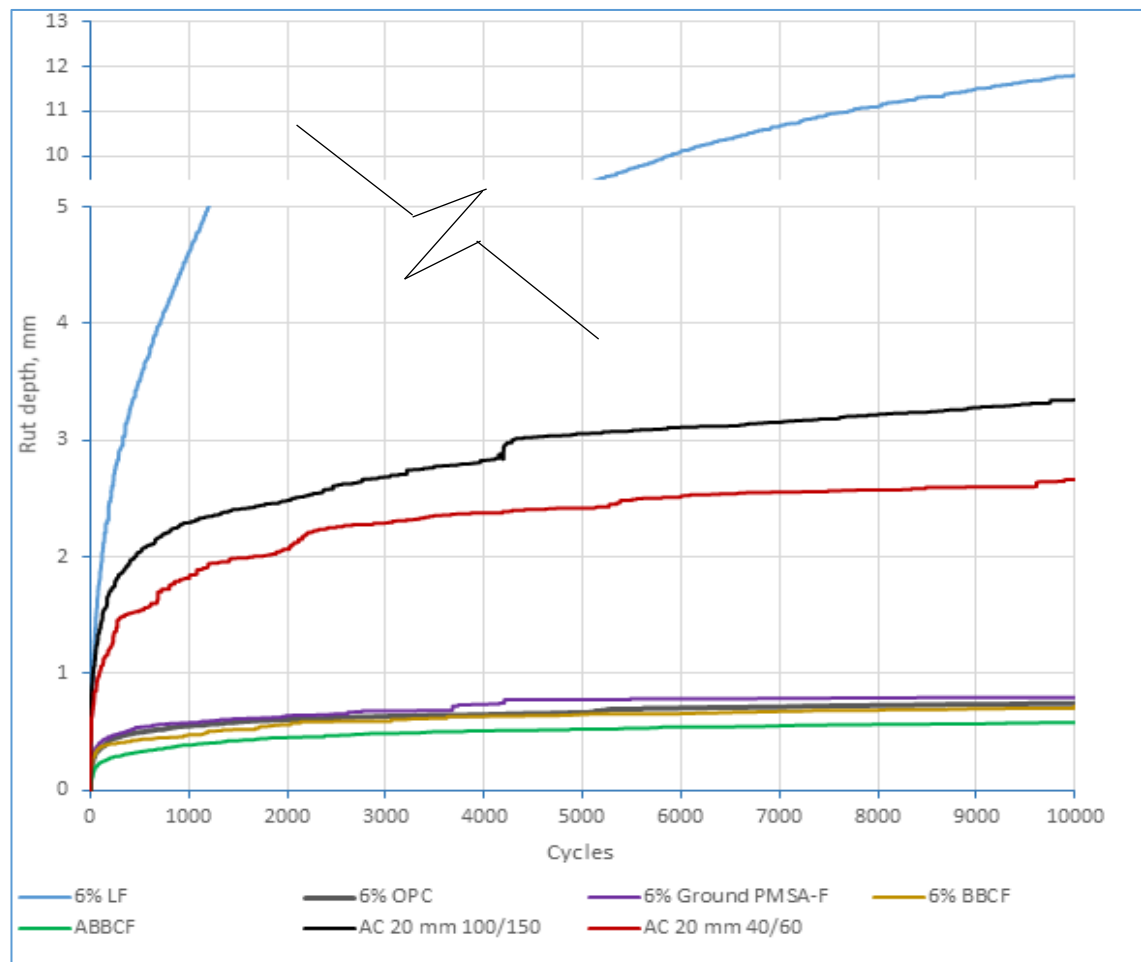
Figure 7.6. Wheel track results for all mixtures at 45°C

Figure 7-7 illustrates the proportional rut depth after 10000 cycles at 45°C for the optimised mixtures, ground PMSA, OPC, BBCF and ABBCF in comparison to the control LF, AC 100/150 and AC 40/60 mixtures. It can be seen that the PRD is dramatically reduced for these mixtures, comprising substantial reductions of approximately 15, 16, 16.5 and 20 times in comparison to the LF mixture. This demonstrates superiority of the ABBCF mixture, in terms of PRD after 10000 cycles at 45°C, in comparison to the other reference mixtures.

In general, it can be concluded that both the BBCF and ABBCF mixtures have reduced permanent deformation susceptibility, demonstrating the potential advantages of applying such materials on heavily trafficked roads. Table 7-2 details a summary of the wheel track tests for all the mixtures. The WTS_{AIR} and PRD_{AIR} for the optimized CBCEA mixtures are significantly lower relative to the control LF and both asphalts. It can be seen that the LF mixture falls outwith the BS EN specification in terms of PRD_{AIR} according to PD 6691 (European Committee for Standardization, 2015) where the maximum limit is 9%.
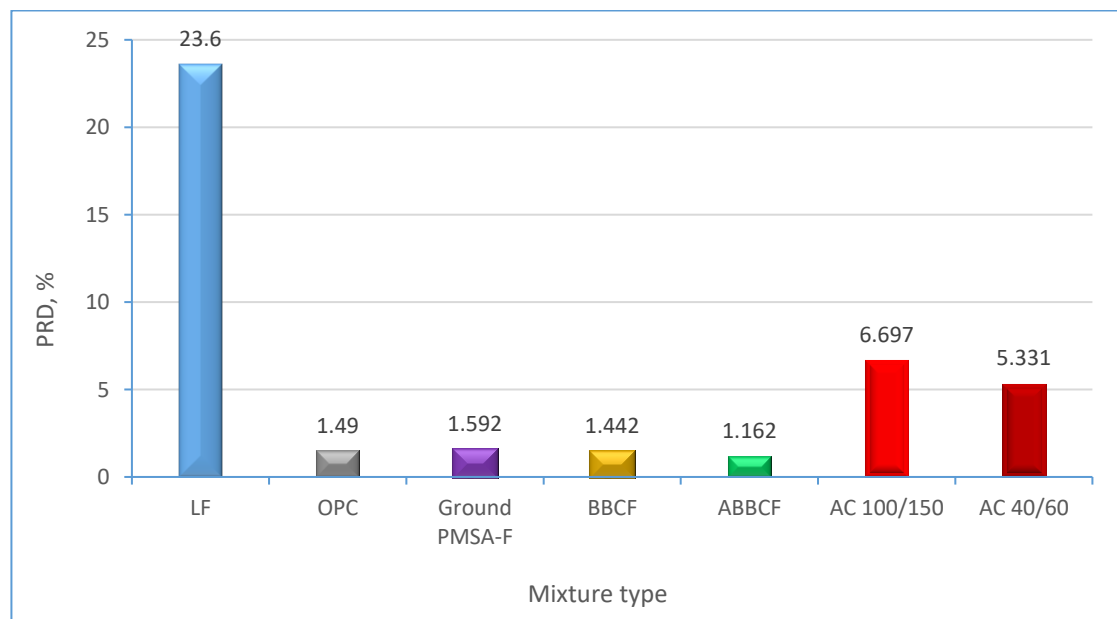
Figure 7.7. Proportional depth of the rut after 10000 cycles for all mixtures at 45°C

Table 7-2. Summary of the wheel track test results at 45°C

Mixture type	Wheel track test results			
	WTS$_{AIR}$, mm/1000 cycle	PRD$_{AIR}$, %	Rut depth, mm	ITSM after 3 days, MPa
LF	0.486	23.6	11.8	183
OPC	0.015	1.49	0.748	3417
Ground PMSA-F	0.018	1.592	0.796	3181
BBCF	0.014	1.442	0.721	3730
ABBCF	0.011	1.162	0.581	4978
AC 100/150	0.058	6.697	3.349	2152
AC 40/60	0.049	5.331	2.666	4946

7.2.2.2 Wheel Track Results at 60°C

Temperature plays a critical role in susceptibility to permanent deformation in asphalt mixtures, therefore, all the mixtures in the second stage were subject to high temperature (60°C) to study the influence of this. This will represent very heavily stressed sites which require higher rut resistance in accordance with PD 6691 (European Committee for Standardization, 2015).

The results revealed that as the temperature increases, there is an increase in the susceptibility of the LF samples to permanent deformation as depicted in Figure 7-8. Most of the deformation took place in the first 1000 cycles, the samples completely destroyed at this temperature (Figure 7-9) under the wheel track load. This illustrates the weakness of such mixtures in hot regions and summer weather, also indicating the disadvantage of applying it on heavily trafficked roads. The poorer performance of the LF mixture results from low early stiffness and high air void content.
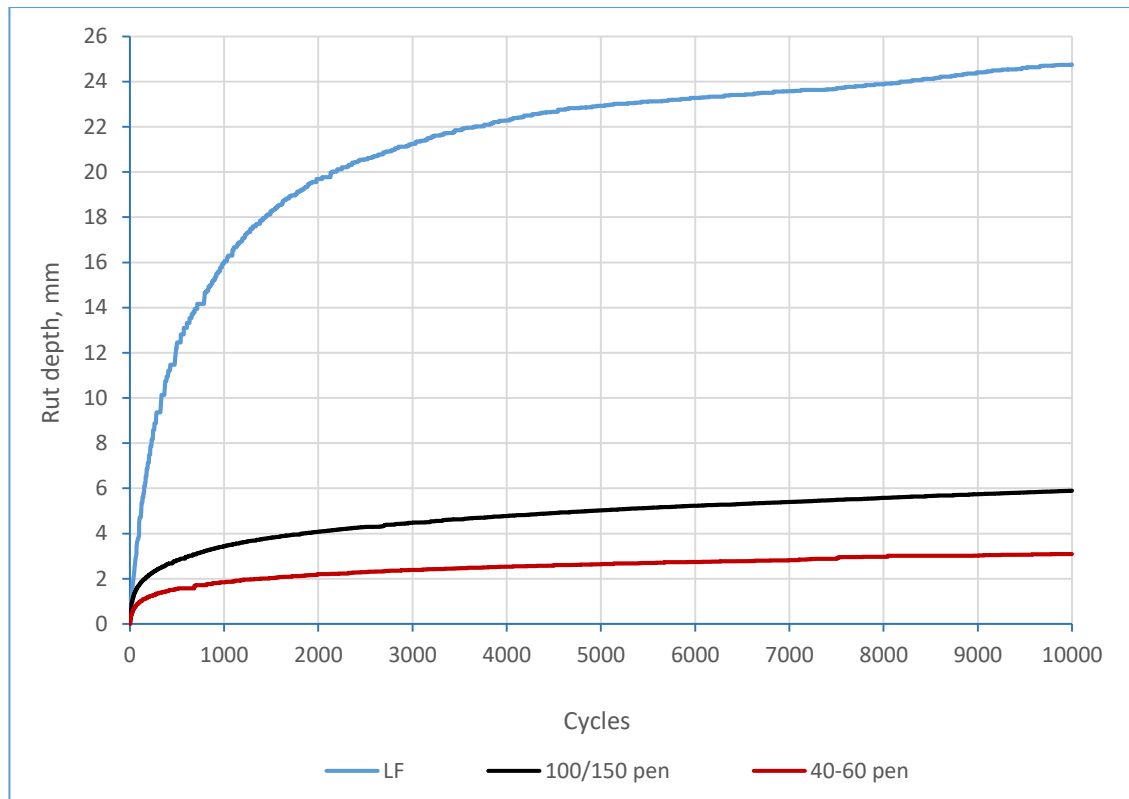
Figure 7.8. Wheel track results for LF sample at 60°C

Figure 7.9. Total failure of the LF slab at 60°C

Figure 7-10 presents the results of all mixtures under wheel tracking at 60°C. The ground

PMSA-F, BBCF and ABBCF mixtures show a remarkable improvement in resistance to

permanent deformation with substantial increments of 15, 24 and 34 times respectively, in comparison to the LF mixture. Figure 7-11 presents the proportional depth of the rut after 10000 cycles for all mixtures at 60°C, confirming the results in Figure 7-10. These results establish that the inclusion of FC3R and W-NaOH to the BBCF and ABBCF mixtures improves resistance to permanent deformation. Therefore, after fulfilling all the wheel track testing requirements to BS EN specifications, it can be concluded that such mixtures can be used in heavily trafficked road pavements even when subject to high temperatures subject to in situ trials. The LF mixture produced the poorest performance under these conditions by having the highest rut depth in comparison to the optimized mixtures. Table 7-3 provides a summary of the test results confirming the superiority of the optimized mixtures in terms of WTS_{AIR}, RPD_{AIR} and rut depth over the reference LF and both AC mixtures.
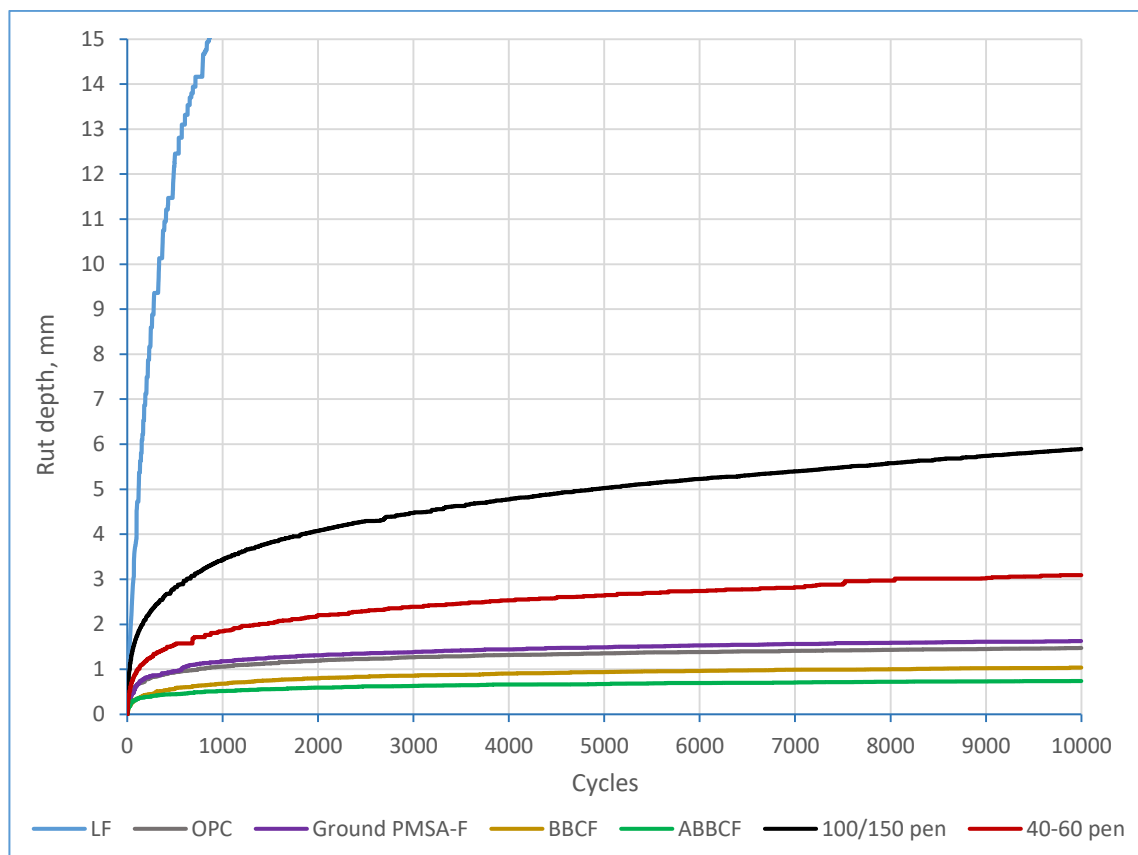
Figure 7.10. Wheel track results for all mixtures at 60°C
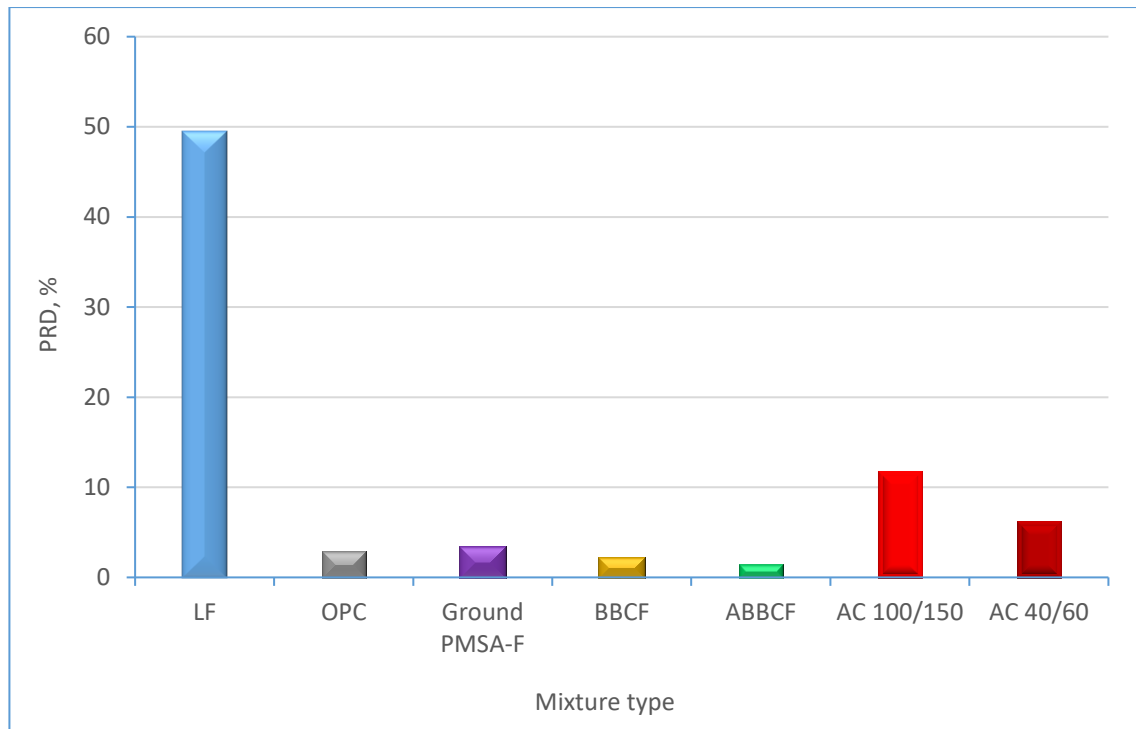
Figure 7.11. Proportional rut depth after 10000 cycles for all mixtures at 60°C

Table 7-3. Summary of the wheel track test results at 60°C

Mixture type	Wheel track test results		
	WTSAIR, mm/1000 cycle	**PRDAIR, %**	**Rut depth, mm**
LF	0.365	49.508	24.754
OPC	0.024	2.946	1.473
Ground PMSA-F	0.028	3.256	1.628
BBCF	0.020	2.075	1.038
ABBCF	0.013	1.478	0.739
AC 100/150	0.174	11.792	5.901
AC 40/60	0.091	6.182	3.091

7.3 Resistance to Fatigue

Fatigue is a major source of failure in asphalt pavements. Fatigue cracking is a phenomenon which happens in pavements as a result of the repeated application of traffic loads. From a mechanical viewpoint, fatigue mechanisms can be divided into two parts: the appearance of tensile stresses/strain in the base layer and the repetitive appearance of such tensile stresses/strains under traffic repetitions. An accumulation of micro damage in the bottom of the base layer, as a result of the repetition of tensile stress/strain over time, causes a break between the aggregate and binder, creating cracks (Maggiore, 2014).

Thom (2008) stated that micro cracking initially appears at the bottom of an asphalt concrete layer as a result of horizontal tensile strain; this compromises the contact between the aggregate skeleton and the binder (particle-to-particle contacts). Water trapped in cracks in addition to repeated loading, causes a reduction in the strength of the mixture. Micro cracking begins to propagate towards the layers above causing pavement collapse. This phenomenon is termed bottom-up cracking.

Different factors affect the fatigue behaviour of asphalts such as: specimen construction method (compaction); loading (axle loads, modes and patterns); rest periods; the characteristics of the material, and traffic and environmental variables such as temperature, ageing and healing (Maggiore, 2014). The impact of temperature and initial air voids on fatigue performance is substantial, while an increase in temperature is harmful to fatigue performance (Hu et al., 2016). It has been reported that in terms of the characteristics of the materials, the two main factors effecting fatigue life for continuously graded mixes are asphalt content and air void content. It appears that while the type of aggregate has a minimal effect on fatigue (Read, 1996), Pell (1973) found that mixture stiffness is important. Mixtures with higher stiffness had a longer fatigue life when tested in stress control modes, while using a control strain mode reduced fatigue life. Aggregate

grading, as reported by Thanaya (2003), also has a significant influence on fatigue life. Asphalts prepared with finer gradings were found to perform better than mixtures comprising coarser gradings.

Crack growth is generally thought to comprise of two major stages: crack initiation and crack propagation. The former is the forming of a macro-crack from an accumulation of micro-cracks as a result of cyclic load application and thermal changes, while the latter is the growth of macro cracks through the asphalt layer, generated by additional applications of traffic load and temperature variation.

Crack initiation can be studied to specify fatigue life by applying a test such as an indirect tensile fatigue test or four-point load test, while crack propagation can be investigated by various approaches including the Semi Circular Bending (SCB) test. These will be reviewed in the next section.

7.3.1 Four-Point Bending Test- Test Procedure and Sample Preparation

Huang (1993) reported that fatigue tests can be carried out in two different types of controlled loading modes: constant stress and constant strain. The former is usually considered to represent the response of a thick layer (more than 150 mm thick), the major loading component of a pavement for traffic loading, whereas the latter is appropriate for thin pavement layers. In the controlled stress test, the applied stress is kept constant, the strain increasing with number of repetitions. In contrast, in the controlled strain test, the applied strain remains unchanged, the load reducing with number of repetitions (Kuna, 2014).

A four-point load (4PL) test was utilized to ascertain the fatigue characteristics of the CBCEA mixtures because it simulates the stress and strain conditions in pavement layers in a more realistic way in comparison to other fatigue tests. Jitareekul (2009) stated that

the benefit of this test is the presence of a constant bending moment over the middle third portion of samples, meaning that failure will show up at a weak spot due to non-uniformity of the material. This is not the case in other tests, such as the centre point loading, where failure is forced to occur at a specific point. In addition, Maggiore (2014) stated that the 4PL test simulates pavement failure very well in terms of fatigue under traffic loading since repeated loading leads to tension at the bottom of the sample. Cracking will initiate that will propagate to the top until failure. Fracturing usually occurs in the area of constant maximum value of bending moment between the two inner clamps.

The 4PL test involves the application of a continuous sinusoidal waveform at the top of a prismatic sample by means of two load points (inner clamps). The sample is controlled at four points by using four clamps. The two outside clamps stay motionless and can only move horizontally while the two inner clamps bend in relation to the strain/stress applied. Free translation and rotations are allowed for all loads and reactions points. Sample deformation is measured at the bottom between the two inner clamps through LVDT. In the current study, the test was performed using a 4PL bending machine following BS EN 12697:24 (European Committee for Standardization, 2012b).

It should be noted that fatigue life (N_f), can be investigated by other methods in accordance with BS EN 12697- 24 (European Committee for Standardization, 2012b). These include bending tests such as two-point bending tests on trapezoidal samples, two-point tests on prismatic-shaped samples, three-point bending tests on prismatic-shaped samples and indirect tests represented by an indirect tensile test on cylindrical-shaped samples.

Different approaches can also be used to define the fatigue life of asphalts. A decrease of 50% in the initial stiffness modulus has been widely used as an indicator of fatigue life in

the controlled strain mode and has been adopted in fatigue tests by Pramesti et al. (2013) and Dulaimi et al. (2016b). Fatigue life is also accepted as present when the stiffness modulus is at 10% of its original value in the controlled stress mode.

Turning to the dissipated energy approach, this concept may also be of value in the evaluation of fatigue life of asphalts (Hopman et al., 1989; Rowe, 1996; Pronk, 1997; Rowe and Bouldin, 2000). The idea here is that the quantity of energy dispersed per loading cycle changes during fatigue testing. Hopman et al. (1989) proposed a proportion of energy dissipation, others, for example, Bahia et al. (2002) and Anderson et al. (2001) labelling it as a dissipated energy ratio (DER). Anderson et al. (2001) also suggested using DER to define fatigue failure. A non-linear transition is seen between two linear phases when plotting DER against number of cycles for the controlled strain mode of loading, failure happening at the point on the curve where the curve becomes nonlinear.

It was reported that failure due to fatigue in asphalts usually happens between 30-200 microstrain (Read, 1996). Brown and Needham (2000b) suggested that the strain levels experienced in a pavement structure are likely to be below 200 microstrain with the actual value depending on variables that include mixture type, subgrade thickness, load and layer thicknesses.

In the current study, prismatic test samples were produced from sawing slabs of LF, OPC, ground PMSA-F, BBCF, and ABBCF mixtures that had been fabricated, compacted and cured in the same manner as the wheel track slabs. The curing conditioning was carried out in two stages, according to Thanaya (2003), as mentioned in the previous section. The first stage was to leave the slabs in their moulds for 1 day at a lab temperature of 20°C. Following this, the slab samples were placed into a ventilated oven at 40°C for 14 days to achieve their constant mass. They were then allowed to cool at lab temperature, five

prismatic test samples fabricated per slab. After the samples were trimmed, they were placed on a flat surface at room temperature in the lab before testing began.

7.3.2 Test Results of 4-Point Bending Tests

The fatigue tests were performed in a strain control mode at a temperature of 20±1°C. The input strain was waveform sinusoidal shaped, tested at a frequency of 10 Hz. Fatigue lives at microstrains of 100, 125 and 150, following Read (1996) and Brown and Needham (2000b) recommendations, were calculated. Actual fatigue life was determined as the number of pulses that result in a 50% reduction of stiffness from initial values.

It can be seen in Figure 7-12 that the LF mixture, which is based on 150 microstrain, has the lowest resistance to fatigue; its fatigue life was short, the mixture performing poorly in comparison to both AC binder course mixtures. This is attributed to having less cohesive characteristics represented by low early stiffness and higher air voids. This implies that the performance of LF mixture is inferior to the two hot mixtures.

