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Faculty of Engineering – Department of Civil Engineering

UNDERSTANDING AND IMPROVING COLD BITUMINOUS EMULSION MIXTURES

By

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the degree of Doctor of Philosophy

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إذا كنت تريد أن تعيش حياة سعيدة ، فربطها إلى هدف ، وليس بالناس أو الأشياء
(Arabic)

如果你想过上幸福的生活，那就把它与目标联系起来，而不是与人
或事物联系在一起
(Chinese)

If you want to live a happy life, tie it to a goal, not to people or things
(English)

Si vous voulez vivre une vie heureuse, attachez-la à un objectif, pas à des
personnes ou à des choses
(French)

यदि आप एक खुशहाल जीवन जीना चाहते हैं, तो इसे किसी लक्ष्य के साथ बांधें, न
कि लोगों या चीज़ों के लिए
(Hindi)

Si quieres vivir una vida feliz, áatala a un objetivo, no a personas o cosas
(Spanish)

Albert Einstein

Abstract

Cold Asphalt Mixture (CAM) is a pavement material usually produced by mixing bitumen emulsion, aggregate, water, and cement at ambient temperature. CAM has many economic, environmental, energy-saving, and health and safety advantages compared to other types of mixtures used in roads, but it has weak mechanical performance as a structural layer, mainly due to containing trapped water. Consequently, studies attempting to increase the mechanical performance of CAM have attempted to dispose of its water content by promoting suction, absorption and consumption of water using cementitious and/or pozzolanic materials. Despite numerous attempts, CAM still has weak final performance, characterised by high porosity and slow development of performance in comparison to Hot Mix Asphalt (HMA). This is due to the lack of a deeper understanding of the dynamics of water evaporation, moisture and temperature profiles in CAM. Therefore, this research aims to investigate, understand and predict: the dynamics of water evaporation and the mechanical performance of CAM (with and without cement); and the affects of CAM components on performance (curing and strength).

Water evaporation dynamics are explored by comparing CAM with soil/granular materials without binder. Dynamic water evaporation and hydraulic conductivity test results were correlated to mechanical performance through a semi-empirical model. The pore size distribution index (n) for samples was estimated based on the hydraulic conductivity tests. Results indicate a reliable relationship between internal pore distribution and water dynamics during drying. In addition, bitumen emulsion was

found to be the main component delaying the curing process of cold mix asphalt. The predictive model for CAM stability was accurate, fast and easy to use.

Prediction of cement's mechanical performance during hydration reduces construction costs. A new model based on apparent activation energy (E_a), that fits the experimental data significantly, was obtained and can be used to predict the performance to different types of cement.

CAM samples with different contents and types of cement were tested by dynamic evaporation, hydraulic conductivity, hydration and Marshall stability test. The results show that cement does not significantly shorten the drying process, while bitumen emulsion delays cement hydration. Finally, a new predictive model with accurate fit was obtained to estimate the contribution of cement hydration products to the total stability of CAM.

Detailed investigation of the impact of aggregate on curing is explored, predicting the rate of water evaporation in unbound granular materials and cold asphalt layers, with and without cement. In addition, the thesis calculates the recommended time to open roads to traffic loads. The correlation between different properties related to material gradation, microstructure and hydraulic conductivity was investigated and their effect on the dynamics of water evaporation was analysed. Among other conclusions, it was found that porosity, surface area of voids, and mean size of aggregate particles of unbound materials significantly affect the time of full drying. In addition, a predictive model was obtained, able to significantly fit the rate of water evaporation in these materials, which enables estimation of the time necessary to open roads to traffic.

Dedication

To Those Who Supported and Prayed For Me

Tahseen Diwan Saadoon

Acknowledgements

Firstly, lastly and forever, thanks be to **ALLAH** for all things which led me to the light during the critical time. Thanks be to **ALLAH** who give me patience, faith and strength during all of my life.

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In British doctoral studies, there is a major and influential exam every year, which includes overall discussion with regards to the project progress. The opinion of the examiner (internal assessor) is very important in correction and evaluation of the project in order to stay on track and improve the project. The internal assessor of my project, Dr. **Nick Thom**, had an important and clear role in evaluating the project, and he offered in-depth discussions and good scientific opinions that gave me direction in my project. My deep thanks to you today and every day.

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My family (father, mother, brothers, sisters), my wife: after **ALLAH**, my success is entirely due to your support and prayers. In brief: you are everything in my life.

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Tahseen,

30th May 2019

Declaration

The research described in this thesis was conducted at the Nottingham Transportation Engineering Centre, Civil Engineering Department, the University of Nottingham between October 2015 and September 2018. I declare that the work is my own and has not been submitted for a degree of another university.

Tahseen Diwan Saadoon,

30th May 2019

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List of Abbreviations

AFt	Ettringite
AMS	Anionic Medium-Setting
ARS	Anionic Rapid Setting
ASS	Anionic Slow Setting
ASTM	American Society for Testing and Materials
CAC	Calcium Aluminate Cement
CAM-CAC	Cold Bituminous Emulsion Mixture Replaced of limestone filler with CAC
CAM	Cold Bituminous Emulsion Mixture (With or Without Cement)
CAM-C	Cold Bituminous Emulsion Mixture With Cement
Cem	Cement
CH	Calcium Hydroxide
CMA	Cold Mix Asphalt
CMS	Cationic Medium-Setting
CRS	Cationic Rapid Setting
CSA	Calcium Sulfoaluminate Cement
CAM-CSA	Cold Bituminous Emulsion Mixture Replaced of limestone filler with CSA
C-S-H	Calcium Silicate Hydrate
CSS	Cationic Slow Setting

CT	Computed Tomography
E	Ettringite
FA	Fly Ash
FBA	Furnace Bottom Ash
G	Gypsum
GGBS	Ground Granulated Blast Furnace Slag
HL	Hydrated Lime
HMA	Hot Mix Asphalt
HWMA	Half Warm Mix Asphalt
IEC	Initial Emulsion Content
IRBC	Initial Residual Bitumen Content
MS	Medium Setting
N	Newton
CAM-N	Cold Bituminous Emulsion Mixture Without Cement
OPC	Ordinary Portland Cement
CAM-OPC	Cold Bituminous Emulsion Mixture Replaced of limestone filler with OPC
OPWC	Optimum Pre-Wetting Water Content
ORBC	Optimum Residual Bitumen Content
OTLC	Optimum Total Liquid Content
PFA	Pulversied fuel ash
PTR	Pneumatic Tyred Roller
PVC	Polyvinyl Chloride
RAP	Reclaimed Asphalt Pavement

RBC	Residual Bitumen Content
RH	Relative Humidity
ROI	Region of Interest
RS	Rapid Setting
RSC	Rapid Setting Cement
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy
SF	Silica Fume
SS	Slow Setting
w/c	Water/Cement Ratio
WFA	Waste Fly Ash
WMA	Warm Mix Asphalt

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Chapter One

Introduction

1.1 BACKGROUND

Asphalt pavements are a mixture of aggregates bound with bitumen. Modern roads are conventionally dated to the early 20th century, but bitumen pavement (asphalt) is a primordial material in road construction, having first been used in ancient Mesopotamia (Byrne, 2005). ‘Asphalt’ is from the Greek for ‘secure’, and bitumen is fundamentally used to secure pavements (i.e. roads) for users, including heavy vehicles (Soleimani, 2009). Generally, the proportion of aggregate to binder in an asphalt mass is 95:5% (Ahmad, 2011).

It is very difficult to mix bitumen with aggregate under normal conditions (at ambient temperature) because of its high viscosity. Read and Whiteoak (2003) indicated that there are three methods used for reducing the viscosity of the bitumen (i.e. increasing its liquidity):

1. The use of heating to reduce the viscosity (as in hot mix asphalt).
2. The use of petroleum solvent to make the bitumen more liquid (cutback bitumen).

3. Converting the bitumen to bitumen emulsion by emulsifying it in water (as for cold bituminous emulsion mixtures).

Additionally, Thanaya (2003) explained a fourth method, which includes foaming hot bitumen by injecting water and air at a certain pressure.

There are three basic types of bituminous pavement, depending on the method (temperature) of binding the bitumen with aggregate. Hot mix asphalt (HMA) is the most common variety of mix used in the construction of roads in most countries. HMA is manufactured at temperatures of approximately 150-190°C. Warm mix asphalt (WMA) is safer during the manufacturing process than HMA, because it uses lower temperatures (70-150°C), which also enables faster opening of roads than HMA, adding economic and logistical benefits for clients (D'Angelo et al., 2008).

The number of countries using cold mix asphalt (CMA) is increasing (Lafon, Samanos and Tyllgren, 1993). In CMA, the aggregate and binder do not need to be heated during the mixing operation, and mixing and compaction operations can be conducted at ambient temperature, making it a cheaper and more expedient method. Figure 1.1 shows the temperature distribution used in the manufacturing of bituminous pavement for the various methods described.

This research focuses on CMA, specifically cold bituminous emulsion mixtures (CAM), which consist of bitumen emulsion and aggregate, which have been in use since the 1930s in the USA (Usmani, 1997). According to Testa (1997) and James (2006), the first development of bitumen emulsion was in the 1900s. A distinguishing feature of CAM is its large water component, in addition to bitumen and aggregate.

Bitumen emulsion consists of three fundamental parts: base bitumen, water, and emulsifier (James, 2006; Salomon and James, n.d.).

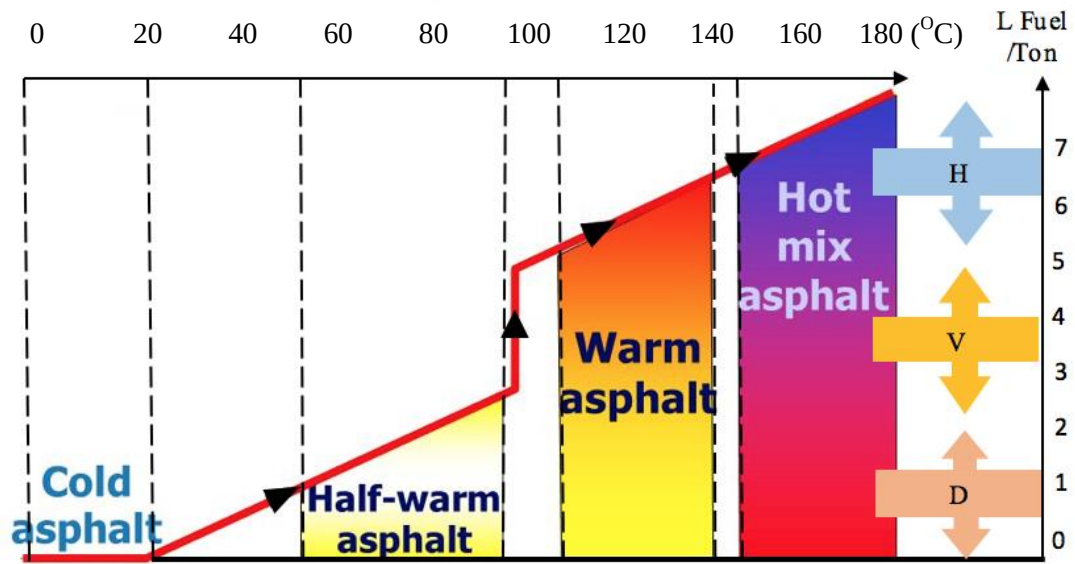


Figure 1.1 The temperature degrees to manufacture hot, warm and half warm, and cold bituminous pavement (Note: H = Heating, V = Vaporization, D = Drying) (D'Angelo et al., 2008)

There are two types of bitumen emulsion, cationic and anionic. Cationic emulsion has a positive electrical charge, $\text{pH} < 7$; anionic emulsion has a negative charge, $\text{pH} > 7$. The main distinction between them is that anionic emulsions hold more water and do not dry out easily (Dash, 2013).

Cationic and anionic emulsions come in three types: rapid setting (RS), medium setting (MS), and slow setting (SS). The setting of bitumen emulsion fundamentally depends on the amount and type of the emulsifying agent (Banerjee, De Fortier Smit and Prozzi, 2012; Dash, 2013).

CAM is similar to other types of bituminous mix (such as HMA) in its need for mixing, storage, laying and compaction during production, but CAM needs an additional stage of curing. The curing stage involves the evaporation of water/volatiles from the CAM and the beginning of setting (breaking) (Thanaya, Forth and Zoorob, 2009), which results in increased bonding among bitumen particles, and between them and other materials in CAM, such as aggregate. Therefore, curing is a fundamentally important stage in CAM performance.

Compared to the other types of construction materials used in pavements (e.g. HMA), CAM has positive impacts in terms of its environmental, economic, energy saving, and health and safety performance (Frazer, 2008; Gómez-Meijide and Pérez, 2014; Gómez-Meijide et al., 2015). However, CAM is generally restricted to the construction of the non-structural course of a pavement, and it is not viewed as a viable alternative to HMA because of weak mechanical performance, especially in its initial period (Oruc, Celik and Akpınar, 2007). This is due to the high proportion of water used in the manufacture of CAM, which remains trapped inside the structure (Robinson, 1997). This water takes a long time to evaporate completely (Read and Whiteoak, 2003), and the impact of the trapped water on CAM's mechanical performance is significant, particularly in colder climates.

From the pioneering uses of CAM to the present, many studies have aimed to improve its performance by different means in order to promote suction, absorption and consumption of water, including the use of:

1. Cementitious and/or pozzolanic materials (Kishore et al., 2008; Niazi and Jalili, 2009; Al Nageim et al., 2012; Nassar et al., 2016).
2. Different methods of curing (Jan Ebels, 2008; Müller, 2012).
3. Different methods of compaction (Jnr, 2002; Thanaya, 2007; Dash, 2013).

Since the 1970s researchers have been using cementitious materials (specifically cement) with bitumen emulsion in attempts to improve the mechanical performance of CAM. Terrel and Wang (1971) added cement to the mixes of bitumen emulsion and found that cement accelerated its performance development. Moreover, the addition of cement to CAM leads to an improvement in a number of properties of CAM, such as stiffness, compressive strength, Marshall stability, and hardness (i.e. the interfaces between cement, bitumen and aggregates become harder) (Oruc, Celik and Akpinar, 2007; Wang and Sha, 2009). On the other hand, it has negative effects, including increased rigidity (i.e. less flexibility in CAM than HMA) (Li et al., 1998). The small size of cement particles leads to quick absorption of a large quantity of water during mixing with the emulsion, and this water absorption leads to an accelerated rate of emulsion breaking. As a result, the distribution of bitumen emulsion is non-homogeneous, and does not cover the whole aggregate surface (Nataatmadja et al., 2002).

Despite numerous attempts to use different cementitious/ pozzolanic materials, compaction and curing methods to accelerate the curing and improvement of CAM performance (e.g. as presented in Appendices A1, A2, and A3), CAM still has weak final performance (high porosity), and slow development of performance in

comparison to HMA, which is the main barrier to the widespread deployment of CAM as an alternative to HMA.

1.2 PROBLEM STATEMENT

The production of CAM requires bitumen and aggregate, like other types of asphalt (e.g. WMA and HMA), but bitumen in CAM is in an elastic liquid form (bitumen emulsion), which makes mixing and compaction of CAM possible at ambient temperature. According to this feature, CAM has economic, environmental, energy saving, and health and safety advantages relative to WMA and HMA (Frazer, 2008; Gómez-Meijide and Pérez, 2014; Gómez-Meijide et al., 2015). The elastic liquid form is characterised by the uniform distribution of bitumen particles inside water, which maintains stability due to the emulsifier in bitumen emulsion (James, 2006; Salomon and James, n.d.).

Water accumulates in CAM at various phases, including water inclusion with bitumen emulsion during manufacturing, and water added to the aggregate before mixing (pre-wetting of aggregate ensures that the bitumen emulsion covers aggregate uniformly) (Thom, 2009; Lanre, 2010). Additionally, in service, water from saturated subbase layer and rain water penetrates CAM (i.e. in road applications).

Breaking of bitumen emulsion normally happens because of water loss from bitumen emulsion, due to evaporation or the hydration of cementitious materials used in the manufacture of CAM. Due to the formation of trapped water inside CAM, water takes 2-24 months to evaporate completely, thus the development of its mechanical performance is slow (Thanaya, Forth and Zoorob, 2009). Therefore, although CAM

has a number of advantageous features compared to other types of asphalt (in terms of economic, environmental, energy saving, and health and safety advantages), its practical application is limited by its drawbacks in terms of mechanical properties due to water-related issues, such as in the structural layers of roads, particularly during the early phase of curing.

Even when water in CAM has completely evaporated, usually after many months, it is characterised by high porosity (weak final strength) (Needham, 1996; Al-Busaltan et al., 2012; Yao and Sun, 2012). To accelerate drying and reduce associated CAM porosity, different methods of compaction and curing have been investigated by previous studies (see Appendices A2 and A3). Using cementitious materials in CAM increases costs and reduces environmental benefits, yet many different cementitious materials have been suggested and used by other researchers (Appendix A1). Despite such attempts, CAM still has slow development of mechanical performance, and weak final performance compared to HMA. Thus, HMA continues to be ubiquitously used in roadworks.

Previous attempts to improve CAM were inefficient due to: a lack of deeper understanding of the dynamics of water evaporation in CAM; relationships between bitumen emulsion, aggregate, and cement materials; the evaporation, moisture, and temperature profiles of CAM; and methodological issues in the correlation between laboratory and site results. These points have not been comprehensively investigated by previous studies, thus this study is necessary to discover the basic reasons for the delayed drying of CAM, and to understand why previous contributions have not yielded suitable solutions.

1.3 RESEARCH OBJECTIVES

Numerous solutions suggested to accelerate curing in CAM have failed to make CAM a viable alternative to HMA for high-intensity applications, including the use of cementitious materials and new techniques of curing and compaction. CAM still takes much longer to be ready for traffic due to its relatively inferior mechanical performance. This is due to a lack of full understanding of the curing of CAM (e.g. movement and distribution of water, and temperature profile in CAM), the effects of bitumen emulsion and aggregate on drying, and the impacts of suggested solutions (e.g. cementitious materials) on the dynamics of water evaporation. Given these considerations, the purpose of this project is to understand and predict the curing process on surfaces built of CAM and the effect of the previous solution (specifically the use of cementitious materials) on this process. This main aim will be achieved from the following objectives:

Understanding the dynamics of water evaporation in cold asphalt mixtures

- In order to assess this, the project studies: (1) evaporative flux evolution, (2) liquid phase distribution, (3) dominant mechanisms supplying and controlling the drying rate, and (4) effect of grain and pore size distributions on drying behaviour

Investigating the effect of components of cold asphalt mixtures (bitumen emulsion, aggregate) on the curing process of CAM

- It is unclear how these components affect the dynamics of water evaporation during drying. Therefore, this objective seeks to understand whether delayed

evaporation in CAM is mainly attributable to bitumen emulsion or aggregate, and to assay the nature and extent of this delay. This is achieved by studying the water evaporation dynamics in CAM outlined above (under the previous objective) and with regard to unbound materials, in order to compare these dynamics.

The role of cementitious materials in the curing behaviour of cold asphalt materials

- Most previous investigations adopted cementitious materials as the natural choice to accelerate CAM curing, but resultant mixes needed longer curing time to achieve traffic-bearing capacity (compared to HMA). Therefore, this objective investigates why cementitious materials do not accelerate CAM curing as desired, and their actual impacts on water evaporation dynamics and mechanical performance. The effect of cementitious materials is studied and compared in terms of the dynamics of water evaporation and mechanical performance in CAM with and without cement (of different types and quantities).

Prediction of the characteristics of CAM during the curing process in CAM

- Normally the characteristics of CAM are measured by casting and testing samples in laboratory or site settings, entailing significant time, economic resources, and effort; these costs can be reduced by the prediction of the performance of CAM. Many statistical models can be devised and developed for these purposes, including to predict: the dynamics of water evaporation

(rate of water evaporation, depth of dry layer, capillary action length, and pore size distribution); mechanical performance of CAM; and the time required to open road surfaces built with CAM.

1.4 THESIS OUTLINE

Chapter One: Introduction

This chapter presents the background of the research topic, identifies the research problem, and delineates the objectives of the study. The methodology is outlined with the rationale and steps undertaken in order to conduct the research, and a list of publications associated with this research is presented.

Chapter Two: Literature Review

Chapter two critically reviews previous literature concerning CAM, especially its benefits, problems, composition, mix design, manufacturing, fillers (mineral admixtures), and previous attempts to improve its performance. It also explores the dynamics of water evaporation in porous media. Finally, suggestions to understand and accelerate the curing of CAM are mentioned.

Chapter Three: Methodology and Materials

This chapter explains the experimental work undertaken to achieve the research objectives, detailing the materials used (e.g. bitumen emulsion, aggregate, cement, and water) and explaining the laboratory tests conducted for the required properties (e.g. weight loss, temperature and moisture profiles, Marshall stability, compressive strength, hydraulic conductivity, porosity, hydration, X-ray computed tomography (CT) scans, and scanning electron microscopy (SEM) tests). Setups of tests are also

explained, alongside procedures, and specimen preparation (e.g. proportions of materials, mixing, compaction and curing).

Chapter Four: Dynamics of Water Evaporation in Cold Asphalt Mixtures

This chapter discusses the dynamics of water evaporation during CAM curing and relates them to the acquisition of mechanical properties, with particular emphasis on evaporative flux evolution, liquid phase distribution, dominant mechanisms supplying and controlling the drying rate, and the effect of grain and pore size distributions on drying behaviour.

The experimental work in chapter four includes making samples of aggregate with different sizes (with and without bitumen emulsion). The study of the dynamic of water evaporation includes evaporation properties, moisture and temperature profiles, hydraulic conductivity and porosity. In addition, the stability of CAM is studied relative to changes in its structure over time, therefore hydraulic conductivity and porosity of CAM are investigated longitudinally, while unbound materials were tested at one time. Theoretical considerations are addressed in this chapter. Moreover, models to predict the dynamics of water evaporation of CAM/unbound materials are explained. The mechanical performance of CAM was predicted from the model developed and presented in this chapter.