It can also be observed that the addition of OPC clearly resulted in an increase in the resistance to fatigue of such mixtures; the fatigue life of the OPC mixture was enhanced in comparison to the LF mixture. The inclusion of OPC has also been found to enhance the cohesion of such mixtures. 4-point bend testing has also shown that ground PMSA-F, BBCF and ABBCF mixtures have a high fatigue life in comparison to LF by 14, 19 and 29 times, respectively, when they were subjected to the same strain levels. The number of cycles to failure (N_f) for ABBCF at a value of 150 microstrain, was higher than that of the other mixtures. This demonstrates that incorporating cementitious materials considerably improves the fatigue performance of such mixtures. It is worth noting that the fatigue performance for the high performance ABBCF mixture is superior to that of ground PMSA-F, OPC, BBCF and the two AC binder course mixtures. The inclusion of

FC3R and W-NaOH in the ground PMSA-F mixture resulted in an increase in fatigue resistance indicating that these materials have a positive influence on the fatigue properties of such mixtures. These results also show that the presence of W-NaOH in the ABBCF mixture had a greater impact than OPC as a filler. This is due to alkaline activated materials which have created higher level mechanical characteristics in comparison to cement. In such an alkaline environment, it is expected that glass phases of fly ash particles will be broken and react with $Ca(OH)_2$ creating CSH gel.

Figure 7-13 shows the fatigue lines for the LF, OPC, ABBCF and the AC 100/150 pen mixtures. These fatigue lines were obtained by plotting the maximum tensile strain at the centre of the sample against the corresponding number of cycles to failure. The spread of data for LF, OPC and ABBCF was quite narrow with an R^2 of 0.9214, 0.9505 and 0.9609, respectively. Referring to this figure, it can be observed that the fatigue life of ABBCF was better than the LF and OPC mixtures across all tensile strains. This mixture also had a higher fatigue resistance performance than the corresponding AC 100/150 pen mixtures. This greater fatigue life is related to improvements in the hydration process as explained in Chapter 9. Consequently, according to Read (1996) and Brown and Needham (2000b) who stated that fatigue failure in asphalts usually occurs below 200 microstrain, the incorporation of ABBCF substantially extends fatigue life.
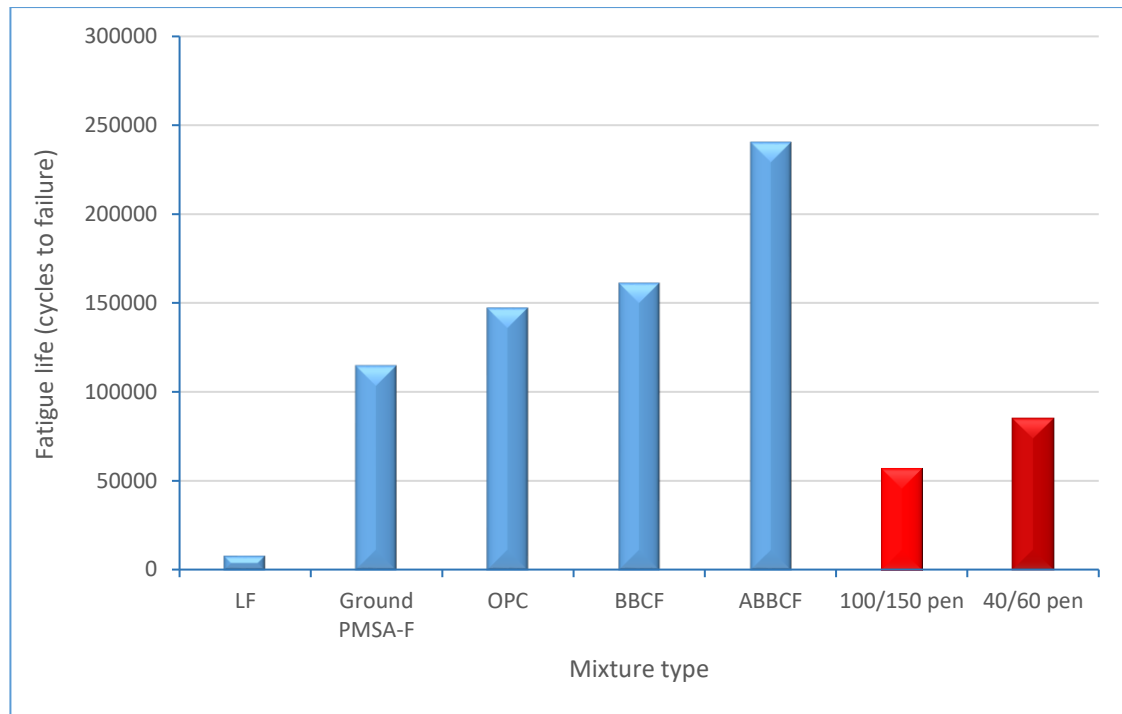
Figure 7.12. Fatigue lives for all cold and hot mixtures at 20°C
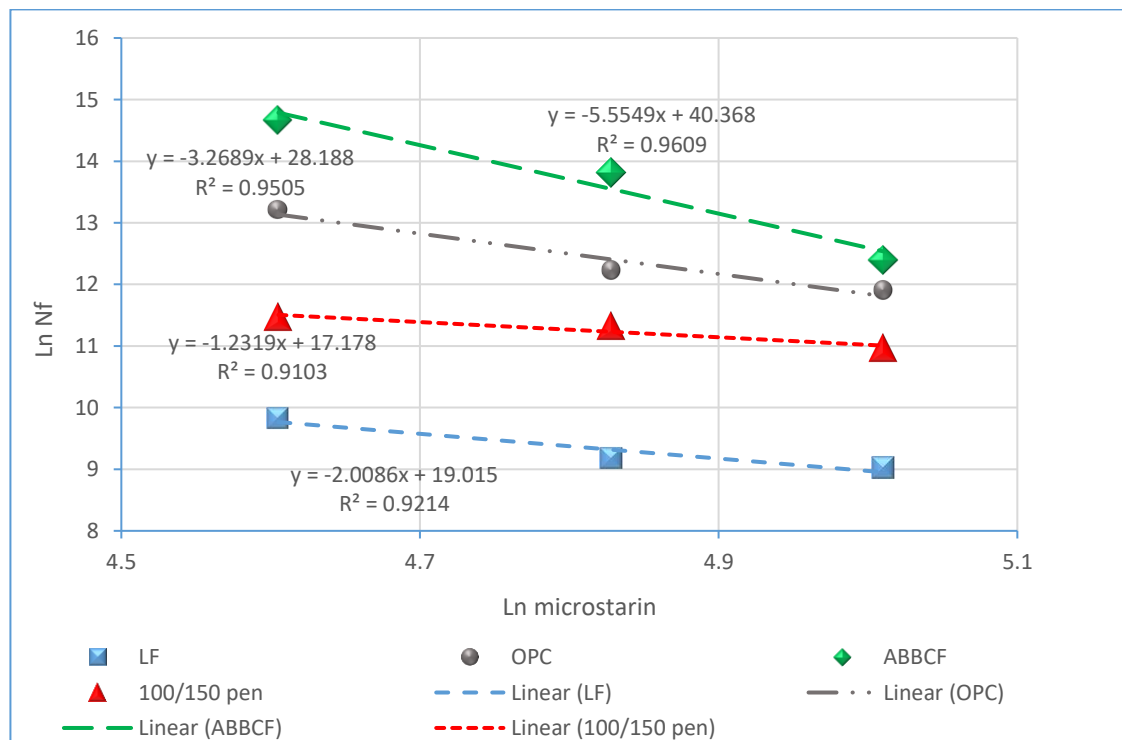
Figure 7.13. Fatigue line for the LF, ABBCF and AC 100/150 mixtures at 20°C

The initial stiffness and number of cycles to failure were compared for LF, OPC, ABBCF and AC 100/150 mixtures as detailed in Figure 7-14. The initial stiffness is normally

measured at cycle 100 in the 4PL test, this representing 100% stiffness of the mixture. After loading, the stiffness decreases until failure at 50% of the initial stiffness, this representing the fatigue life. Figure 7-14 displays the initial stiffness and fatigue failure cycles of these mixtures where it is seen that the ABBCF mixture had higher fatigue failure cycles in comparison to its hot and cold counterparts. The ABBCF mix achieved an average fatigue failure cycle of 240470, constituting 29, 2 and 4 times that of the LF, OPC and AC 100/150 mixtures with 8322, 147977 and 57299 failure cycles, respectively.

The initial stiffness values for ABBCF (2617 MPa) are more than 6 times higher than those of LF and 42% and 22% higher than the OPC and AC 100/150 mixtures, respectively. This is consistent with the ITSM results discussed in the previous chapter where it was reported that ABBCF had a higher ITSM in comparison to LF, OPC and AC 100/150 mixtures.
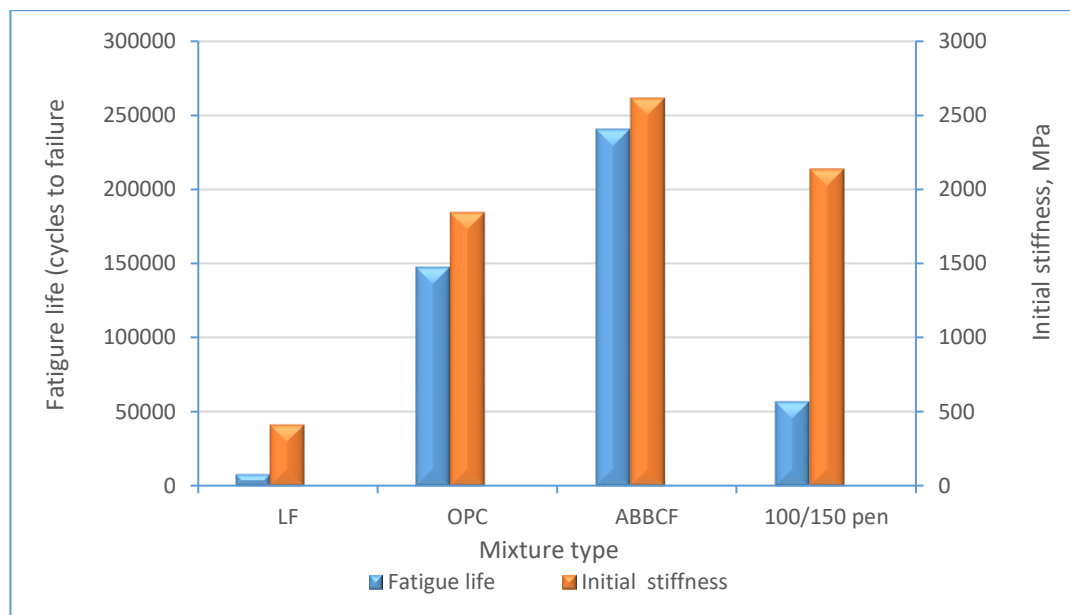
Figure 7.14. Comparison of initial stiffness and fatigue life

7.4 Fracture Toughness Performance

Traffic loading on pavement surfaces generates tensile stresses, in addition to other stresses, at the bottom of the asphalt concrete layers. Fatigue cracks begin when traffic

loading continues, propagating through the asphalt concrete layer. Asphalt commonly exist as a brittle material at low temperatures meaning that stress intensity factors can be utilized as essential parameters to describe asphalt mixture failure (Ameri et al., 2011). Brittle fracturing is the main failure mode of asphalt pavements at low temperatures due to the elastic and brittle nature of the binder (Aliha et al., 2015). Said fracturing creates considerable expense to pavement rehabilitation agencies every year (Pirmohammad and Ayatollahi, 2015).

Measuring the fracture resistance of asphalts has been achieved using various test samples including, a) a single edge notched bend beam subjected to three point bend loading, b) a single edge notched bend beam subjected to four point bend loading, c) a Semi-Circular Bend (SCB) specimen subjected to three-point bend loading, d) a centre cracked circular disc specimen subjected to diametral compression (the Brazilian disc specimen) and e) a disc shape compact tension (DCT) specimen (Mansourian et al., 2016).

In this study, SCB tests were employed to gauge the fracture toughness of the LF, ABBCF and AC mixtures because this test has so many benefits including i) ease and efficacy in the production of samples; ii)) appropriateness for field cores; iii) repeatability in results and v) a clear crack progresses with smashing near the loading strip (Molenaar et al., 2002; Li and Marasteanu, 2009; Aragão and Kim, 2012; Im et al., 2014). Because of these benefits, the SCB test has been used by many researchers to measure the fracture toughness of asphalt mixtures (Molenaar and Molenaar, 2000; Pérez-Jiménez et al., 2013; Ban et al., 2015).

The SCB test is primarily a three-point bending test applied to a semi-circular shaped sample with a notch at the bottom of the sample as shown in Figure 7-16. Tension will be induced at the bottom of the sample leading to crack propagation. Artamendi and Khalid

(2006) defined fracture toughness as a measure of crack propagation resistance for an asphalt when the stress state near the crack tip is mainly plane strain and when tensile mode monotonic loading is applied. Fractures may occur under mode I (also known as opening or tension mode), mode II (sliding or inplane shear mode), mode III (tearing or anti-plane shear mode) or a combination thereof (Mansourian et al., 2016) as can be seen in Figure 7-15. Mode I occurs when crack faces open without any sliding. Mode II occurs when the crack faces slide at right angles to the crack front without any opening, while mode III occurs when the crack faces slide parallel to the crack front without any opening (Pirmohammad and Ayatollahi, 2015). In this study, the tensile mode (mode I) is used to appraise crack propagation performance of the reference and optimised mixtures as this mode is normally the most frequently seen, associated with local displacement as the surfaces of the cracks move directly apart.

A comparison between calculated stresses, dependent on the tensile strength of the asphalt, was applied to describe fracture behaviour; tensile strength is used to describe fracture criteria. Although higher fracture resistance can be achieved with higher tensile strength, fracture mechanics theory states that such materials are sensitive to fracturing, these cracks acting as stress concentrators (Artamendi and Khalid, 2006).
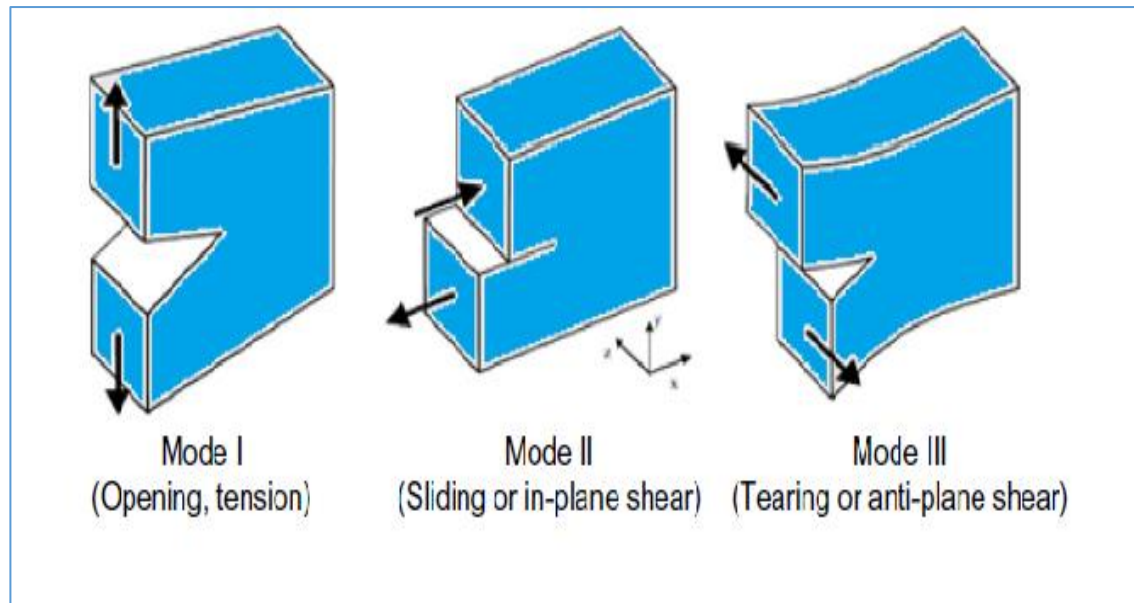
Figure 7.15. Different fracture modes (Mansourian et al., 2016), permission to reproduce this figure has been granted by Elsevier

7.4.1 Sample Production

To obtain samples for the fracture toughness test configuration, slabs of 400 x 305 x 50 mm were prepared and compacted with the roller compactor. The same two stages of curing as used for the wheel track samples and the fatigue samples, were employed here, according to Thanaya (2003) recommendations. Following curing, three cylindrical specimens with a diameter of 150 mm, were cored from the slabs (Figure 7-16). Each specimen was cut in half, perpendicular to the axis, to produce two SCB samples which were notched (length 10 mm) using a diamond saw. This introduced notch works as crack initiators at the mid-point of load direction to characterize the fracture properties of mixtures during cracking propagation. Metal bearing strips with a length of at least the thickness of the sample and a width of 20 mm, were glued to the specimens, after which the samples were placed on the rollers. The samples were then allowed a minimum of four hours conditioning by placing them inside a temperature controlled cabinet at 5°C (Figure 7-17) before positioning them on a three-point bending to carry out the test.

Figure 7.16. Cored samples for the SCB test

Figure 7.17. SCB samples conditioned at 5°C

7.4.2 Semi-Circular Bending (SCB) Test Results

The fracture behaviour of the cold and hot mixtures was examined by carrying out three-point bending tests at 5°C, using an SCB test on semi notched samples. The SCB test results in Figure 7-18, detail the load vs load-line displacement curves of the samples of LF, ABBCF, AC 100/150 and AC 40/60 mixtures. These graphs illustrate the generation of two load deflection responses, both linear and non-linear relationships. The load

deflection responses switched to non-linear a short time before the ultimate load was reached as a result of plastic zone generation ahead of the crack tip. Cracks propagated until failure when the ultimate load was reached.

The behaviour of the LF mixture is not the same as that of the ABBCF mixture as seen by the non-linear region formation and crack propagation rate after reaching the ultimate load. The behaviour of the LF mixture is however similar to the AC 100/150 mixture. The ABBCF is similar to the AC 40/60 mixture as seen by their load deformation relationship shape. The response of the ABBCF mixture during loading was almost linear elastic until the maximum load was reached. A non-linear response for these mixtures was observed when reaching peak loading, beginning near to the deformation corresponding to the maximum load where cracks propagated very quickly. This produced sudden failure due to the development of a plastic zone ahead of the crack tip. The stiffness value for each mixture category (cold and hot) caused this similarity in behaviour where a wide, non-linear zone can be observed for the low stiffness mixtures such as that of fully cured LF. High stiffness cold and hot mixtures are characterized by rapid failure within the narrow non-linear zone.

Figure 7-19 presents the fracture toughness calculated in accordance with equations 5-6 and 5-7 for both cold and AC mixtures. It can be seen that the fracture toughness of treated ABBCF mixtures is better than the control LF mixture by around 30%. This means that the inclusion of cementitious materials improves resistance to crack propagation in comparison to the untreated cold mixture. This appears to increase the required peak load for initiation of fracture from the tip of the pre-existing crack. This result is in contrast to that found by Al-Hdabi et al. (2014b) who reported that there was no difference in fracture toughness of CBEM treated with 6% OPC and untreated CBEM. However, while the treated ABBCF mixture has an improved stiffness, the fracture toughness for such

mixtures is less than the corresponding AC mixtures. The failure loads for the ABBCF samples are less than that for AC samples. One of the reasons for this is high air voids in such mixtures (see Chapter 11 for details), which affects crack propagation resistance. Air voids in the LF and ABBCF mixtures are 10.93% and 10.25%, while they are only 5.63% and 6.06% for AC 100/150 and AC 40/60, respectively. It can also be seen from Figure 7-20 that for all specimens (LF, ABBCF, AC 100/150 and AC 40/60), the propagation of cracks starts from the tip of the notch moving towards the point of load application. The displacement of the crack surfaces are perpendicular to the plane of the crack which complies with Mode I (Monney et al., 2007).
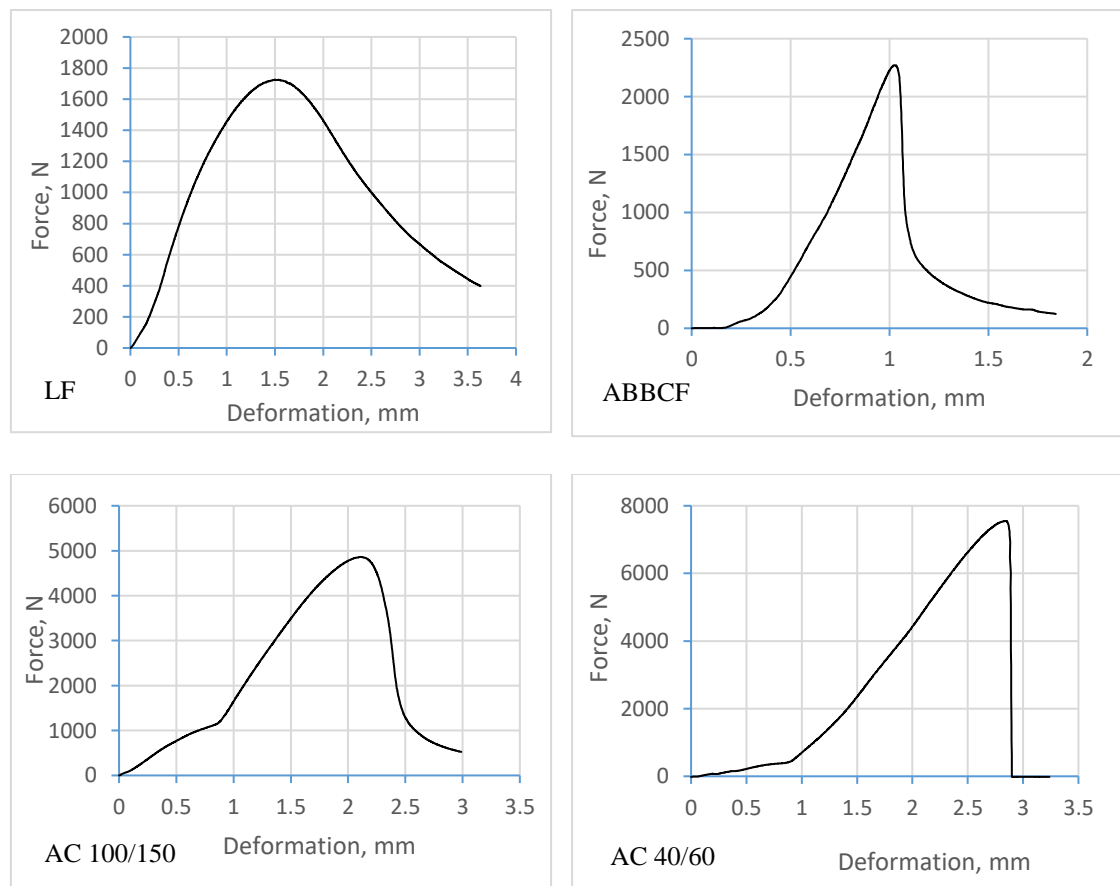
Figure 7.18. Force-deformation curves for SCB samples of all cold and hot mixtures
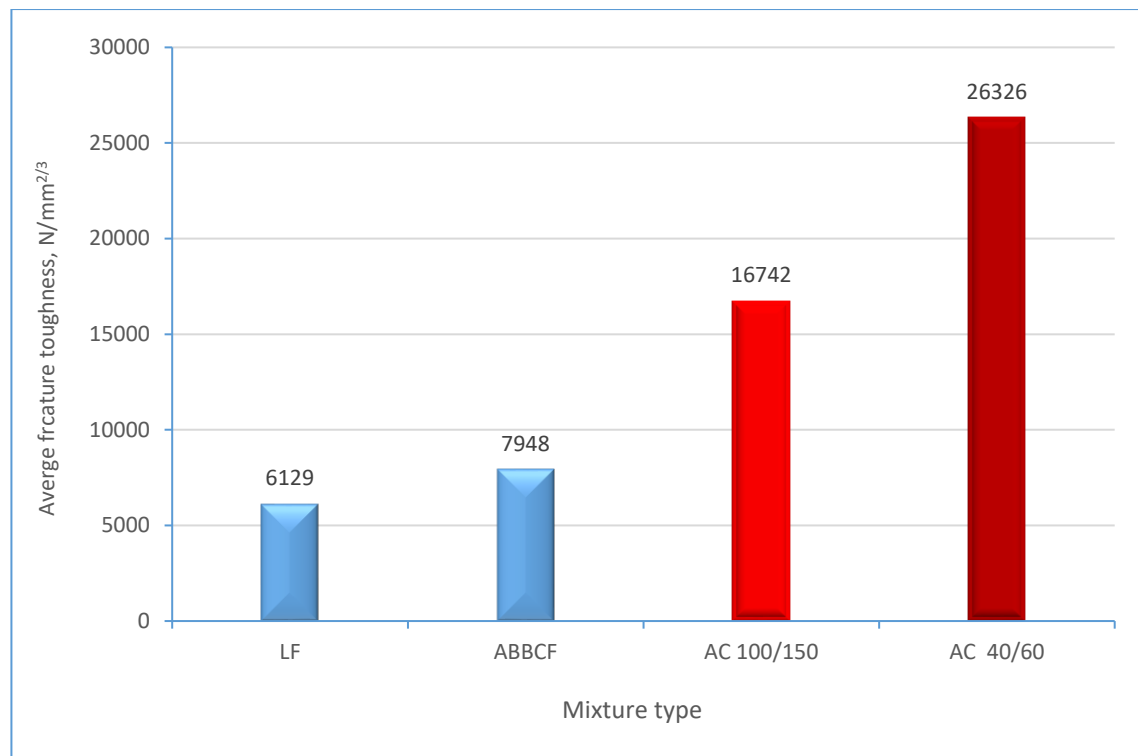
Figure 7.19. Fracture toughness for all cold and hot mix
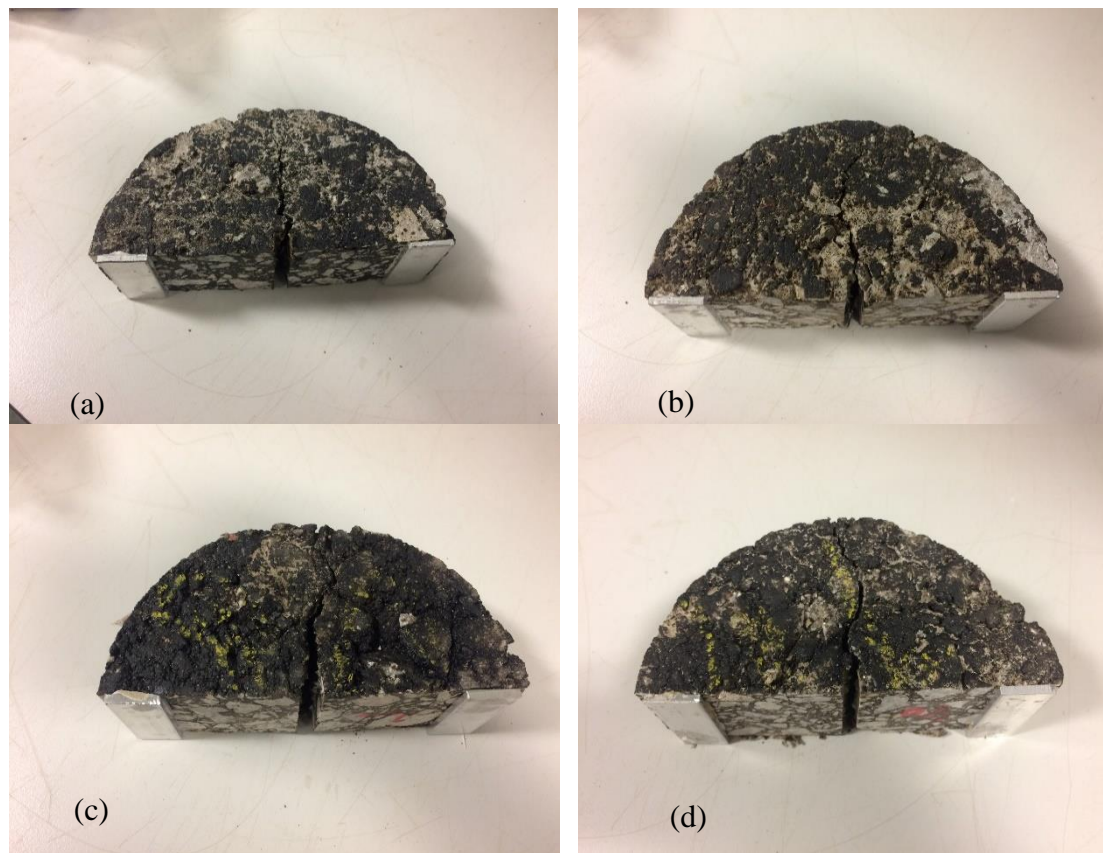
Figure 7.20. SCB samples for all cold and hot mixtures (a- LF, b- ABBCF, c- AC 100/150, d- AC 40/60)

7.5 Summary

Based on the results of the mechanical testing performed on the CBCEA mixtures, the following conclusions can be drawn.