Chapter Five: New Predictive Methodology for Apparent Activation Energy and Strength of Conventional and Rapidly Hardening Concretes

The main aim of this thesis is to understand and accelerate the curing of CAM; one of the secondary aims related to this is investigating the affect of different types of

cement on CAM performance. Therefore, chapter five aims to study and predict the performance of cement concrete, and the resultant data presented in this chapter then provides the basis for subsequent investigations on the affect of cement on CAM performance, presented in subsequent chapters.

Compressive strength and scanning electron microscopy (SEM) tests were carried out on cement concrete samples over time, at different curing temperatures. As in chapter four, theoretical considerations are addressed in this chapter, and the apparent activation energy and mechanical performance of the cement concrete are calculated. The results of this part are used to: investigate the influence of temperature on microstructure and the mechanical performance of concrete made with different types of cement; calculate the apparent activation energy of the normal and rapid hardening cement; and create innovative models to predict the apparent activation energy of cement, and the mechanical performance of cement concrete.

Chapter Six: Prediction of Water Evaporation and Stability of Cold Asphalt Mixtures Containing Different Types of Cement

The objective of chapter six is to identify the effect of cementitious materials on water evaporation dynamics and CAM mechanical performance by testing evaporation properties, temperature and moisture profiles, Marshall stability, hydraulic conductivity, porosity, and hydration. Three types of cement with different quantities were used to manufacture the CAM samples tested in this chapter. The chapter presents the results of normal CAM (without cementitious materials, from chapter four) and the results of energy activation of cementitious materials (from chapter five).

Comparing the results of CAM with and without cementitious materials enables understanding the effect of cementitious materials on CAM characteristics (particularly the dynamics of water evaporation and mechanical performance). In addition, the mechanical performance of cement in CAM samples was predicted by the developed model.

Chapter Seven: A General Model to Predict the Time Required to Open Road Surfaces Built of Cold Asphalt Mix

Chapters four and six categorise water evaporation rates in three stages and note that the gradation of aggregate affects the rate of water evaporation; their results are related to the analyses of porosity and CT scans presented in chapter seven. Based on this, correlations between properties of the dynamics of water evaporation and hydraulic, topological, and gradation parameters are investigated in this chapter, discovering the effect of the gradation of aggregate, microstructure of voids, and hydraulic properties on the time of full drying, to identify specifications of aggregate gradation that promote faster drying. Moreover, a model to predict the evaporation rate at every stage of evaporation is presented in the chapter, and another model to predict the necessary time to open roads to traffic loads.

Chapter Eight: Conclusions and Future Work

Conclusions and recommendations based on the results of the current work are expounded in this chapter, and areas for future work based on this thesis are suggested.

1.5 PUBLICATIONS LIST

The majority of findings obtained in this project have been published, accepted for publication, are under review or are to be submitted, as follows:

➤ **Journal papers:**

1. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2017). Dynamics of water evaporation in cold asphalt mixtures. **Materials & Design**, 134, pp.196-206.
(Published)
2. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2018). New predictive methodology for the apparent activation energy and strength of conventional and rapid hardening concretes. **Cement and Concrete Research**, 115, pp. 264-273. **(Published)**
3. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2018). Prediction of water evaporation and stability of cold asphalt mixtures containing different types of cement. **Construction and Building Materials**, 186, pp.751-761.
(Published)
4. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2018). A general model to predict the time required to open road surfaces built of cold asphalt mix. **(To be submitted)**

➤ **Conference papers:**

- I. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2018). Fundamental study of water evaporation in cold asphalt mixture. **International Society for Porous Media, INTERPORE**, 14-17 May 2018, New Orleans, USA. **(Accepted and presented as poster).**

- II. Saadoon, T., Garcia, A. and Gómez-Meijide, B. (2018). Effect of bitumen emulsion and cement on the drying potential of cold asphalt mixtures. **1st International Conference on Sustainable Mega Infrastructures - SMI 2018 and the 3rd International Conference on Sustainable Construction Materials: Design, Performance and Application, SMI2018 SCM2018**, 10-11 August 2018, Wuhan, Hubei, China. **(Published).**

Chapter Two

Literature Review

2.1 INTRODUCTION

This chapter reviews literature concerning types of bituminous pavement, with particular emphasis on cold bituminous emulsion mixtures (CAM), in terms of their benefits, problems, composition, mix design, manufacturing, fillers and the previous attempts to improve the performance of CAM by filler. It also explores chemical admixtures and evaporation in a porous medium (CAM), suggesting developments to improve the performance of CAM.

2.2 BITUMEN PAVEMENT

2.2.1 Background

Bituminous pavement is a mixture of aggregate and binder (bitumen), the latter of which binds the aggregate together. Generally, the proportion of aggregate and binder in bitumen by mass is 95:5%, respectively (Ahmad, 2011). Bituminous pavement has the ability to resist stress because of its flexibility, and its function as a flexible pavement is the main reason for its use (Needham, 1996).

There are three main types of bituminous pavement, depending on the method (temperature) of binding the bitumen with aggregate (EAPA, 2016): Hot Mix Asphalt (HMA), Warm Mix Asphalt (WMA) and Half Warm Mix Asphalt (HWMA), Cold Mix Asphalt (CMA). Figure 2.1 explains the distribution of temperature used in the manufacturing of the bituminous pavement for the various methods described.

2.2.2 Cold Mix Asphalt (CMA)

The number of countries using CMA is increasing (Lafon, Samanos and Tyllgren, 1993). In CMA the aggregate and binder do not need to be heated during the mixing operation in this type of bitumen, and mixing and compaction operations can be conducted at ambient temperature, making it a cheaper and more expedient method.

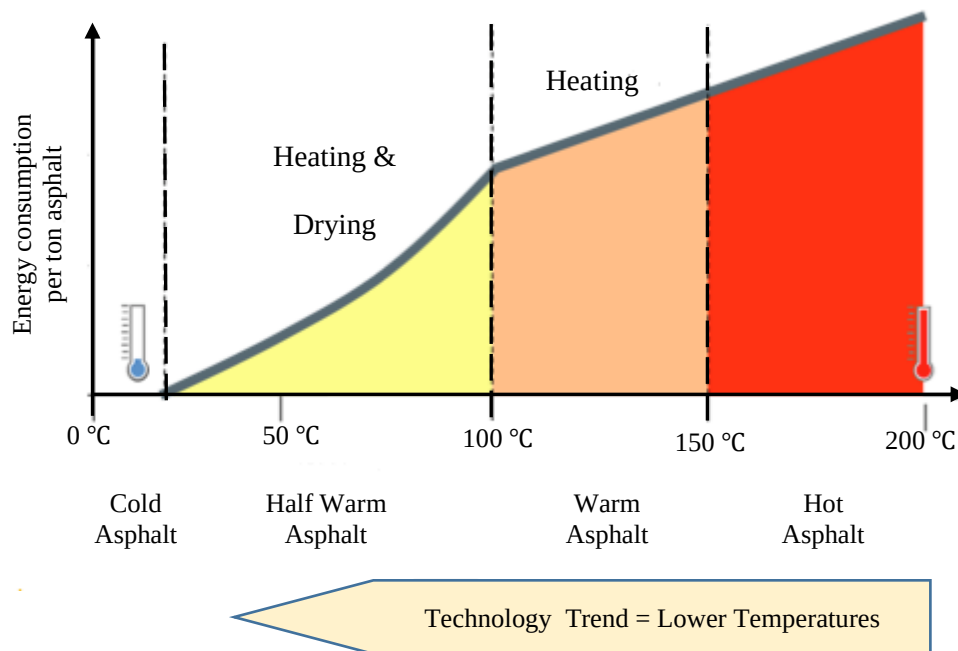


Figure 2.1 The temperature degrees to manufacture the hot, warm and half warm, and cold bitumen pavement (EAPA, 2016)

It is possible to classify cold bituminous mixtures into two types depending on the ability of storage (Needham, 1996):

1. The first type contains a binder (cut-back or fluxed bituminous emulsions) and solvent that keeps the softening of the binder, so this mixture is named a storable or workable mixture.
2. The second type contains emulsion, but is non-fluxed, so this mixture will become stiffer after removing the water in the mixture. This mixture is named non-storable cold mix or cold bituminous emulsion mixture.

2.3 COLD BITUMINOUS EMULSION MIXTURE (CAM)

CAMs have been used in the world for many years; they have been used continuously in the US since the 1930s (Usmani, 1997).

2.3.1 Benefits of CAM

CAMs have a positive effect on the environment, economy, energy saving, safety and health compared to the other types of asphalt.

CAM is more energy efficient than HMA (Oruc, Celik and Akosy, 2006; Thanaya, Forth and Zoorob, 2009; Wang and Sha, 2009; Bouteiller, 2010; Lanre, 2010). Raw materials (bitumen emulsion and aggregate) used in CAM do not need to be heated up. In addition to this, the aggregate must be damp before use, and the mixing process can be conducted at normal air temperature (James, 2006; Lesueur, 2011; Ojum, 2015). Moreover, recycled or waste materials can be used in CAM, without the need for virgin raw materials taken from natural resources (Thanaya, 2003). CAM contributes positively to improving the environment by reducing CO₂ emissions from the bitumen and the other materials used in the industry (Needham, 1996; Wang, and

Sha, 2009; Bouteiller, 2010; Lanre, 2010; Lesueur, 2011). Bouteiller (2010) stated that the carbon footprint of hot bitumen is 21 kg per ton, compared to only 3 kg for cold bitumen.

Health risks resulting from the use of CAM are much less dangerous than with the use of HMA, such as the risk of skin burns (Thanaya, 2003; Wang, and Sha, 2009; Bouteiller, 2010). In addition, bitumen emulsion is non-flammable (Thanaya, 2003). The cost efficiency of CAM is a major factor in its widespread and increasing use, which reflects its low energy requirement during manufacture. Along with the related environmental benefits and its health and safety advantages, it also exhibits good functional performance (Sjoblom, 2005).

2.3.2 Problems of CAM

In addition to their advantages, CAMs have some disadvantages, mainly due to water issues, as described below.

1. There is a high chance of CAM being non-homogeneous because of one or both of the following reasons:
 - Incompatibility (electrical charge) between bitumen emulsion and aggregate leads to weak bonding (Robinson, 1997; Masson and Lacasse, 1999).
 - The thickness of binder film around coarse aggregate is less than the fine aggregate, because the surface area of the latter is larger, attracting the most bitumen emulsion, with an uneven (low) quantity attracted towards the coarse aggregate (Robinson, 1997).

2. High voids and porous content after full compaction (Robinson, 1997; Thanaya, Forth and Zoorob, 2009; Lanre, 2010).
3. To achieve the required performance, CAM need a long time to complete curing (evaporation of water / volatiles and start with the setting) (Needham, 1996; Robinson, 1997; Read and Whiteoak, 2003; Oruc, Celik and Akpinar, 2007; Thanaya, Forth and Zoorob, 2009; Ojum, 2015).
4. Weakness in mechanical properties, especially during early ages (Needham, 1996; Robinson, 1997; Read and Whiteoak, 2003; Oruc, Celik and Akpinar, 2007; Thanaya, Forth and Zoorob, 2009; Lanre, 2010).
5. Impairment in durability properties (Needham, 1996; Robinson, 1997; Read and Whiteoak, 2003; Oruc, Celik and Akpinar, 2007; Lanre, 2010).
6. High water sensitivity leads to stripping of aggregate, especially in early days (Needham, 1996; Robinson, 1997; Read and Whiteoak, 2003; Oruc, Celik and Akpinar, 2007; Thanaya, Forth and Zoorob, 2009; Lanre, 2010).
7. Poor cohesion or adhesion between the components of CAM during early days (Robinson, 1997).
8. The flow of bitumen emulsion during the storage due to low viscosity (Robinson, 1997).

2.4 CONSTITUENTS OF CAM

2.4.1 Bitumen emulsion

A- Background of bitumen emulsion

Generally, it is very difficult to mix bitumen with aggregate in normal conditions (ambient temperature) because of the high viscosity of the former, thus it is necessary to reduce the viscosity of the bitumen if using bitumen in the pavement at ambient temperature. Read and Whiteoak (2003) indicated that there are three methods used for reducing the viscosity of the bitumen (i.e. increasing its liquidity):

1. The use of heating to reduce the viscosity (as in the hot mix bitumen).
2. The use of petroleum solvent to make the bitumen more liquid (cutback bitumen).
3. Converting the bitumen to bitumen emulsion by emulsifying it in water (as for cold bitumen emulsion mixtures).

In addition to the above methods, Thanaya (2003) explained that there is a fourth method which is foaming the bitumen. This research will use bitumen emulsion in cold mix asphalt as a binder material, thus it is necessary to focus on the description of bitumen emulsion.

B- The history of bitumen emulsion

According to Testa (1997) and James (2006), the first development of bitumen emulsion was in the 1900s. Le Coroller (1999), Read and Whiteoak (2003) indicated that bitumen emulsion was applied in spray sealing and dust palliatives by 1906, however the first major use of bitumen emulsion in pavement construction was

pioneered during the 1920s by two English chemists, Hugh Alan Mackay and George Samuel Hay (COLAS, 2016). At that time there were limited types of bitumen emulsion available, and few people with knowledge and skill in its use, but it quickly developed and its use increased in the construction of roads in general (James, 2006).

C- Components of bitumen emulsions

There are many major and minor components used in the manufacture of bitumen emulsion.

➤ *The main components of bitumen emulsion*

Bitumen emulsion consists of three fundamental parts: base bitumen, water and emulsifier (James, 2006; Salomon and James, n.d.).

❖ *Base Bitumen*

Base bitumen is the basic ingredient in cold bituminous emulsion mixtures, and its proportion depends on the expected use of the emulsion. In most types, the bitumen content ranges from 40-70% of the bitumen emulsion (Thanaya, 2003; James, 2006; Senadheera et al., 2011; Salomon and James, n.d.). There is an upper limit to the bitumen content depending on the relative volume ratio to the water and bitumen. Near the upper end of this limit, space becomes insufficient for more bitumen particles, accelerating the coalescence of the emulsion (Thanaya, 2003; Atif, 2006).

The hardness of the bitumen used in bitumen emulsion ranges from 60-250 penetration, weather conditions may necessitate harder or softer bitumen (Lanre, 2010). For example, in hot weather it is required to use bitumen emulsion with hard base bitumen (Thanaya, 2003). The quality of bitumen has an effect on the properties

of the bitumen emulsion (Thanaya, 2003), whose stability is affected by the chemical compatibility between the emulsifying agent and bitumen (James, 2006).

❖ *Water*

Water occupies 30-60% of the total mass of the bitumen emulsion (James, 2006; Senadheera et al., 2011). James (2006) stated that water has an effect on the final required properties, so it cannot be reduced. Moreover, the water must be chosen carefully because impurities can have a negative effect on the quality of bitumen emulsion.

❖ *Emulsifying agent*

The proportion of emulsifying agent ranges from 0.1-2.5% of the mass of bitumen emulsion (James, 2006; Lanre, 2010; Senadheera et al., 2011). Emulsifying agent is used for the purpose of maintaining the particles of bitumen scattered uniformly in all parts of a mixture of bitumen emulsion, whereby the absence of emulsifying agent will lead to the separation of water from the bitumen and forming of two layers, one of water and the other of bitumen (James, 2006), and as shown in Figure 2.2.

Emulsifier consists of a hydrocarbon chain, which includes a anionic or cationic end. These emulsifiers cluster around the bitumen particles and stick to them; every particle of the bitumen will be surrounded with a number of emulsifier particles, thus the number of the latter is always more than that of the former. The emulsifier forms a cover surrounding the bitumen particles and thus prevents the coalescence of bitumen particles. Moreover, every emulsifier molecule has two portions, the oil-loving (hydrophobic or lipophilic) and the water loving (hydrophilic or oleophobic). The hydrophilic portion is in the water zone and the hydrophobic is in the bituminous zone. The bitumen particles are bigger than the emulsifier molecules (ANON, 2016).

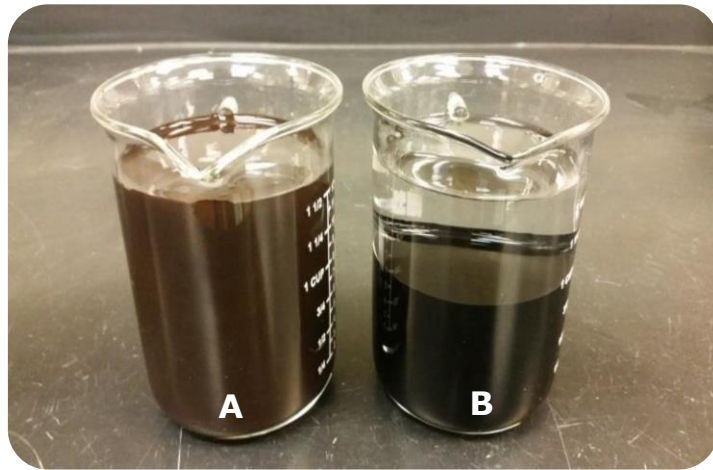


Figure 2.2 The effects of emulsifiers on the mixture of water and bitumen. (A): Bitumen emulsion (Water and bitumen with emulsifier); (B): Water and bitumen without emulsifier (Shoger, 2016)

The emulsifying agent is a surface active agent that provides the bitumen particle with electrical charges on its surface (Lanre, 2010). Bitumen emulsions are classified into three types according to the type of charge: cationic bitumen emulsion, in which the particles are charged positively; anionic bitumen emulsion, which has a negative charge on the surface of the bitumen droplets; and non-ionic bitumen emulsion, which does charge at the surface of bitumen particles (James, 2006; Dash, 2013); a fourth type, clay-stabilised bitumen emulsion, was added by Read and Whiteoak (2003).

Cationic and anionic emulsifiers are the main types used (AEMA, 2010; Lanre, 2010). The letter (C) in front of bitumen emulsion refers to cationic emulsion, while the absence of (C) denotes anionic emulsion (Lanre, 2010; Tia, 2012; Grummoorthy, 2013). The pH (alkalinity or acidity) in the system determines the electrical charge of the emulsifier. Cationic emulsifier has a positive electrical charge, $\text{pH} < 7$, and acidic emulsion; while anionic emulsifier has a negative charge, $\text{pH} > 7$, and alkaline emulsion. An emulsion with cationic and anionic emulsifiers simultaneously would

cause the bituminous droplets to coagulate due to the incompatibility of these emulsifiers (Thanaya, 2003).

Figures 2.3 and 2.4 explain the production of cationic emulsifiers and anionic emulsifiers respectively. Moreover, the structures of bitumen emulsion containing cationic and anionic emulsifier are shown in Figures 2.5 and 2.6, respectively.

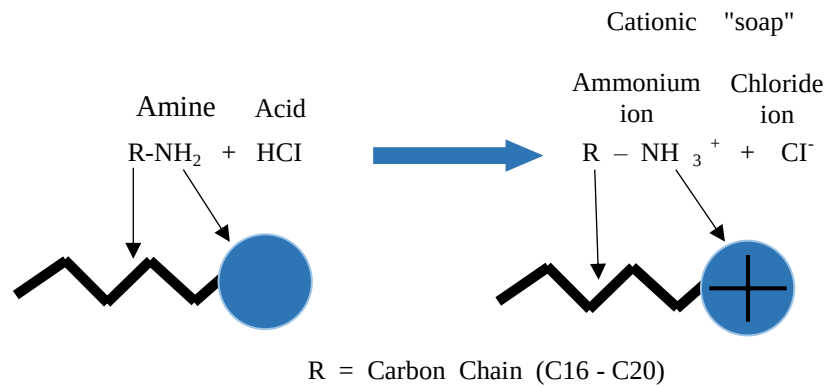


Figure 2.3 Cationic emulsifying agent (Salomon, 2006)

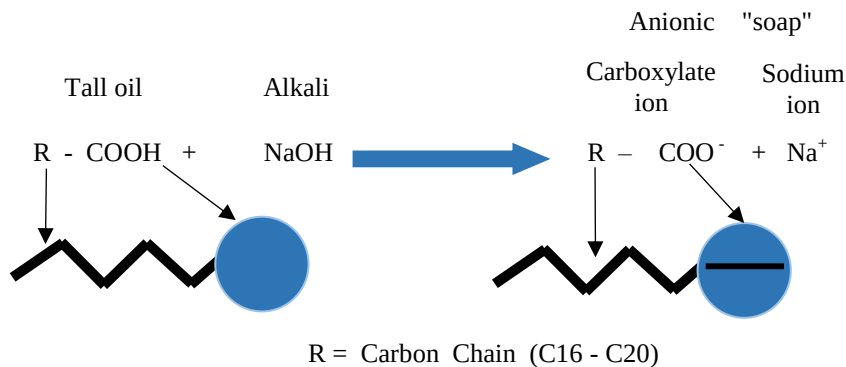


Figure 2.4 Anionic emulsifying agent (Salomon, 2006)

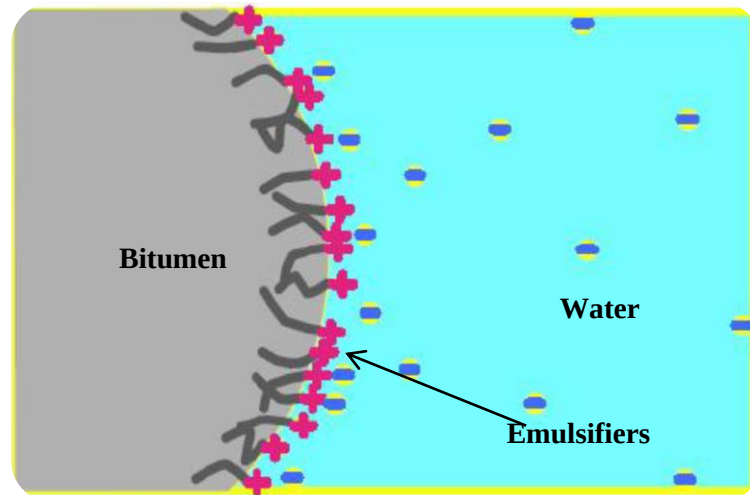


Figure 2.5 Structure of cationic bitumen emulsion (Salomon, 2006)

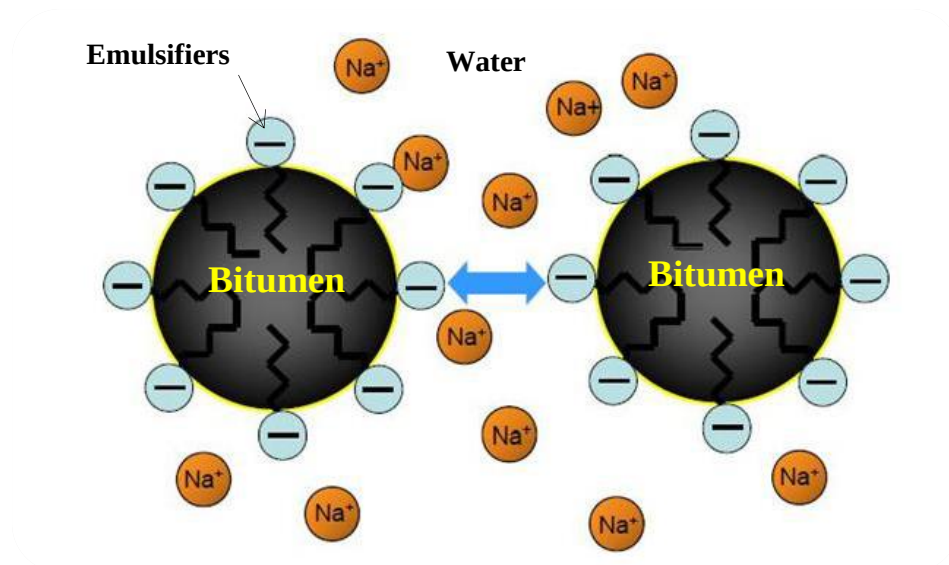


Figure 2.6 Structure of anionic bitumen emulsion (Salomon, 2006)

➤ *The secondary components of bitumen emulsion*

There are secondary compounds used in the manufacturing of bitumen emulsion in addition to the main compounds, some of which are explained below.