➢ The performance of the LF under wheel track testing after 10000 cycles is very weak at 45°C, however at 60°C, this mixture failed at 1000 cycles. The inclusion of ground PMSA-F, FC3R and W-NaOH allows these mixtures to be more resistant to rutting at both 45°C and 60°C by developing a dense microstructure, through improved hydration processes, giving mixtures a high stiffness modulus. This confirms the suitability of such mixtures for use in summer weather and hot regions, demonstrating the possible advantages of using this material on heavily trafficked roads.

➢ In terms of fatigue life, the ground PMSA-F, BBCF and ABBCF mixtures had a significantly longer life under 4PL testing in comparison to the untreated LF mixture. The microstructural integrity of the new mixtures and the formation of hydration products is responsible for this improvement.

➢ In terms of fracture behaviour, the results show that there is improvement in ABBCF in comparison to the reference LF mixture. However, the results for these mixtures are still lower when compared with the two reference AC mixtures, this relating to the presence of air voids in such mixtures.

CHAPTER 8

WATER DAMAGE AND AGE HARDENING PERFORMANCE OF

CBCEA MIXTURES

8.1 Introduction

During their service life, asphalt pavements endure severe traffic loadings under a variety of environmental conditions which have the potential to cause deterioration over time. These pavements must have the capacity to withstand deterioration during their service life in order to satisfy performance demands. Scholz (1995) defined the durability of asphalt pavements as the ability of the materials to resist the effects of water, problems of ageing and temperature variation in the context of a given amount of traffic loading, without substantial deterioration over a long period of time. Thanaya (2003) stated that it is generally agreed that moisture damage and age hardening are the main factors affecting the durability of asphalts. Therefore, in this chapter, both water damage resistance and age hardening performance for the optimised CBCEA mixtures are examined in order to assess these elements. The following mixtures: OPC, ground PMSA-F, BBCF and ABBCF, have been subjected to water sensitivity and long term age hardening tests and compared to the reference LF mixture and the two traditional AC mixtures.

8.2 Water Sensitivity

Moisture damage is considered to be one of the main causes of distress in asphalt pavements resulting in a loss of stiffness and structure strength in pavement layers and eventually, failure of the road structure (Jakarni, 2012). It is defined as the degradation of the structural integrity of the asphalt. This phenomenon can occur through a failure in adhesion between the asphalt binder and the aggregate or loss of cohesion within the asphalt film in the presence of moisture (Souliman et al., 2015). Moisture damage can

have a substantial economic impact as it can result in premature pavement failure leading to increased rehabilitation work and higher maintenance costs.

It has been reported by Jakarni (2012) that the quality, performance and serviceability of asphalts are negatively influenced by environmental factors specifically, water and/or moisture. Pavement distress types including stripping, ravelling, rutting and fatigue cracking can be attributed to water presence or moisture in the pavement structure in addition to having an impact on the properties of asphalts, this termed moisture damage.

Ling et al. (2016) reported that CMA's have higher moisture susceptibility in comparison to conventional asphalts. This is considered the challenge that restricts the more widespread application of CMAs in the field to date. CBEMs are also considered as having higher water sensitivity in comparison to asphalt meaning that knowledge of the moisture sensitivity of CBCEA mixtures plays an essential role in the performance of such mixtures as it provides information with respect to the mixtures' durability.

A range of moisture conditioning procedures exist in the literature, as applied to CBEM specimens, such as capillary soaking and vacuum saturation (Thanaya, 2003). In capillary soaking, half the specimen thickness is soaked in water at room temperature for 24 hours. Following this, the sample is reversed allowing the other half to soak for another 24 hours. Each specimen rests on a bed of 15 to 20 mm of coarse sand during soaking to allow full contact with the water. Afterwards, the specimens are towel dried and subject to water absorption and Marshall stability tests at room temperature. The results of this are referred to as soaked stability values according to the design procedure introduced by the Ministry of Public Works Republic of Indonesia (1990).

According to the Asphalt Institute (1989), moisture exposure using vacuum saturation simulates the influence of exposure of CBEMs to subsurface water. The sample is

positioned in a vacuum device and entirely covered with water. A glass jar connected to a vacuum pump is evacuated at 100mm of Hg and held under vacuum for one hour. The vacuum is gradually released and the sample is permitted to soak in water for a further hour. Following this, the sample is removed from the water, towel dried, weighed in air and then tested for its strength.

In this study, the procedure described in section 5.5.2.1 which conforms to the BS EN 12697-12 (European Committee for Standardization, 2008), has been used to evaluate the water damage resistance of the CBCEA mixtures and the AC mixtures. Stiffness Modulus Ratio (SMR) was adopted as recommended by Al Nageim et al. (2012); Al-Hdabi et al. (2014b); Dulaimi et al. (2016b).

8.2.1 Results and discussion

Figure 8.1 illustrates the ITSM test results for both conditioned and unconditioned LF, OPC and the two AC mixtures. It can be seen that the LF mixture has the lowest SMR compared to OPC and the two AC mixtures. This is due to the low stiffness modulus of the mixtures, experiencing a reduction in this value after the samples were conditioned. The application of the vacuum pressure and saturation of the LF mixture with water at 40°C, lead to a substantial reduction in the stiffness and strength of this mixture, having an average SMR of about 50%. The advantages of the inclusion of OPC are clear. SMR values (ratios of wet to dry ITSM) of OPC (100%) were higher than that for the reference LF mixture and the corresponding two AC mixtures. The hydration process and the generation of a secondary cementitious binder, as stated before, are the main reasons for the increase in ITSM of the conditioned samples.
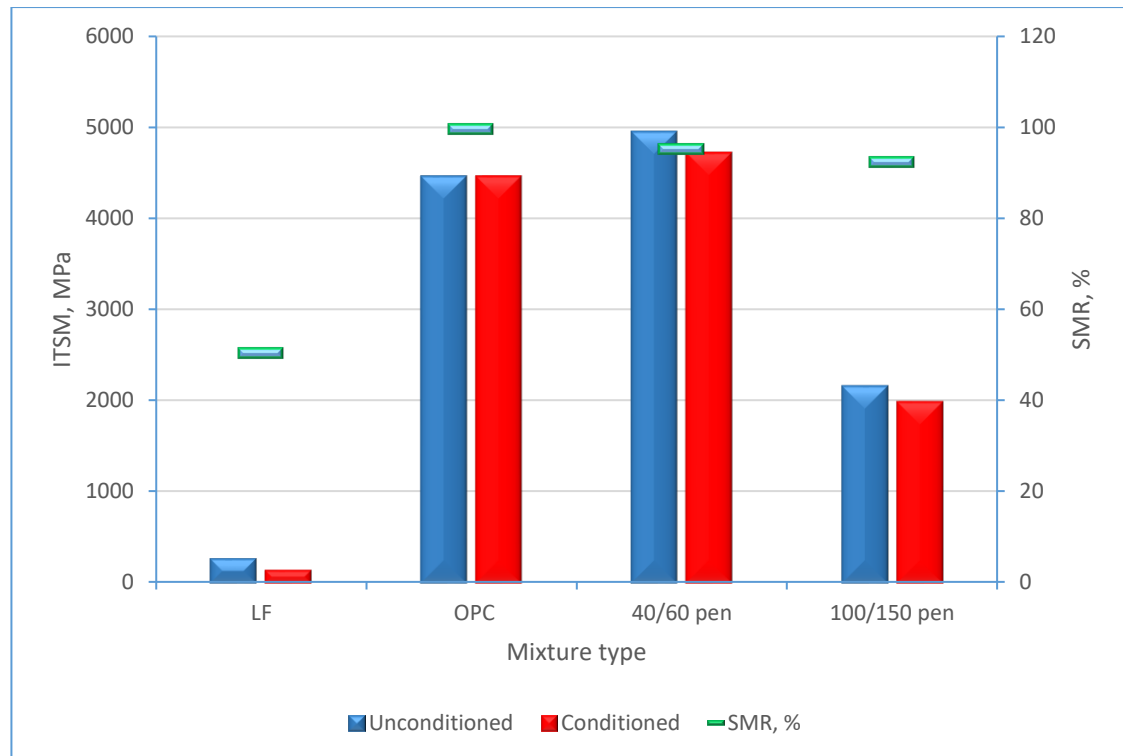
Figure 8.1. Stiffness modulus ratio for the water sensitivity analysis of LF, OPC and AC mixtures

The SMR values of CBCEA treated with ground PMSA-F, BBCF and ABBCF were higher than that for the LF mixtures and the two AC mixtures, as seen in Figure 8-2. The performance of these mixtures, in terms of water sensitivity, were better than the OPC mixtures. It can be seen that the SMR values of ground PMSA-F, BBCF and ABBCF are all are more than 100%, while the control LF has a lower SMR (50%), the AC 100/150 mixture and AC 40/60 mixture at 92% and 95%, respectively. This leads to the conclusion that OPC, ground PMSA-F, BBCF and ABBCF are less sensitive to moisture damage, results which comply with the required specifications recommended by Al-Busaltan et al. (2012); Dulaimi et al. (2016a). The ability of these mixes to preserve their strength after damage, reflected by higher SMR values, is linked to the development of new hydration products caused by the inclusion of cementitious and pozzolanic materials. Furthermore,

increasing the temperature of the water for immersion of samples to 40°C accelerated the

hydration processes for these mixtures.
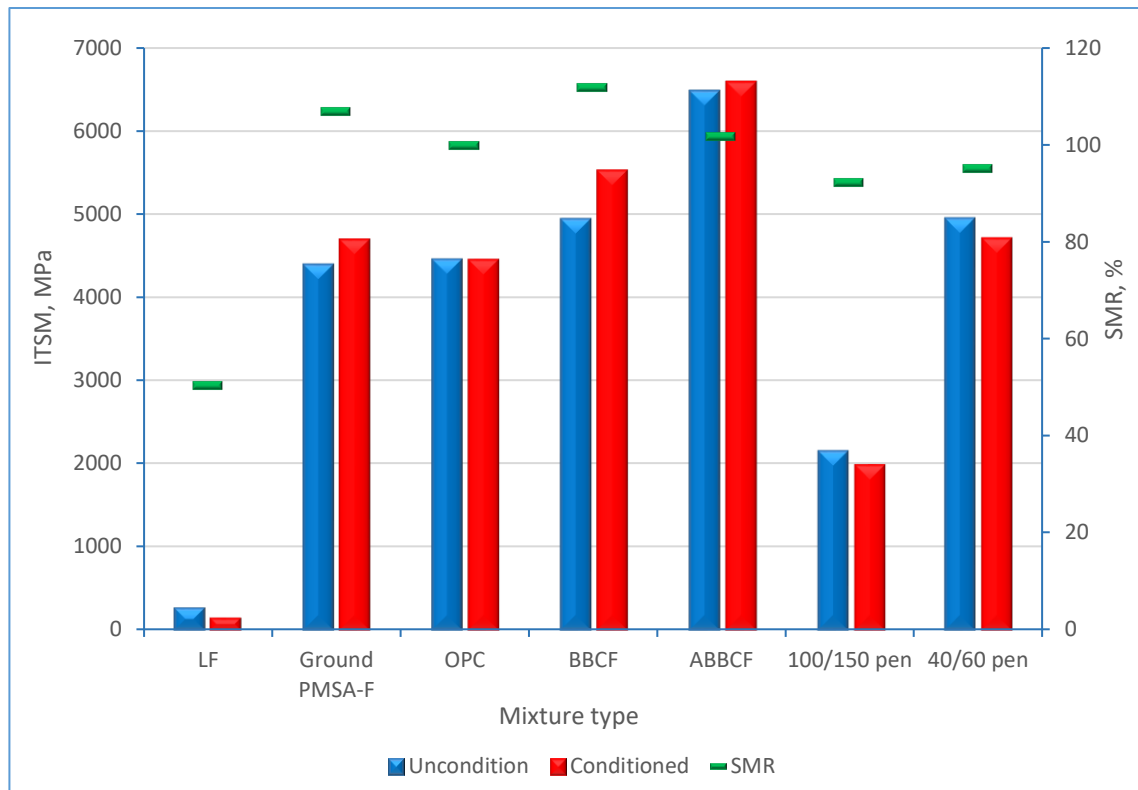
Figure 8.2. SMR of the water sensitivity analysis for all mixtures

8.3 Effects of Long Term Age Hardening

The durability of the asphalt is also influenced by age hardening (ageing) of the bitumen,

primarily during the mixing and construction stages. When the pavement is in service,

the bitumen slowly becomes stiffer as a result of oxidation which affects chemical

composition (Read and Whiteoak, 2003). Ageing is generally related to bitumen

hardening as result of the loss of volatile constituents in addition to oxidation of the

material during construction (short term ageing) and during its service life (long term

ageing) (Sutanto, 2009b). Ageing is often investigated for asphalts, whereas for CMA it

is not considered as the main challenge due to the mix preparation and compaction

features. Both types of age hardening are detailed in section 5.5.2.2. The procedure

adopted to investigate long term age hardening for the CBCEA mixtures is that proposed by the Strategy Highway Research Program (SHRP) A-003A.

When the bitumen comes into contact with air, it gradually oxidises; oxygen in the atmosphere facilitates a rise in viscosity making the bitumen harder and less flexible. The degree of oxidation is dependent on temperature, time and the thickness of the bitumen. The loss of volatile constituents is also dependent on temperature and exposure conditions (Read and Whiteoak, 2003).

8.3.1 Results and Discussion

All the CBCEA mixtures and the two AC mixtures were conditioned in an oven at 85°C for 5 days to simulate the effects of 10 years of age-hardening in order to investigate long term ageing. ITSM tests were then conducted at 20°C to specify the stiffness modulus of the samples according to the standard BS EN 12697-26 (European Committee for Standardization, 2012c).

Long term ageing was evaluated by measuring the ITSM before and after ageing. The SMR was used to assess ageing, defined as the ratio of ITSM before and after ageing. The results of the ageing are detailed in Figure 8.3 where it can be seen that there is improvement for all CBCEA mixtures, i.e OPC, ground PMSA-F, BBCF and ABBCF where the ITSM after ageing is more than the ITSM before ageing. The results for these mixtures are better than the corresponding AC mixtures. The growth of hydration products for the OPC, ground PMSA-F, BBCF and ABBCF mixtures, produces a cover for the bitumen, this cover preventing the loss of volatile fractions and oxidation. The control LF mixture shows a significant improvement in SMR (around 5 times), the ITSM for this mixture after ageing (971 MPa), a promising result. Heating the LF samples at

85°C for 5 days provided cohesion characteristics which resulted in a better ageing performance.
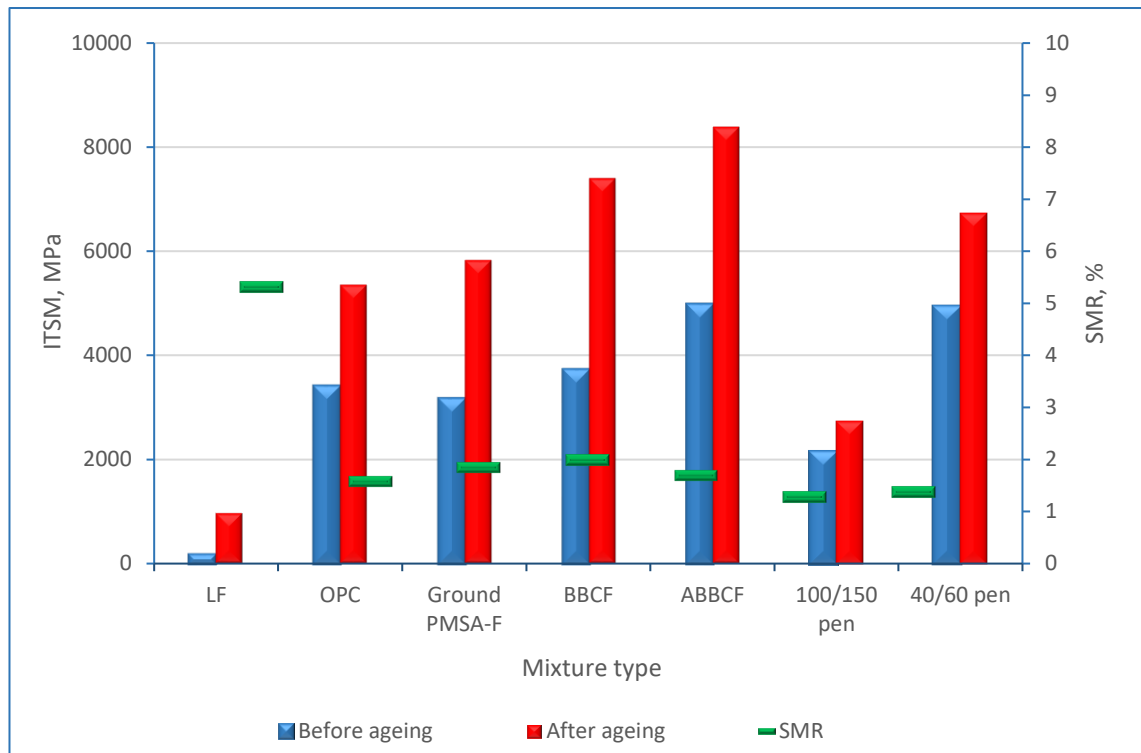
Figure 8.3. Ageing results

8.4 Summary

In this chapter, all the optimised mixtures, i.e. ground PMSA-F, BBCF and ABBCF show a significant enhancement in terms of water damage resistance and ageing in comparison to the control LF mixture and the two AC mixtures.

In terms of water sensitivity, it has been seen that there is more wet stiffness than dry stiffness for the optimised mixtures due to conditioning the samples in water at high temperatures thus providing a good environment to further activate the hydration process.

Long term ageing was studied for all the mixtures confirming the positive influence of conditioning for the CBCEA mixtures. There were significant improvements for the LF mixture as the SMR increased 5-fold. As a result, it can be stated that the new CBCEA

mixtures, containing new cementitious fillers, show promise in terms of water susceptibility and ageing performance. Consequently, these mixtures represent improvements economically, environmentally and with reference to sustainability.

The generation of new cementitious products and the formation of an alternative binder from waste materials, in addition to the bitumen, are the reasons for these improvements. This will be further explained in the next chapter using the analysis from the Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) carried out on these materials.

CHAPTER 9

MICROSTRUCTURAL CHARACTERISATION OF THE NEW CEMENTITIOUS MATERIAL

9.1 Introduction

In previous chapters, it was demonstrated that the ABBCF mixture allowed for significant improvements in ITSM and other important mechanical and durability properties. The new cementitious material will work as a new binder, in addition to the primary bituminous binder, generating a harder mass as a result of the development of bonds between particles. The microstructure of the paste made from fillers, undergoes change due to a chemical reaction between ground PMSA-F, FC3R and W-NaOH and the trapped water present in the mixtures. The combined influence of ground PMSA-F, FC3R and W-NaOH on CBCEA performance has been examined with a series of tests at various ages. Therefore, this chapter aims to establish the role of the new filler i.e. ground PMSA-F, FC3R and the alkali solution W-NaOH, with regards to improvements in the properties of the new ABBCF mixture. The use of both Scanning Electron Microscopy (SEM) and X-Ray diffraction (XRD) to qualitatively and quantitatively identify changes in chemistry and microstructure developments in the paste samples, provides sound and robust justifications for the results obtained.

9.2 Scanning Electron Microscopy (SEM)

SEM imaging has been used extensively in the cement research sector to carry out petrographic analysis of hardened products and to appraise degrees of hydration as it offers a description of elemental structures and helps to distinguish between various phases and products. As a technique, it provides information on the morphology and texture of hydrated phases.

Sarkar et al. (2001) reported that when a beam of primary electrons strikes a solid bulk, the electrons are either reflected (scattered) or absorbed, generating different signals (Figure 9-1). In addition to a secondary electron, backscattered electrons (BSE), x-rays, Auger electrons, and other responses are also generated. Consequently, various modes of observation and/or microanalysis should be applied to the material under investigation. The most common modes in SEM comprise the capture of secondary and back scattered electrons, whereas the most frequent micro-analytical techniques, based on the detection of x-rays, are energy dispersive x-ray analysis and wavelength dispersive (WD) analysis.

SEM observations in this study were carried out by both Inspect S and Quanta 200 scanning electron microscopes with a probe current of 45 nA and counting time of 100 seconds under a resolution of 3-4 nm, high vacuum and test voltage of 5-25 kV.
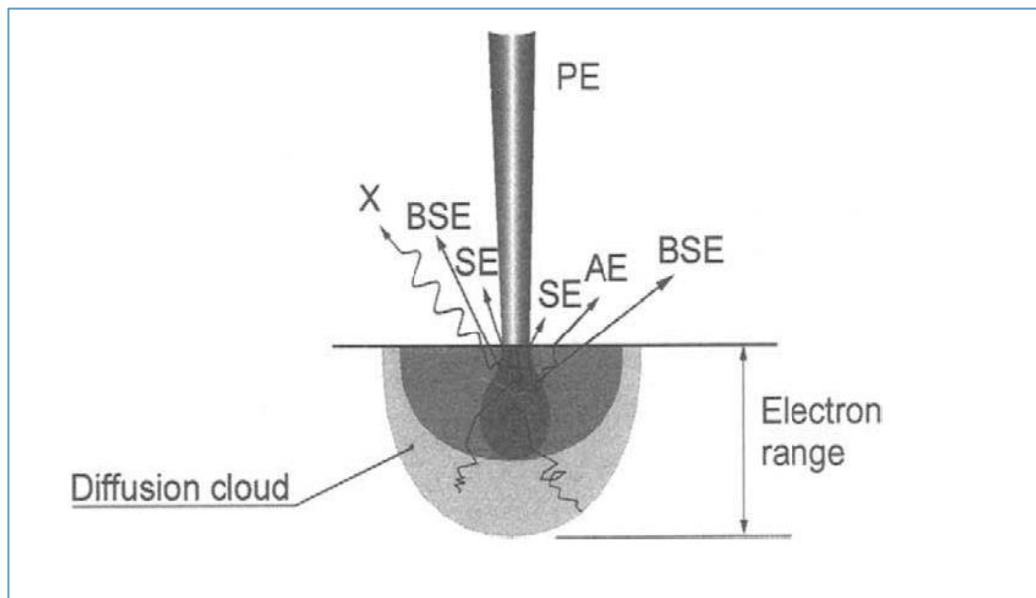
Figure 9.1. Different interactions of an electron beam (PE) with a solid target. BSE = backscattered electron, SE = secondary electron, X = x-ray, AE = auger electron (Sarkar et al., 2001), permission to reproduce this figure has been granted by Elsevier

According to Sarkar et al. (2001), the morphology of different phases occurring within the hydrated cement phase, can be thought of as the gel structure which represents the calcium silicate hydrate (C-S-H) phase in the cement phase at normal temperature. Portlandite, calcium hydrate (C-H) crystals, form in a variety of shapes and sizes, starting as massive crystals plates with a distinctive hexagonal prism morphology or large thin elongated crystals. Ettringite (AFt), appears as needle-like crystals in vacant spaces throughout early hydration, while Monosulfate (AFm) forms hexagonal crystals plates.

As a result, SEM has been used to investigate the microstructure of both ABBCF and LF pastes at different ages. Sarkar et al. (2001) noted that SEM was found to be remarkably effective at characterising the morphology and chemical composition of the C-S-H phase; this phase is recognised as the most significant constituent in concrete because of its binding properties and subsequent contributions towards final strength.

9.3 X-ray Diffraction (XRD)

XRD is used to observe the characterization of crystalline phases and the detection of different chemicals in cement pastes at different ages as each material has a unique fingerprint in terms of its X-ray pattern. This technique is based on the analysis of the intensity and the angle of the diffracted X-ray beam after encountering the plane of atoms in a material (Alizadeh, 2009a). XRD can be used to track the hydration reaction over time as it allows identification of the consumption of mineral phases and their decrease in crystalline nature (Esteves, 2011).