❖ *Stabilizer*

It is possible for the base bitumen to contain some salts, which leads to the swelling of the bitumen particles because of osmotic action on water. As a result, the stability of the emulsion will be affected due to increasing the emulsion viscosity. Therefore, stabilizers are used in order to reduce the negative effects of salts (Thanaya, 2003; Atif, 2006; James, 2006).

❖ *Acids*

The pH in the emulsion must be at the required level. Therefore, some acids are used in the manufacture of bitumen emulsion in order to keep the pH at the desired value (Thanaya, 2003).

D- Manufacture of bitumen emulsions

As explained previously, bitumen emulsion consists mainly of base bitumen, water and emulsifier in addition to other minor components. These components are used in the manufacturing of bitumen emulsion using either the continuous or batch method, as shown in Figure 2.7, but the continuous method is more common, therefore it is explained in detail below.

Akzo Nobel (2008) stated, the continuous method includes the colloid mill and other machines used in the manufacturing of the bitumen emulsion. There is a minimum of two main stages included in the continuous method:

- In the first stage, water is heated and mixed properly with the emulsifier and other chemical materials.
- The final stage includes pumping the bitumen and the mixture prepared in the first stage to the colloidal mill machine, after which the mixing process starts

with materials in the same machine. The result of the mixing is the bitumen emulsion, as shown in Figure 2.7.

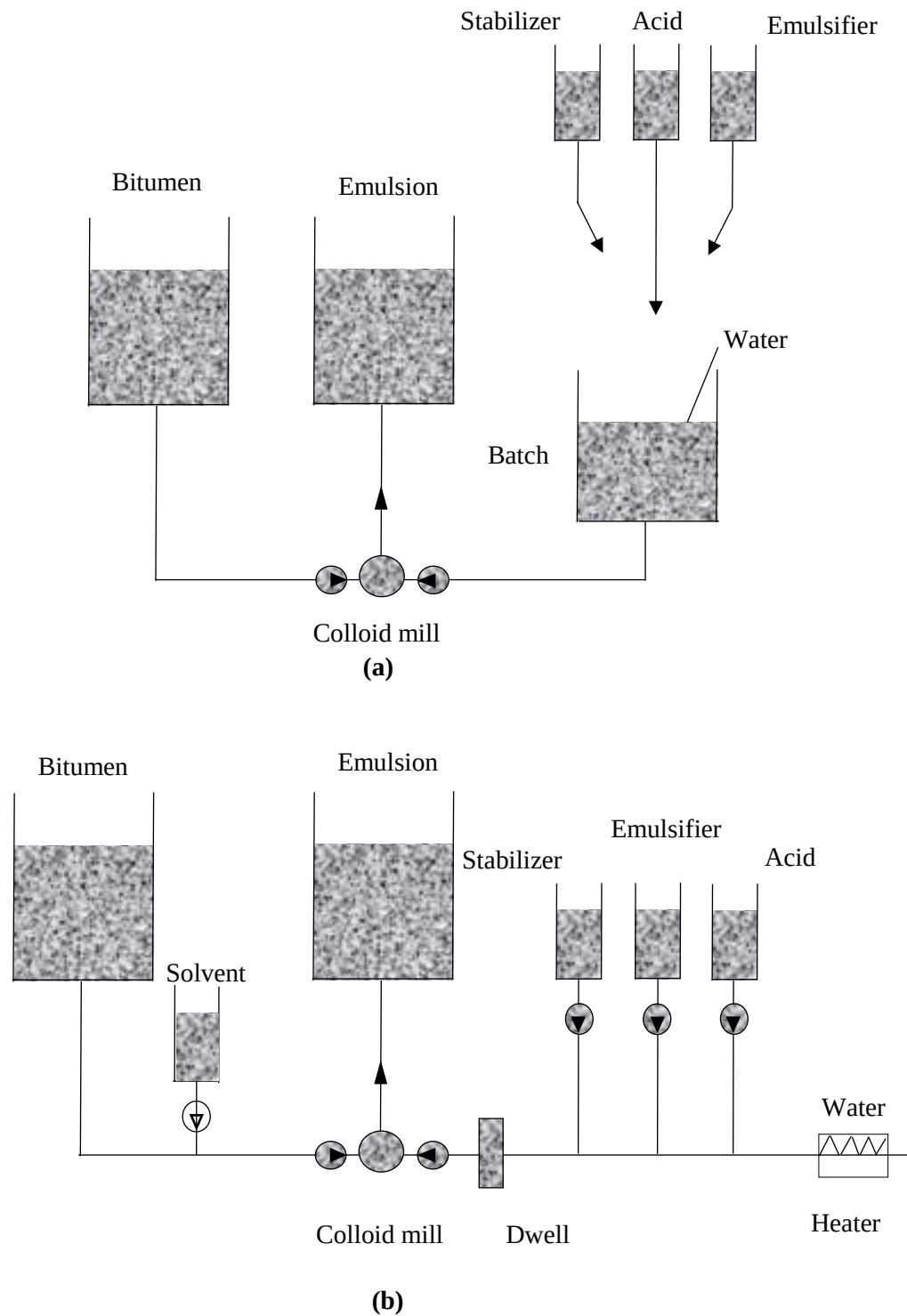


Figure 2.7 The continuous (a) and batch (b) methods used in the manufacture of bitumen emulsion (IRC, 2014)

E- Classification of the bitumen emulsions

The standard specifications and researchers have classified bitumen emulsion into many types depending on the rate of breaking (i.e. the rate at which the water separates from the bitumen). Figure 2.8 explains the mechanism of breaking the bitumen emulsion.

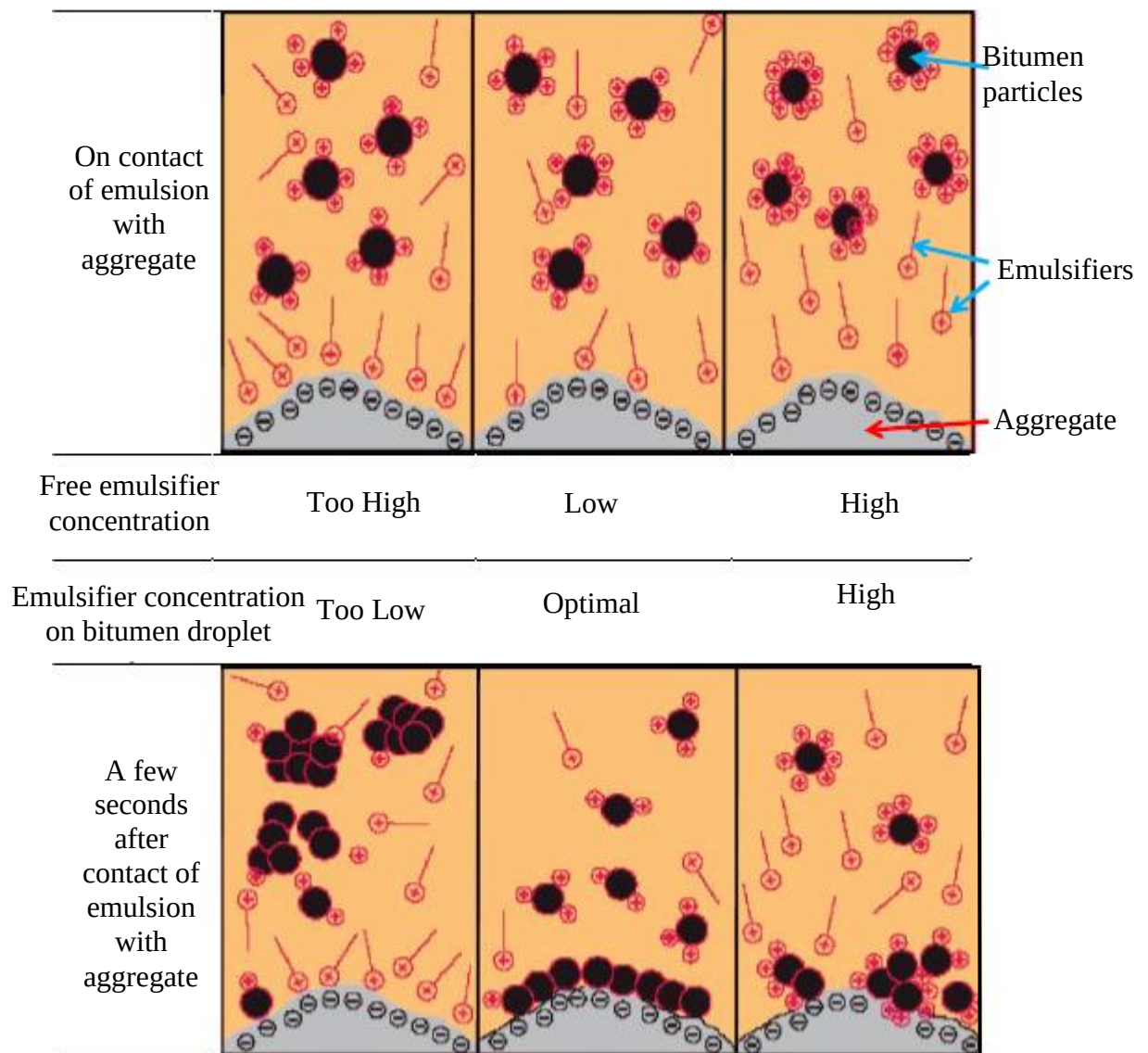


Figure 2.8 The breaking of bitumen emulsion (as example of cationic bitumen emulsion) (Jan Ebels, 2008)

Cationic and anionic emulsion are divided into secondary types depending on the rate of setting into rapid setting (RS), medium setting (MS), and slow setting (SS), as shown in Table 2.1. The setting of bitumen emulsion fundamentally depends on the amount and type of the emulsifying agent (Banerjee, de Fortier Smit and Prozzi, 2012; Dash, 2013). The primary distinction between cationic and anionic emulsions is that the latter surrender water less readily than the former (Dash, 2013).

Table 2.1 Classification of bitumen emulsion depending on the rate of setting (AEMA, 2010; Ojum, 2015)

Setting Mode	Symbol	
	Anionic	Cationic
Rapid Setting	ARS	CRS
Medium Setting	AMS	CMS
Slow Setting	ASS	CSS

Rapid setting emulsion has low or non-ability to mix with the aggregate in the mixture. The medium setting emulsion can be mixed with coarse aggregate, but not with fine aggregate. The slow setting emulsion has the ability to mix with fine aggregate (Lanre, 2010).

AEMA, (2010) confirmed that emulsions used in spray sealing must break quickly to prevent negative responses like run-off and rain damage, but in use to stabilise soil, the emulsion must break slowly to enable sufficient time for mixing.

A- Considerations in selecting the type of bitumen emulsion

According to AEMA (2010), the following are the main factors in choosing the suitable bitumen emulsion: the aggregate specification (type, gradation and

availability); the weather conditions (temperature, humidity, wind, rain); the machines used in construction; the site from a geographical perspective; the control of traffic; and considerations related to the environment.

B- Factors influencing the performance of bitumen emulsion

Bitumen emulsion is considered a sensitive material because of the many factors with effects on its performance. These factors can be understood as described below (AEMA, 2010).

❖ Materials

- Bitumen (hardness, quantity, chemical properties, and size of the particles).
- Emulsifier (properties of the emulsifier, type, concentration).
- Water (quality).
- Additives (like polymer or chemical modifier).

❖ Manufacturing

- The order of the addition of ingredients.
- Pressure, temperature and shear during manufacturing.
- The equipment type utilised in the manufacturing.

❖ The quantity of emulsion in the mixture

C- World consumption of bitumen emulsion

There has been a constant increase in the use of bitumen emulsion worldwide, reaching 7 million tons per annum. The production of bitumen emulsion in many

countries is shown in Appendix A4 (Le Coroller, 1999). Moreover, 3-34% of bitumen was consumed in the manufacturing of the bitumen emulsion. France produces about 50% of total bitumen production in Europe (EAPA, 2016). Many applications use bitumen emulsion, traditionally because of this functional property, and increasingly because of its environmental and economic benefits, along with its ease of use. Appendix A5 explains the main fields using bitumen emulsion.

D- The tests of bitumen emulsion and bitumen residue

All construction materials should be tested before use to verify their safety and functional ability according to required specifications; bitumen emulsion has been exposed to many tests, some of which are stated in Appendix A6 (AEMA, 2004).

2.4.2 Aggregate

Generally, CAM is a mass of aggregate and binder (bitumen emulsion). The aggregate occupies approximately 95% of the mass of CAM, while the remaining 5% mainly comprises the bitumen emulsion (Ahmad, 2011). Therefore, the properties of aggregate play an important role in determining the properties of CAM (Ahmad, 2011; Naidu and Adishesu, 2013).

i- The properties of aggregate

The physical properties of aggregate, such as gradation, surface texture and shape, have an effect on the amount of binder (bitumen emulsion) used. Moreover, physical properties affect the amount of pre-wetting water used to moisten the aggregate before mixing with bitumen emulsion; therefore, there are affects on the quantity of water in CAM. As a result, there are effects on the performance of the mixture (CAM). The

more rough the surface of the aggregate, the more adhesive the bonding between the aggregate and the bitumen (Ahmad, 2011; Naidu and Adishesu, 2013).

The aggregate material has a composition of inorganic polar compounds. The main source of aggregate is rocks; thus the properties of the aggregate vary depending on the type and source of these rocks. The chemical properties of the surface of the aggregate are considered influential on the adhesion and compatibility between aggregates and binder (bitumen emulsion). Some types of aggregate are basic (e.g. limestone), while others are acidic (e.g. quartzite). The content of silica and carbonate can change the nature of aggregate; for example, increasing the silica content causes increased acidity (reduced pH), while enhancement of the content of carbonate has the opposite effect (i.e. reduce of acidity and increased the basic in aggregate) (Tarrer and Wagh, 1991; Ahmad, 2011).

ii- Impurities in the aggregate

The aggregate may contain impurities between or around particles that lead to problems in the structure of the mixture. For instance, clay particles will increase in volume when they absorb water, therefore acting as a barrier between the binder and aggregate, resulting in weak adhesion. Furthermore, the expansion of clay applies internal pressure of the mixture and contributes to deterioration (Ahmad, 2011).

2.5 FILLER

Filler is part of aggregate and a component of the bitumen mixture in addition to the binder and the other aggregate parts (fine and coarse). The quantity of filler in the mixture depends on the binder quantity, and filler-to-bitumen ratios range from 1-1.5 by mass (Thanaya, 2003 cited that Zoorob, 2000). Most materials in the filler pass a 0.063 mm sieve (Nikolaides, 2015). The function of filler varies from one type to

another, depending on chemical composition, surface area of filler particles (fineness) or size of filler particles. A previous study classified filler in cold bituminous mixtures as reactive and non-reactive (Thanaya, 2003) cited that (Zizi, 1997). Reactive filler has the ability to interact chemically with water in bitumen emulsion, and any other water (e.g. water used in wetting the aggregate) in the CAM. Conversely, non-reactive filler does not have the ability to interact with water (the water in bitumen emulsion, and any other water). Cement and silica fume are examples of reactive and non-reactive fillers (respectively) (Thanaya, 2003).

2.5.1 The relation among reactive, non-reactive filler and water

The reactive filler has two effects on the microstructure of mixtures containing water:

- (a) The chemical effect, which happens when there is a connection between the water and the reactive filler. This connection leads to a chemical reaction (the hydration interaction) between them, which produces bonding materials (C-S-H gel and Ca(OH)_2), as shown in Figure 2.9. As a result, the products of hydration contribute to enhance the bonding among the aggregate particles, increasing the ability of waterproofing in the mixture (Mier, 1997; Taylor, 1997; Rendell, Jauberthie and Grantham, 2002; Lamond and Pielert, 2006; Protus, 2014).
- (b) The physical effect, which occurs when the connection between the water and the reactive filler does not happen because of the lack of water, or the amount of water being insufficient (e.g. consumed by some particles of reactive filler), or the water not reaching some of the reactive filler due to a lack of permeability in the mixture. In this case, hydration interaction will not occur and reactive filler works as very small aggregate particles in the mixture; as a result, the filler particles help to fill pores and voids in the aggregate

gradation, thus reducing the porosity and permeability of the mixture (Mier, 1997; Lamond and Pielert, 2006).

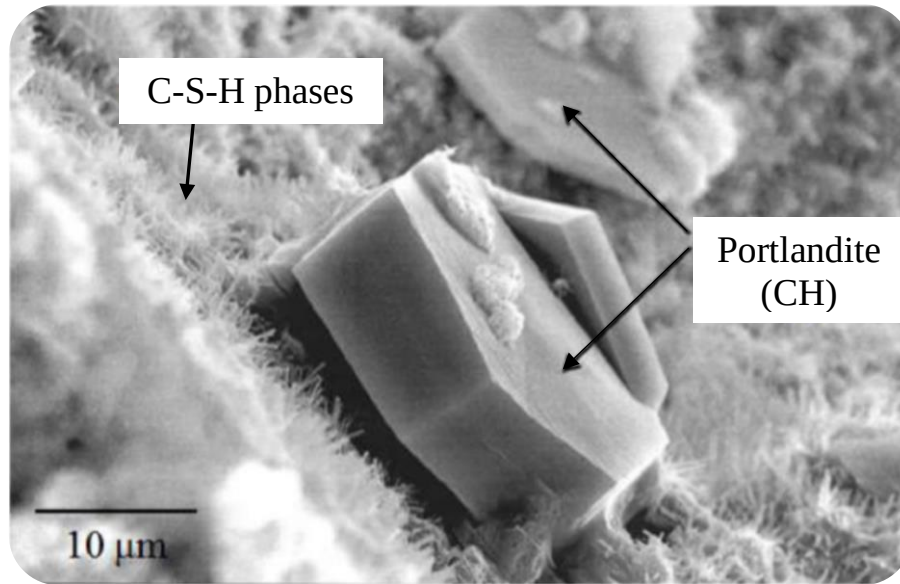
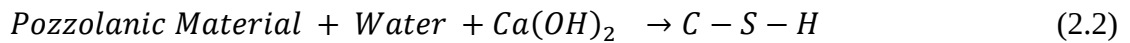
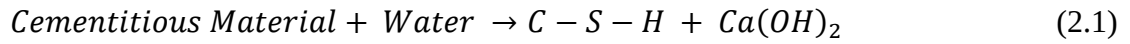


Figure 2.9 Products the hydration of the cement (Lummer, 2010)

At the same time, the non-active filler has a physical effect, whether or not there is a connection between the water and the non-reactive filler. It will fill the pores and voids between the aggregate particles and improve the performance of the mixture as the physical effect of reactive filler (Mier, 1997). However, the non-reactive filler can become reactive when mixed with water and reactive filler at the same time. Moreover, the non-reactive filler will interact chemically with water and calcium hydroxide (Ca(OH)_2) (one of products the interaction between water and reactive filler). As a result, Ca(OH)_2 will interact with non-reactive filler and water and produce calcium silicate hydrate (C-S-H) (Frías, de Rojas and Cabrera, 2000; Rendell, Jauberthie and Grantham, 2002; Siddique and Khan, 2011). Equation 2.1 explains the interaction (the hydration interaction) between water and reactive filler (e.g.

cementitious materials) (Taylor, 1997). Equation 2.2 presents the pozzolanic interaction among water, Ca(OH)_2 and non-reactive filler (e.g. pozzolanic materials) (Shi and Day, 2000; Poon et al., 2001).



2.5.2 The benefits of non-reactive and reactive fillers in the manufacture of CAM

Use of non-reactive and reactive fillers in the production of CAM has numerous positive effects, as described below.