Different atoms occur in the structure of a crystalline material in a repeating pattern. This can generate similar atomic planes as seen in Figure 9-2. The distance between these planes is termed the *d*-spacing or basal spacing. X-ray beams are partially diffracted when

they hit different parallel layers, these beams detected if they are in phase. This happens

following Bragg's law:

$n\lambda = 2d\sin\theta$ ……………………………………………. (9-1)

where λ, is the wavelength of the X-ray, d is the distance between the atomic planes, θ is

the angle of incidence and n is an integer.
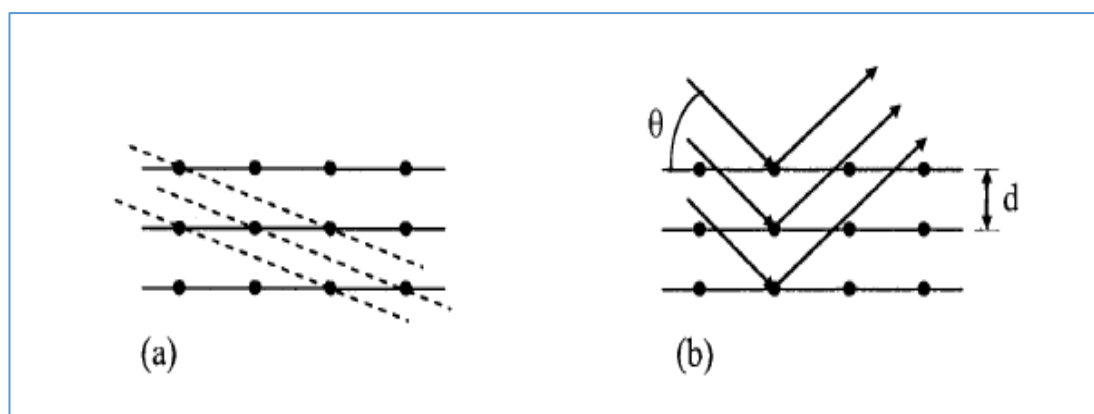
Figure 9.2. (a) Two possible atomic planes in a crystalline structure, (b) Diffraction of X-rays expressed by Bragg's law (Alizadeh, 2009a), permission to reproduce this figure has been granted by Dr Rouhollah (Aali) Alizadeh

The X-ray tube rotates around the specimen so that beams are emitted at angles between

2 to 30 degrees. Only the diffraction from atomic planes parallel to the surface of the

specimen is detected since the detector rotates at the same angle to receive these diffracted

beams. The intensity of the X-ray is plotted against 2θ, the angle between the emitted and

diffracted beam. This spectrum is then matched with reflections identified in the database

in order to classify the compounds in the specimen.

In keeping with the above, X-ray diffraction analysis was adopted to track changes in

material mineralogy by recording the intensity of the material crystals at different times;

3, 7, 14 and 28 days. XRD patterns can be appraised before and after reaction with water

to reveal whether crystallisation has occurred. In this research, the XRD patterns were

identified using a Rigaku Miniflex diffractometer (Miniflex goniometer), a Wolfram cathode and aluminium sample holder as an anode (Cu Ka), a voltage of 30 kV and current of 15 mA registering from 3 to 60 with a scanning speed of 2.0 deg./min in a continuous scan mode.

9.4 Sample Preparation

The microstructural analysis of the raw materials, BBCF and LF powders as well as ABBCF and LF pastes, was undertaken on fractured surfaces by SEM and with powder through XRD analysis. Changes in the morphology of the materials were investigated at 3, 7, 14 and 28 days to identify the development of the new binder. A comparison was made with the raw filler materials to detail differences before and after the hydration process. The use of the ABBCF mixture for microstructure investigation was because of its performance in terms of mechanical properties and durability. The LF mixture was used for comparison purposes. SEM observation and XRD analysis were also applied to dry powder raw materials to identify changes at different times.

The ABBCF and LF samples were used to identify changes in the materials in terms of SEM and XRD at different curing ages. The pastes were prepared at the optimum water/cement ratio, mixed by lab spatula and moulded into cylinder specimens which were kept at room temperature for 24 hours. The next day, the specimens were demoulded and allowed to dry at lab temperature. Suitable fragments were taken off from the core of the paste at due age, i.e. 3, 7, 14 and 28 days, for SEM observations. It was very important to ensure that the pieces were snapped out of the cylinders by impact without touching any tools otherwise the surface would not be natural and would not correctly represent the features of the materials. Figures 9-3-a and 9-3-b show the samples for SEM observations. Prior to the SEM observations, the samples were dried in a vacuum pump to eliminate any water. Following this, they were mounted onto aluminium stubs using

double-sided adhesive carbon disks. Since the specimens were not electrically conductive, the fractured surfaces of the hydrated paste specimens were coated with a thin layer of palladium using an auto fine sputter coater before being processed by the SEM equipment (Figure 9-3-c). The SEM samples were approximately 0.75 x 0.75 x 0.1 cm in size. Other fragments from the ABBCF and LF pastes were selected, after drying, and pulverized into powder for XRD analysis at design ages 3, 7, 14 and 28 days. The powder produced by pulverizing and sieving the fragments, was placed on an aluminium holder, the surface flattened using a small lab spatula to ensure a uniformly flat surface for the x-ray beam to hit. In addition, suitable fragments were taken from the ABBCF mixture after 28 days and tested using SEM to identify the hydration products inside this mixture.
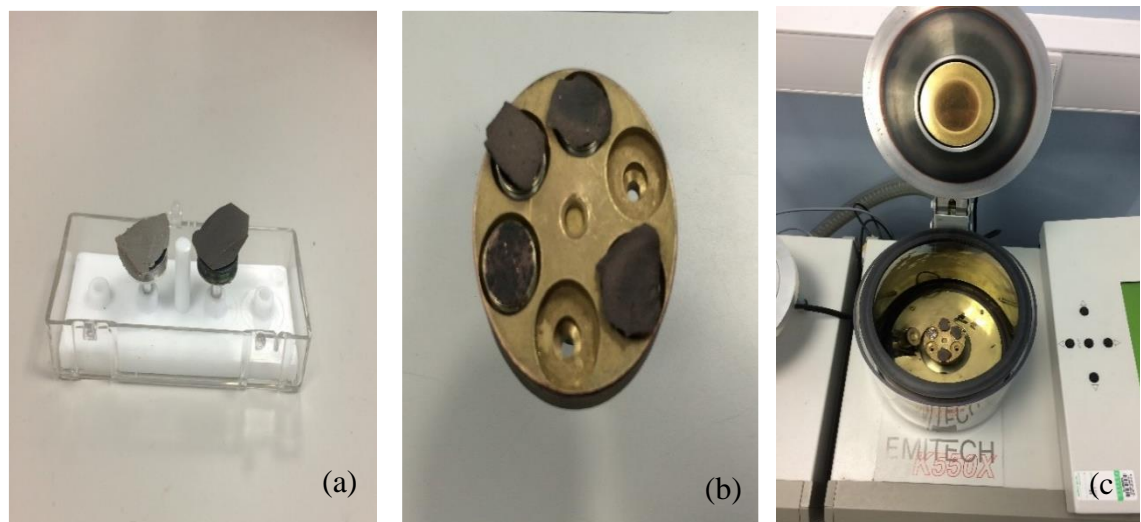
Figure 9.3. Fracture samples taken for SEM observation

9.5 Microstructure Analysis Results and Discussion

9.5.1 SEM Observations

Scanning electron microscopy (SEM) was performed to analyse the microstructure of the alkali activated binary blended cement filler (ABBCF) and limestone filler (LF) paste samples. The microstructures of the fractured surfaces of the ABBCF samples and the

reference LF specimens (made under the same test conditions) provide information about chemical reactions in the materials.

In cement chemistry, hydration is characterized as the reaction of anhydrous cement with water; to generate a hydrate as a new compound. The anhydrous phases of cementitious materials convert into hydrated phases through hydration via a sequence of chemical reactions.

Figure 9-4 displays the LF powder micrographs, while Figures 9-5, 9-6, 9-7 and 9-8 present the LF paste micrographs at 3, 7, 14 and 28 days, respectively. It is evidenced here that the LF filler consists of irregularly shaped particles. It can be considered an inert material as there is no noticeable change in the morphology of the LF paste sample. There is no evidence of the formation of hydration products at any age. Accordingly, there was a slight improvement in ITSM for the LF mixture, this due to water evaporation. These results are in agreement with the results of the ITSM test for the LF mixture as presented in Chapter 6.
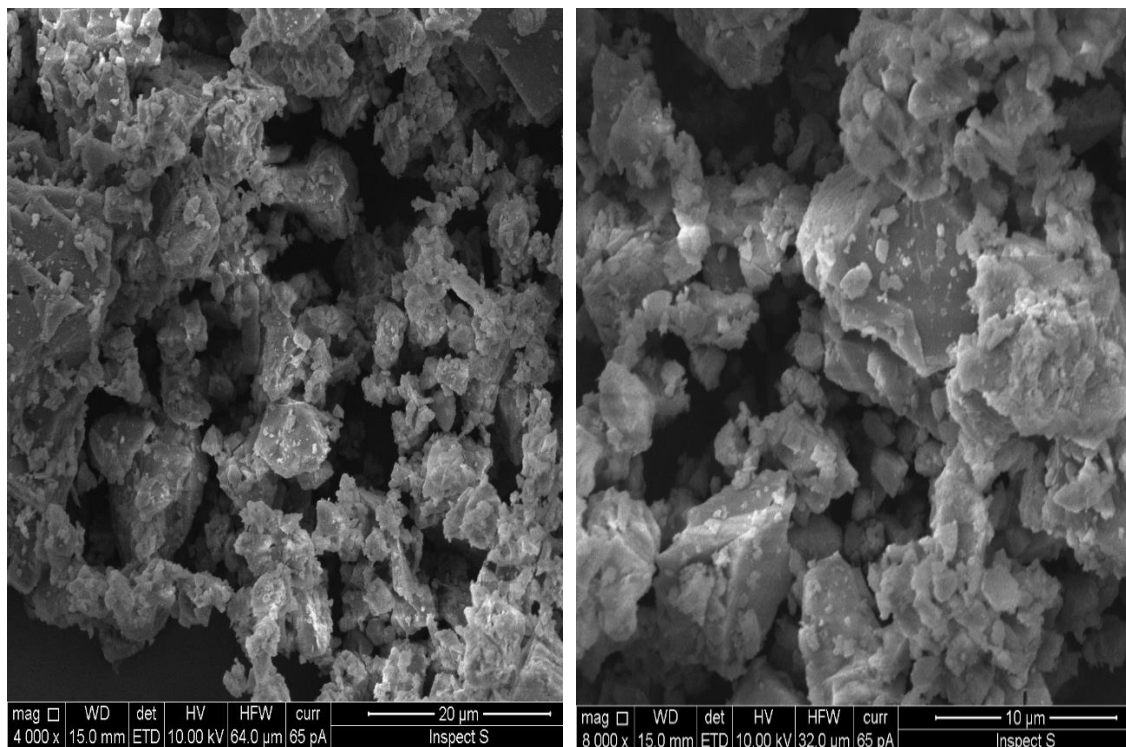
Figure 9.4. SEM micrograph of LF powder
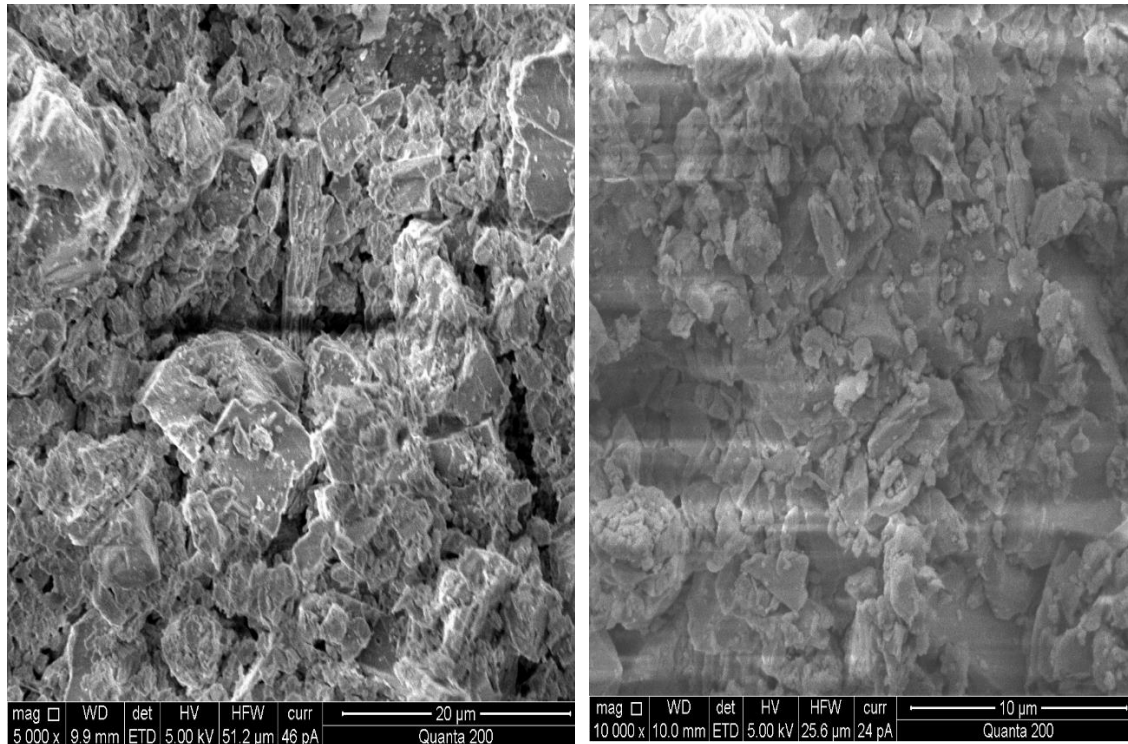
Figure 9.5. SEM micrograph of LF paste after 3 days
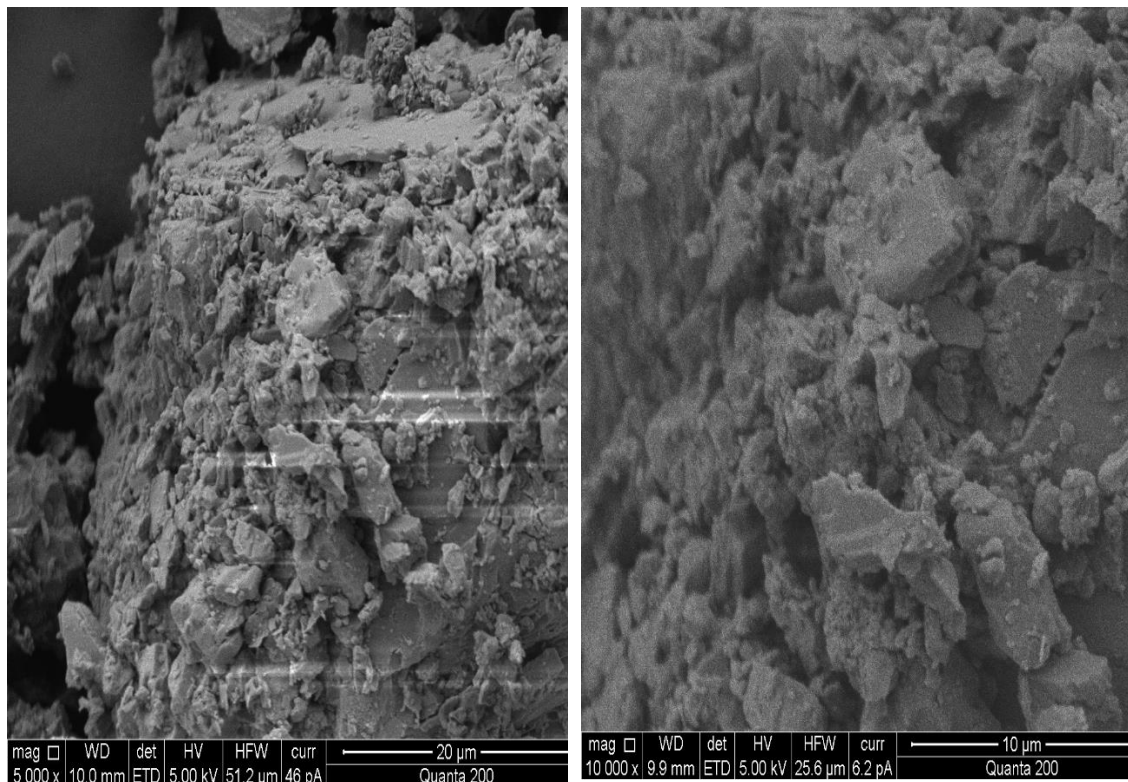
Figure 9.6. SEM micrograph of LF paste after 7 days
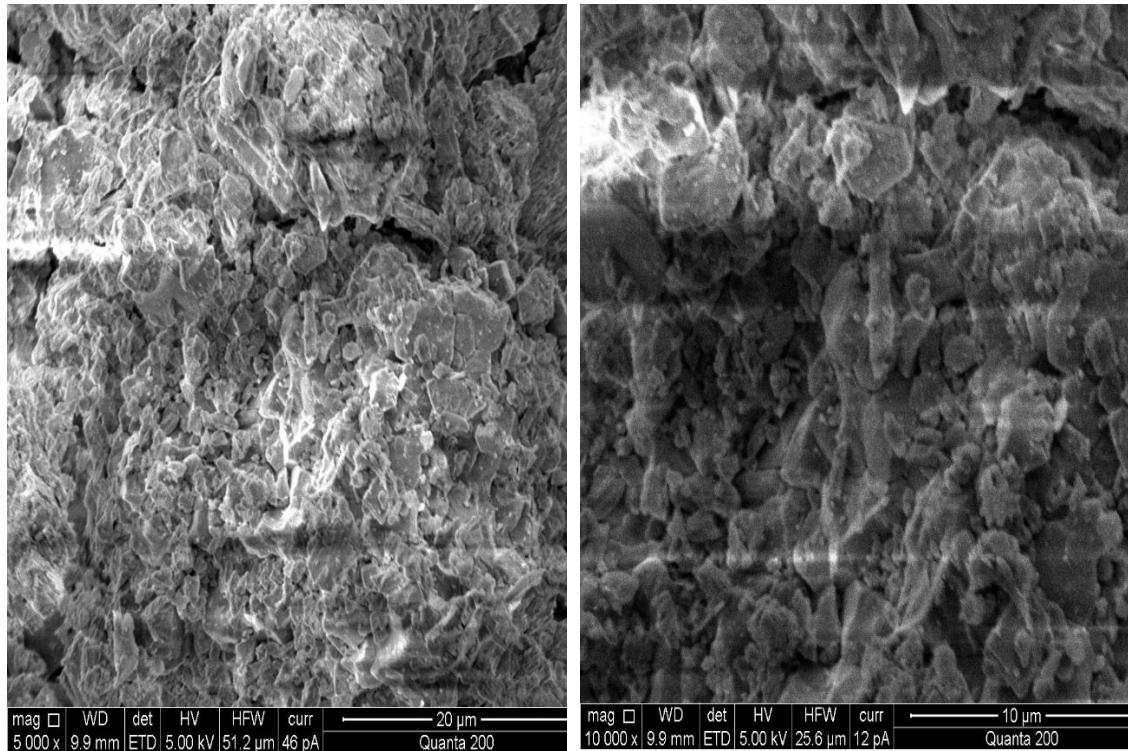
Figure 9.7. SEM micrograph of LF paste after 14 days
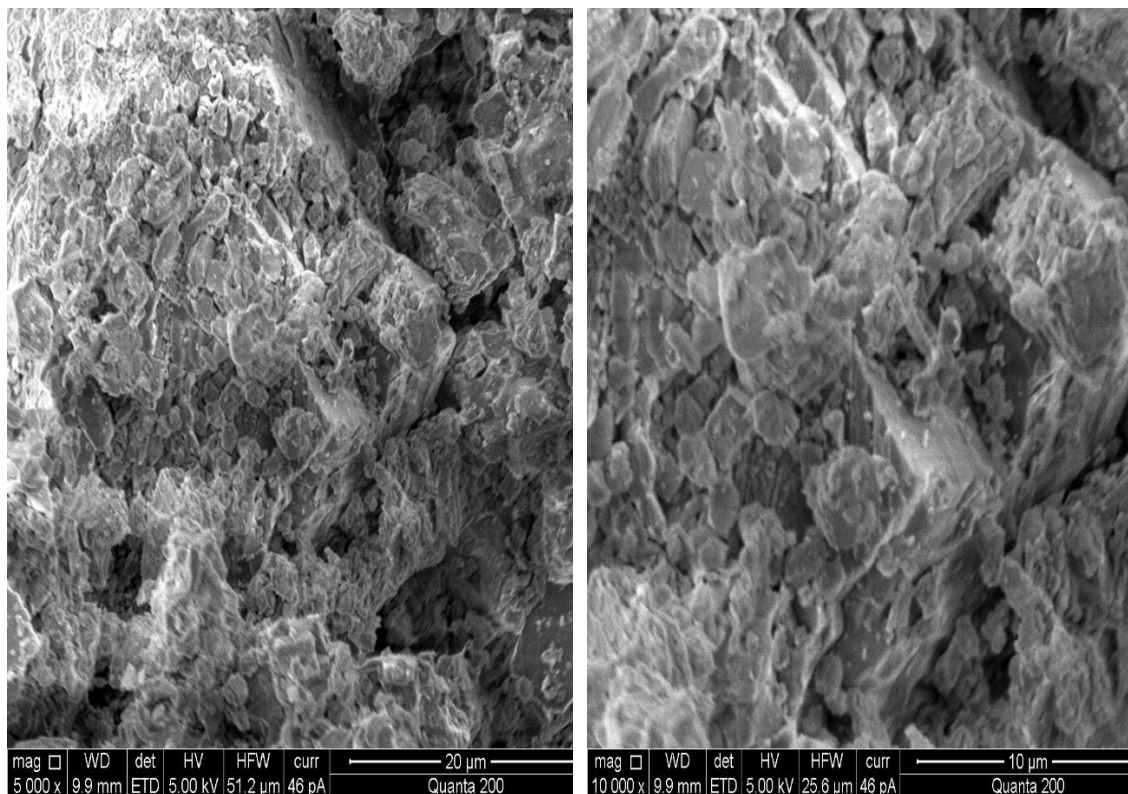
Figure 9.8. SEM micrograph of LF paste after 28 days

Figure 9-9 displays the micrograph of the BBCF powder, Figures 9-10, 9-11, 9-12 and 9-13 illustrating the microstructures of the ABBCF paste samples after 3, 7, 14 and 28 days. It can be seen from Figure 9-9 that the BBCF particles are agglomerated and non-spherical. Significant amounts of hydrates were formed at the early stages of curing within ABBCF (Figure 9-10). In this study, the reaction between ground PMSA-F, FC3R and W-NaOH was noticeable after 3 days, SEM analysis revealing a more pronounced micro-structural evolution after 3 days. There were no intact filler particles detected and the ground PMSA-F and FC3R powder particles were found to be converted into hydrates due to a successful hydration reaction. This illustrates that when the BBCF was activated by W-NaOH, hydration was speeded up, the hydration products generating a dense binding mass material. Its hardness increased over curing time producing improved mechanical properties, this consistent with the development of a high stiffness modulus in the ABBCF mixtures which were tested. The structure of the ABBCF was much denser with crystalline products found filling the pore areas.

Figure 9-11 presents the images after 7 days showing that ABBCF particles were in the form of particles with a dissolved surface and a covering layer made of hydration products, indicating a high degree of reaction in the system.

In 14 days (Figure 9-12), the ABBCF particles had been replaced by hydrates. The alkali activation of W-NaOH increased the amount of C-S-H consumed. It can be clearly observed that the surface of the ABBCF sample is covered by C-S-H gel which is characterised as the most important element in cement hydration as it is responsible for its binding characteristics and contribution to strength.

The succeeding conversion of constituent particles with age towards dense and compact microstructures within ABBCF pastes from pozzolanic reaction between ground PMSA-F, FC3R and W-NaOH is evident in Figure 9-13. The SEM micrograph of the fractured

surface of ABBCF paste after 28 days reveals the generation of a C-S-H gel creating dense microstructures confirming that C-S-H is their common hydration product.

The surface of the ABBCF sample had changed into C-S-H gel, Portlandite (CH) and calcium aluminum silicate hydrate (C-A-S) and in consequence, high stiffness of the material was recorded after 28 days. C-S-H phases are the major phases which contribute to cement strength as they are the major binding materials. They constitute approximately 70wt% of the hydrated products and are consequently the most significant phases for characterising the properties of the paste (Feldman and Sereda, 1968). The Portlandite phase contributes to 20wt% of the final cement waste form (Bensted and Barnes, 2008). Consequently, ABBCF displayed improved properties due to the alkali activation of W-NaOH, this accelerating the appearance of hydrate products. Research has found that alkali-activators will increase the pH of the hydration medium which, in turn, improves breaking and dissolution in the glassy phase of pozzolanic material (Bakharev et al., 1999; Shi and Day, 2000).

In summary, it can be seen that successful hydration in a high pH environment impacts the generation of dense, impermeable C-S-H. The C-S-H phase is the most significant one because it offers essential cementitious or binding characteristics for the final product. The reaction between active BBCF and W-NaOH generates an ABBCF mixture with improved properties. It was stated by Nassar et al. (2016a) that a higher degree of hydration in CBEMs as a result of active fillers can generate a dense, internal structure with less porosity.