❖ *Performance*

As shown previously, the use of non-reactive filler (e.g. silica fume), reactive filler (e.g. cement) and water has positive effects (improved performance) on the structure of CAM:

(a) The interaction (hydration) between the reactive filler with water leads to improved performance of CAM through the production of new bonding materials (C-S-H and Ca(OH)_2) in addition to the binder of bitumen; and it accelerates the curing process through the use of some water found in the internal structure (used for the hydration of reactive filler) (Protus, 2014).

(b) The interaction (pozzolanic) among Ca(OH)_2 , non-reactive fillers (e.g. silica fume) and water converts Ca(OH)_2 , which has high porosity, high

permeability, little mechanical resistance and low bonding to calcium silicate hydrate (C-S-H), which has low porosity, low permeability, high mechanical resistance and more bonding, as shown in Figure 2.10 (Bentur and Cohen, 1987; Malhotra and Mehta, 1996; Rendell, Jauberthie and Grantham, 2002; Setina, Gabrene and Juhnevica, 2013; Mohamed Sutan et al., 2015). Moreover, the curing process to CAM is accelerated through the use of water found in the internal structure of CAM (the use of water for the purpose of completing the interaction between Ca(OH)_2 with non-reactive filler) (Protus, 2014).

If some filler (reactive or non-reactive) stays dry, it will work as a very small aggregate and fill voids and pores, which improves the performance of CAM (Mier, 1997; Lamond and Pielert, 2006).

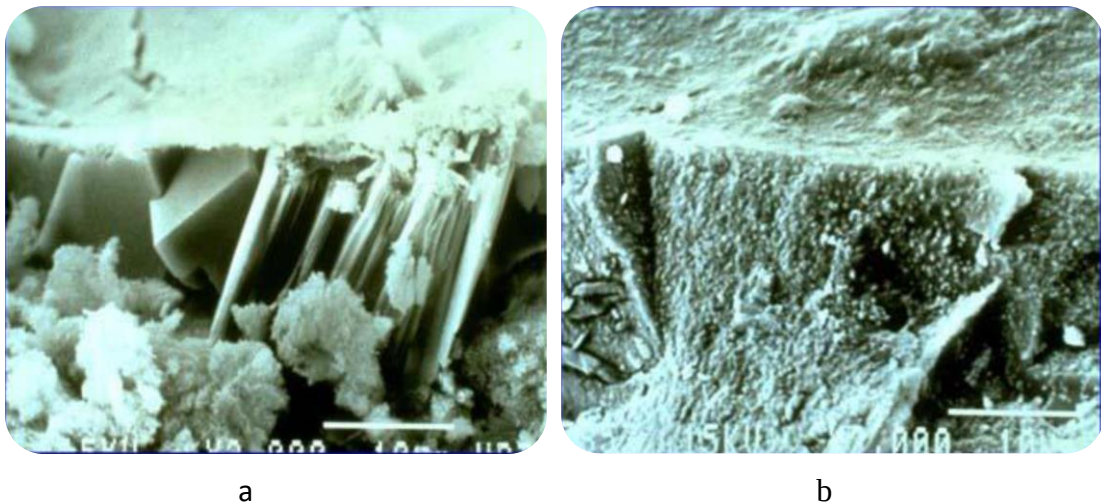


Figure 2.10 The internal structure of the material after reaction between water and reactive filler (cement): without non-reactive filler (a), with non-reactive filler (b)
(Bentur and Cohen, 1987)

❖ ***Economic***

The use of reactive and nonreactive filler in CAM has numerous economic benefits. From the initial preparatory stage, most reactive and non-reactive fillers are industrial by-products, thus they are relatively cheap for use in the manufacture of CAM (Malhotra and Mehta, 1996; Rendell, Jauberthie and Grantham, 2002). Furthermore, the use of such materials accelerates the rate of construction and enables quicker opening of the road, with reduced maintenance requirements and delayed need for replacing or resurfacing the road, thus saving on materials, workers, machines, transportation and energy.

❖ ***Environmental***

As mentioned previously, most reactive and nonreactive fillers are by-products, thus their use is inherently a form of recycling, saving virgin materials and reducing pollution and carbon emissions. It also serves to embed toxins from these by-products within roads (and mitigate their spread into natural habitats and water systems) (Malhotra and Mehta, 1996).

2.5.3 Types of reactive and non-reactive fillers

Reactive and non-reactive fillers have been widely used in construction, especially in concrete, for decades. For example, silica fume was used for the first time in 1952 in the construction of a tunnel in Norway (Nagataki, 1994; ACI 234R, 1996). The classification of these materials is different for concrete and bitumen. The reactive and non-reactive fillers in bitumen are the same as in concrete, but they are named cementitious and pozzolanic materials, respectively.

a- The cementitious materials

The cementitious materials have the cementing property (i.e. the ability to adhere to other materials) after reaction with water (hydration interaction), as shown in Equation 2.1. Their particles are very fine, and their chemical composition is weakly crystalline or non-crystalline (i.e. similar to pozzolanic materials), but the calcium content is high and enough to be cementitious in interaction with water. Cement, high calcium fly ash, lime and granulated blast-furnace slag (GGBS) are some of the cementitious materials widely used in construction.

o Cement

Cement is the most ubiquitous construction material in the world, because of the presence of its raw materials in all countries, its relatively low price, its ease of use and its structural properties. In 1995 annual global production of cement was estimated to reach 1453 million metric tons. Cement is an inorganic, nonmetallic material. It has the capability to react with water (the hydration interaction) and to produce hydrate (cement paste) with a binding property. Hardened cement paste due to hydrate formation retains its strength after hardening (Worrell et al., 2001).

The chemical composition of cement

Generally, cement has many oxides that combine with each other partially or completely to produce four main compounds, as shown in Appendix A7.

The relation between the main cement compounds and its properties

The compounds of cement differ from each other in terms of the quantity of water used in the hydration reaction, the rate of interaction with water (hydration), the heat released during hydration, the effect on strength, and the value of CO₂ emitted in the manufacture of cement.

The quantity of water

Compounds C_3S and C_2S consume almost the same quantity of water. The compound C_3A consumes a larger quantity than the rest of the compounds, as explained in Table 2.2.

Table 2.2 The hydration water required by the Portland cement compounds
(Lamond and Pielert, 2006)

Cement component	Coefficient (g of water per g of component)
C_3S	0.24
C_2S	0.21
C_3A	0.4
C_4AF	0.37

The effect on strength

The aluminate compounds (C_3A and C_4AF) have an influence on the strength of cement, but not more than the silicates (C_3S and C_2S). As can be seen from Figure 2.11, the order of compounds from most to least strength is as follows: C_3S , C_2S , C_3A and C_4AF . However, the compounds C_3S and C_2S are of greater quantity in Portland cement, so they will exert a correspondingly greater effect on the strength of cement than other compounds.

The rate of hydration

As in the effect on strength, the compounds of cement have different rates of hydration, as shown in Table 2.3.

The heat of hydration

The chemical interaction between the cement and water results in exothermic heat. There is variation in heat values among compounds of Portland cement, as shown in Table 2.4.

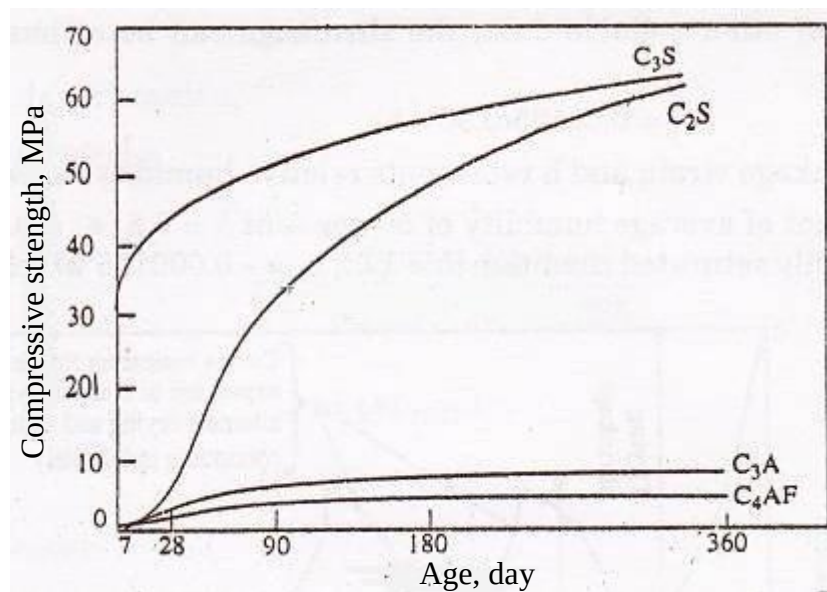


Figure 2.11 Developing the strength of different cement compounds with age (Protus, 2014)

Table 2.3 The rate of hydration of the cement components (Bensted and Barnes, 2002; Neville and Brooks, 2010; Aïtcin and Flatt, 2015)

Cement component	The Rate of Hydration
C ₃ S	Very Rapid
C ₂ S	Rapidly
C ₃ A	Rapidly
C ₄ AF	Slow

Table 2.4 The heat of hydration of the cement compounds (Neville and Brooks, 2010)

Main Compounds	Heat of hydration	
	J/g	Cal/g
C ₃ S	502	120
C ₂ S	260	62
C ₃ A	867	207
C ₄ AF	419	100

The total heat released from cement is distributed by the following amounts with time (Neville and Brooks, 2010), as follows:

1. Half the amount of heat is released during the first 1-3 days.
2. Three-quarters during the first seven days.
3. Almost 90% during the first six months.

The values of CO₂ emitted during the manufacture of cement

Cement compounds contribute to the emission of different amounts of CO₂. Aluminate compounds (C₃A and C₄AF) contribute to air pollution (emissions of CO₂) less than silicates (C₃S and C₂S), as shown in Table 2.5.

Table 2.5 The value of CO₂ of the cement compounds (Gartner, 2004)

Cement compounds	CO ₂ (g/g)
C ₃ S	0.578
C ₂ S	0.511
C ₃ A	0.489
C ₄ AF	0.362

The types of cement

Several types of cement (which differ in their properties) are produced and used in the construction sector, such as rapid hardening cement for use in roads and low-heat cement for use in dams. The different types of cement are achieved by changing the proportions of components (e.g. C_3S etc.); using different additives (e.g. silica fume) for the purpose of modifying properties; and the fineness of cement (Neville and Brooks, 2010). There are five main types of Portland cement used in the world, all of which have the same main chemical compounds in composition but in different proportions, as shown in Table 2.6. The development of strength with time, and the heat of hydration with time relative to type of cement is explained in Figures 2.12 and 2.13, respectively.

Table 2.6 Shows the typical values of chemical compounds used in manufacturing the main types of Portland cement (ASTM C150, 2016)

Cement		Main Compounds (%)			
Symbol	Type	C_3S	C_2S	C_3A	C_4AF
I	Ordinary Portland cement	50	24	11	8
II	Modified Portland cement	42	33	5	13
III	Rapid-hardening Portland cement	60	13	9	8
IV	Low heat Portland cement	26	50	5	12
V	Sulfate-resisting Portland cement	40	30	4	9

○ ***Ground granulated blast furnace slag (GGBS)***

The manufacture of iron and steel is the source of GGBS (Ramezaniapour, Atarodi and Sami, 2016). A slag (molten waste) produced during the manufacturing process (Arivalagan, 2014), it was first used in Germany in 1853 (Thanaya, 2003). GGBS is

used widely with cement at different proportions, ranging from 25-70% of the cement mass. Blended Portland-blast furnace slag cement includes ordinary Portland cement and GGBS (Aktan et al., 2003).

- ***Fly Ash***

The cementitious property (adhesion) is directly proportional to the content of calcium oxide. There are two main types of fly ash classified according to chemical composition (i.e. calcium content) (Nagataki, 1994): Class F: has high calcium content (more than 10%), with properties of pozzolanic and cementitious material; Class C: has the properties of pozzolanic material only, because of low calcium content (equal to or less than 5%).

The main source of fly ash is the use of coal as combustible fuel in power stations. The intense heat of this combustion produces highly fine ash. Approximately 75-85% of fly ash is produced by coal burning (Sherwood, 1995; Siddique, 2008). Mechanical and electrostatic operations are used to separate and precipitate fly ash or pulverised fuel ash (PFA) from the flue gases (Sherwood, 1995; Bech and Feuerborn, 2011); coarser ash falls to the bottom surface of the furnace and is later collected as furnace bottom ash (FBA) (Sherwood, 1995; Bai and Basheer, 2003).

b- The pozzolanic materials

Pozzolanic materials have negligible cementitious properties. Their composition is siliceous and aluminous, or siliceous only. As mentioned previously, pozzolanic materials (non-reactive filler) can be rendered cementitious in combination with water (moisture) and cementitious materials (e.g. cement) that produce Ca(OH)_2 . Pozzolanic

materials will interact with $\text{Ca}(\text{OH})_2$ and water to form a binder C-S-H gel (ASTM C618, 2016). There are many types of pozzolanic material, such as silica fume, calcined clays, metakaoline, volcanic ashes, rice-husk ash and pulverized coal ash (Malhotra and Mehta, 1996). Silica fume, metakaoline, and rice-husk ash are classified as materials with high activity pozzolan because they have an amorphous nature (i.e. the particles of materials have different shape or form), very fine particles and high silica content (Rendell, Jauberthie and Grantham, 2002).

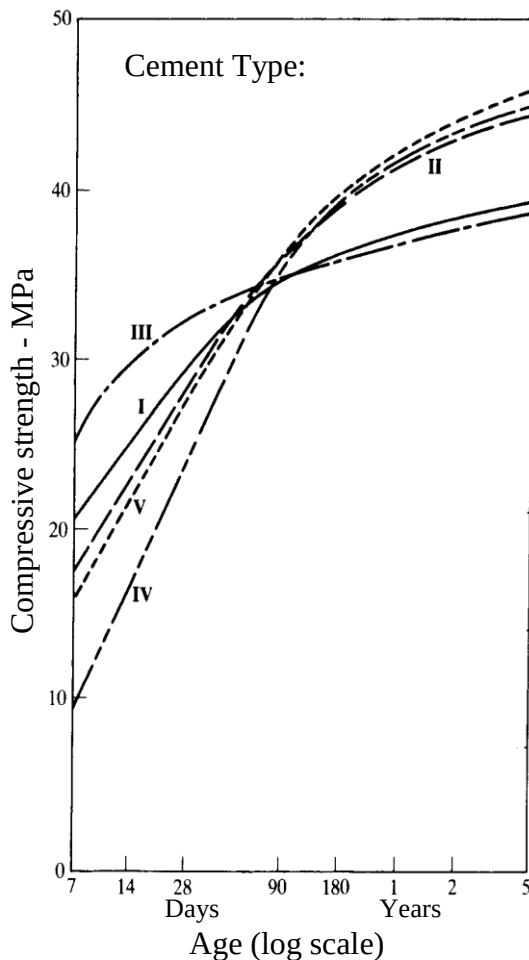


Figure 2.12 Effect of cement type on the development of strength with age
(Neville and Brooks, 2010)

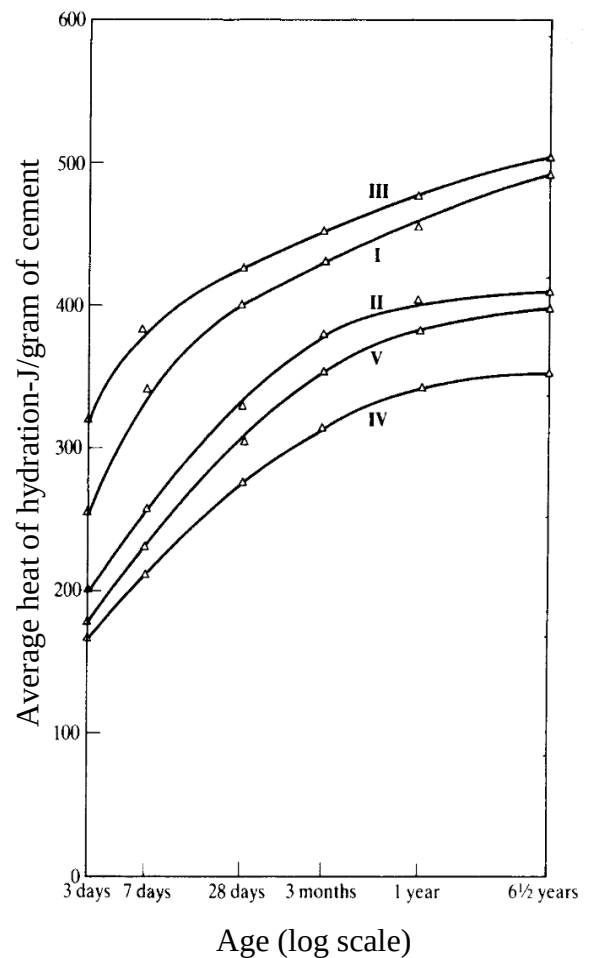


Figure 2.13 The heat of hydration of cement with age for the different types of cement
(Neville and Brooks, 2010)

▪ ***Silica fume***

Silica fume is produced as a by-product from electric arc furnaces (ACI 116R, 1978; Malhotra and Mehta, 1996). It began to be widely used from the 1980s (Aïtcin, 1998). SiO₂ occupy more than 78% in the composition of silica fume (Malhotra and Mehta, 1996). Particles have a surface area between 13000-30000 (m²/kg), and up to 95% of particles have a diameter of less than 1µm (Siddique and Khan, 2011). Moreover, as densified powder or slurry, silica fume is handled and transported easily due to the high fineness and low bulk density of particles (ACI 234R, 1996).

▪ ***Metakaoline***

Although kaolinitic clay exists naturally, this cannot be used directly. Three processes are necessary to produce metakaoline suitable for use in construction:

1. The kaolinitic clay must be of high purity. This can be achieved by washing the clay to remove any un-reactive impurities.
2. Washed clay is calcined at a temperature of 700-800 °C.
3. The clay is finally milled into particles of an average diameter of 1-2 µm (Thanaya, 2003). The product of milling is white metakaoline.

▪ ***Rice-husk ash***

The mass production of rice in many countries results in a massive volume of rice husks (Kumar et al., 2012), that can be used in numerous applications, including as fuel in power stations (Sasaki, 2007). The resultant rice-husk ash contains a high proportion of silica, and has a large surface area, so proposed as a pozzolanic material (Xu et al., 2016).

2.5.4 The chemical composition of cementitious and pozzolanic materials

One the differences among the types of cementitious and pozzolanic materials is the chemical composition, which leads to a difference in the behaviour and activities of materials. Table 2.7 explains the chemical analysis of cementitious and pozzolanic materials discussed previously. It can be seen that the increase in (CaO) oxide content leads to development of the cementitious properties in the material, while increased (SiO₂) oxide enhances pozzolanic properties.

Table 2.7 Chemical analysis of typical Portland cement, silica fume, metakaoline, rice hull ash, fly ash, and GGBS

Type of material		Chemical Analysis (Weight Percent)				
		Component				
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃
Portland Cement (Neville and Brooks, 2010)		20	6	3	63	2
Silica Fume (Kosmatka and Panarese, 1988)		90	0.4	0.4	1.6	0.4
Metakaoline (Kosmatka and Panarese, 1988)		53	43	0.5	0.1	0.1
Rice Hull Ash (Patentscope.wip-o.int, 2016)		94.3	0.06	0.04	0.48	0.01
Fly Ash (Kosmatka and Panarese, 1988)	Class C	52	23	11	5	0.8
	Class F	35	18	6	21	4.1
GGBS (Kosmatka and Panarese, 1988)		35	12	1	40	9

2.5.5 Previous attempts to improve CAM performance with fillers

Since 1971 researchers have been using cementitious materials (specifically cement) with bitumen emulsion in an attempt to improve the performance of CAM. Terrel and

Wang (1971) added cement to the mixes of bitumen emulsion and found that cement greatly accelerated the performance development of the CAM. However, the use of cement leads to positive and negative effects, such as:

✓ ***Positive effects***

The addition of cement to CAM leads to an improvement in a number of properties of CAM such as: the stiffness (Oruc, Celik and Akpinar, 2007); the compressive strength (Oruc, Celik and Akpinar, 2007); the Marshall stability (Oruc, Celik and Akpinar, 2007); the hardness (the interface between cement, bitumen and aggregates becomes harder) (Wang, and Sha, 2009).

✓ ***Negative effects***

Increased rigidity of CAM (i.e. less flexible than HMA) (Li et al., 1998). Also, the small size of cement particles leads to absorption of a big quantity of water after mixing with the emulsion. The water absorption leads to an accelerated rate of emulsion breaking. As a result, the distribution of bitumen emulsion is non-homogeneous and does not cover the whole aggregate surface (Nataatmadja et al., 2002).

However, after Terrel and Wang (1971) and till now, many attempts have been started with the purpose of improving the performance of CAM by means of filler. Most of these attempts to improve CAM by filler stated in Appendix A1

2.6 THE DESIGN METHOD OF CAM

CAMs are highly advantageous types of bitumen because of their positive environmental, health and safety and economic features (IRC, 2014), but their use is

generally restricted to low or medium traffic load roads (Lanre, 2010), maintenance and repair (IBEF, 2016), small areas at different locations, and remote areas (IRC, 2014). CAMs have mechanical properties and durability properties inferior to HMA, therefore, they can not be used in major applications such as the structural layer of roads. Therefore, most of the specifications and the researchers (Asphalt Cold Mix Manual, 1989; Ministry of Public Works Republic of Indonesia, 1990; Nikolaides, 1994; A Basic Asphalt Emulsion Manual, 1997; MORTH, 2001; Thanaya, 2007) have aimed at attempting to develop CAM, by proposing several procedures to design the mixture and to test different possibilities using laboratory and field tests; however, there is no universal method to design CAM. Generally, most design methods use sequential steps such as those described below, or similar steps for the purpose of completing or finding a suitable design for the mixture as follows:

2.6.1 Determining the gradation of aggregate

To determine the appropriate aggregate gradation, most procedures have adopted a simple approach that relies on the recommendations of other researchers or standard specifications, such as HMA specifications.

2.6.2 Determining Initial Residual Bitumen Content (IRBC)

This step includes determining residual bitumen content, which is an initial content and not the final amount. Initial residual bitumen content is determined using the empirical Equation 2.3:

$$IRBC = (0.05A + 0.1B + 0.5C) * (0.7) \quad (2.3)$$

where:

A = The aggregate retained on sieve 2.36 mm (as percentage of total aggregate)

B = The aggregate passing from sieve 2.36 mm but retained on 0.075 mm (as percentage of total aggregate)

C = Aggregate passing from sieve 0.075 mm (as percentage of total aggregate)

2.6.3 Determining Initial Emulsion Content (IEC)

IEC (the initial emulsion content) is calculated by using the following Equation 2.4:

$$IEC = \frac{IRAC}{x} \quad (2.4)$$

where x = the bitumen content in the emulsion (as a percentage)

2.6.4 Determining Optimum Pre-Wetting Water Content (OPWC)

OPWC can be estimated using the coating test, which includes the following: Mix the dry aggregate with water (using different amounts of water). Then, add the bitumen emulsion (IEC) to the pre-wetting aggregate, and mix the mixture for about three minutes. Optimum pre-wetting water content that gives a homogeneous mixture (mixture is not sloppy or stiff) and good uniform covering (the uniform covering is checked by visual inspection and must cover not less than 50% of the aggregate surface).

2.6.5 Determining Optimum Total Liquid Content (OTLC)

OTLC is the total quantity of liquid in the bitumen emulsion and pre-wetted water (water used to damp aggregate). OTLC is selected depending on the result of the dry stability test as follows: The first sample is made by mixing the dry aggregate, initial

emulsion content (IEC), and the water content (OPWC) selected in the previous steps. After that, many samples are made by using the same material quantities as the first sample except increasing the water content (pre-wetting water content) by 1% in each sample compared to the previous. All the loose samples are compacted by the Marshall method (100 Marshall blows (50 blows on each side of the sample)). Upon completion of compaction, all samples are kept in the mould for 24 *h*. Subsequently, samples extracted from the mould are kept in an oven for 24 *h* at a temperature of 40°C. After the required period of time (24 *h* in the oven), the samples are placed in the room under normal conditions for one day. The dry samples are subsequently tested by the Marshall test (Marshall stability) and the results are the values of dry stability. OTLC is chosen depending on the test results of dry stability. For the sample that has maximum dry stability, the total liquid content in that sample is the OTLC.

2.6.6 Determining Optimum Residual Bitumen Content (ORBC)

To estimate the values of ORBC, the values of soaked stability, air void, and flow need to be calculated. The soaked stability can be found by applying the following steps:

- a- The samples are made from aggregate and filler (using the same quantities used in making the dry stability samples), OTLC (as previously calculated and fixed in all samples), and the quantity of residual bitumen content (RBC) ranging from 7-10% bitumen emulsion content (increasing by 0.5% between samples).
- b- After the samples are mixed, compacted and cured as in the samples of dry stability in the first two days (24 *h* in the mould at room conditions + 24 *h* in oven at 40°C), but on the third day half the thickness of sample is put in the

water for 24 h at room temperature. On the fourth day, the second half of the sample is put in the same water and in the same conditions. The specimens are then dried with a towel and are ready to test for Marshall stability at room temperature. These samples are not cured fully.

- c- The results of Marshall stability are the results of soaked stability. ORBC is achieved by optimizing the main parameters, which are maximum soaked stability, air void and flow (The air void and flow must meet the required specification, such as around 5% air voids by volume). The main parameters are calculated at all the values of residual bitumen content examined. If the values of air void and flow are not within the required specification, the curing efforts must be increased.

2.6.7 Determining retained stability

The ratio of soaked stability to dry stability is retained stability. At ORBC only, the values of soaked stability over dry stability are estimated. 50% is the minimum value of retained stability that must be achieved at ORBC.

2.6.8 Determining ultimate strength

After the full curing of samples at ORBC, the value of ultimate strength is achieved.

2.7 MANUFACTURING OF CAM

CAM manufacturing is similar to HMA in following the three main stages of mixing, laying, and compaction, but in addition to those stages CAM need the curing stage. Moreover, as explained previously, CAM does not need to use heat (both in heating materials before or during the manufacturing process), unlike HMA.

The stages of manufacturing (mixing, laying and compaction) can be done by hand, or by using machines or both. Moreover, the curing stage can be done naturally (e.g. sun curing) or industrially (such as by using of machines to generate temperature).

2.7.1 The mixing stage

This stage includes mixing aggregates with bitumen emulsion and any other materials required for use in CAM, like cement. The mixing process can be completed by using one of the following types of machine: pavers by motor, the specialized plant for mixing, or mixing bitumen on-site with a simple concrete mixer.

The parts and distribution of the types of CAM manufacturing lines, which include batch and continuous lines, are clarified in Figures 2.14 and 2.15, respectively.

The mixing process includes the following steps and considerations:

The first step in the mixing process includes transferring the aggregate to a mixing bowl (drum). The aggregate can be used without drying, and it must be damp before mixing with the bitumen emulsion, because dry aggregates absorb water from the bitumen emulsion and lead to premature and undesirable breaking. Water is added to the aggregate for the purpose of wetting the surface (Thanaya, Forth and Zoorob, 2009; Swaroopa, Sravani and Jain, 2015). Lanre, (2010) cited that Thom (2009) confirmed that the aggregate needs to be damp before mixing with bitumen emulsion to ensure covering the aggregate surface with reasonable binder.

The bitumen emulsion is placed in a mixing bowl with aggregate. After that, the mixture (aggregates and bitumen emulsion) is mixed until the whole aggregate surface is sufficiently covered with bitumen emulsion. Mixing for more than the necessary time causes faster breaking of the bitumen emulsion, with negative effects

on CAM such as covering the aggregate surface incompletely, high voids and pores content, and unworkable mixture (Needham, 1996).

2.7.2 The storage and laying stage

After the mixing stage, the mixture is ready to use (ready for storage and laying). The storage and laying can be done by a machine (large job) or hand (small job). As with the mixing stage, the person responsible for this stage must have skill and pay attention, because any increase in the rolling process leads to increased breaking of the bitumen emulsion, which contributes to the sealing of the material surface, which can delay curing (Needham, 1996). During the laying stage, bitumen emulsion must remain workable and be set or broken slightly, for the purpose of ensuring that the emulsion has resistance to moisture, such as rain. Bitumen emulsion has low viscosity, so there is fear of flow (segregation) of bitumen emulsion from the aggregate, thus it must be ensured that it does not flow from the aggregate after mixing (Thanaya, Forth and Zoorob, 2009).

Based on the mechanical performance of CAM achieved in several studies, there is no restriction to its use as a base, binder or surface layer (Leech, 1994; Kim, Im and Lee, 2011; Al-hdabi, 2014; Redelius, Östlund and Soenen, 2016). CAM will need more time to cure when used as a base or binder course layer and overlaid by another material such as hot mix asphalt; as a result, the mechanical performance will improve more slowly (Leech, 1994; Kim, Im and Lee, 2011). However, due to flexibility of CAM, its use as a base layer will help to reduce the probability of base-initiated cracking due to deflection in the surface layer (Gómez-Meijide and Pérez, 2014). On the other hand the use of CAM as a surface layer will allow the required performance

to be achieved in a shorter time due to faster curing (Leech, 1994; Kim, Im and Lee, 2011)

2.7.3 The compaction stage

When the laying stage is finished, the compaction stage is undertaken using various technologies and machines. Needham (1996) stated that the preferred method for the compaction of CAM involves: the use of a steel rolles, followed by the use of a very heavy pneumatic tyred roller (PTR); then the use of the steel rolles again.

Bitumen emulsion must be broken and returned to the original composition (base bitumen) quickly after finishing compaction (Thanaya, Forth and Zoorob, 2009). CAM can be used in making pavement courses with various thicknesses, ranging from 3-22 cm. When the grading used in the CAM is open, the surface of the CAM must be sealed by a coat after compaction (Needham, 1996). Appendix A2 includes previous studies to develop cold bitumen mixture by compaction

2.7.4 The curing stage

Curing is a widely used term in the concrete industry to refer to the improved properties of concrete over time due to chemical reactions between cementitious and pozzolanic materials and water (Kosmatka and Panarese, 1988; ACI 308R, 2008; Taylor, 2014). Concrete curing is a chemical process influenced by several factors: the conditions (temperature, relative humidity, wind velocity, and rain) (ACI 308R, 2008; Doran and Cather, 2014); water (purity, pH, quantity, and temperature) (Lamond and Pielert, 2006; Naganathan, Lin and Mustapha, 2014); aggregate (chemical composition, texture and impurity) (West, Darwin and Browning, 2010; Ahmad, 2011); the chemical admixtures (quantity and type) (Rixom and

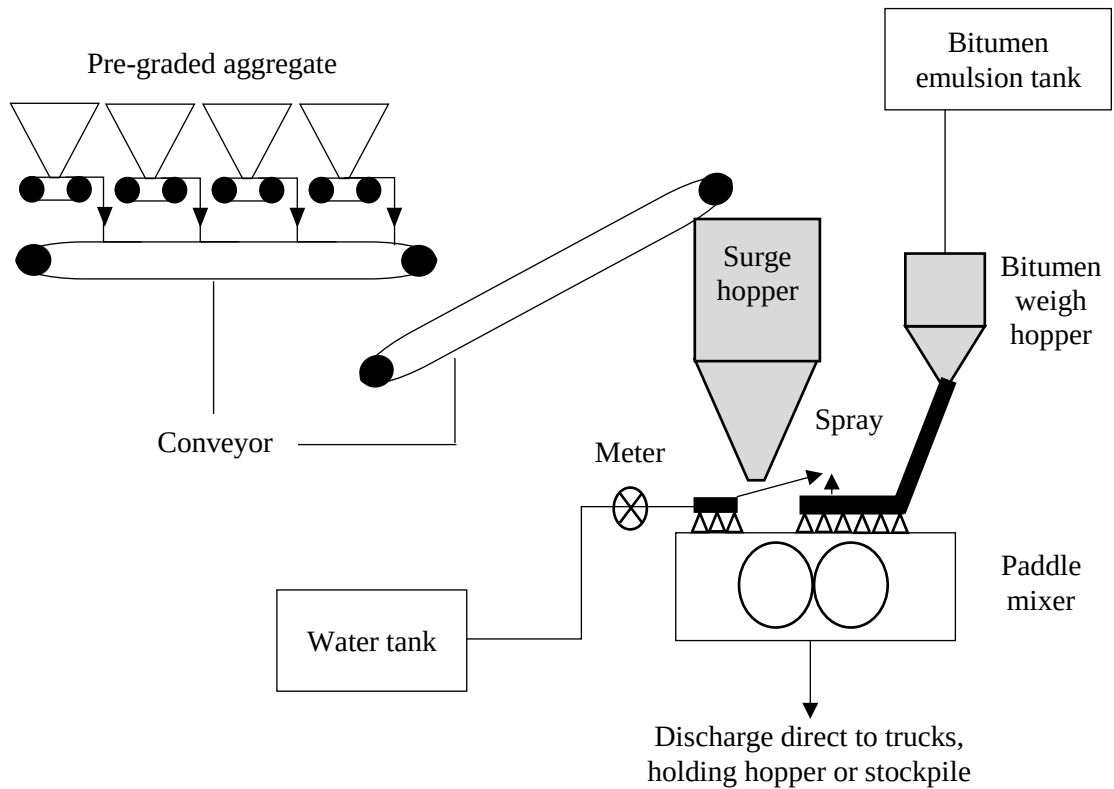


Figure 2.14 The production of cold asphalt by batch line (Needham, 1996)

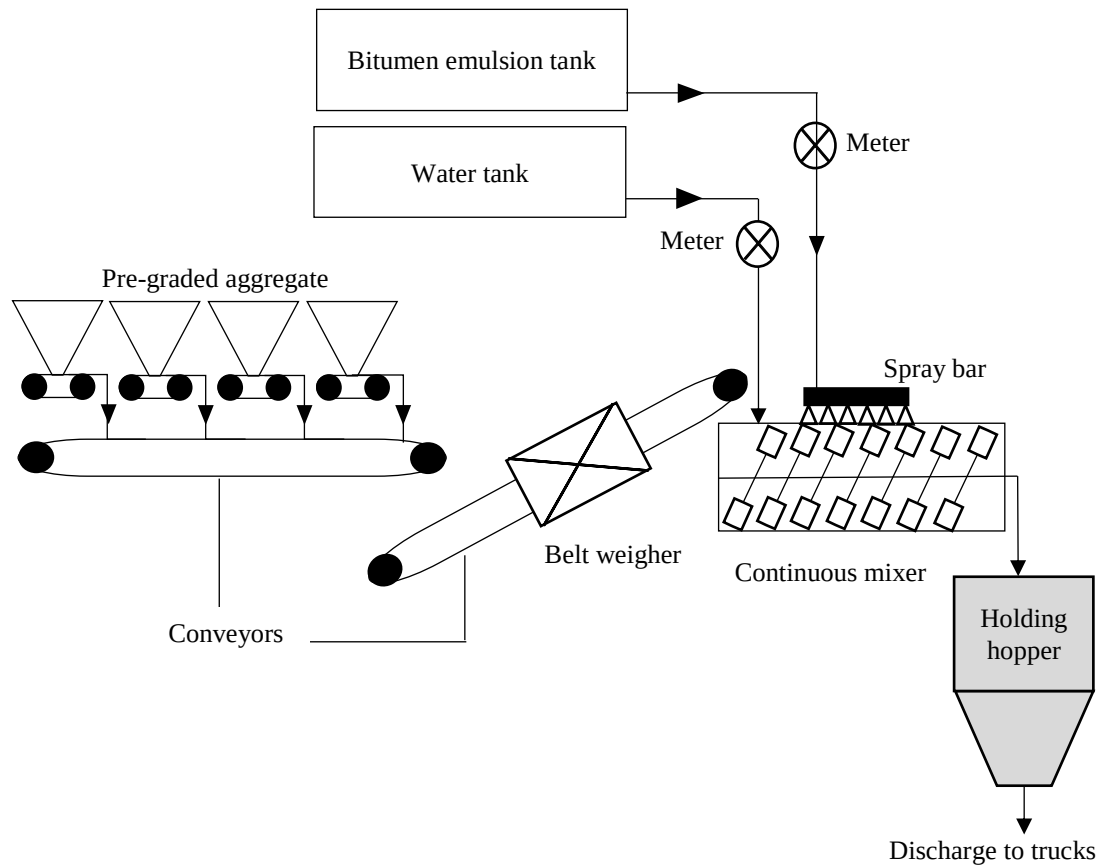


Figure 2.15 The production of cold asphalt by continuous line (Needham, 1996)

Mailvaganam, 1986; Rixom and Mailvaganam, 1999); and the thickness of concrete (ACI 308R, 2008).

The relationship between these factors and the rate of curing is different; some factors have a positive correlation (increased curing rate) to varying degrees, while others have a negative correlation, also to varying degrees.

The same term (curing) is used in the world of cold bitumen emulsion mixture. The curing of CAM is a distinctive process in the world of bitumen, due to all kinds of bitumen (except CMA) not needing water in the manufacturing process, and requiring high temperatures in the formation stage, which leads to the non-existence of any significant quantities of moisture between its components. Therefore, these types of bitumen do not have any delay in the acquisition of the required properties, and can gain them shortly after formation. On the other hand, CAM needs water in its manufacture under normal temperatures, which leads to the presence of water amounts within its structure after its formation. There are three sources of water in CAM:

- That added to aggregate during mixing. Lanre (2010) cited Thom (2009) that the aggregate must be pre-wet to ensure that the bitumen emulsion has covered the aggregate uniformly.
- That included with the bitumen emulsion during its manufacturing process.
- That added to CAM when pozzolanic/ cementitious materials are used, because these materials need water in pozzolanic/ hydration reactions.

Lanre (2010) cited Thom (2009) the stated that some water is trapped inside the CAM, and there is restriction on using CAM widely in construction because of weak performance, especially during the early age. This weak performance is due to the

trapping of water inside CAM, which leads to many negative effects. For instance, it reduces the mechanical properties of material due to the high content of voids and pores (Thanaya, Forth and Zoorob, 2009); reduced bonding between bitumen particles and between the aggregate and bitumen (Kassem et al., 2009; Ahmad, 2011); water freezes inside the CAM and thus increases in size (causing internal pressure within the pavement and ultimately producing cracks) (Taylor, 2014); compression force in the internal structure of CAM when applying a compression load on the bitumen (Li, 2004); and reduced durability because of increased permeability of the material, which leads to accelerated degradation due to inappropriate material entering into the internal structure of the CAM (e.g. motor oil, water and rain) (Li, 2004).

Therefore, it is necessary to accelerate the evaporation of the water trapped in CAM for the purpose of development of the performance of the material. Moreover, all the trapped water in the CAM should be evaporated to ensure the material has the required properties. The performance development of CAM due to the evaporation of water in its internal structure represents the curing process (AEAM, 1997). This means that the curing of CAM is a physical process, while the curing of concrete is a chemical reaction. The curing of CAM improves functional performance because of the evaporation of water, which contributes to increased cohesion between bitumen particles and adhesion between the bitumen and the aggregate. Figure 2.16 shows the breaking process of bitumen emulsion with time. However, many researches confirm that CAM needs between 2-24 months for the purpose of final completion of the curing process (evaporation of all water in the material) (Leech, 1994; Thanaya, 2007).

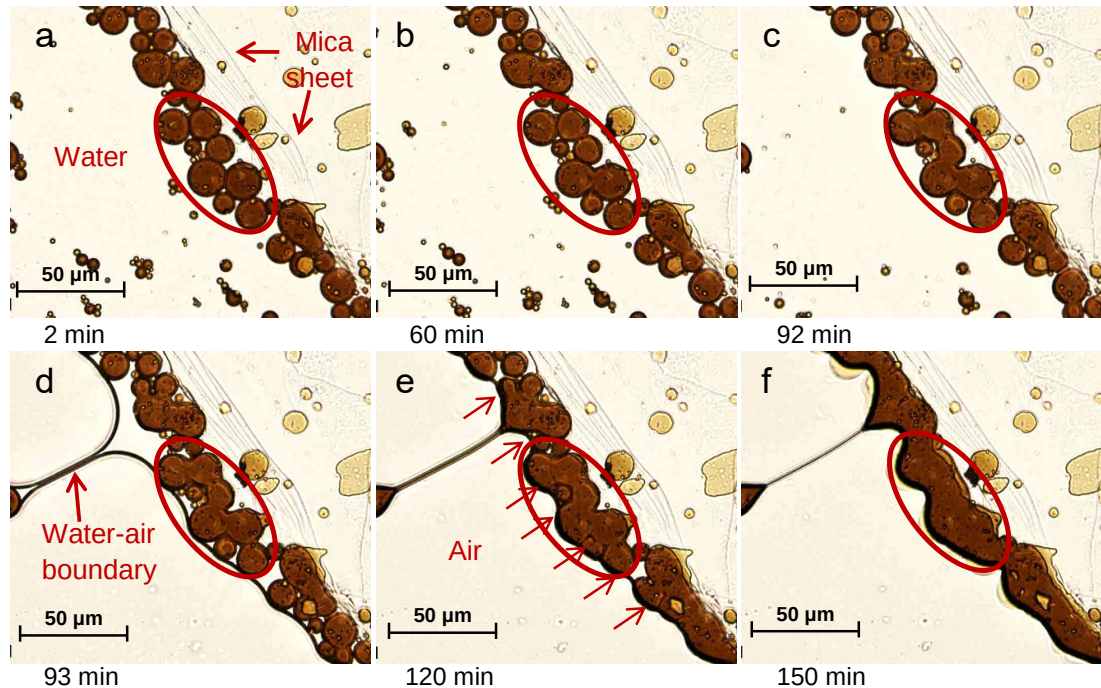


Figure 2.16 Breaking process of bitumen emulsion with time (Fang, 2016)

The curing of CAM accompanies change in the color from brown to black (Lanre, 2010). According to previous research, there are several factors that affect (positively or negatively) the rate of curing in the CAM, which include: the quantity of water (Ojum, 2015); bitumen emulsion (quantity, type, and the temperature of emulsion) (Lanre, 2010); aggregate (absorption, the temperature of aggregate, surface chemistry, and surface area) (Ojum, 2015); filler (active or not) (Jan Ebels, 2008); compaction (Needham, 1996; Ojum, 2015); environmental conditions (temperature, relative humidity, and rain) (Needham, 1996; Ojum, 2015). If cementitious/pozzolanic materials are used in CAM, the factors affecting the curing of concrete must be borne in mind also.

To-date, locally and globally, an enormous number of curing methods are used for CAM to accelerate the process after the compaction of specimens, as shown in Appendix A3.

2.8 CAM MIXES USED IN REALITY

Many road have been built using CAM, and over their service lives, several have performed well under traffic (Muncy, 1990; Davidson, 2005; Khalid and Monney, 2009; Redelius, Östlund and Soenen, 2016; Lundberg et al., 2016). Based on this experience, the design and performance properties of these mixtures are summarised in Tables 2.8 & 2.9 respectively:

Table 2.8 Mix design (type and quantity) of CAMs used in practice

Materials	Description	Quantity (as average) of mixture
Aggregate	• Virgin or RAP • Typically 10-14 mm (Maximum size) • Open or dense graded	≈ 95% (after water evaporation)
Emulsion	• Cationic	≈ 9 % (5% residual bitumen)
Water	• Water in aggregate and emulsion	≈ 5%

Table 2.9 Some properties of CAM in practice

Property	The measured value	Note
Dry density (kg/m ³)	• 2156	• Variation in values depends on: 1- Mixture (mix design and manufacturing) and 2- Age when tested • As found in Khalid and Monney (2009), the values of dry density, compaction and ITSM present means ranging over different values
Void content (%)	• 6 to15	
Compaction (%)	• 89	
Residual water content (%)	• ≈ 3	
Recovered binder R&B (°C)	• 26 to 48	
ITSM at 20°C (MPa)	• 1155	
Stiffness modulus at 2°C (MPa)	• 750 to 5840	

2.9 THE POROUS MEDIUM (CAM/UNBOUND LAYER) AND EVAPORATION

2.9.1 The porous media

The porous medium is a scientific concept used in many applications such as biology, geosciences (geophysics, hydrogeology and petroleum geology), filtration, mechanics (soil mechanics, acoustics, geomechanics and rock mechanics), engineering (construction engineering, petroleum engineering) and material science. Moreover, the porous medium concept is applicable to many materials (natural or man-made), like soil, cement, concrete, bitumen, ceramic, wood, bone, cork etc.