In general, there are substantial differences in the microstructural configuration in ABBCF in comparison to the LF paste samples. LF particles did not react at early ages and performed as a filler material. The crystalline components in the ABBCF paste were considerably more characterized than the LF paste, producing a harder binder.
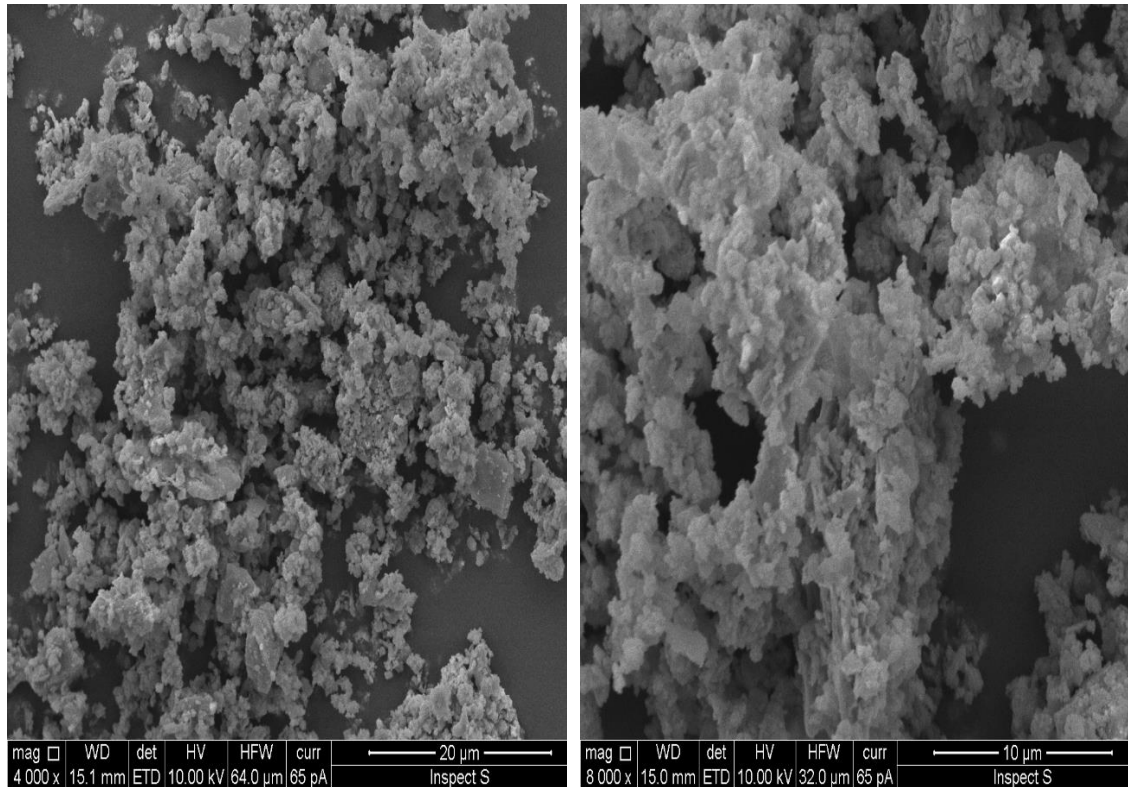
Figure 9.9. SEM images of BBCF dry powder
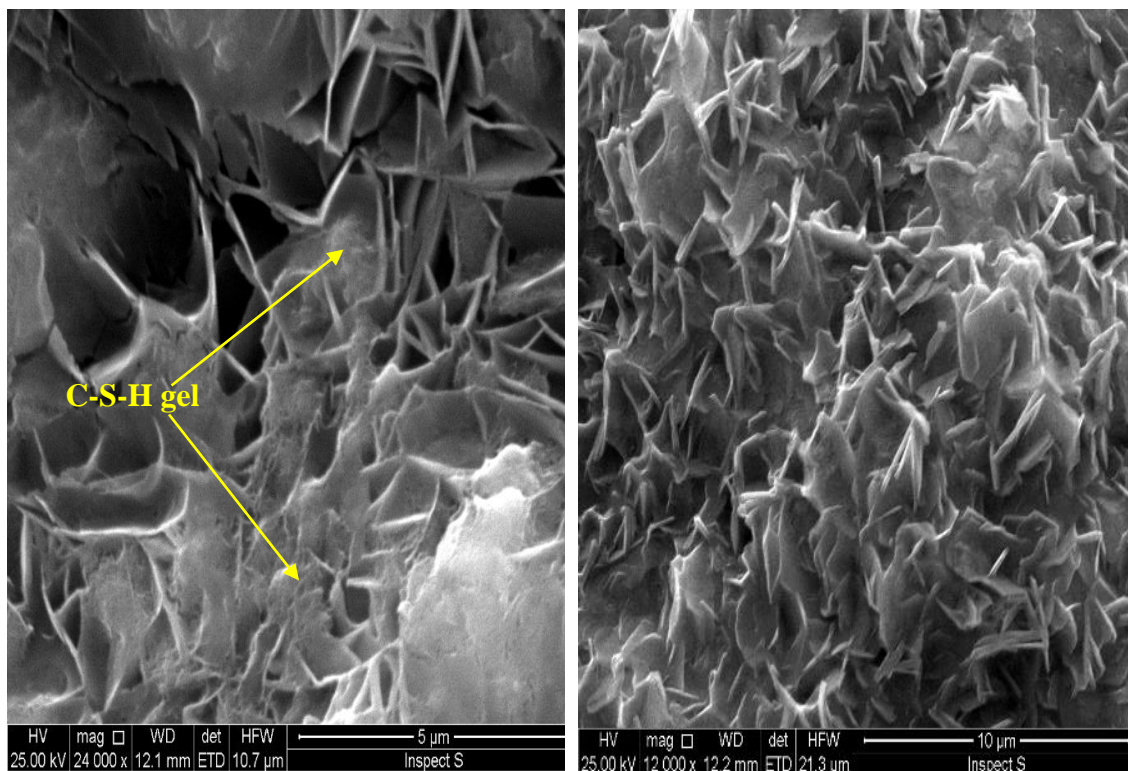
Figure 9.10. SEM micrograph of ABBCF paste after 3 days
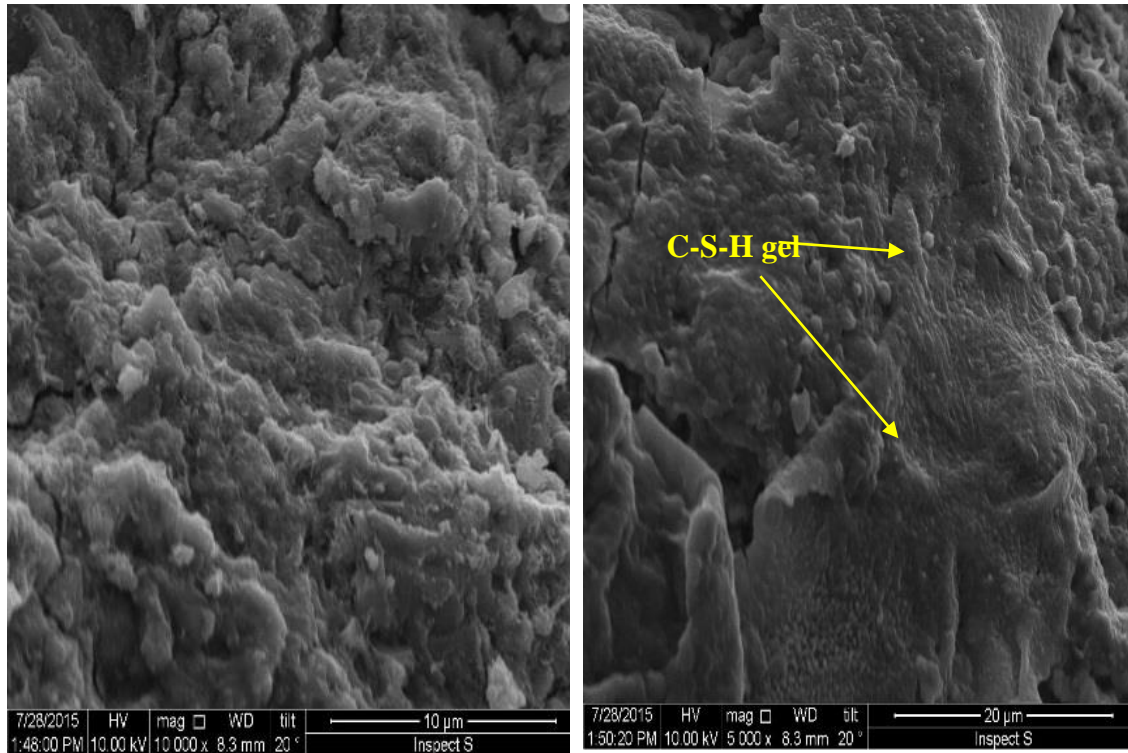
Figure 9.11. SEM micrograph of ABBCF paste after 7 days
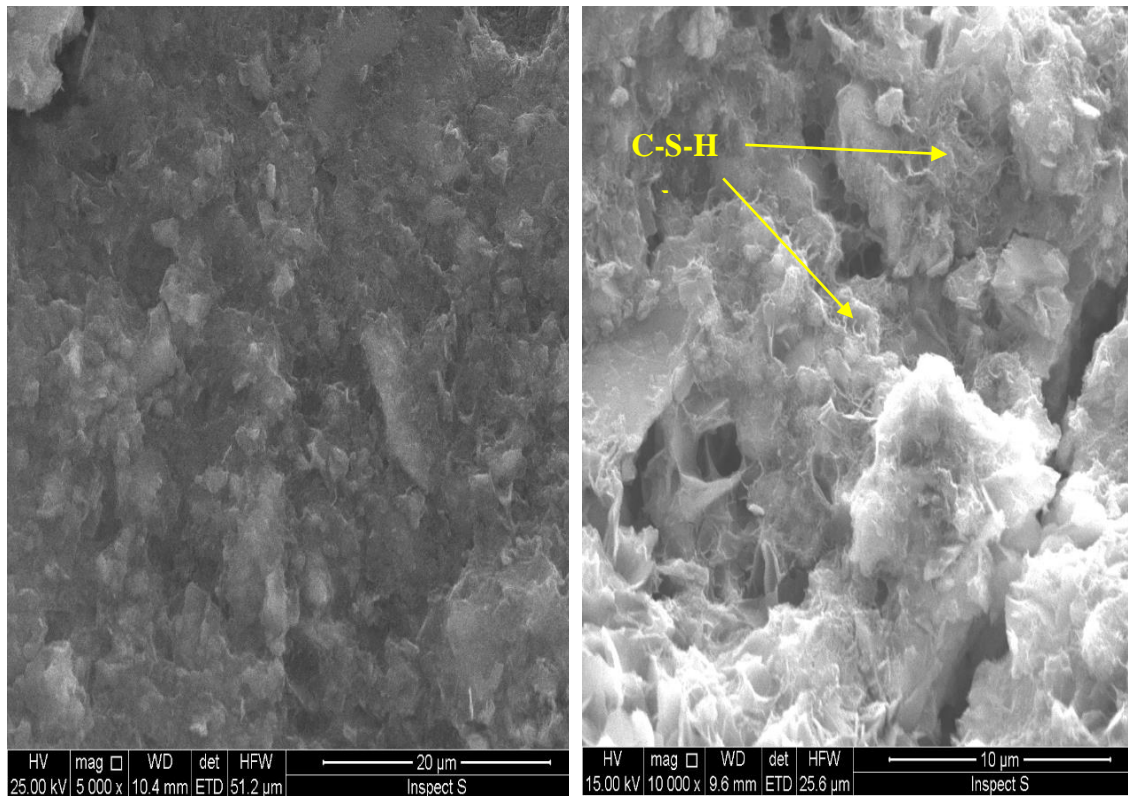
Figure 9.12. SEM micrograph of ABBCF paste after 14 days
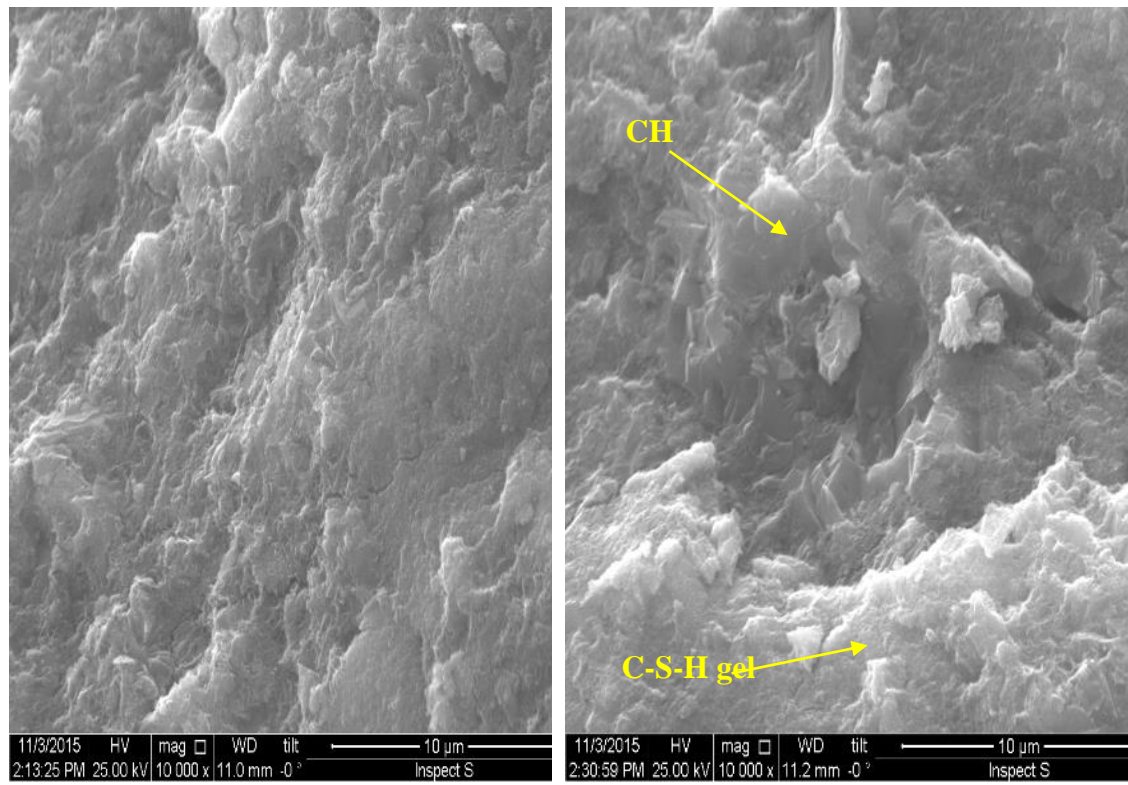
Figure 9.13. SEM micrograph of ABBCF paste after 28 days

It can be seen in Figure 9-14 that ABBCF hydrate products work as a secondary binder in asphalts when included in CBCEA mixtures, the ITSM increasing substantially with curing time (see Chapter 6), as a result of the production of a new binding material alongside the bitumen. It is clear that the two binders, cementitious and bitumen, work together inside the ABBCF mixture to provide strength. More interestingly, Figure 9-15 shows the C-H products that generate C-S-H gel inside the ABBCF mixture after 28 days. This is evidence for the hydration process that facilitates products responsible for improvements in ITSM alongside the residual bitumen.
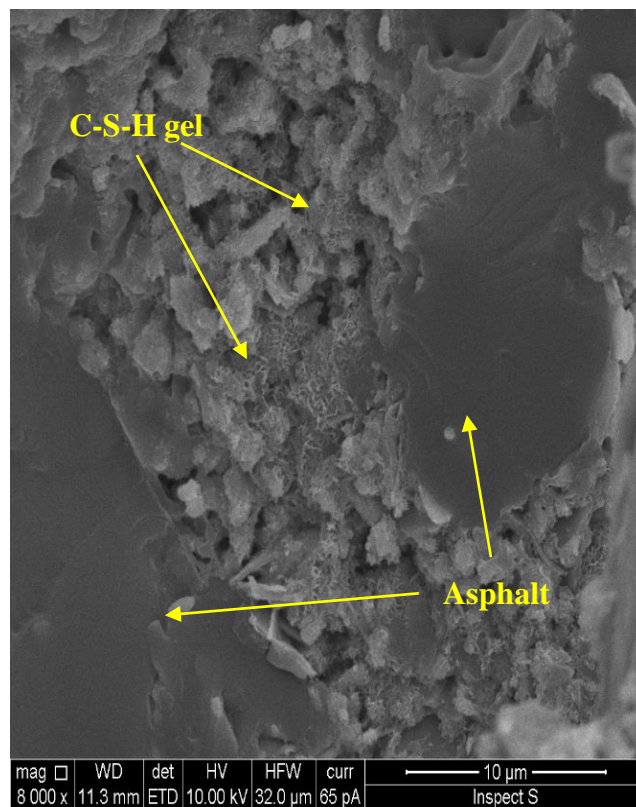
Figure 9.14. SEM micrograph of ABBCF mixture after 28 days
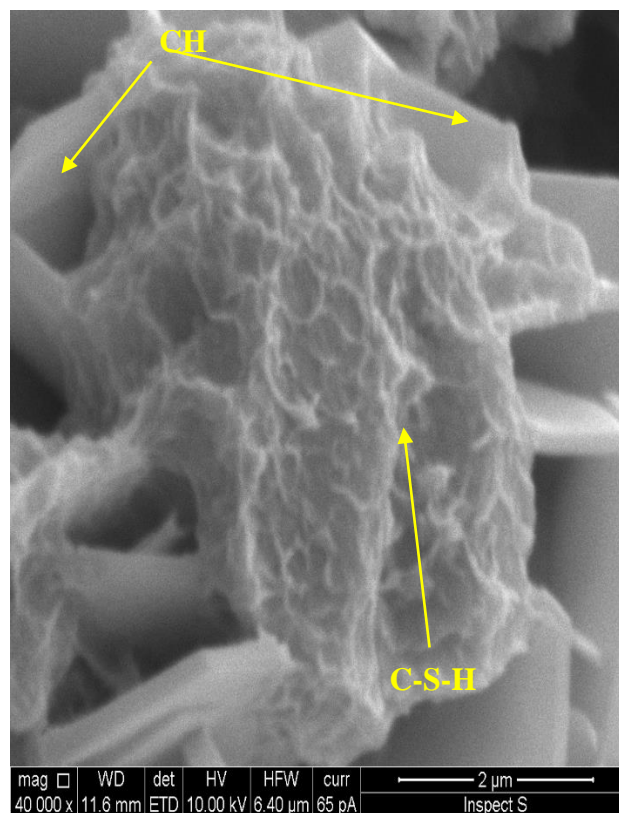
Figure 9.15. Development of hydration products inside ABBCF mixture

9.5.2 XRD Analysis

In this study, X-ray diffraction was used to identify potential variation in hydration products produced by the use of both ABBCF and LF in CBCEA mixtures. Samples were taken from ABBCF and LF paste specimens at 3, 7, 14 and 28 days, ground into a powder form ready for analysis via their XRD patterns. In order to identify unspecified materials, the XRD pattern is recorded using a camera or a diffractometer, a list of d-values and the relative intensities of diffraction lines prepared. A comparison was made between this data and the standard patterns which exist for various compounds in a database called Powder Diffraction File (PDF). For a supplementary cementitious material, tracking the mineral phases of hydration reactions can be classified into five categories: appearance of new peak/s, disappearance of peak/s, expansion of previous peak/s, decrease in previous peak/s and unchanged peaks.

The chemical reactions that occur between anhydrous cementitious material and water are usually complex and can be affected by a variety of factors. Chatterjee (2001) detailed the common features of reaction sequences and cement hydrates involved in XRD analysis. He stated that unreacted phases coexist in various proportions, with different reactants, at various ages. Silicate phases result in the creation of CH and amorphous or poor crystalline C-S-H, while the reactions in both aluminate and ferrite phases in gypsum cause the early formation of AFt. The most important AFt phase is ettringite $[(Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O]$, which forms during the early hydration of cement and later converts to AFm ($C_3A.CaSO_4.12H_2O$).

Figure 9-16 presents the XRD for LF before mixing with water, in addition to the XRD patterns for the LF paste after 3, 7, 14 and 28 days, respectively. It can be observed that there is no significant change in the chemical phases (i.e. calcite and quartz) in the material both in its original state and when mixed with water at different ages. This

reveals the inert characterisation of the limestone filler. These results strongly comply with previous SEM observations for the LF paste samples. The CBCEA mixture with LF only had a very slight improvement in terms of ITSM due to the inert characterisation of the LF; these findings confirm and substantiate this outcome.
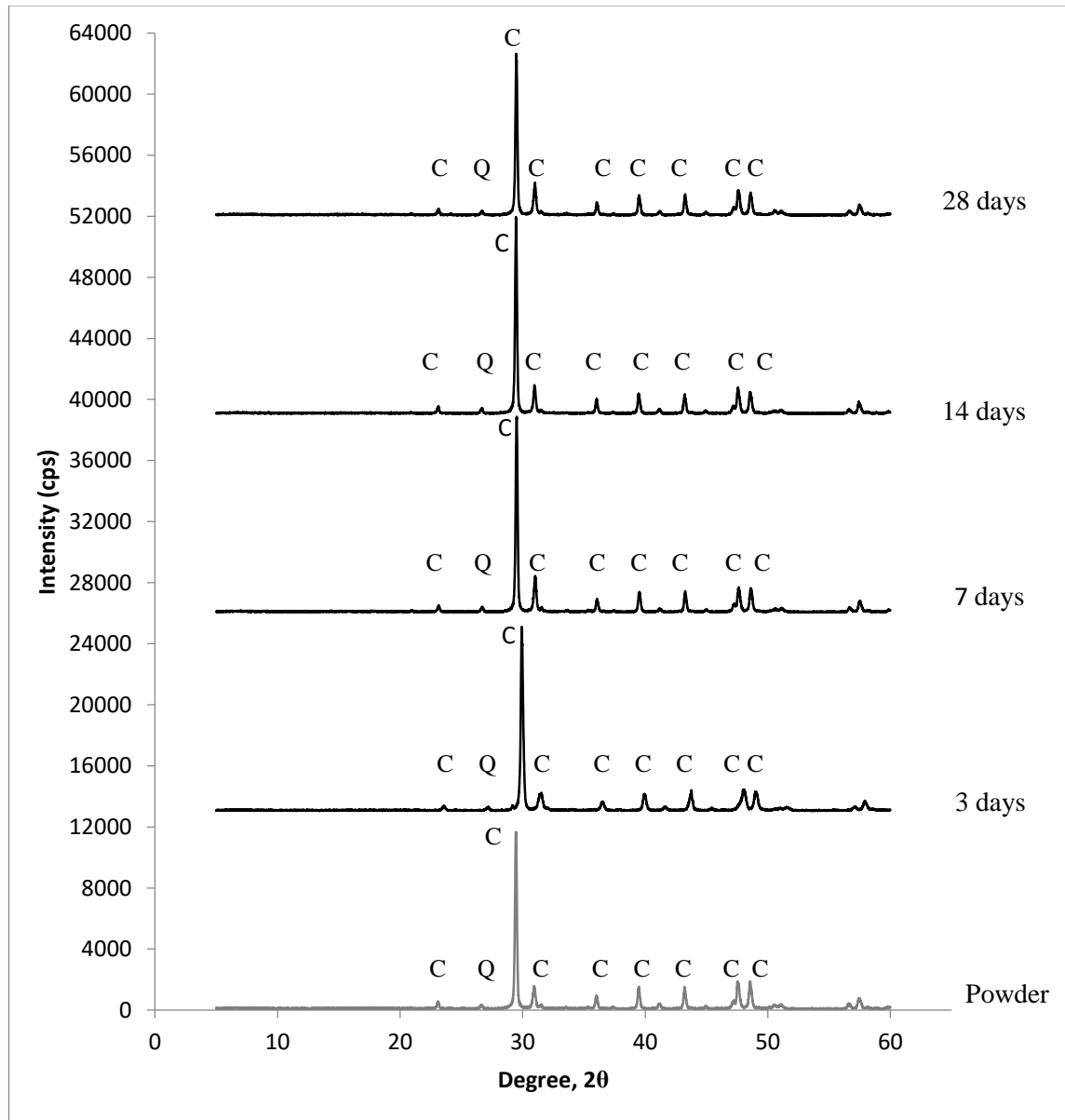
Figure 9.16. XRD profile of LF at different ages

On the other hand, Figure 9-17 reveals the main components of the raw ABBCF powder: L: lime; C: calcite; G: gehlenite; B: belite; M: mayenite; Mr: mowinite; K: kyanite and Z: dehydrated Ca-A zeolite. Reduced crystallinity is seen in the XRD of the raw ABBCF

powder in comparison to the crystallinity found in the individual materials of ground PMSA-F (Figure 5-14) and amorphous FC3R (Figure 5-16).