The porous medium consists of two kinds of structure: that of pores and voids, and that which is solid or semi-solid material. Usually, the structure of pores or voids and the structure of solid or semi-solid may be continuous or non-continuous structure. Generally, models of porous structures are divided into three types: networks of capillaries; arrays of solid particles; and trimodal formation.

Porosity is the basic property used in the description of porous material, albeit there are other pertinent properties associated with this, such as permeability, tensile strength and electrical conductivity. In any case, the pores or voids in a porous medium are filled either with a gas (e.g. water vapor) or liquid (such as water). The following section discusses the life cycle of water in a porous medium.

2.9.2 The life cycle of water in a porous media

The life cycle of the water in porous media includes water and gas (water vapor) phases. The water changes from liquid to vapor by evaporation (drying). Therefore, evaporation in porous media includes transfers of mass and heat (Coussot, 2000; Yiotis et al., 2006; Shokri, Or and Lehmann, 2007; Shokri, Lehmann and Or, 2009a;

Vorhauer, Metzger and Tsotsas, 2010; Gran et al., 2011; Shokri and Or, 2011; Deol et al., 2012).

2.9.3 The evaporation dynamic in porous media

Water dynamics in porous media have been intensively studied for several decades (Fisher, 1923; Battistelli, Calore and Pruess, 1997), because of their significant role in many industrial sectors, including biological, hydrological, environmental, agricultural, engineering and construction applications (Shokri, Or and Lehmann, 2007; Lehmann, Assouline and Or, 2008; Gonçalves, Pel and Rodrigues, 2009). The inception of evaporation differentiates three zones, saturated, semi-saturated and film region, as shown in Figure 2.17 (Fisher, 1923). The interface between the saturated and semi-saturated zone is the receding drying surface, while the interface between the dry and semi-saturated zone is the receding or second evaporation surface; the surface of material is the primary evaporation surface at all the stages of evaporation (Graham, 2004). The concept of the film region has been used by many researchers to define the space between the surface of evaporation and the receding drying front (Lehmann, Assouline and Or, 2008), functioning like a hydraulic bridge that transports water by capillarity action between both regions.

In addition, as shown in Figure 2.17, the dynamics of water evaporation in porous materials are divided in three stages: (i) first, (ii) transition and (iii) second. Fisher, (1923) classified the evaporation into these stages depending on differences in evaporation rate, location of drying front and mechanisms that control the evaporation (transport).

➤ ***The first stage***

The primary phase of evaporation is characterised by high and constant evaporation rate over time (Graham, 2004; Lehmann, Assouline and Or, 2008; Shokri, Lehmann and Or, 2010a). The weather is the main factor in this evaporation rate, with drying of the porous body being determined by the ambient temperature, relative humidity, solar radiation and wind velocity (Hide, 1954; Lemon, 1956; Graham, 2004; Shokri and Or, 2011; Han and Zhou, 2013; Rad, 2014; Garcia et al., 2015).

The rate of evaporation during the first stage can be assumed equal to that of the open pan, when the atmospheric conditions are equal between them (Graham, 2004). At this stage, the evaporation occurs in the material surface (Han and Zhou, 2013).

The water moves to the evaporation surface (the material surface) by capillary action (capillary tubes) that connect the receding drying surface (interface between the semi-saturated and saturated zone) to the evaporation surface. The zone that contains these capillary tubes is the capillary fringe (Garcia et al., 2015). Large pores in this stage are invaded by air due to the differential with atmospheric pressure, as well as a small capillary pressure inside the large pores, so these large pores are unable to retain water. As a result of this, evaporation during this phase happens at the surface of the material, specifically at small pores which pull water by capillary action from the large pores at a receding drying front (Van Brakel, 1980; Scherer, 1990; Shokri, Lehmann and Or, 2008; Shokri, Lehmann and Or, 2009a; Shokri, Lehmann and Or, 2010a; Shokri, Lehmann and Or, 2010b, Yiotis et al., 2012).

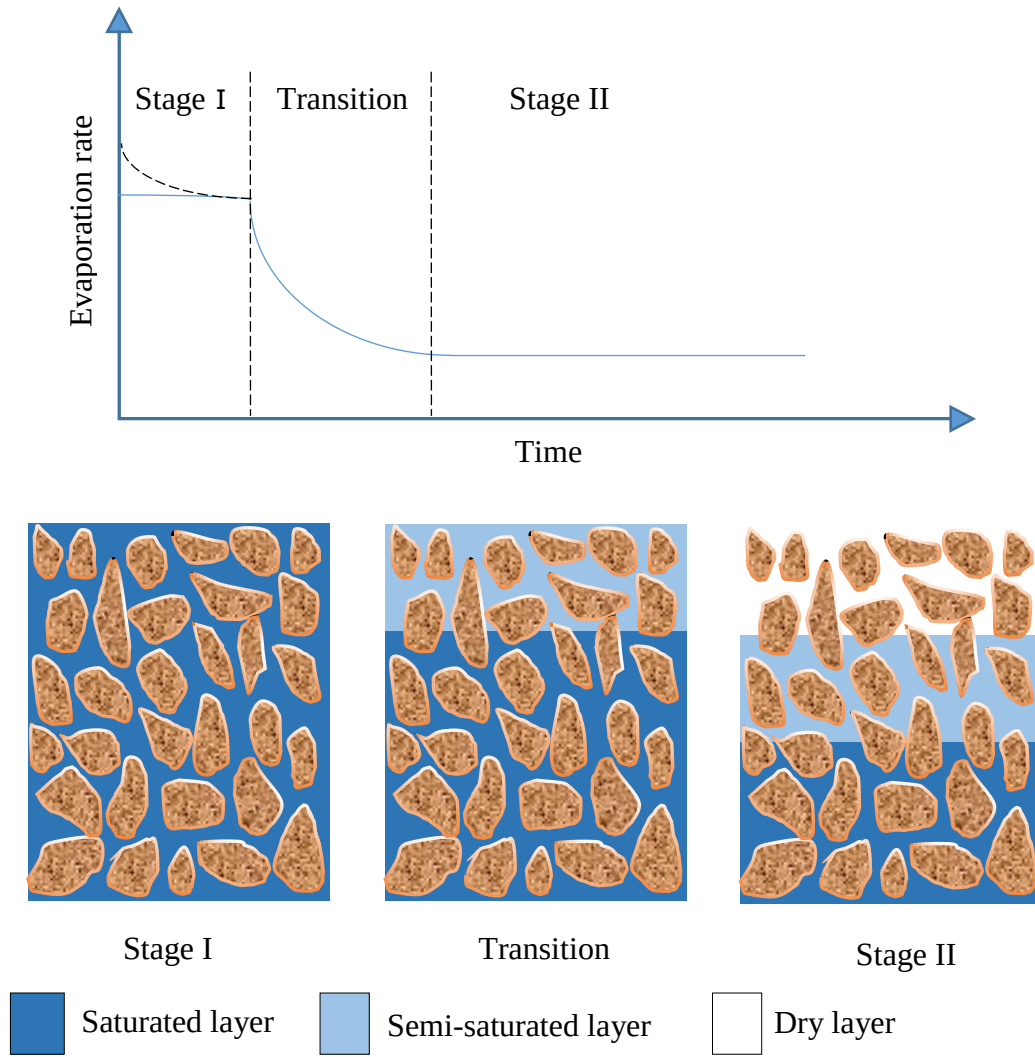


Figure 2.17 The evaporation stages of porous media (Graham, 2004)

➤ ***The transition from the first stage to the second stage***

As explained previously, and shown in Figure 2.17, the first stage of evaporation happens as long as the film region provides full hydraulic contact between the receding drying front and the upper surface, which depends on the capillary properties of the material (Lehmann, Assouline and Or, 2008; Shokri and Or, 2011). When the capillary front reaches a certain depth (characteristic length (L_C) defined by downward gravity (L_G) and viscous forces (L_V)), the saturated capillaries between the surface and the saturated region may get cut. The progressive collapse of the saturated

capillaries is known as the transition stage, and finishes when there is no more hydraulic contact between the saturated region and the surface of the material. At this point the second stage starts (Han and Zhou, 2013). The thickness of the film region is controlled by the capillary action of the porous material.

➤ ***The second stage***

The transition stage stops when the capillary pathways between the evaporation surface and the receding drying front are disconnected because the capillary action is no longer sufficient to push the water to the material surface. At that time, the second stage begins (Fisher, 1923; Nissan, Kaye and Bell, 1959; Kowalski, 2000; Saravanapavan and Salvucci, 2000; Graham, 2004; Lehmann, Assouline and Or, 2008; Shokri et al., 2008; Shokri and Or, 2011; Or et al., 2013).

At the second stage, the surface evaporation turns from the surface of the material to a deeper surface, therefore, the material presents two evaporation surfaces: the proper surface of the material and the secondary evaporation surface placed at a lower level. The evaporating water from the secondary surface needs to travel throughout the superficial dry layer in order to reach the top of the material. In this process the rate of travelling vapor is low because: (1) it is produced by vapor diffusion (Or et al., 2013); and (2) also reduced due to the energy dissipation produced throughout the dry layer (Gowing, Konukcu, and Rose, 2006). Due to these differences, the rate of evaporation of the last stage is low compared with the primary and transition stages (Shokri, Lehmann and Or, 2009b).

2.10 THE CAPILLARY ACTION OF POROUS MEDIA

The capillary action of porous media is represented by a pair of capillaries (Figure 2.18). The capillaries are hydraulically connected. According to Figure 2.18, there is a relationship (Equation 2.5) between the characteristic length and the sizes of the pores of the porous material, whereby the former is affected by the size and distribution of pores (i.e. the ratio between the sizes of the pores) in the porous media (Lehmann, Assouline and Or, 2008).

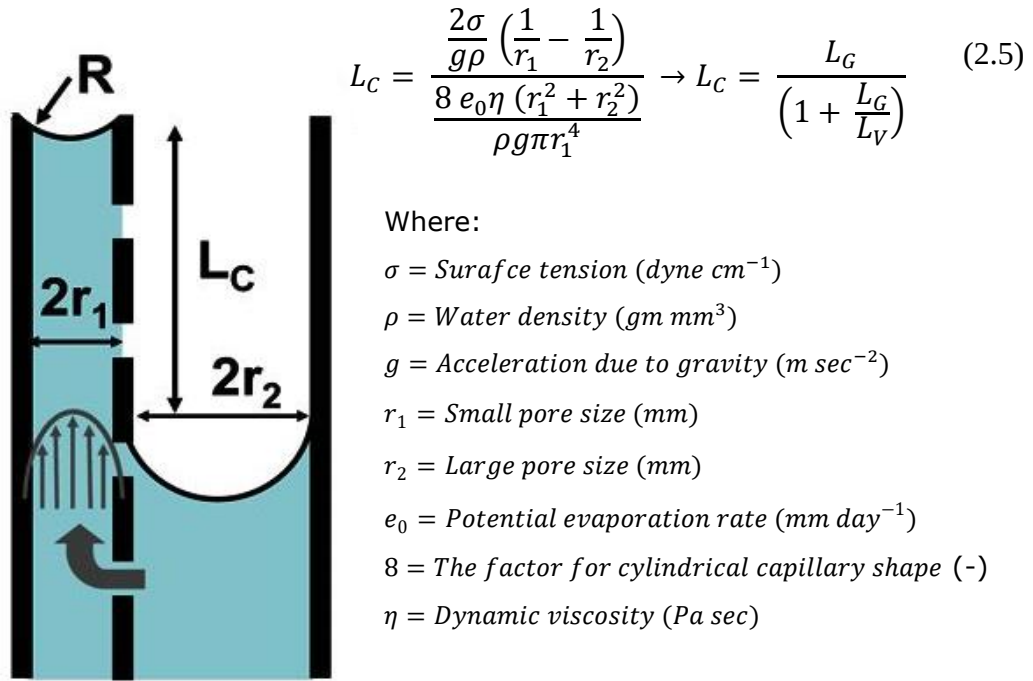


Figure 2.18 The characteristic length of porous media (Lehmann, Assouline and Or, 2008)

2.10.1 The size of pores

The relation between the size of pores and the capillary length (front depth) is explained in Figure 2.19. It is clear that the size of the pores has an effect on the value of L_C . The relation between the size of the pores and the value of L_C is negative: a

decrease of pore size leads to an increase in the length of the film region (L_C), but there is a limit to the relation for pores that have very fine size. When the size of pores becomes finer than this limit, then the relation becomes positive, because when the size of pore becomes very fine, the movement of water to the surface of material slower (Li, Chang and Salifu, 2014); as a result, the length of the film region will become shorter.

2.10.2 The pore size distribution (n)

Various parameters are used in the description of soil structure; one of these parameters is the pore size distribution, which is the mean variation in sizes of pores in a porous material (Cary and Hayden, 1973). One of methods used in the calculation of this parameter is the hydraulic conductivity test method (Lehmann, Assouline and Or, 2008), which was followed in the current research (Chapters 4 and 6). The ratio between the sizes of the pores in the porous material has an affect on the characteristic length, as shown in Figure 2.20. The relation between the pore size distribution and the characteristic length is positive in some regions and negative in others. It is clear from Figure 2.20 that when the ratio between the size of pores becomes approximately 0.3 (as defined in Lehmann, Assouline and Or, 2008), the thickness of the film region will be maximum.

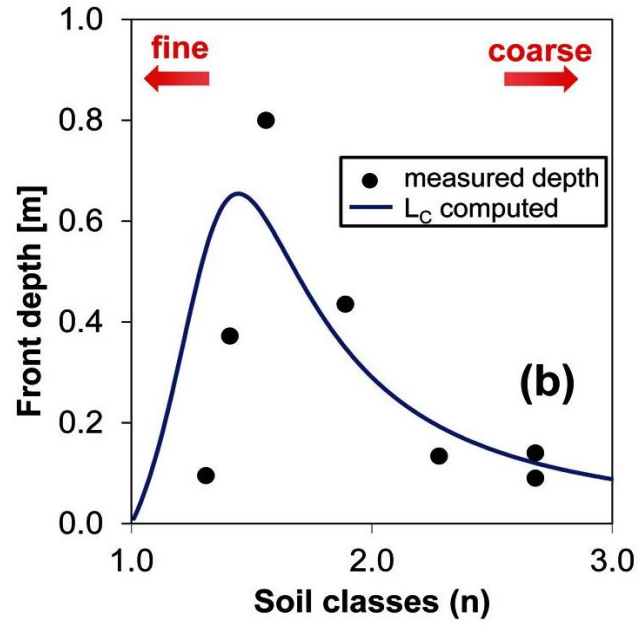


Figure 2.19 The relation between the front depth and the size of pores (Or et al., 2013)

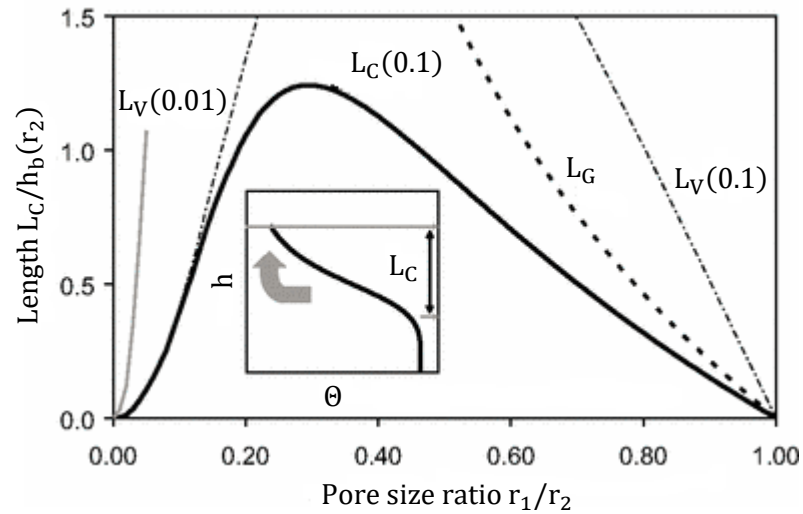


Figure 2.20 The effect of pore size distribution on the thickness of film region (Lehmann, Assouline and Or, 2008)

2.10.3 The rate of evaporation in the porous media

The rate of evaporation depends on the four main categories, as shown in Table 2.10 (Coussot, 2000; Yiotis et al., 2006; Shokri, Lehmann and Or, 2009a; Vorhauer, Metzger and Tsotsas, 2010; Gran et al., 2011; Shokri and Or, 2011; Deol et al., 2012).

Table 2.10 Factors affecting the rate of evaporation of the porous media

Type of group	Properties
External condition around porous medium	• Temperature • Thermal radiation • Relative humidity • Wind velocity • Rain
Thermal properties of porous medium	• Thermal conductivity • Thermal diffusivity • Volumetric heat capacity
Hydraulic properties of porous medium	• Hydraulic conductivity • Porosity • Soil retention
Mechanisms of internal transport	• Vapor diffusion • Capillary flow • Film flow

It is clear that there are interactions among these factors, whereby the properties of porous medium interactions with the properties of the atmosphere ultimately have an impact on the results of evaporation (Sakai et al., 2006).

SUMMARY

Low performance is the main problem of CAM, especially at early stages, because trapped water requires a long time to evaporate completely. Most previous researches have worked on solving that delay in curing by adding cement, but this does not accelerate the curing of CAM as required (i.e. roads cannot be opened road to traffic quickly, as in hot mix asphalt). Moreover, cement has negative effects on the generally positive features of CAM (i.e. economic, environmental, energy-saving, and health and safety features). It is necessary to address the problem of the delayed curing of CAM without undermining its positive features. Suggested solutions depend on understanding the dynamics of water evaporation in CAM. A summary of previous

research reviewed by the researcher targeted to understanding and developing the performance of CAM yielded the following observations:

1. The dynamics of evaporation, moisture and thermal profiles in CAM have not been adequately researched, therefore it is important to study these parameters for the purpose of increasing knowledge about CAM, which will help in developing new and improved versions.
2. The relationship between the evaporation of water and the mechanical properties of the CAM is also under-researched, therefore investigating this relationship will be important to understand the correlation between the water evaporation and mechanical properties.
3. The aggregate is the greatest component in the bitumen mixture, comprising 95% of its mass. However, this crucial component has rarely been explored by researchers in terms of the impact of aggregate specifications in solving the problem of trapped water inside CAM. This area must be researched in order to develop the structure of CAM to accelerate evaporation of the water inside the bituminous mixture, such as developing the grading of aggregate to increase the rate of evaporation.
4. Research is needed for prediction of the performance of CAM in order to know if CAM will give appropriate performance on site or not, and when.

Chapter Three

Methodology and Materials

3.1 INTRODUCTION

This chapter presents the experimental work undertaken to achieve the research objectives explained in chapter one. Therefore, the following sections describe the properties of materials, the experimental setup, preparation of the sample and test procedures.

3.2 DESCRIPTION OF MATERIALS

The materials used in the current work comprised water, cementitious materials, bitumen emulsion and unbound materials (limestone aggregate), as explained below.

3.2.1 Water

Tap water is used in this work in the manufacturing and saturation of unbound materials/ CAM, manufacturing and curing of cement concrete, hydraulic conductivity and porosity tests.

3.2.2 Unbound materials

The crushed limestone aggregate was supplied to the University of Nottingham by a local supplier (Tunstead Quarry, Derbyshire, UK) in five different sizes: 20 mm, 14 mm, 10 mm, 6 mm and dust.

The limestone aggregate was used to manufacture compacted aggregate samples with different gradations: six of them single-sized and five compound-sized. The single-size samples had uniform size 0.6, 2, 5, 8, 14 and 20 mm respectively, referenced as S0.6, S2, S5, S8, S14 and S20 (Figure 3.1), and the five compound-sized gradations had maximum size: 6.3, 8, 10, 14 and 20 mm, named as C6.3, C8, C10, C14 and C20 (Figure 3.2).



Figure 3.1 Single sized-aggregate of uniform size (0.6, 2, 5, 8, 14 and 20 mm)

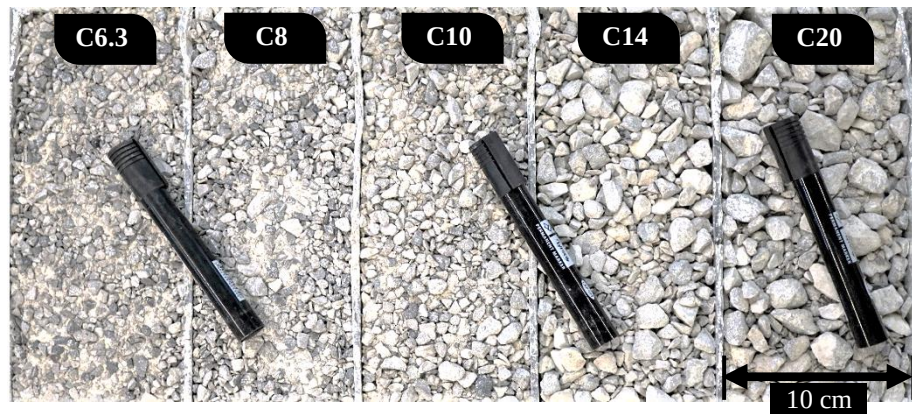


Figure 3.2 Compound sized-aggregate of maximum size (6.3, 8, 10, 14 and 20 mm)

The proportions of the sizes of aggregate used to make the gradations of compound aggregate are shown in detail in the Table 3.1. The particle size distribution of compound aggregate used in this research is given in Figure 3.3.