The trend for peak amplification across the spectrum of materials from 3 days to 28 days for the powders (generated from pulverizing hydrated pastes), indicates that crystallisation becomes stable after 3 days. Most crystals appear by then signifying that there is substantial hydration over these 3 days. The major hydration products which are present are C-S-H (calcium silicate hydrate), CH (Portlandite), C-A-S (calcium aluminum silicate hydrate) and AFt (Ettringite AFt Phase). These are found to intensify with age seen by the increase in the line of the pattern with age. The continuous formation of these products reflects accelerated hydration and consequent progressive improvements in strength. Furthermore, the rapid consumption of mineral phases (lime, gehlenite) with a decrease in crystallinity, appearance of new crystal peaks of hydrates, and conversion of the silicate phase (gehlenite) to C-H phase was in accordance with observations reported by Chatterjee (2001) and Esteves (2011). These results are in good agreement with the results of SEM where the generation of C-S-H/C-A-H gel and CH is obvious in both tests. The XRD pattern reveals sharp reflection peaks, this phenomenon in agreement with the development of stiffness revealed in the test results. This means that hydrate products form a secondary binder in the ABBCF mixture which is responsible, in addition to the bitumen emulsion, for ITSM improvement. In addition, hydrate products in the ABBCF paste seen after 3 days, leads to a denser microstructure. It should be noted that three samples were tested for each material at each specific age to verify the reliability and validity of the results.
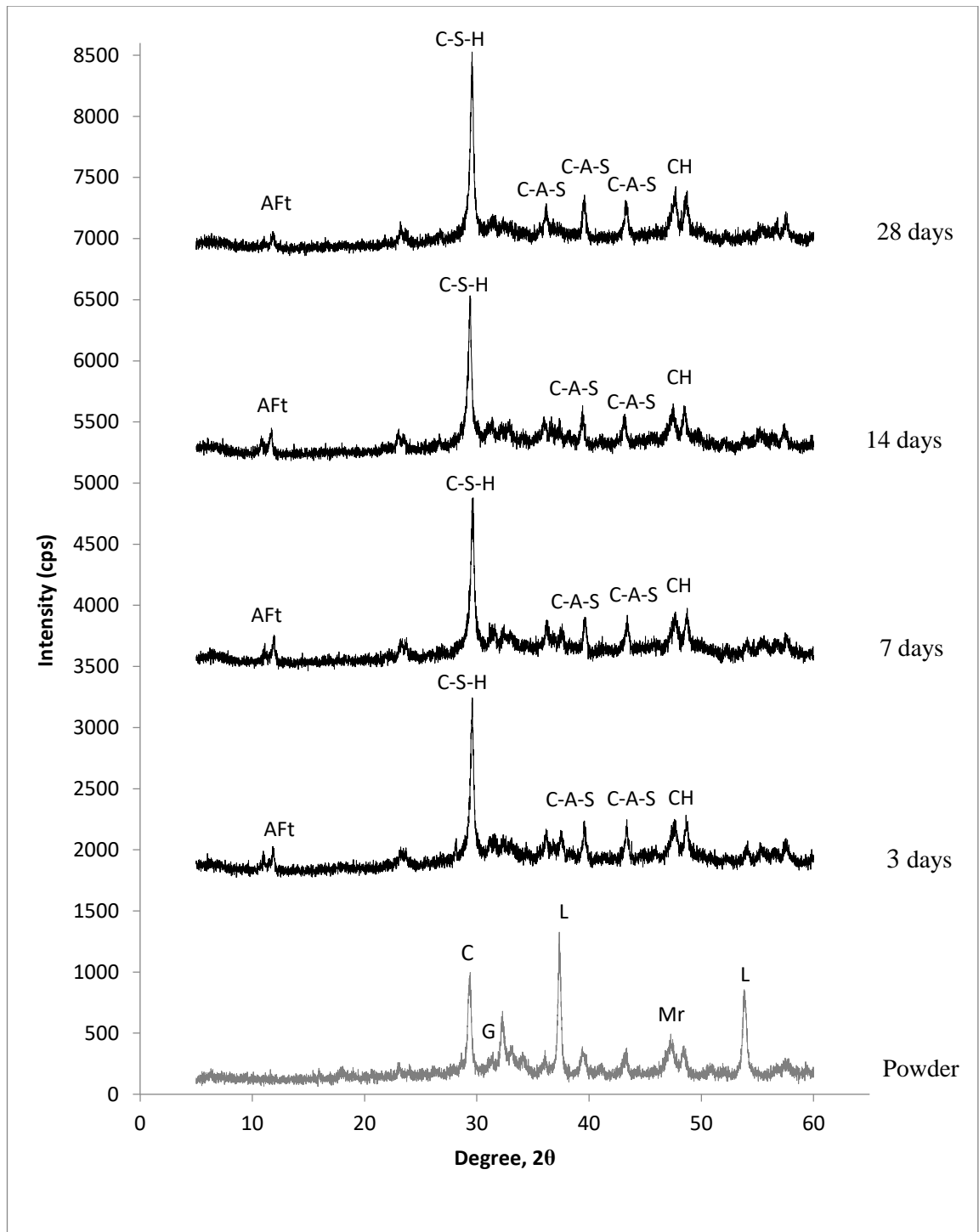
Figure 9.17. XRD-pattern of investigated ABBCF

L: lime; C: calcite; G: gehlenite; Mr: mowinite; C-S-H: calcium silicate hydrate; CH: portlandite; C-A-S: calcium aluminum silicate hydrate; AFt: Ettringite AFt Phase

9.6 Summary of Microstructure Outcomes

The analysis of the microstructure results of the binding paste within ABBCF in terms of SEM observations and X-ray diffraction, explain the improvements in both the mechanical and durability properties regarding the new CBCEA mixture. Differences in the morphology of the ABBCF paste sample, compared to ground PMSA-F and FC3R, were investigated using SEM in order to identify changes in the material during hydration. A dense microstructure was seen which increased over curing time. It was found that the presence of the hydrated products C-S-H, CH and C-A-S, are significant for ABBCF paste. The abundance of C-S-H in ABBCF paste was found to be consistent with the corresponding XRD analysis. The SEM observation on fragments of the ABBCF mixture revealed that the hydration products were not affected when included in the CBCEA mixture. It was also found that there were no changes in the morphology of LF before and after mixing with water.

Regarding the XRD analysis, it was found that the most substantial changes in the ABBCF paste in the mineralogical phase, occurred during the first three days where the existence of C-S-H, C-A-S, CH and AFt was noticeable. There was no notable change in the XRD patterns for the LF as all the chemical phases are inert components. Consequently, the SEM observation and the XRD analysis together confirm improvements in stiffness in the CBCEA mixture that contains ABBCF, and that can be attributed to the generation of a new secondary binder from the hydration process in addition to the bitumen emulsion.

CHAPTER 10

ENVIRONMENTAL INVESTIGATION: LEACHING OF HEAVY METALS INTO WATER

10.1 Introduction

Previous sections of this study have identified opportunities to overcome deficiencies in the mechanical and durability properties of CBCEA mixtures by the inclusion of waste and by-product materials, namely ground PMSA-F, FC3R and W-NaOH. However, wastes produced from industrial applications comprise numerous potentially hazardous heavy metals including nickel (Ni), copper (Cu), lead (Pb), chromium (Cr), zinc (Zn), strontium (Sr), barium (Ba) and cadmium (Cd), which constitute serious threats to both human and non-human life when they are released into the environment. Consequently, using waste materials in pavement construction brings the risk of groundwater contamination. Leachates introduction into this water could result in drinking water contamination. The ingestion of water or foodstuffs contaminated with heavy metals can mean that humans become subject to the negative effects of such heavy metals. Therefore, in this chapter an environmental assessment has been performed by applying Toxicity Characteristic Leaching Procedure (TCLP) tests to determine whether the above mentioned wastes are hazardous by virtue of their toxicity.

10.2 Toxicity and Health Effects

The inclusion of waste and by-product materials in CBCEA mixtures can mean that heavy metals will leach into the surrounding soil and groundwater. Halim et al. (2003) stated that pavement layers which are continuously in direct contact with surface and underground waters, increase the risk of water pollution because of the leaching of hazardous materials, for example heavy metals, into underground water resources. Heavy metals can also impact soil ecology, agricultural production, animals and plants, product

quality, quality of water and the environment in general (Babish et al., 1984; Cui et al., 2005). In developed countries, levels of heavy metals are now a major problem as hazardous levels of heavy metals could enter the food chain (Pepper et al., 1996).

Heavy metals have a tendency to decrease growth, lead to tissue damage and even cause death in humans. They can become toxic, if concentration levels increase, to plants and animals. That said, at low concentrations, some heavy metals, or Essential Trace Elements (ETEs), are needed for growth and the maintenance of health (Askari, 2007). Some heavy metals such as chromium, cobalt, iron, copper, manganese, selenium and zinc contribute to cellular reactions as either enzyme elements or as chemical reaction controllers.

Heavy metals affect the main bodily functions in humans including kidneys, liver, heart, nervous system, immune system and joints. Children exposed to heavy metals from hazardous materials at a young age can suffer from memory impairment, problems with learning, behavioural problems, for example, aggression and hyperactivity and a general reduction in rate of growth (Askari, 2007). Consequently, while heavy metals are necessary for health in small quantities, too much may result in severe or chronic toxicity.

10.3 Toxicity Characteristic Leaching Procedure (TCLP) Test

Leaching is defined as the mechanical or chemical percolation of waste constituents from stabilized layers in pavements to the ambient environment because of the passage of water or other solvents (Ling and Poon, 2014). The leaching of some pollutants such as heavy metals, is a significant threat to the health of humans and the environment in general. The presence, for example, of low concentrations of arsenic, more than 10 μg/l, in drinking water, leads to skin cancer and damage to the central nervous system (Garcia-Lara et al., 2009; Wan et al., 2011). The leachability of these heavy metals can be determined using the Toxicity Characteristic Leaching Procedure (TCLP) test (Modarres and Ayar, 2016), who state that the TCLP test is an effective method for determining the potential for

organic and inorganic wastes to leach hazardous chemicals concentrations into the environment. The TCLP test was established by USEPA in order to decide whether a waste was dangerous by virtue of its toxicity. It can be considered as one of the major leaching technique tests used to examine the risk of leachability of heavy metals from stabilised layers (Xue et al., 2009).

In this study, the TCLP test has been adopted to determine the leached concentrations of nickel (Ni), copper (Cu), lead (Pb), chromium (Cr), zinc (Zn), strontium (Sr), barium (Ba) and cadmium (Cd) from the new CBCEA mixtures according to the procedure used by Xue et al. (2009) and Modarres and Ayar (2016) to analyse the possibility of heavy metal leachability from the CBEM mixtures. This procedure follows the method recommended by the US Environmental Protection Agency (SW846-1311).

10.4 Sample Preparation

In this research, the TCLP test was first conducted on both the ground PMSA-F and FC3R powder samples. The test was also performed on CBCEA mixtures treated with ground PMSA-F, BBCF and ABBCF containing waste materials. The CBCEA specimens were prepared in the laboratory then tested along with the original two waste materials, using the TCLP test. A stock of TCLP leachant was prepared by mixing stoichiometric amounts of deionised water and acetic acid (pH 2.88) supplied by Hach-Lang and used as supplied. Weighted amounts, 10 grams, of the crushed samples were placed in bottles that contained 200 ml of the TCLP leachant. These bottles now containing the powders, the crushed specimens and the TCLP leachant, were agitated using a rotary extractor (type: Labent 222 DS) at 30 rpm for 18 hours (Figure 10-1). All investigations were performed at a temperature of 20°C, which was precisely controlled by a rotary extractor. After the extraction process, the solutions were filtered using a 47 mm glass fibre filter supplied by Hach-Lang, the filtrates then acidified using acetic acid to a pH below 2. Concentrations

of heavy metals were measured using an atomic adsorption spectrophotometer (type: Thermo, Model: ICE 3300 (Figure 10-2)).
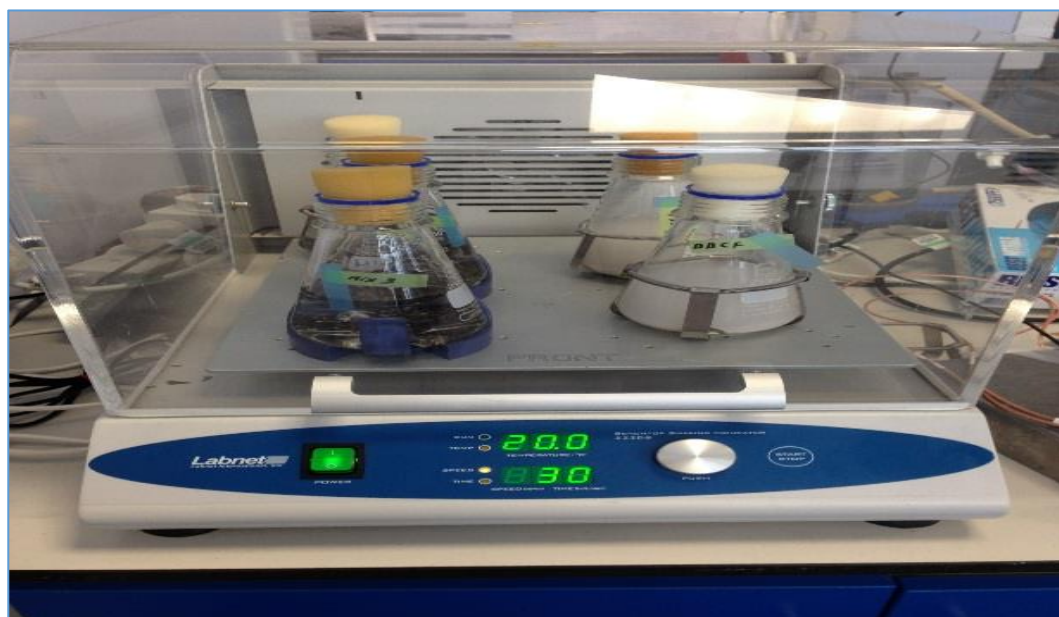
Figure 10.1. Rotary extractor

Figure 10.2. Atomic adsorption spectrophotometer – sample under test

10.5 TCLP results and Discussion

The concentrations of heavy metals, Ni, Cu, Pb, Cr, Zn, Sr, Ba and Cd in the leachates according to the TCLP test, are tabulated in Table 10-1. It can be seen that there was a

high concentration of Sr in the ground PMSA-F leachate. This concentration was lower in the BBCF as the ground PMSA-F amount was reduced in this filler. In contrast, concentrations of heavy metals in the leachates of ground PMSA-F-, BBCF- and the ABBCF-treated mixtures were considerably reduced; they were several times lower than those of the powder of ground PMSA-F and BBCF, and met the standard limits required by set regulations (Modarres and Nosoudy, 2015; Modarres et al., 2015b).

According to atomic adsorption, concentrations of Sr in the raw materials were higher than those of other heavy metals, which explains the high Sr leachate concentration compared to the other heavy metals. However, the concentration of Sr leachate in the ground PMSA, BBCF and ABBCF treated mixtures was less than the Health Reference Level (HRL) for strontium which is currently set at 4.2 mg/l (Alfredo et al., 2014). This means that these mixtures have stabilised and solidified the heavy metals found in both the ground PMSA-F and the BBCF.

Based on these results, it can be stated that not only did the inclusion of the three waste materials in the new CBCEA mixtures have technical advantages, they also decreased potentially harmful effects on the environment. Table 10-1 shows regularity standard levels, the minimum limits to classify the hazardous materials.

Table 10-1. TCLP test results (mg/l)

Heavy metal concentration (mg/l)	Reference water quality	Ground PMSA-F filler	BBCF filler	Ground PMSA-F mixture	BBCF mixture	ABBCF mixture	TCLP regulatory level
Nickel (Ni)	0.0	0.007	0.004	0.0	0.0	0.0	25
Copper (Cu)	0.0	0.0	0.0	0.0	0.0	0.0	25
Lead (Pb)	0.0	0.0	0.0	0.0	0.0	0.0	5
Chromium (Cr)	0.0	0.020	0.017	0.009	0.008	0.008	5
Zinc (Zn)	0.0	0.0	0.0	0.0	0.0	0.0	25
Strontium (Sr)	0.0	5.841	3.616	0.367	0.257	0.087	-
Barium (Ba)	0.0	0.0	0.0	0.0	0.0	0.0	100
Cadmium (Cd)	0.0	0.0	0.0	0.0	0.0	0.0	1

10.6 Summary

The TCLP test was performed to study the environmental impact of the waste materials in the new fast-curing CBCEA mixtures. The environmental analysis of the three waste materials in the CBCEA mixtures reveals that there are no negative effects on the environment. The concentrations of heavy metals of the specimens which incorporated ground PMSA-F, BBCF, ABBCF and their waste materials were observed to be less than the regulatory levels determined for hazardous materials; minimum requirements were satisfied. Bitumen emulsion and allied hydration process are an active stabilisation and solidification agent for heavy metals meaning that leachates will not have any harmful effects on underground and surface water resources.

CHAPTER 11

MICROWAVE HEATING APPLICATION IN CBCEA MIXTURES

11.1 Introduction

The previous chapters have addressed the potential to overcome the shortfalls of CBCEA mixtures in terms of mechanical and durability properties by the inclusion of three waste materials namely ground PMSA-F, FC3R and W-NaOH. Problems related to long curing times and low early strength of CBCEA mixtures with LF have been tackled resulting in a much improved, new ABBCF mixture that has outstanding mechanical and durability properties in addition to environmental, economical and safety benefits. However, the air void content of such mixtures is too high, according to road engineers, making it unacceptable as a binder course layer. In response to this, a new method was implemented, a microwave technique, to decrease these air voids at the same time making sure that improvements already gained have not been compromised. This technique is widely used as an alternative to conventional heating methods because it allows the volumetric, rapid heating of samples with no air emissions. For clarity, a brief review of the relevant literature is included in this chapter.

11.2 Characteristics of Microwaves

The principle of microwaving is to transform electrical energy to microwave energy to heat items using the high voltage system supplied in the microwave. Wang (2005) reported that microwaves cover a wide spectrum of frequencies ranging from 0.3 to 300 GHz, as can be seen in Figure 11-1. Microwaves also have comparable attributes to light waves as they are reflected by metallic materials, absorbed by some dielectric objects and transmitted without substantial absorption through other dielectric materials travelling at the speed of light in free space (Figure 11-2).
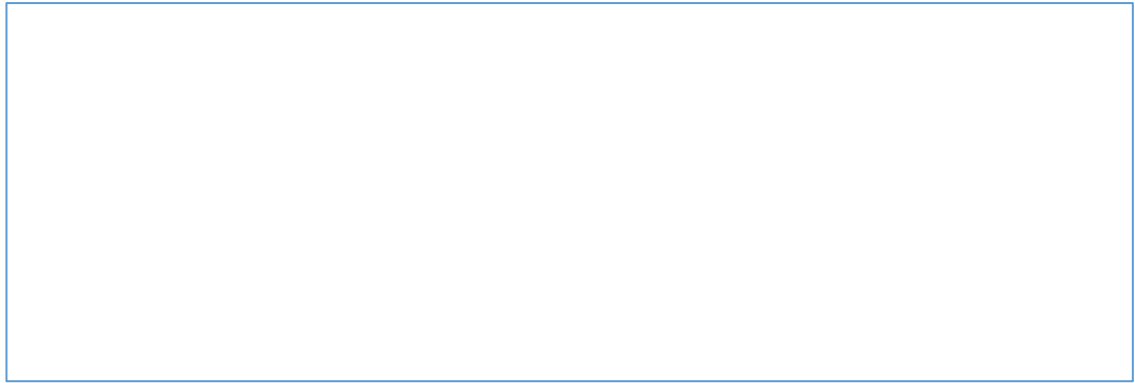
Figure 11.1. The electromagnetic spectrum (Wang, 2005)

The diagram originally presented here cannot be made freely available via LJMU Digital Collections because of 'copyright'. The diagram was sourced from Wang (2005)

The free space wavelength, λ_0, is associated to the frequency by the equation:

$$\lambda_0 = c/f \qquad\qquad \text{……………………………………………..11.1}$$

Where λ_0 is the free space wavelength, c is the speed of light and f is frequency.
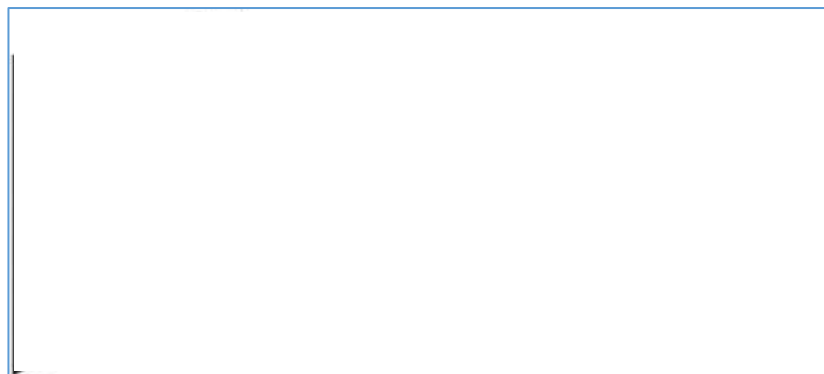
Figure 11.2. Propagation of the plane wave (Wang, 2005)

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Different materials react in various ways when subjected to microwave radiation; some materials are transparent or opaque towards microwaves while others absorb them (Figure 11-3). Some materials which are transparent at room temperature, can increase their capacity to absorb microwaves when heated above a critical temperature (Sutton, 1989).

It was reported by Sutton (1989) that dielectric materials generate an internal electric field in the affected volume when microwaves penetrate and propagate through it. The rotation of complex charges from this field are seen as dipoles and translational motion of free and bound charges (electrons or ions) which is forced onto the charges. Consequently, the inertial, elastic and frictional forces, which are frequency dependent, generate a resistance to this induced motion. Therefore, the electric field is reduced by this resistance which generates heat, giving rise to volumetric heating.
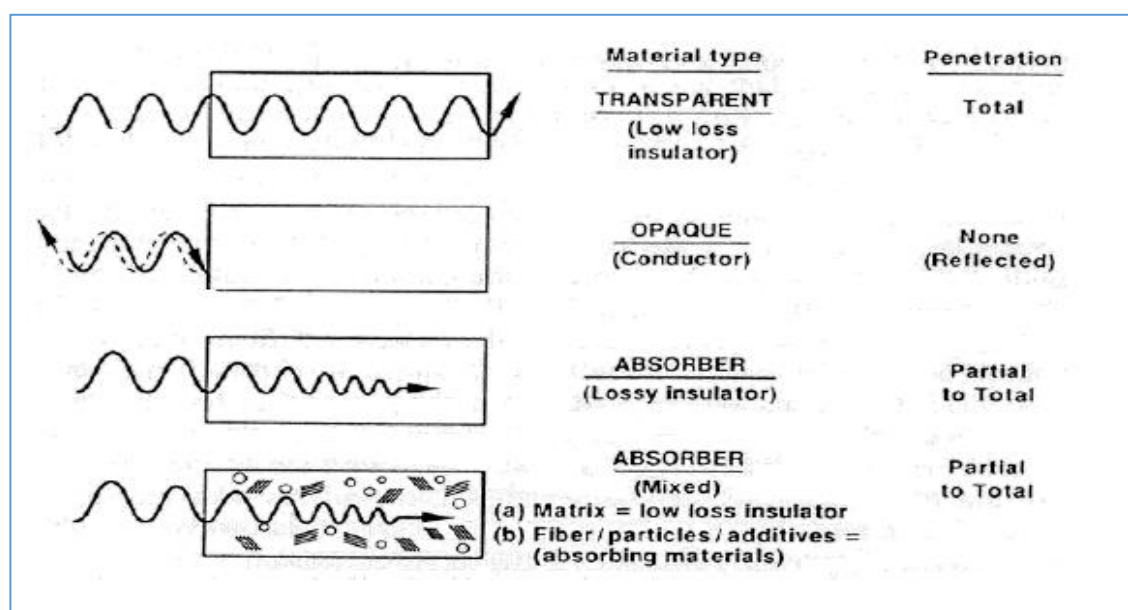
Figure 11.3. Schematic diagram illustrating the interaction of microwaves with material power absorption caused by dielectric losses (Sutton, 1989), permission to reproduce this figure has been granted by American Ceramic Society

Numerous studies have been performed comparing microwave heating with traditional heating of materials, demonstrating the advantages of the former (Hagerty et al., 1990). The main difference between conventional heating techniques and microwave is that the thermal energy in the former is delivered to the surface of the material by radiant or convective heating, which is then transferred to the bulk via conduction. This generates thermal gradients and non-uniform heating in materials that can result in less desirable

properties. In the latter, microwave energy is delivered directly to the material through interactions at the molecular level with the electromagnetic field. Microwaves can penetrate materials thereby heating from the inside, this resulting in volumetric heating (Somaratna et al., 2010). This direct heating of materials eliminates the need for heat transport from an external heat source to the material and from the surface to the core. This is in comparison to conventional heating which depends on an external heat source to create the heat that is transported by thermal convection and radiation to the materials' surface. Using this method, when the surface temperature rises, heat is transported towards the core of the material (Meredith, 1998). Consequently, microwave energy is a very attractive option because it uses less energy and less time to manufacture composites (Ku and Yusaf, 2008; Das et al., 2009). Benedetto and Calvi (2013) summarise the advantages of microwave heating as follows:

- ➢ no air emissions or liquid pollutants
- ➢ rapid heating
- ➢ easy control and isolation of hazardous conditions
- ➢ very small thermal gradients, little loss of energy and negligible time needed to heat up
- ➢ ability to strictly control automatic applications of heat
- ➢ allows volumetric heating of samples because of the penetrating capacity of microwaves
- ➢ direct action on polar bonds and entropy of the material to be heated.

In consequence, there are many potential advantages when using microwaves to process materials. The differences between microwave heating and conventional heating have been summarised in Table 11-1 (Kobusheshe, 2010).

Table 11-1. Differences between microwave heating and conventional heating

	Microwave	**Conventional**
Source	Energy transfer	Heat transfer via conduction
Start up	Immediate	Dependant on heating chamber
Rate	Rapid heating possible	Dependant on thermal diffusivity
Uniformity	Volumetric and selective heating	Temperature gradient from surface
Energy loss	Waveguide to reduce loss	Loss due to radiation externally

11.3 Microwave application in asphalt mixtures

Microwave energy has received a great deal of attention from researchers over a wide range of applications. For example, the technology of microwave heating is not a new concept in construction sectors. Recently, the use of industrial microwave heating of concrete materials has been examined and further developed, some researchers confirming its efficiency for the rapid curing of concrete (Leung and Pheeraphan, 1995). Microwave energy has also been shown to be effective in the highway engineering field. Jeppson (1981) examined the application of microwave heating in the context of road repairs, this considered one of the first such investigation into the use of this technology in the field. Al-Ohaly and Terrel (1988) described how microwave energy heats asphalt. They found that aggregates heat well due to factors such as absorbed moisture in the aggregate which heats up first then contributes to the heating of bitumen coatings. Microwave radiation has been used by Shoenberger et al. (1995) to heat Reclaimed Asphalt Pavement (RAP) based on the assumption that this would lead to less damage in comparison to directly applied heat.

Wave propagation techniques have been used by Li and Soheil (1995) to determine the degree of ageing in asphalts under the assumption that the non-destructive nature of this technique makes it an attractive option to use and to observe the difference in modulus of asphalts samples. It was also reported that microwave heating techniques can improve the road properties of asphalt mixes in terms of Marshall stability, flow value, dynamic stability and splitting strength at low temperatures (Wang et al., 2011).

The microwave heating of materials decreases processing time and saves energy (Benedetto and Calvi, 2013) so is therefore more efficient re asphalt production. Both the water and bitumen in asphalts are influenced by microwave heating. The alternating magnetic field causes polar molecules to change their orientation leading to internal friction resulting in an increase in the temperature of the material. It was also reported by Norambuena-Contreras and Garcia (2016) that microwave technology is more efficient in comparison to induction heating to heal cracks in asphalt roads and that it has shown the potential to promote self-healing in steel slag asphalt mixtures (Sun et al., 2014).

Nieftagodien (2013) investigated the use of microwave technology (for heating reclaimed bituminous mixtures and crushed aggregates) as a way of heating and generating Half-Warm Foamed mix (HWF), a relatively new material manufactured at a temperature higher than ambient temperature but below 100°C as reported by Jenkins (2000) and Rubio et al. (2013). This technique will bring many advantages such as improving tensile strength, particle coating and durability. In comparison to both WMA and traditional asphalts, HWF offers advantages in terms of its shear strength and possible energy-saving elements over both WMA and traditional asphalts. The energy saving benefits of this approach can be explained by its volumetric heating capability, in addition to rapid heating, which enhances productivity when using appropriate materials. HWF

characteristics are a compromise between those of Foamed Bitumen Stabilized materials (BSM-foam) and traditional asphalts characteristics.

11.4 The effect of Air Voids on the Performance of Asphalts

Water is an important component of CMA, its role of advantage in the early life of the material, but it is harmful afterwards. It is essential for the production of emulsion and ionises the medium, allowing coalescence and breaking to take place. Other useful roles for water include the facilitation of lower binder viscosity and compaction, and lubrication of aggregates. However, it delays the formation of a firm binder film and the development of cohesion as well as increasing fragility during early ages (Serfass, 2002). Serfass (2002) reported that the higher air void content in compacted CMA mixtures was the result of water evaporation which can increase the risk of stripping of the asphalts and water ingress to the layers underneath. If a comparison is made between CMA and asphalts, many tiny voids are present in the former due to the film made by coalescence and because the viscosity of the bitumen is higher at ambient temperature. These features of void distribution confirm that the initial densities of emulsion cold mixes are lower those of equivalent asphalts.

It was reported by Ibrahim (1998) that reducing the air void content in asphalts will increase its stiffness modulus. The consequent strain will be smaller at given stress levels leading to longer fatigue life, this the same as in the case of CMA. He also confirmed that the stiffness modulus increased significantly by increasing the compaction efforts cause by a decrease in air voids which, in turn, increased the interaction between the binder and aggregate particles. Jenkins (2000) revealed that when HWF mixtures are compacted at higher temperatures, 45°C to 90°C soon after mixing, air voids can be reduced by up to 30%. Thanaya (2007) reported that the target for air void contents ranges from 5-10% for CBEMs. He recommended a heavy compaction effort for such mixtures to achieve this

target. Increasing the compaction effort can easily lead to a reduction in air voids of CBEMs to comply with target values. Drying or aeration prior to compaction may be required, especially for gradations comprising finer materials, this producing CBEMs with less air voids, higher density and superior strength (Asphalt Institute and Asphalt Emulsion Manufacturers Association, 1997).

It was recently reported by Nassar et al. (2016a) that the presence of Ettringite with a needle shape (AFt) resulting from the use of OPC and fly ash (as a filler replacement) in the capillary voids of CBEM, can enhance the volumetric properties (less porosity) by decreasing both the pore size and their continuity. This prevents the movement of water and other aggressive fluids into the mixture.

11.5 Sample Preparation

Low workability during compaction of CBEMs results in high porosity in such mixtures. In contrast to asphalts, where workability depends on bitumen viscosity subject to mix temperature, CBEMs workability depends on pre-wetting water and bitumen emulsion content. Therefore, increasing the temperature of CBEMs will result in an increase in workability by reducing binder viscosity leading to less porosity. Because of the reasons detailed above, microwave heating techniques have been selected for use in this study.

Microwaving has been used to manufacture a Half-Warm Asphalt Concrete (HWAC) by adopting a pre-heating process prior to mixture compaction. This technique has been applied to reduce the air voids of the ABBCF mixture by decreasing the base bitumen viscosity, leading to enhanced mixture workability.

A domestic microwave oven was used to heat the ABBCF mixture which was placed on a ceramic plate at a working frequency 2.45 GHz, which corresponds to an approximate wavelength of 120 mm (Gallego et al., 2013), full output power and a 220 V, 50 Hz power

supply. The mixing procedure was the same procedure as explained in Chapter 5. After processing, the mixtures were conditioned in the microwave at different times, the materials moulded and subjected to compaction. All the tests described previously such as the ITSM, wheel track, 4-point load fatigue, SCB toughness and durability tests, were conducted on the conditioned samples. The reference mixtures were LF, ABBCF and the two AC mixtures. Figure 11-4 shows the loose specimens examined in the laboratory tests.

Figure 11.4. Materials used for microwave conditioning

11.6 Air Voids-ITSM Optimisation for the Half-Warm Asphalt Concrete (HWAC) Mixture

In this study, volumetric properties were calculated according to Asphalt Institute (1989) recommendations. The loose specimens were heated in the microwave for different times, i.e. 1.5, 3, 4.5 and 6 minutes. Both LF and ABBCF constituted control mixtures, subject to no heating. After removing the samples from the microwave, their temperatures were measured and recorded immediately.

The volumetric properties for the Marshall samples are defined in terms of air voids for the dry specimens; ITSM was measured after 1 day to identify the optimum microwave conditioning time. Figure 11-5 presents the optimized air voids and ITSM after 1 day while Table 11.2 presents the volumetric properties summary as well as the ITSM results.

The increase of microwave conditioning time from 1 up to 6 minutes, causes a reduction in air voids of 10.25% for the non-heated samples to 5.18% for the specimens heated for 6 minutes (Figure 11-5). This increase in time also leads to an increase in the temperature of the mixtures from 20°C to 99°C (Table 11-2). It can also be seen from Figure 11-2 that the increase in microwave conditioning time from 0 to 1.5 minutes caused a rise in the stiffness modulus by around 6% more than the stiffness generated by normal curing. This increment results from improvements in the workability of mixtures leading to an improved level of bonding between mixture constituents by decreasing the viscosity of the base bitumen. This lead to a drop in the air voids content from 10.25% to 7.36%. In addition, increasing the temperature to 44°C at this early stage activated the hydration process, which, in turn, enhanced the stiffness modulus. This effect is in agreement with Kong et al. (2016) who found that microwave curing improved the compressive strength of cement mortar at early ages.

In contrast, an increase of microwave conditioning time from 1.5 to 3 minutes, lead to a decrease in the stiffness modulus caused by the loss of trapped water (necessary for the hydration process) through the increase of mixture temperature. Finally, increasing the mixture temperature to 89°C for 4.5 minutes gave an increase in the stiffness modulus. At this point, a rise in the temperature of the mixture causes a reduction in the air voids content because of evaporation of the trapped water as well as improvements in workability. This increment in the ITSM after 4.5 minutes because of mixture densification, facilitated an increase in the ability of particles in the mixture to interlock.

In addition to this, there is a drop in the viscosity of the bitumen because of the increase in mixture temperature (to 89°C), leading to an increase in bond reaction between the bitumen film and aggregate particles.

In accordance with the results presented in Figure 11-5 and Table 11-2 for the ITSM with air voids and microwave conditioning time, conditioning of the ABBCF mixture can be optimized. Treating the ABBCF mixture for 1.5 minutes at 44°C was chosen because of the following: i) an increase in ITSM from 3138 to 3328 MPa ii) a reduction in air voids from 10.25% to 7.36% iii) the compaction temperature at this point (44°C) can be consider as a low conditioning temperature. Therefore, a new, optimised CBCEA mixture was generated at low temperature termed Half-Warm Asphalt Concrete (HWAC).
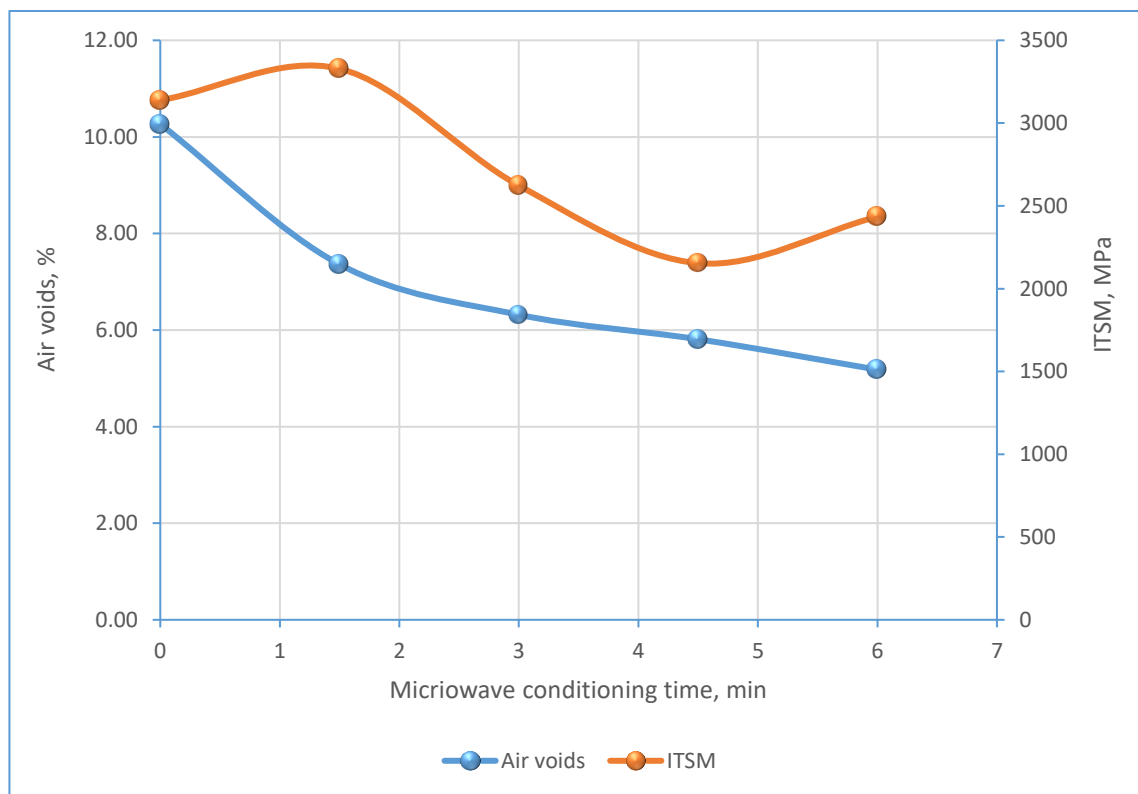
Figure 11.5. Air voids and ITSM optimization for ABBCF mixture after 1 day

Table 11-2. Summary of air voids and ITSM results of the ABBCF mixture

Microwave conditioning time, min.	Air voids, %	Dry density, mg/m^3	Temperature, °C	ITSM after 1 day, MPa
0	10.25	2.09	20	3138
1.5	7.36	2.13	44	3328
3	6.32	2.14	67	2623
4.5	5.81	2.16	89	2154
6	5.18	2.18	99	2435

11.7 Mechanical and Durability Properties of the HWAC

Performance tests for the HWAC mixture comprised the stiffness modulus, rutting resistance, fatigue resistance, SCB, moisture damage resistance and ageing tests.

11.7.1 ITSM Performance of the HWAC Mixture

The evolution of ITSM at different curing times (1, 3, 7, 14 and 28 days) is shown in Figure 11-6. The test was performed at a temperature of 20°C according to the standard BS EN 12697-26 (European Committee for Standardization, 2012c). HWAC offers a 6% improvement in ITSM compared to the ABBCF mixture after 1 day. It was expected that the microwave heating temperature of 44°C would cause improvement in the workability of the mixture by reducing the viscosity of the bitumen and by activation of the hydration process. The results also indicate that the ITSM of the HWAC mixture increased considerably over the first three days, in comparison to the ABBCF mixture. After that, a reduction in increment rate was detected. At early ages, microwaving can accelerate the hydration process, however, HWAC samples generate dense hydration products wrapped around its particles, hindering further hydration at later ages. These findings are consistent with those obtained by Kong et al. (2016) who found that the hydration of cement mortar at early ages can be promoted by microwave curing by producing fine and dense C-S-H

gels around the cement particles, these impeding the later hydration process. Microwave

conditioning appears to be an important and noteworthy heating technique as the ITSM

of the HWAC mixture after 3 days was higher than that of the corresponding references

mixtures i.e. LF, OPC, AC 20mm with 100/150, AC 20mm with 40/60. The increase in

mixture temperature facilitates these results.
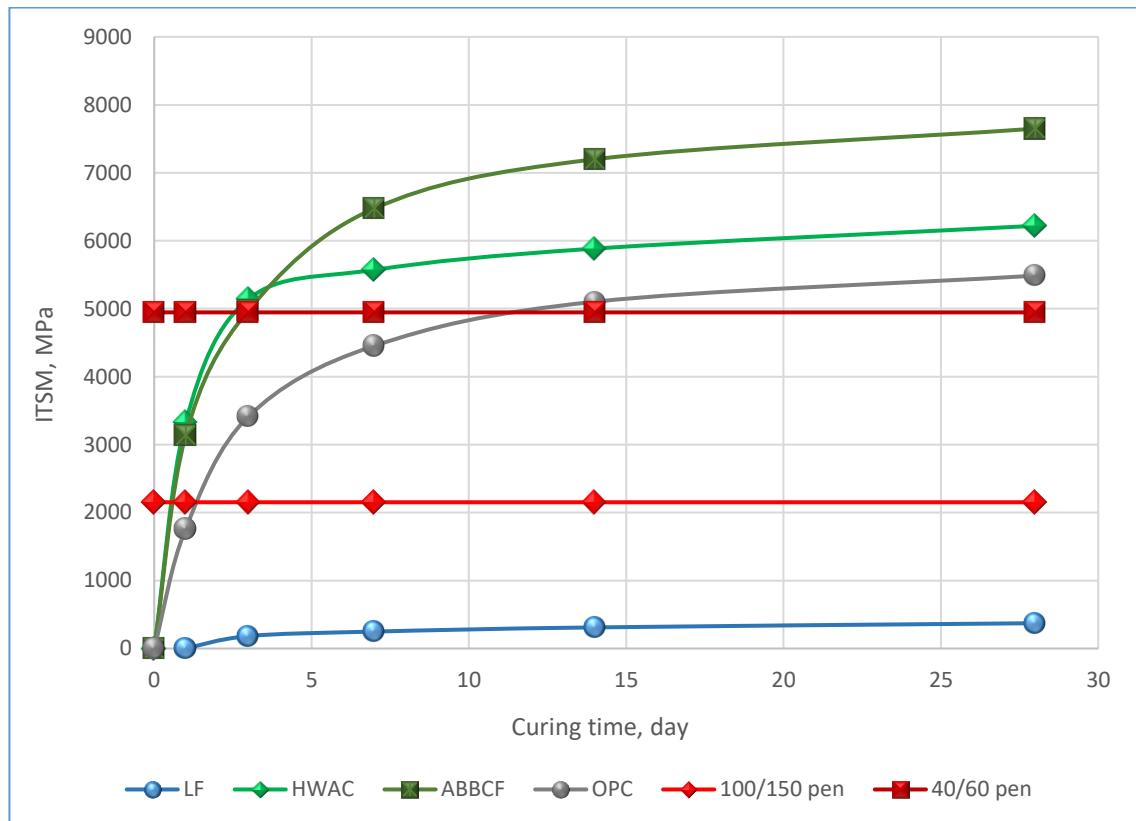
Figure 11.6. ITSM results

11.7.2 Performance in the Wheel Track Test for the HWAC Mixture

The rutting resistance in the HWAC mixture is assessed by a wheel tracking test,

following the standard procedure in BS EN 12697-22 (European Committee for

Standardization, 2003a). The wheel tracking test was applied to assess the deformation

resistance of all mixtures at 45°C. Slab sample preparation, as well as curing, has been

detailed in sub section 7.2.1. but in addition to this, HWAC mixtures were subjected to

microwave heating for 1.5 minutes before being compacted by the roller compactor. It

can be observed from Figure 11-7, that microwave conditioning of the HWAC mixture led to an increase in the permanent deformation resistance giving a better performance than the reference mixtures, i.e. LF, OPC, ABBCF and both AC mixtures. This is due to an increase in particle interlock. These results confirm the validity of microwave heating in the production of a HWAC mixture comparative to both AC's.
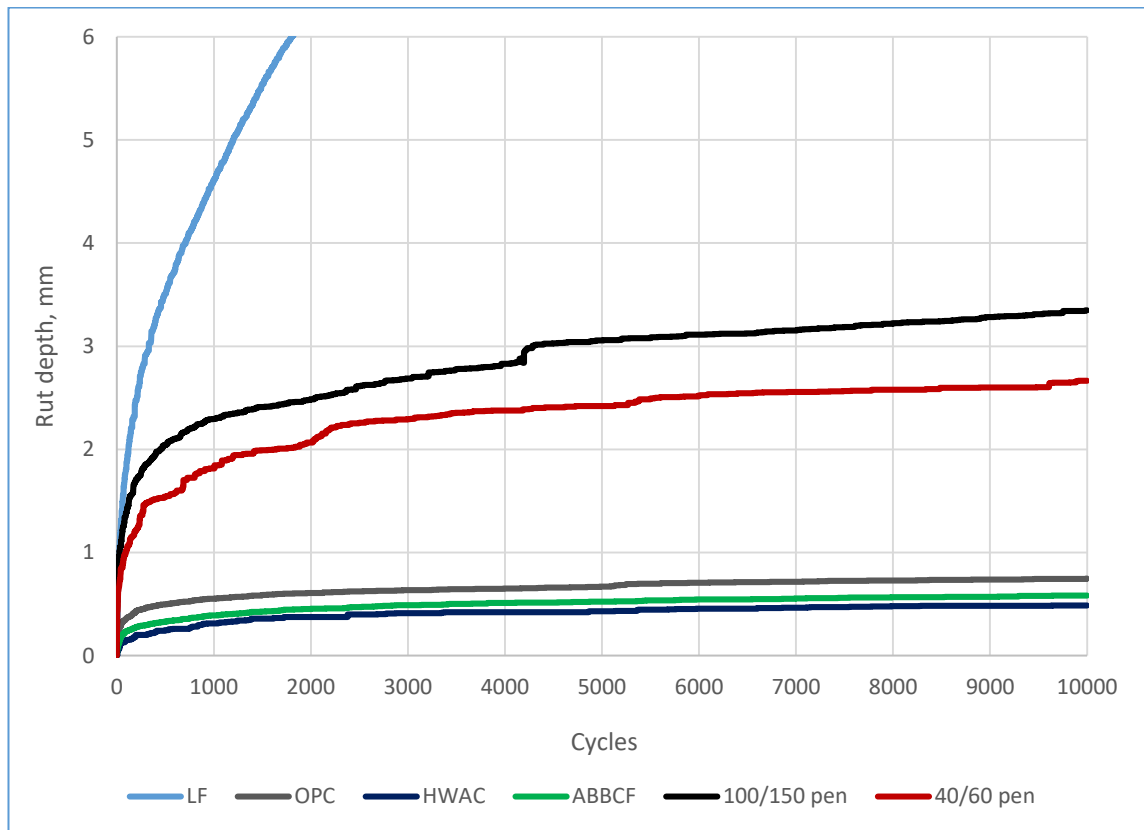
Figure 11.7. Comparison of rut depth growth at 45°C

11.7.3 Fatigue Performance for the HWAC Mixture

The HWAC specimens for the fatigue test were prepared and cured following the same procedure described in Chapter 7. The samples were exposed to microwave heating for 1.5 minutes prior to compaction. Fatigue life, which represents the crack initiation stage, has been measured by the four-point bending (4PL) test using prismatic samples following the standard BS EN 12697-24 (European Committee for Standardization, 2012b). Constant strain tests were performed at the 150 microstrain level using sinusoidal

loading at a frequency of 10 Hz. Fracture toughness which represents crack propagation, has been assessed by conducting the semi-circular bending (SCB) test. The fatigue life results of the HWAC compared with the LF, ABBCF and the two hot mixes are presented in Figure 11-8 where it can be seen that fatigue life for the HWAC is 32 times better than that of the LF mixture. It is also better that the ABBCF by about 12%. The reduction in air voids and the improvement in coating percentage as a result of the reduction in the base bitumen viscosity lead to this improvement. The air voids are 7.36% and 10.25% for the HWAC and the ABBCF mixture, respectively.
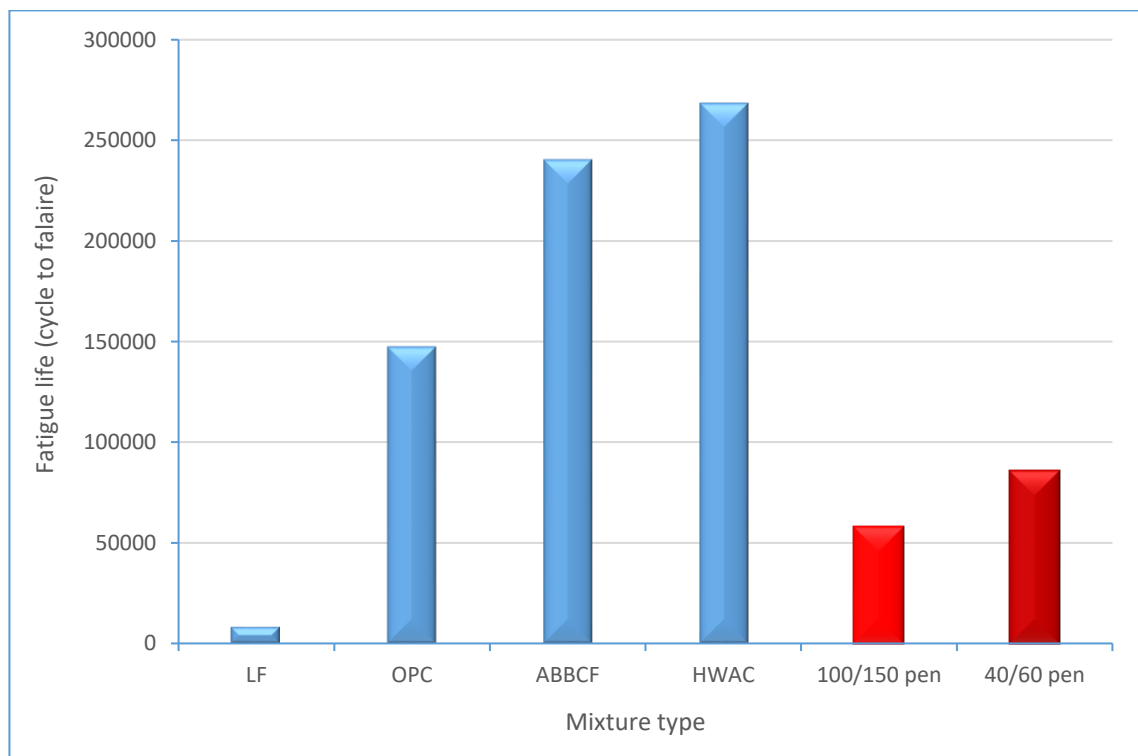
Figure 11.8. A comparison of fatigue lives

Figure 11-9 shows the results of the SCB test for the HWAC and reference mixtures. One of the most important effects of microwave conditioning is an increase in consistency by decreasing viscosity. This leads to an improvement in the interlock between mixture constituents that reduce the percentage of air voids in the mixture. In consequence, the HWAC mixture shows improved performance in the SCB test in comparison to the

ABBCF mixture. Less air voids in the HWAC mixture (7.36%) compared to ABBCF

(10.25%) have enhanced the behaviour for HWAC by around 10%. However, the results

are still less than the reference hot mixes due to one of the main parameters that effects

crack propagation performance; there are less air voids in hot mixtures in comparison to

HWAC mixtures. That said, these findings are in agreement with those of Aliha et al.

(2015) who observed that air void content markedly affects the fracture toughness of

asphalts.
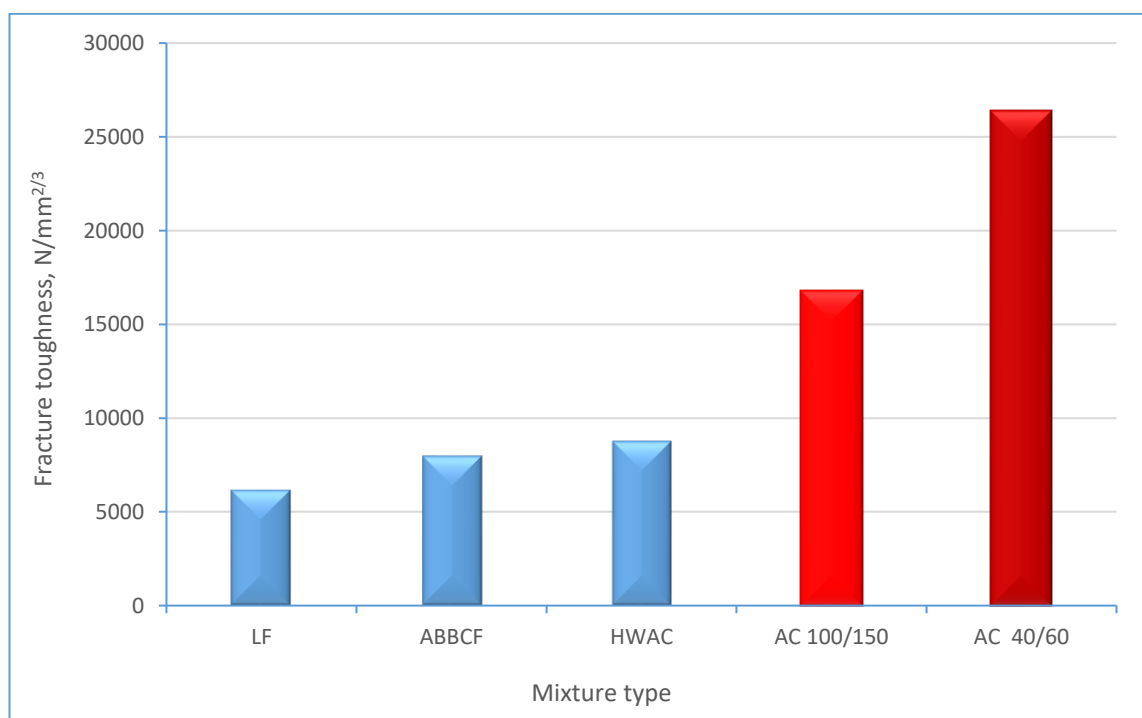
Figure 11.9. SCB test results

11.7.4 Durability Performance of the HWAC

The durability of mixtures in terms of moisture susceptibility and long term ageing was

measured by determining the stiffness modulus ratio (SMR) following the standard

procedure in BS EN 12697-12 (European Committee for Standardization, 2008), to

examine the influence of microwave conditioning of the HWAC mixture. It is important

to establish if improvements in air voids due to microwave conditioning, have affected

durability in terms of water damage and long-term ageing. HWAC needs to resist the impact of the environment from a durability perspective, otherwise it will not meet the requirements of carrying heavy traffic loads.