To determine the appropriate aggregate gradation, most design procedures in CAM have adopted gradations of standard specifications, such as HMA specifications. Therefore, all compound aggregate mixtures in the research were chosen in accordance with standard specifications BS EN 13108-1:2006 (BS EN 13108-1, 2006) and BS 4987-1:2005 (BS 4987-1, 2005).

In the current work, in addition to binder, compound-sized gradation (C10) was used in the manufacturing of CAM and cement concrete samples.

Table 3.1 Proportion of mixture of compound aggregate

Compound aggregate (maximum size, mm)	% by weight of aggregate						
	Size of aggregate (mm)						
	Dust*	6	6.3	8	10	14	20
6.3	58	41.92	0.08	0	0	0	0
8	51	43	---	6	0	0	0
10	50	30	---	---	20	0	0
14	26	27	----	---	28	19	0
20	40	20	---	---	15	10	15

* Aggregate $\leq$ 4 mm size

3.2.3 The binding material

➤ Bitumen emulsion

Slow-setting cationic bitumen emulsion with 60% residual bitumen content and classified according to BS EN 13808:2013 (BS EN 13808, 2013) as a C60B3 was used. Cationic emulsion has high stability and high adhesion (Nikolaides, 1994; Thanaya, 2003), thus it was used in the current investigation. Table 3.2 lists the properties of the slow-setting cationic bitumen emulsion, which was supplied in large containers (30 kg).

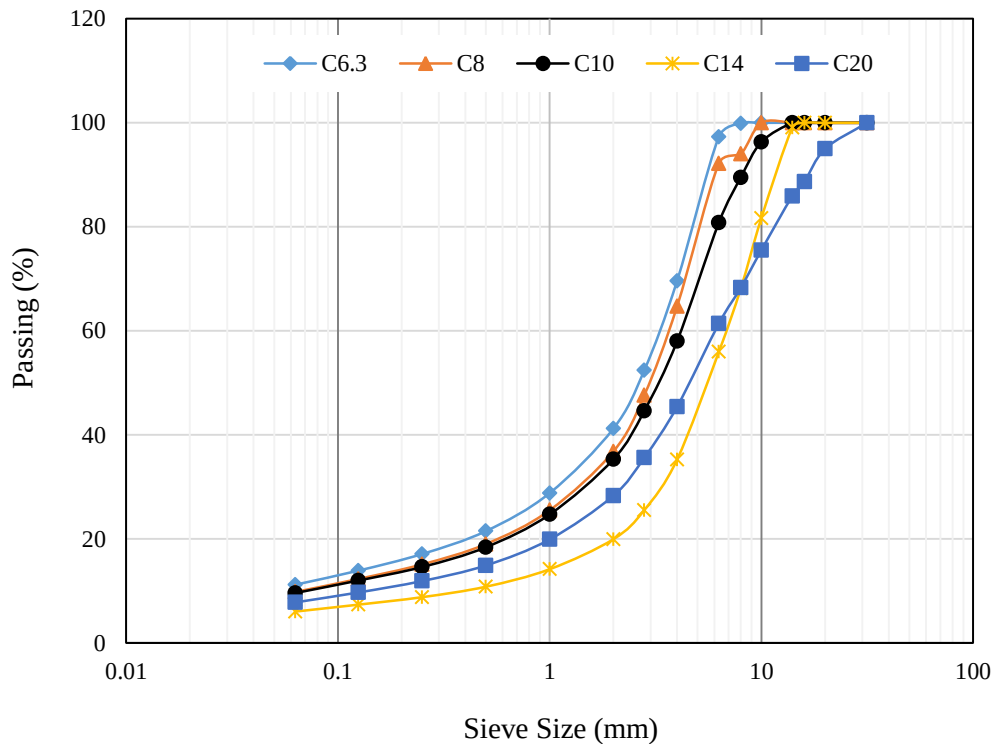


Figure 3.3 The particle size distribution of compound aggregate (6.3, 8, 10, 14 and 20 mm)

During storage, solid particles will settle at the bottom of the container, consequently causing non-homogeneity in the bitumen emulsion, therefore the emulsion must be agitated (i.e. remixed) before use in manufacturing cold asphalt mixtures.

Vigorous or sustained remixing of bitumen emulsion could cause sudden (fast) breaking of the emulsion itself because of collision among particles. Consequently, to avoid laboriously remixing bitumen emulsion multiple times over an extended period, the large container was homogenized by a single remixing, and then apportioned into smaller batches stored in air-tight, sealed containers of equal volume and shape (bottle = one litter), for single use as required in subsequent experiments (see Figure 3.4). This improves the homogeneity of all samples, both individually and as a group, as well as offering practical efficiency.

Table 3.2 Bitumen emulsion properties

Property	Value	Standard
Appearance	Thick Black	
Bitumen content (%)	60	EN 1428
Breaking behaviour	70 - 155	EN 13075-1
Softening point (°C)	≥ 46	EN 1427
Adhesiveness	≥ 90	EN 13614
Viscosity - Efflux time 2mm - 40°C (sec)	15-70	EN 12846
Particle surface electric charge	Positive	EN 1430
Penetration (dmm)	≤ 100	EN 1426
Density at 20°C (kg/m ³)	1010	

➤ **Cementitious materials**

Three types of cement with different hardening rates were used: CEM I, 42.5 N (OPC), which is an ordinary Portland cement; and two types of rapid hardening cement, Calcium Aluminate Cement (CAC) and CSA (Calcium Sulphoaluminate Cement). The hydration and hardening behaviour of these cements are well known as they have been extensively researched (Neville and Brooks, 2010; Winnefeld and

Barlag, 2010; Juenger et al., 2011; Winnefeld and Lothenbach, 2012). Their chemical compositions and surface areas are shown in Table 3.3. During storage, all bags of cement were kept in well-sealed plastic bags in order to prevent any reaction with atmospheric moisture, which leads to abnormal hardening of cement.



Figure 3.4 Preparing the bitumen emulsion to mix

3.3 MANUFACTURING OF MOULDS

The current work required forming of special cylindrical (100 mm height x 95 mm diameter, Figure 3.5) and prismatic (300x300x105 mm³, Figure 3.6) moulds for some tests designed to achieve the research aims.

The moulds were enclosed from all sides except the top, which was open to the atmosphere. The moulds were made of transparent acrylic. Silicone, which has resistance to temperature and moisture, was used to join the parts of the moulds and aluminium corners were used to support the sides of the prismatic mould to prevent water leakage and collapse during and after compaction.

Table 3.3 Chemical composition and surface areas of cements used in the present investigation (main phases) (Fang, 2016).

OPC		CSA		CAC	
Phase	Content* (%)	Phase	Content* (%)	Phase	Content* (%)
Blain (m ² /kg)	305.0	Blain (m ² /kg)	481.0	Blain (m ² /kg)	367.0
C ₃ S	0.561	MgO	0.001	C ₂ S	0.109
C ₂ S	0.155	C ₄ A ₃ s	0.502	C ₄ AF	0.111
C ₃ A	0.048	CT	0.045	CT	0.040
C ₄ AF	0.115	C ₂ AS	0.146	C ₂ AS	0.035
MgO	0.010	CA	0.064	CA	0.601
		CA ₂	0.024	C ₁₂ A ₇	0.033
		MA	0.014	C ₃ FT	0.009
		Cs	0.006	Ff	0.034
				MA _{0.1} F _{0.9}	0.009
				C ₂₀ A ₁₃ M ₃ S ₃	0.018

*by mass of cement; *A = Al₂O₃, C = CaO, F = Fe₂O₃, S = SiO₂, s = SO₃, T = TiO₂, f = FeO, M = MgO

3.4 PREPARATION OF SAMPLES

3.4.1 Proportions of materials

- CAM

The mixture compositions used in this study are summarized in Table 3.4. CAM-N samples were produced by mixing crushed limestone aggregates, tap water and slow-setting cationic bitumen emulsion (C60B3). The emulsion content was calculated to leave 5% residual bitumen content in the mix after curing. Following previous investigations (Oke, 2011), 1.5% pre-wetting water (by mass of dry aggregate) was

used to avoid excessive bitumen absorption when the emulsion is mixed with the aggregates. In addition to water in emulsion and pre-wetting water, an extra amount of water was used in order to saturate CAM-N samples during compaction. In total, the initial water content was 19 g/100 g of CAM-N. These mix proportions are close to mix design for the application of CAM, on site (section 2.8).

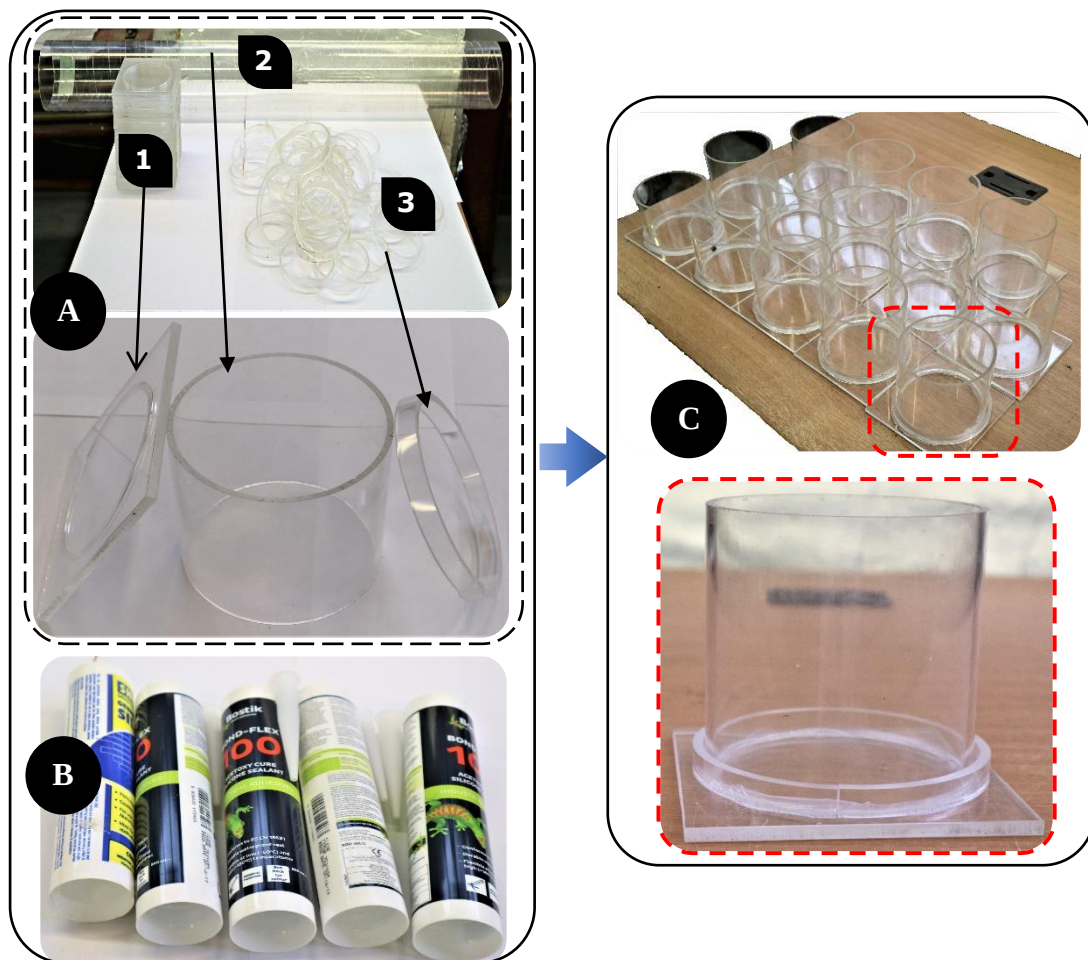


Figure 3.5 Cylinder mould. A: Parts of mould: 1 and 2 – base and wall of mould, respectively; 3 – ring to prevent leakage of water at contact zone between base and wall of mould. B: Silicon material to glue parts of mould. C: Mould after sticking (ready to use)

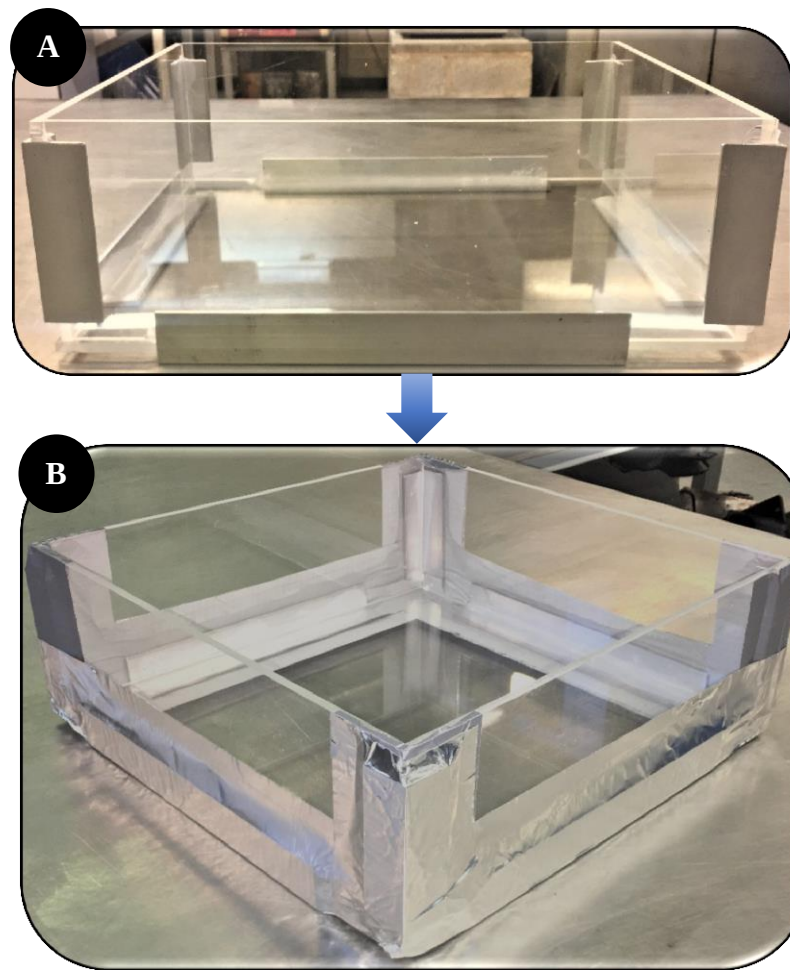


Figure 3.6 Prismatic mould. A: The first stage, which included glue of the parts of mould by silicon; aluminium angles at the corners of the mould were then used. B: Waterproof tape was used at the sides and corners of the mould

Table 3.4 Amount of materials in 100 g of cold asphalt mixture (CAM)

Emulsion (g)	Pre-wet water (g)	Aggregate (g)		Cement		
		≥ 0.063 (mm)	< 0.063 (mm)	(g)	(%)*	W/C
			8.64	0	0	0
			6.82	1.82	2	2.418
7.60	1.36	82.40	5.00	3.64	4	1.209
			3.18	5.46	6	0.806
			1.36	7.28	8	0.604

* Percentage of cement by mass of dry aggregate

The cold asphalt mixture samples (CAM-C) were produced using the same constituents and mixture proportions to CAM-N samples, but the latter replaced 2, 4, 6, and 8% (by mass of dry aggregate) of limestone filler with OPC, CAC and CSA. These mixtures are referred to below according to the type of cement contained (OPC, CAC or CSA) and their content by mass of dry aggregate. For example, sample OPC6 is made of CAM with 6% OPC.

- **Cement concrete**

The mix proportions used are shown in Table 3.5. Mix proportions, except water quantity, were selected according to previous investigation on cement activation energy (Schindler, Dossey and McCullough, 2002). The water/cement ratio (w/c) necessary for CSA to completely hydrate is 0.75 (Fang et al., 2015), therefore w/c = 0.8 was used to ensure that all types of cement completely hydrated for comparison.

Table 3.5 The mix proportions of concrete used in tests

Water (kg/m³)	Cement (kg/m³)	Aggregate (kg/m³)	w/c	Aggregate- cement ratio
280	350	1800	0.8	5.14

3.4.2 Procedures of manufacturing

- **Unbound materials**

The manufacturing of the aggregate samples included the mixing, placement, compaction and saturation of aggregate with water according to the customary method (Sakaki and Illangasekare, 2007; Smits et al., 2011; Smits et al., 2012; Han and Zhou, 2013), which led to the production of samples with uniform density that were fully saturated when filled with water. In addition, this method prevented

damage to the moulds and other parts of the experimental setup, such as sensors, which are commonly damaged when using vibrating methods. The manufacturing of the aggregate samples included the following steps:

1. In order to homogenise the manufacturing process between unbound materials and CAM, the same water content (4.85%) was used to blend and compact samples of unbound materials as in the manufacture of CAM, which involves 3.35% of water provided by the emulsion and 1.5% of water addition.
2. After that, aggregates were poured into a prismatic 300x300x105 mm³ mould in 2 cm thick layers and compacted by hand. The mould walls were tapped to achieve higher compaction. Every layer of aggregate was saturated and covered with water for 3 mm thickness, then after waiting for 10 min (to be sure of full saturation of the aggregate layer) the placement of the next layer of aggregate began.
3. Once the whole mould was filled with aggregates and water, an extra 1 mm of water was added on top. The mould was covered with a plastic wrap to prevent evaporation and left for 2 h to ensure full saturation.
4. After this time, the water level was checked. If it had decreased, more water was added and the test sample was left to rest again. Once the water level was constant, the samples were ready to be tested.

In order to reduce uncertainty in the results due to manual compaction, every test was repeated three times and the final results were obtained as the average value of all iterations.

On average, the water needed to saturate aggregate test samples ranged from 5.55% to 10.30% by mass of dry compound-sized aggregates samples, while for single-sized aggregate, higher contents were needed, from 10.85% to 27.85%.

Although full saturation of specimens does not represent a likely situation in the field, for the present research work and with the aim of obtaining the most universal conclusions possible, tests were performed by covering the whole range of water contents that a sample can present. This is from fully saturated to fully dry.

➤ **CAM**

For the present investigation, CAM samples were produced by mixing crushed aggregates, tap water, bitumen emulsion and cement. Limestone aggregate with a maximum size of 10 mm was used, in accordance with BS EN 13108-1:2006 (BS EN 13108-1, 2006) (Figure 3.3), which has been found to promote fast drying (Saadoon, Garcia and Gómez-Meijide, 2017).

The same placement and compaction method as for the unbound materials was followed in the manufacturing of CAM. The mixing method followed was previously used in other studies (Oke, 2011), leading to the production of CAM with uniform coating of bitumen emulsion.

➤ **Cement concrete**

The cement concrete used for the present investigation was manufactured by mixing crushed aggregates, tap water and cement. Limestone aggregate with a maximum size of 10 mm was used based on previous research, as it showed fast water evaporation (Saadoon, Garcia and Gómez-Meijide, 2017) and high strength, especially when used with CAC (Amour, Monteiro and Scrivener, 2001).

The mixing process was carried out in two rotary mixers to produce concrete with appropriate workability and homogeneity. First, the aggregates were mixed at ambient temperature for 5 min to ensure homogeneity. Then, these aggregates were placed in the second mixer in two layers, with a layer of dry cement in between. These materials were mixed for 1.5 min before adding the required quantity of water and mixing for another 2 min.

Concrete was cast in two layers using 100x100x100 mm³ cubic moulds previously cleaned and oiled. Each layer was compacted by a vibrating table for about 25-30 sec. Once the top layer was compacted, it was smoothed and levelled using a steel trowel. The whole process was carried out at $20 \pm 2^\circ\text{C}$.

3.4.3 Curing of cement concrete

After demoulding the cement concrete samples, they were completely immersed in water at the required curing temperature. The water surface was periodically monitored and more water was added when necessary to ensure that the specimens remained completely immersed at all times. Different temperatures are necessary to test the activation energy of cement (ASTM C1074, 2011). Heat chambers were used to conduct the curing work (Figure 3.7).

Due to effect of temperature on the characteristics of CAC microstructure (Odler, 2000), CAC cement samples were cured at 16 different curing temperatures (4°C, 7°C, 9°C, 12°C, 15°C, 20°C, 24°C, 27°C, 32°C, 35°C, 38°C, 40°C, 48°C, 50°C, 53°C and 56°C). These temperatures were chosen according to previous studies (Odler, 2000; Kirca, 2006) that classified the curing temperature into four ranges according to the resulting hydration products: (a) 0–10°C produces CAH_{10} ; (b) 11–27°C produces CAH_{10} and $\text{C}_2\text{AH}_8 + \text{AH}_3$; (c) 28–40°C produces $\text{C}_2\text{AH}_8 + \text{AH}_3$; and (d) $> 40^\circ\text{C}$

produces $C_3AH_6 + AH_3$. For the case of OPC and CSA cements, 7 different curing temperatures (10°C, 20°C, 30°C, 35°C, 40°C, 50°C and 55°C) were considered sufficient, as the resulting composition does not depend significantly on the temperature (Beaudoin et al., 1998; Canut, 2011; Neville, 2012).