In terms of water sensitivity, HWAC samples were subject to the same curing as described in Chapter 8. Figure 11-10 presents the SMR results for LF, OPC, HWAC, ABBCF and the two AC mixtures. The HWAC mixture has an SMR that is superior to that of the reference LF and the two AC mixtures which makes this new mixture comply with BS EN standards. The SMR of the HWAC mixture is more or less the same as the ABBCF mixture, however the dry and wet stiffness of the HWAC mixture is less than that of the ABBCF, this consistent with the ITSM results (Figure 11-6). This improvement is due to an enhancement in porosity, because of a reduction in air voids, in addition to the activation of the hydration process leading to a better stiffness modulus.

Regarding long term ageing performance, the same procedure used to prepare and test the samples detailed in Section 8.3, has been applied. Figure 11-11 shows the ageing results of the HWAC mixture and the reference mixtures. It can be seen that HWAC is comparable to the ABBCF mixture indicating the improvement in the strength rate of the former. In addition, the performance of HWAC was better than the reference two AC mixtures. These results constitute strong evidence for the validity of microwave heating.
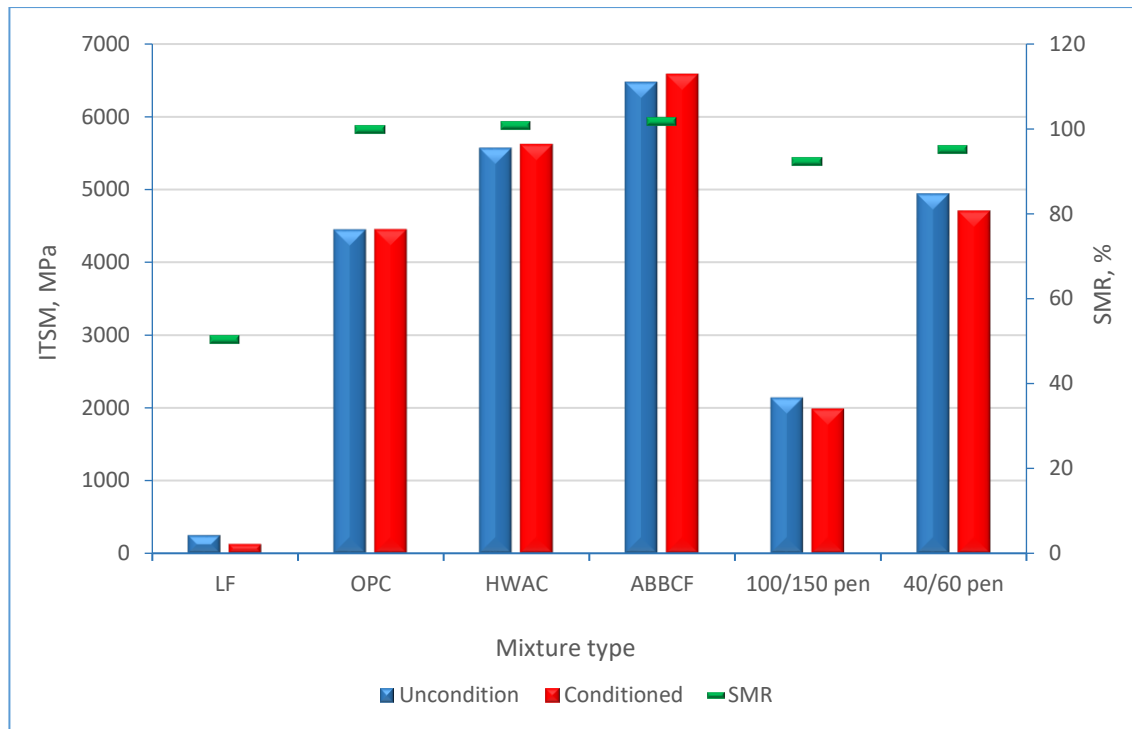
Figure 11.10. Water sensitivity results
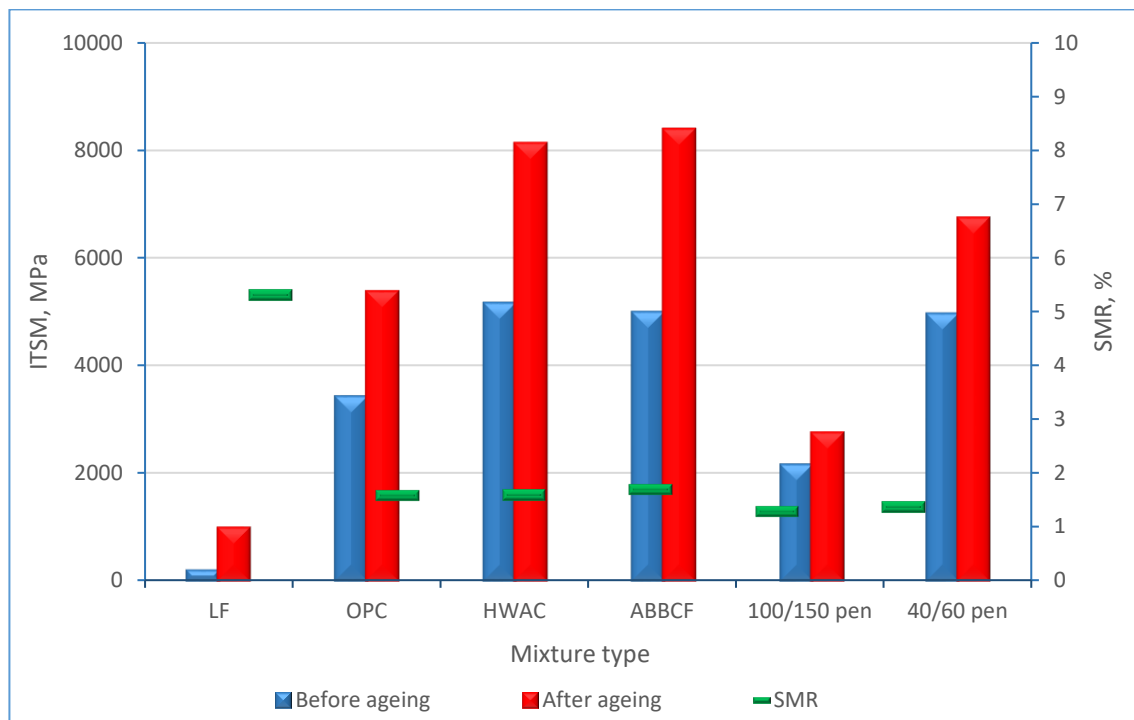
Figure 11.11. Long-term ageing results

11.8 Summary

Microwave conditioning has been used to enhance the volumetric properties of the ABBCF mixture and assess whether or not mechanical and durability properties were kept within acceptable and comparable ranges. Heating in this way offers several advantages in comparison to conventional heating including savings in energy and volumetric heating. Therefore, microwave heating was applied to the ABBCF mixture over different times, i.e. 1.5, 3, 4.5 and 6 minutes, resulting in increases in the mixture temperatures of 44, 67, 89 and 99°C, respectively. 1.5 minutes has been selected as the optimum microwave conditioning time based on the ITSM, air voids and the pre-compaction temperature of the mixture. A Half-Warm Asphalt Concrete mixture (HWAC) has been created through using microwave heating which decreased air voids to 7.36% in comparison to 10.25% for the ABBCF.

The consistency of the bitumen is enhanced by reducing its viscosity which, in turn, improves workability leading to improved bonding between mixture constituents. In addition, microwave heating improves the compressive strength at early ages by the activation of hydration process. The mechanical properties of the HWAC mixture were evaluated in terms of ITSM, wheel track, 4PL and SCB tests, while durability properties were appraised through water sensitivity and ageing tests. The performance regarding these mechanical and durability properties is promising in comparison to the reference LF and two AC mixtures.

CHAPTER 12

CONCLUSIONS AND RECOMMENDATIONS

12.1 Introduction

This research aimed to develop a new, fast-curing, cold emulsion asphalt mixture for use as a binder course in bituminous pavements. The new mix contains ground PMSA-F and FC3R as a replacement for limestone filler; a waste NaOH alkali activator was used as a substitute for pre-wetting water. Characterizations of the new mixture in terms of mechanical and durability properties were supported by studying SEM and XRD to explain the improvement of both properties due to the use of the new filler in addition to pre-wetting with the W-NaOH solution. The environmental impact of the new mixture has also been examined. The following conclusions are based on the findings revealed in this study. Recommendations for future research are suggested at the end of this chapter.

12.2 Conclusions

A new, fast-curing, high performance and environmentally friendly, cold emulsion asphalt for use as a binder course mixture (CBCEA) in road pavements was developed at the Liverpool Centre for Material Technology (LCMT). The new CBCEA mixture provides significant advantages by being an environmentally friendly, energy efficient and cost-effective mixture which is safer to use than its predecessors. In this research, a novel alkali activated binary blended cementitious filler (ABBCF), created from waste materials, was developed as a substitute for conventional mineral filler in CBCEA mixtures. This ABBCF mixture is a new material with both a mechanical and durability performance comparable to traditional AC in binder course mixtures. This mixture will overcome concerns related to the use of traditional CBEM in binder course vis à vis its poor early strength, the need for long curing times and high air void contents. Based on

the results achieved in the current research, the conclusions fall into the following main categories:

1. **The new novel alkali activated binary blended cementitious filler (ABBCF)**

   1.1. The new ABBCF is made of ground Fine Paper Making Sludge Ash (PMSA-F) (4.5%) and Fluid Catalytic Cracking Catalyst Residue (FC3R) (1.5%), activated by waste sodium hydroxide alkali (W-NaOH).

   1.2. Blending and mixing various types of wastes and by-products, i.e. PMSA, FC3R and W-NaOH, was found to be crucial in developing a novel cementitious material for use in the new CBCEA mixture.

   1.3. The characteristics of PMSA are that it is rich in hydraulic minerals such as lime, mayenite and gehlenite; the presence of Ca, Al and Si are significant for the development of new cementitious materials.

   1.4. It was found that increasing the fineness of the PMSA-F lead to improvements in the hydration process due to an increased surface area.

   1.5. The amorphous nature of FC3R means that it will show high reactivity during the hydration process when used as an activator with $Ca(OH)_2$. The presence of a high silica-alumina content allows the formation of a dense microstructure creating a Binary Blended Cementitious Filler (BBCF).

   1.6. The creation of a high alkali environment to activate the BBCF has been achieved by using a W-NaOH solution as the alkali activator to provide said ambient environment to activate reactivity in the cementitious components.

2. **The performance characterization of cold binder course emulsion asphalt (CBCEA)**

   2.1. Substantial improvements were achieved in the stiffness modulus in both early and later ages for the ABBCF mixture. When compared with the control LF

mixture, the stiffness modulus increased more than 27 times after just 3 days. In addition, the new ABBCF mixture achieved the required stiffness for a conventional hot asphalt concrete binder course 100/150 pen (2152 MPa) in less than one day. The ABBCF mixture offers a stiffness modulus value of 3138 MPa after one day. This means that using this mixture, roads can be opened the same day of laying; there is no longer the need to wait for 2-24 months as in case of traditional CBEMs. This will overcome restrictions around the time required to achieve acceptable stiffness for traditional CBEMs. The generation of a new binder from the cementitious reaction of ABBCF is responsible for this enhancement.

2.2. The ABBCF considerably improved resistance to temperature sensitivity because of significantly lower thermal susceptibility in comparison to that of traditional AC binder course mixtures. This will provide an appropriate solution to issues around resistance to temperature variations. Such mixtures can be used in the asphalt binder layer to offer significant rutting resistance because of its high stiffness modulus as well as stability at higher temperatures.

2.3. The ABBCF mixture offered a considerably longer life under wheel tracking tests at both 45°C and 60°C when compared to the results of the reference LF mixture. Said LF reference mix developed a high rut depth in the wheel tracking test, indicative of poor permanent deformation resistance. These results are an improvement on two asphalt concrete binder course mixtures using two different grading of bitumen, meaning that they can carry heavy traffic loads in hot climate conditions. Successful hydration, specifically with ABBCF, was responsible for creating high resistance to permanent deformation, demonstrating the possible advantages of using this material in heavily trafficked roads.

2.4. The ABBCF mixture extended fatigue life to around 29 times that of the control LF mixture at strains of less than 200 microstrain. In terms of crack propagation, there was an improvement in the ABBCF mixtures (30%) in comparison to the LF mixture.

2.5. In terms of durability properties, the ABBCF mixture has a high resistance to water damage. Improved performance in the ITSM test for conditioning samples resulted in an SMR of more than 100%. The water sensitivity of these mixtures is more than twice that of the LF mixture. This also better than traditional soft and hard asphalts. Progressive hydration during curing within said mixtures accounted for higher resistance to water damage. The performance of the ABBCF mixture regarding long term ageing is promising. This is an improvement in comparison to traditional AC mixtures.

3. **Mixture microanalysis investigations**

3.1. Microanalysis techniques, in terms of SEM observation and XRD analysis, show an increase in hydrated products within the ABBCF paste which explains the improvements in ITSM in the ABBCF mixture. The formation of hydration products can be detected by SEM observation at an early age explaining the stiffness improvement.

3.2. Concerning XRD analysis, the generation of new cementitious components such as C-S-H, C-A-S, CH and Aft, are noticeable in the mineralogical phase which occurs during the first three days; this was confirmed by SEM observations. It was also confirmed that the presence of emulsion does not affect the hydration process in the ABBCF mixture.

4. **The toxicity characteristic leaching procedure (TCLP)**

4.1. Investigation of the influence of PMSA, FC3R and W-NaOH in the CBCEA mixtures by TCLP reveals that there are no negative impacts on the environment as the heavy metals do not leach into the environment. Therefore, there will be no pollution as a result of using these materials in the new CBCEA and, consequently, no detrimental effect on the surrounding environment.

4.2. Accordingly, the waste material used in CBCEA mixtures are non-hazardous. This will encourage pavement and asphalt agencies to promote their use.

5. **Microwave application**

5.1. Microwave conditioning of the ABBCF mixture enhanced the bitumen consistency by decreasing its viscosity. This enhanced mixture workability resulted in an improved bonding action between the mixtures' constituent parts.

5.2. Microwave conditioning activates the hydration process and thus improves the mixture strength at early ages. The lower viscosity value of the bitumen achieved at 1.5 minutes of microwave conditioning, was responsible for producing a more workable Half-Warm Asphalt Concrete mixture (HWAC) mixture.

5.3. An increase in temperature from 20°C to approximately 44°C, lead to an improvement in the stiffness modulus of HWAC. This temperature is required to create air void contents which are comparable to that of traditional asphalts.

5.4. It must be noted that a further increase in microwave conditioning, both time and temperature, facilitated moisture evaporation in the mixture, leading to a decline in the stiffness modulus by inhibiting the hydration process.

6. **The new CBCEA: sustainable advantages**

    Substituting traditional limestone filler with ABBCF will reduce cement usage in CBEMs and thus offer a positive sustainability effect. Problems related to carbon emissions (during production) and mixture temperature maintenance (during transportation and laying) in the case of asphalts will be mitigated by using this novel CBCEA mixture. These results confirm that it is possible to produce CBCEA mixtures which have a stiffness modulus equal to, or greater than, conventional asphalt concrete. Road engineers consider this as a suitable material for use as a binder course layer for heavy trafficked motorways and airfields, allowing early and temporary trafficking where site restrictions inhibit the application of a surface course prior to the elimination of traffic management. These materials also eliminate the restrictions imposed by road engineers on ABBCF by reducing curing time to less than one day.

12.3 Recommendations for Future Research

Recommendations for further studies are as follows:

1. Due to time constraints, only AC 20 mm has been used in this research. Future works can be undertaken to produce CBEMs by introducing reclaimed asphalt pavement (RAP) contents with PMSA, FC3R and W-NaOH to examine these new mixes in terms of their mechanical and durability properties.

2. Currently, there are substantial ongoing developments regarding the manufacture of bitumen emulsions. Further research could be carried out on the use of different bitumen emulsions types containing polymer modified bitumen emulsions, to examine the properties of these mixtures including stiffness, rutting, fatigue and fracture toughness.

3. A new mix design method for CBEMs with fillers from SCMs should be developed. The type and grading of the aggregate, as well as emulsion content and type, should be covered by the design method. The new mix design should consider the optimization of both optimum bitumen emulsion content and pre-wetting water content.

4. The outcomes presented in this research are from laboratory investigations and require field trials for the validation of the laboratory results to effectively bridge the gap between laboratory tests and field conditions. There are several practical difficulties with field trails so ways by which to overcome these have, and are still being discussed with industrial partners.

5. Future research is needed to examine the influence of grinding waste filler materials to nano particles to study the effect on hydration products as well as the mechanical and durability properties of CBEMs.

6. In order to reduce CBEMs air void contents, trials with different heating techniques such as infrared heating, are recommended. This should take into consideration the correlation between frequency and time of treatment, and the correlation between waste materials content and treatment time.

7. A detailed economic study for the new CBCEA mixture is recommended, taking into consideration that waste materials are a low cost resource.

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APPENDIX I: RESEARCH CONTRIBUTIONS

List of peer-reviewed published journal papers

1. Dulaimi, A., Al Nageim, H., Ruddock, F. & Seton, L. (2017), High performance cold asphalt concrete mixture for binder course using alkali-activated binary blended cementitious filler, **Construction and Building Materials**, 141, 160-170. doi.org/10.1016/j.conbuildmat.2017.02.155.

2. Dulaimi, A., Al Nageim, H., Ruddock, F. & Seton, L. (2017), Performance analysis of a Cold Asphalt Concrete Binder Course Containing High Calcium Fly Ash Utilizing Waste Material. **Journal of Materials in Civil Engineering**, 29, 7. doi. 10.1061/(ASCE)MT.1943-5533.0001883.

3. Dulaimi, A., Nageim, H. A., Ruddock, F. & Seton, L. (2017), Laboratory Studies to Examine the Properties of a Novel Cold-Asphalt Concrete Binder Course Mixture Containing Binary Blended Cementitious Filler, Journal of Materials in Civil Engineering, 29, 9. DOI: http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0001975.

4. Dulaimi, A., Al Nageim, H., Ruddock, F. & Seton, L. (2016), New developments with cold asphalt concrete binder course mixtures containing binary blended cementitious filler (BBCF), **Construction and Building Materials**, 124, 414-423. doi.org/10.1016/j.conbuildmat.2016.07.114.

5. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. (2015). A Novel Cold Asphalt Concrete Mixture for Heavily Trafficked Binder Course. **International Journal of Civil, Environmental, Structural, Construction and Architectural Engineering**. Vol: 9, No: 8, 734-738.

List of peer-reviewed published conference papers

1. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. A Novel Cold Bituminous Emulsion Mixture for Road Pavement using A New Cementitious Filler. **The 3rd BUiD Doctoral Research Conference, the British University in Dubai**, 13th May 2017, UAE.

2. Dulaimi, Anmar, Al Nageim, Hassan, Ruddock, Felicite and Seton, Linda. Microwave Technique to Develop Cold Asphalt Concrete Bituminous Emulsion

Mixture Using New Cementitious Filler. **The 16th Annual International Conference Asphalt, Pavement Engineering and Infrastructure**. 22nd-23th Feb 2017. Liverpool, UK.

3. Dulaimi, Anmar, Al Nageim, Hassan, Ruddock, Felicite and Seton, Linda. Performance Assessment and Microstructure of New Cold Asphalt Concrete Binder Course Mixture with GGBS and CKD. **The 16th Annual International Conference Asphalt, Pavement Engineering and Infrastructure**. 22nd-23th Feb 2017. Liverpool, UK.

4. Anmar Dulaimi, Hassan Al Nageim, Khalid Hashim, Felicite Ruddock and Linda Seton. Investigation into the stiffness improvement, microstructure and environmental impact of a novel fast-curing cold bituminous emulsion mixture. **The 6th Eurasphalt & Eurobitume Congress.** 1st – 3rd June 2016. Prague Congress Centre, Czech Republic. (DOI): dx.doi.org/10.14311/EE.2016.425.

5. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Microanalysis of Alkali-Activated Binary Blended Cementitious Filler in a Novel Cold Binder Course Mixture. **The 38th International Conference on Cement Microscopy**, April 17th-21st, 2016, Lyon, France.

6. Hassan Al Nageim, Anmar Dulaimi, Felicite Ruddock and Linda Seton. Development of a New Cementitious Filler for Use in Fast-Curing Cold Binder Course in Pavement Application. **The 38th International Conference on Cement Microscopy**, April 17th-21st, 2016, Lyon, France.

7. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Assessment the Performance of Cold Bituminous Emulsion Mixtures with Cement and Supplementary Cementitious Material for Binder Course Mixture. **The 38th International Conference on Cement Microscopy**, April 17th-21st, 2016, Lyon, France.

8. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. The Effect of High Calcium Fly Ash Fineness on the Stiffness Modulus of a New Cold Asphalt Concrete for Binder Course Mixture. **The 2nd BUiD Doctoral Research Conference**, the British University in Dubai, UAE, 14th–15th May 2016.

9. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. High Performance Cold Asphalt Concrete Mixtures Using Alkali-Activated Binary Blended Cementitious Filler System. **The 15th Annual International**

Conference Asphalt, Pavement Engineering and Infrastructure. 24th -25th Feb 2016. Liverpool, UK.

10. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Microanalysis of a New Cementitious Material to Use as a Filler in a Cold Dense Graded Binder Course Mixture. **The 15th Annual International Conference Asphalt, Pavement Engineering and Infrastructure**. 24th-25th Feb 2016. Liverpool, UK.

11. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. A Novel Cold Asphalt Concrete Mixture for Heavily Trafficked Binder Course. **The 17th International Conference on Civil, Environmental and Geological Engineering.** August 13th-14th 2015, Venice, Italy. ISSN: 1307-6892, ISBN: 2010-376X.

12. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Development of sustainable cold asphalt concrete binder course mixtures using waste fly ash and new waste activator. **Post Graduate Research Conference, Faculty of Technology and Environment Liverpool John Moores University**. 15th-19th June 2015. Liverpool, UK.

13. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Development of Sustainable Cold Asphalt Concrete Binder Course Mixtures Using Waste Fly Ash and Metakaolin. **The 12th International Postgraduate Research Conference**, Media City, Manchester on 10th-12th June, 2015. Manchester, UK.

14. Anmar Dulaimi, Hassan Al Nageim, Felicite Ruddock and Linda Seton. Improving the Stiffness Modulus of Cold Asphalt Concrete Binder Course. **The 14th Annual International Conference Asphalt, Pavement Engineering and Infrastructure**. 11th -12th Feb 2015. Liverpool, UK.

15. Hassan Al Nageim, Anmar Dulaimi, Felicite Ruddock and Linda Seton. Cold Mix Binder Course for Roads & Highways. **The 14th Annual International Conference Asphalt, Pavement Engineering and Infrastructure**. 11th-12th Feb 2015. Liverpool, UK.

16. Dulaimi, A., Al Nageim, H., Ruddock, R., Seton, L. Development of A Cold Binder Course Bituminous Emulsion Mixture, **BEAN (Built Environment & Natural Environment) 8th Annual Conference**. 2014. Liverpool, UK.

List of conference papers – poster presentation

1. Dulaimi, Anmar, Al Nageim, Hassan, Ruddock, Felicite and Seton, Linda. Microanalysis of a New Cementitious Material to Use as a Filler in a Cold Dense Graded Binder Course Mixture. **The 9ᵗʰ Manchester Metropolitan University Postgraduate Research Conference. 22ⁿᵈ February 2017.**

List of under preparation journal papers

1. Dulaimi, Anmar, Al Nageim, Hassan, Ruddock, Felicite and Seton, Linda. Mechanical Performance and Microstructure of New Cold Bituminous Emulsion Mixtures Containing GGBS and CKD. **Construction and Building materials journals.**

APPENDIX II: AWARDS, HONOURS AND RECOGNITIONS

1. **An Honourable Mention Award** by the Association of British Turkish Academics (ABTA) in the Engineering category of the 2017 Doctoral Researcher Awards competition at University College London (UCL), on Saturday, 20 May, 2017.

2. Awarded the **Medal of Excellence** by the Minister of Higher Education in Iraq on 24th January 2017 at the Iraqi embassy on London for **achieving first place among around 2000 Iraqi PhD students in the UK** due to the publication of 17 journal and conference papers up to that point in time.

3. Awarded the **Certificate of Excellence** by the Iraqi Ambassador in London on 5th March 2017 at the Iraqi embassy on London due to excellent academic achievements.

4. Awarded the **Certificate of Excellence** by the Iraqi students society in the United Kingdom on 5th March 2017 at the Iraqi embassy on London due to excellent academic achievements.

5. Award for the paper with **best potential impact: 2nd place** at the Faculty Research week (LJMU Faculty of Technology and Engineering) 2016.

6. Award for the **best poster presentation: joint 3rd place** at the Faculty Research Week (LJMU Faculty of Technology and Engineering) 2016.

7. Award for the **best poster presentation: 2nd place** at the Faculty Research Week (LJMU Faculty of Technology and Engineering) 2015.

8. Award for the **best extended abstract: runner up** at the BEAN conference (LJMU School of Built Environment) 2014.

Medal of Excellence by the Minister of Higher Education in Iraq

CERTIFICATE *of* EXCELLENCE

AWARDED TO

Anmar Falih Diekan Dulaimi

TO RECOGNISE HIS OUTSTANDING ACADEMIC ACHIEVEMENTS DURING HIS STUDY IN THE UK

MARCH 05
2017

H.E. DR SALIH HUSAIN ALI
AMBASSADOR OF THE REPUBLIC OF IRAQ TO
THE UNITED KINGDOM - LONDON

IRAQI STUDENTS SOCIETY
Certificate of Excellence

This certificate is awarded to

Anmar Falih Diekan Dulaimi

TO RECOGNISE HIS OUTSTANDING ACADEMIC ACHIEVEMENTS DURING HIS STUDY IN THE UK
on 05 March, 2017
London – United Kingdom

Zeyad Yousif Al-Shibaany
Chair of Iraqi Students Society

This Event is sponsored by the Embassy of the Republic of Iraq in the United Kingdom