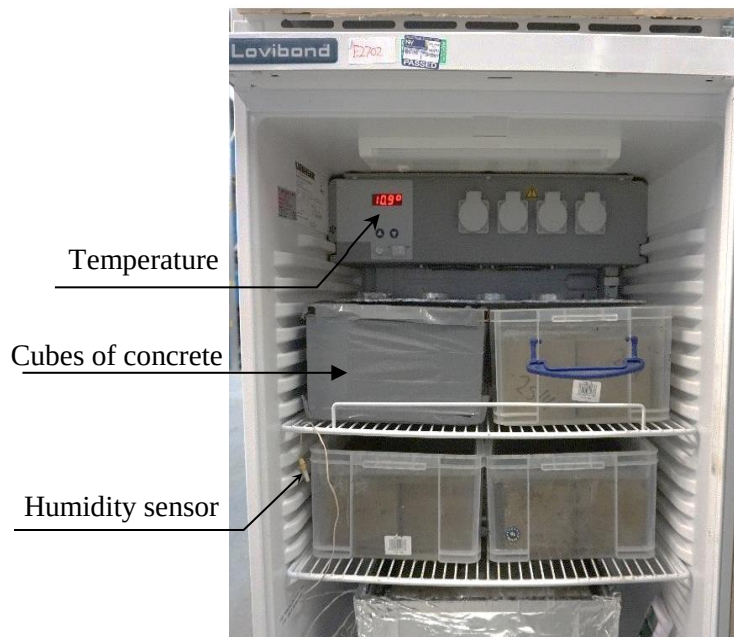


Figure 3.7 The curing process of the cement concrete samples.

3.5 LABORATORY TESTING PROGRAM

The experimental work in the current investigation involved many variables including evaporation, mechanical, hydraulic, microstructure, cement interaction dynamics, which affected tests in numerous ways, as explained below. As explained in chapter one, the purpose of this project is to understand and predict the curing process on

surfaces built of CAM, therefore most of these tests, especially evaporation tests, employ to the usage of CAM as a surface layer.

3.5.1 Dynamics of water evaporation in unbound materials /CAM

➤ Setup of test

The dynamic water evaporation test was carried out using the test device described in Figure 3.8,

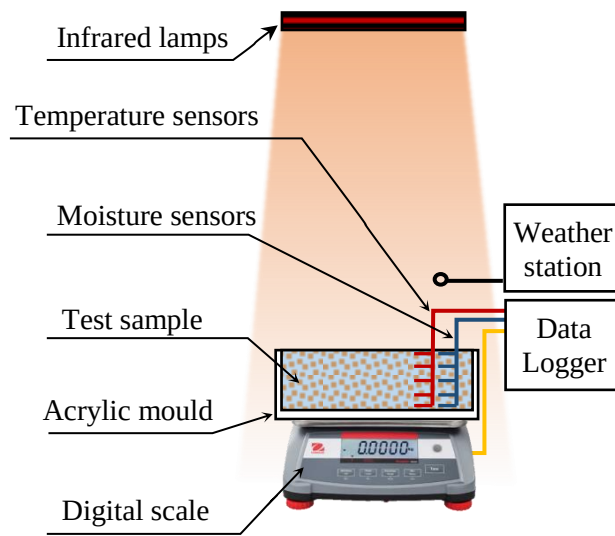


Figure 3.8 Experimental setting and instrumentation for dynamic water evaporation test

The water content and temperature of samples were monitored during the test period by moisture sensors (DFRobot Moisture Sensor) and thermocouples (K-type) respectively. Both types of sensor were selected based on their small size and flexibility, being suitable to be left embedded and compacted within the material. The total number of moisture sensors and thermocouples used in every sample was seventeen (five moisture sensors and twelve thermocouples), installed as follows:

1. Two PVC pipes of 1.5 cm diameter were used to install the moisture sensors and thermocouples.
2. Every PVC pipe was perforated with holes equal to the number and cross sections of moisture sensors and thermocouples.
3. The bottom opening of pipes was adhered to the base of the mould by epoxy, while the top side was left open to pass cables (for moisture sensors and thermocouples) through it.
4. Two PVC pipes were installed equidistant from the centre of the mould (acrylic square).
5. Insulation tape was used to cover all the walls of the pipe and the top side (after the cables were passed), to prevent the entry of water or aggregate particles to the inside of the pipe.
6. The moisture sensors and thermocouples were arrayed from a distance of 0.5 cm from the surface of sample until 8.5 cm for moisture sensors and 9.5 cm for thermocouples. Moisture sensors were 2 cm apart, while thermocouples were 1 cm apart.
7. The temperature at the top and bottom surfaces of the sample were controlled by thermocouples installed at the surface and bottom of the sample.

The temperature and relative humidity of air just above the surface of the sample were monitored during the test by using weather station (PCE Instruments) installed adjacent to (but not touching) the mould of the sample. The moisture sensors, thermocouples, geothermal heat flux transducer, and weather station were set to record the data automatically by connecting to a data logger type DFRduino UNO R3 for the moisture sensors, Omega OMB-DAQ-54 for thermocouples and geothermal heat flux transducer, and PCE Instruments for the weather station. The acrylic mould

of the sample was placed on a digital weight scale to record the loss of weight with time automatically by connecting directly with computers. The type of weight scale was Ohaus Ranger 3000, which has a capacity of 30 kg and accuracy of 0.001 kg.

Moisture sensors, thermocouples, geothermal heat flux transducer, weather station and digital weight scale were set to record data at the same time and at 15 min intervals. The air above the surface of the sample was controlled at $12 \pm 2\%$ (humidity), $40 \pm 3^\circ\text{C}$ (temperature) using four infrared lamps, with an energy capacity of 250W, as a heat source. The lamps were arrayed in square formation, with the centre of each lamp 7 cm distant from the others. The lamps were suspended above the surface of the sample from a steel frame. The vertical distance between the top surface of the sample and the bottom of the lamps was 65 cm.

➤ **Test procedures**

After ensuring that the aggregate sample became fully saturated (section 3.4.2), the open boundary of the mould was covered with a plastic sheet to prevent evaporation until the start of the evaporation test. Infrared lamps and the weather station were then turned on and the temperature of the air was monitored. When the temperature reached approximately 40°C , the plastic sheet was removed and the test began (i.e. the weight scale, the data loggers for moisture sensors, thermocouples and geothermal heat flux transducer were turned on simultaneously). When the data of all moisture sensors was zero, the water quantity in the sample was less than 0.1% of the water quantity used to saturate the sample, and the loss of weight of the aggregate sample (i.e. loss of water) was less than 0.5% between the previous weight and the next; and the temperature in the sample became constant, then the sample was considered dry and the test was finished.

3.5.2 Hydraulic properties

➤ Hydraulic conductivity test

The hydraulic conductivity was measured at room temperature ($20 \pm 2^\circ\text{C}$) by following the Florida Method (falling head method) (Florida, 2004). Figure 3.9 shows the setup of the hydraulic conductivity test.

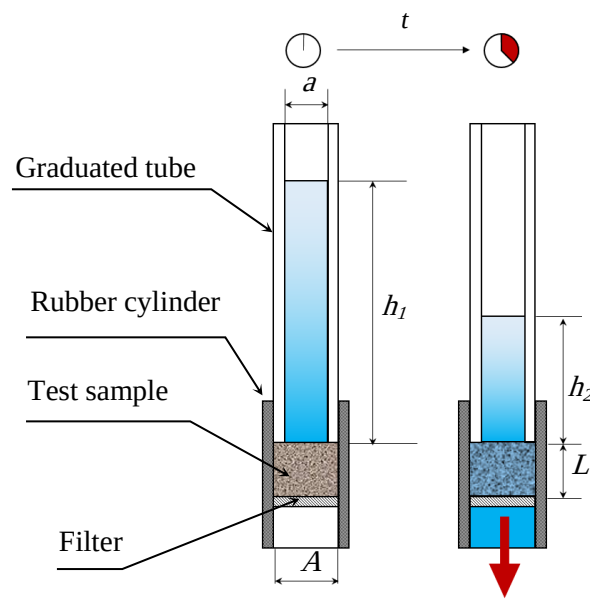


Figure 3.9 Hydraulic conductivity test

CAM samples were tested at different curing times in order to assess the evolution of these mixes. Before the test, each sample was conditioned at $20 \pm 1^\circ\text{C}$ for 4 h. Then, mould and sample were confined into a hollow rubber cylinder and a graduated acrylic tube was placed and sealed on the upper end of the cylinder.

A sufficient amount of water was poured from the upper side of the acrylic tube while blocking water flow through the bottom side of the specimens. Once the required water level was achieved, the samples were allowed to rest for 3 h to ensure that they were completely saturated. Then, the water was allowed to run out of the sample and

the time until 700 ml of water drained was measured. Hydraulic conductivity (K_s) was calculated based on Darcy's law (Florida, 2004) as:

$$K_s = \frac{a L}{A t} \ln \left(\frac{h_1}{h_2} \right) \quad (3.1)$$

Where a is the inner cross-sectional area of the graduated tube (cm^2), L is the test sample thickness (cm), A is the test sample cross-sectional area (cm^2), t is the time elapsed between the initial head and the final head (sec), h_1 is the initial head across the test specimen (cm), h_2 the is the final head across the test specimen (cm).

➤ Porosity test

The porosity was calculated once for each aggregate because it is a constant property. For the CAM, porosity was calculated at different ages because the structure of CAM changes with time. Samples for porosity tests had the same description (dimensions, manufacturing, curing) as for hydraulic conductivity tests (section 3.4.2). According to the manufacturing method of the samples in the current work, initial total water in the samples was used to calculate initial porosity ($t=0$). With regard to aggregate, porosity at initial age is also the porosity at all remaining ages. Porosity of CAM was calculated by adding water to the sample until it became stable for 7 h at the surface of the sample (water level was stable at the surface of all samples over this period (7 h) and did not move inside of sample though this period, which means that all samples became fully saturated. Equation 3.2 is used to calculate porosity (Φ).

$$\Phi(t) = \frac{V_w(t)}{V_m} = \frac{W_w(t) \cdot \rho_w}{V_m} = \frac{(W_m(t) - W_{bw}(t) - W_s) \cdot \rho_w}{V_m} \quad (3.2)$$

where V_m is volume of specimen, $V_w(t)$ is volume of total water inside the sample at the time (t) , $W_w(t)$ is the weight of total water inside the sample at time (t) , ρ_w is density of water, $W_m(t)$ is weight of specimen at time (t) , $W_{bw}(t)$ is the quantity of water reacted with cement at time (t) and W_s is the weight of solid materials in the sample (mould, aggregate, bitumen and cement) at the beginning of the test. The final weight (W_s) was calculated according to the mixture proportion of the CAM (see section 3.5.4). According to the oven-dry method, used in other references (Saadoon, Garcia and Gómez-Meijide, 2018 a), water bound by cement was calculated against time.

3.5.3 Evolution of water in CAM

The total amount of water included in CAM is provided through three ways: (1) water provided by the asphalt emulsion; (2) pre-wetting water added to the aggregates to reduce their absorption before mixing with the binder; and (3) extra water added to obtain the optimum compaction of the mix. Over the drying process, most of this water will be evaporated and a small amount will remain trapped inside cavities even after long curing times. If cement is added to the mix, the water will also react with it during its hydration.

The quantity of water that is evaporated during the drying process was determined by the oven-drying method (Carino, 1991; Scharf and Odler, 1992; Amour, Monteiro and Scrivener, 2001; Winnefeld and Barlag, 2010; Saadoon, Garcia and Gómez-Meijide, 2018a). This simple method consists of subjecting the samples to a temperature of 105°C until the sample mass becomes constant. At that time, all the water that had not reacted with cement and was not trapped in closed pores had been evaporated. Hence, the evaporation water can be determined as the mass lost during the drying process.

Control CAM samples (CAM-N) without cement were used to measure the trapped water. These samples were first cured at 40°C until a steady-state mass was reached (typically, less than 0.5% of mass change per day). After that, samples were gently crushed into pieces with size smaller than 5 mm and fully dried again at $105 \pm 1^\circ\text{C}$. The mass of trapped water could then be calculated using Equation 3.3:

$$W_{tr} = W_t - (W_{ec} + W_{ed}) \quad (3.3)$$

where W_{tr} is the total trapped water inside the sample; W_t is initial water content at time zero; W_{ec} is the evaporated water during curing at 40°C; and W_{ed} is evaporated water during drying at 105°C.

In the present research, the volume of evaporated water during drying at 105°C was negligible, which means that practically all the water remaining inside the samples without cement is trapped water. The content of the trapped water, calculated as the average of 20 different samples, was 0.63% for the CAM-N mixture, which can be compared to the residual water content (3% of the mixture) on site found by Muncy, (1990). Clearly, on site not all potentially evaporable water actually evaporates.

In order to obtain the hydration degree of cement with time, after the trapped water is known, the same procedure was repeated on samples containing also cement. Hence, these samples were first cured at 40°C until the required age, then they were gently crushed into pieces with less than 5 mm size and fully oven-dried at $105 \pm 1^\circ\text{C}$. In order to avoid increases in sample weight due to carbonation of cement during the drying process in the oven (Canut, 2011), CO_2 was removed by introducing containers filled with NaOH (Zhang and Scherer, 2011; Korpa and Trettin, 2006). Finally, the degree of cement hydration, $\alpha(t)$ could be also calculated using Equation 3.4, once

evaporation and trapped water were known (Garcia et al., 2013; Korpa and Trettin, 2006):

$$\alpha(t) = \frac{w_b(t)}{w_{bt}} = \frac{W_t - W_e(t) - W_{tr}}{W_h * Q_c} \quad (3.4)$$

where $\alpha(t)$ is the hydration water reacted with cement at a given time (t); w_{bt} is hydration water reacted with cement at full hydration; W_t is the initial total water in the sample at time $t=0$; $W_e(t)$ is the evaporated water at a given time (t); W_{tr} is the amount of trapped water; W_h is the amount of water required to produce full hydration of 1 g of cement; and Q_c is the quantity of cement in the sample.

It should be noted that there is a conversion in the internal structure of hydration products when using CAC, which produces the release of some water that has already reacted with cement (Odler, 2000). In the present research, this phenomenon was taken into account and calculations were corrected. The hydration water obtained per gram of cement at full hydration is 0.7 g/g for CAC, 0.75 g/g for CSA and 0.42 g/g OPC (Powers and Brownyard, 1948).

3.5.4 Mechanical performance

❖ Marshall stability test

The mechanical performance of CAM was evaluated by the Marshall Stability test, which gives an idea of the compressive resistance of the material. The samples were prepared and cured as explained for the dynamic water evaporation test, but by using cylindrical moulds of 95 mm diameter and 100 mm height. In order to compare the results of tests with previous work in which the Marshall test was conducted at 20 °C

(Fang et al., 2015), each sample was left at $20\pm1^\circ\text{C}$ for 4 h before the test. The test was performed at a temperature of $20\pm3^\circ\text{C}$ by applying an increasing compression at a rate of 50 mm/min (strain control). The stability is defined as the maximum load resisted by the sample before breaking. In this study, every result of stability was obtained as the average of three samples.

The addition of cement to CAM accelerates the gain of stability provided by the broken emulsion, but the maximum level reached at the end of the curing process is practically the same (Fang et al., 2015). Hence, it was also assumed that the stability $S_c(t_1)$, provided to CAM by the products of cement hydration at a certain time t_1 can be estimated as the difference between the stability $S_{CAM-C}(t_1)$, registered by CAM with cement at time t_1 , and the stability $S_{CAM-N}(t_2)$ of the mix without cement at a time t_2 , at which the breaking degree of the emulsion is the same as that for mixes with cement at time t_1 . As the cement produces a significant effect on the breaking process, the times t_1 and t_2 are not necessarily the same:

$$S_c(t_1) = S_{CAM-C}(t_1) - S_{CAM-N}(t_2) \quad (3.5)$$

In addition, the stability of mixes without cement can be calculated as:

$$S_{CAM-N}(t_2) = S_{fn} * D_b(t_1) \quad (3.6)$$

where S_{fn} is the final stability of CAM-N when the material is fully dried and $D_b(t_1)$ is the breaking degree of bitumen emulsion in mixes with cement at time t_1 . This can be calculated as follows:

$$D_b(t_1) = \frac{W_{eb}(t_1)}{(W_t - W_{tr})} \quad (3.7)$$

where $W_{eb}(t_1)$ is the quantity of water evaporated and reacted with cement in CAM at time t_1 , W_t is the total initial water at the beginning of the test and W_{tr} is the trapped water. The procedures to obtain these amounts of water were described in Section 3.5.4.

❖ Compressive strength test

The mechanical behaviour of concrete was evaluated through uniaxial compressive tests on 100 x 100 x 100 mm³ cubic specimens, according to BS EN 12390-3 (BS EN 12390-3, 2009). A standard testing machine (Contest) with a maximum capacity of 2500 kN was used. The tests were performed at different curing times, 0.50, 1.0, 1.5, 2, 4, 8, 16 and 28 days. For CSA and CAC, additional measurements at 0.13 and 0.25 days were also possible. For each material and curing time, three specimens were tested and the average value was obtained. The compressive strength (fcs) was calculated as:

$$fcs = P/A \quad (3.8)$$

where P is the maximum load registered (N) and A is the initial cross section area of specimens (mm²).

3.5.5 Microstructure of samples

➤ X-ray computed tomography (CT scans) test

The test samples used for the hydraulic conductivity tests were fully saturated and scanned by using a Phoenix v|tome|xL scanner. The X-ray source was operated with an acceleration voltage of 290 kV and a current of 1300 μ A. The test samples were scanned on a rotational surface, leaving a distance from the X-ray source of 906.84 mm. The spatial resolution was 96 μ m/pixel, also between consecutive slides. The 16-

bit images were processed by the software Avizo 8.1 and ImageJ, Version 1.49 [Abràmoff, Magalhães and Ram, 2004], to convert them into 8-bit greyscale resolution and cropped into a region of interest (ROI) of $6 \times 6 \times 4 \text{ cm}^3$. Then, 3D Gaussian and Median filters ($1 \times 1 \times 1$ kernel size) were used to reduce image noise. Reconstructions of the microstructure were prepared by segmenting the materials in the ROI, based on greyscale thresholding, which made possible the separation between air voids and aggregates.

The microstructure parameters defined in Table 7.1, were determined by BoneJ particle analyser plugin (Version 1.3.11) in ImageJ software [Abràmoff, Magalhães and Ram, 2004]. The length of macropores was obtained by Analyse Skeleton and Skeletonize 2D/3D modules in ImageJ [Doubé et al., 2010].

➤ **Scanning electron microscopy (SEM) test**

Scanning electron microscopy (SEM) was used to investigate the effect of curing temperature on the morphology of cement concrete over the curing time. Samples with a largest dimension shorter than 7 mm were taken from the centre of crushed concrete blocks and weighed before starting the test; the samples must be dried and the hydration process stopped. The specimens were immersed in 1000 ml beakers containing organic solvent (solvent exchange), diffusing the solvent into the samples to replace the pore solution (water) and decrease the relative humidity (RH) (Canut, 2011). Isopropyl alcohol or isopropanol with a density of 0.78 g/cm^3 is commonly used as a solvent (Feldman and Beaudoin, 1991; Beaudoin et al., 1998; Kocaba, 2009) and was selected for the present investigation. Although a high concentration was used (solution/sample volume ratio $> 100:1$) solvents were renewed every 1 h for the first 5 h, then once a day for a week as previously described (Zhang and Scherer,

2011). The immersion time of specimens into organic solvent to fully replace interstitial water depends on the porosity, diffusivity and dimensions of the samples, as given by the following equation (Zhang and Scherer, 2011):

$$\frac{\langle c(r,t) \rangle - C_1}{C_0 - C_1} = \sum_{n=1}^{\infty} \frac{\beta}{n^2 \pi^2} \exp \left[-n^2 \pi^2 \left(\frac{Dt}{a^2} \right) \right] \approx \frac{\beta}{\pi^2} \exp \left[-\pi^2 \left(\frac{Dt}{a^2} \right) \right] \quad (3.9)$$

where C_0 is the initial concentration, C_1 is the constant surface concentration, $\langle c(r,t) \rangle$ is the average concentration in the particle, β is a constant whose value is $\beta = 6$ according to Zhang and Scherer (2011), D is the diffusivity, t is the equilibration time and a is the characteristic dimension.

In the present research, solvent penetration was continuously monitored by measuring changes in the specimen weight. However, it could be checked that the time obtained by Equation 3.9 (8 days on average) was shorter than the time required by samples to reach a steady-state weight (variations lower than 0.1% per day). Hence, the latter (19 days) was selected to make sure that tests were performed once all the water was removed from the samples.

Once the hydration was stopped, isopropanol was removed simply by ambient drying, as recommended by Zhang and Scherer (2011). The weight of specimens was continuously monitored until the variations were lower than 0.1% per day. At this time, the samples were considered fully dried (Zhang and Scherer, 2011). Finally, the electric conductivity of specimens was enhanced by applying a high vacuum to remove dust particles with a diameter < 15 nm and by coating the samples in platinum. SEM was performed on a FEI Quanta 600 MLA SEM machine set to an accelerated voltage of 15 kV. More information about parameters used with the SEM setup to make the images is included below every image.

Chapter Four

Dynamics of water evaporation in cold asphalt mixtures

4.1 INTRODUCTION

Water dynamics in porous materials have been studied for several decades (Keen, 1914). It is known that when evaporation is started, three zones can be differentiated: saturated, semi-saturated or film region, and dry (Fisher, 1923). In addition, the dynamics of water evaporation in porous materials are divided in three stages: (i) first, (ii) transition and (iii) second (Fisher, 1923). The evaporation rate changes depending on the stage, being higher during the first stage and reducing during transition and second stages (Shokri, Lehmann and Or, 2010 a).

The main objective of the present chapter is to understand the dynamics of water evaporation during the curing process in CAM and relate them to the acquisition of mechanical properties. In order to assess this, (1) evaporative flux evolution, (2) liquid phase distribution, (3) dominant mechanisms supplying and controlling the

drying rate, and (4) effect of grain and pore size distributions on drying behaviour, will be studied.

In addition to CAM samples, the dynamics of water evaporation of 11 different samples of unbound material will be investigated in the current chapter. This higher number of different samples was necessary to: (1) validate the proposed methodology, based on the theory of water dynamics in soils, at the most universal level possible; and (2) to establish a wide scale where the performance observed for CAM can be placed and compared.

4.2 THEORETICAL CONSIDERATIONS

The film region is the zone of maximum hydraulic conductivity and is located between the main evaporation surface and the receding drying front. It might be considered dry but due to capillary forces it contains columns of water rising through the pores from the lower saturated zone. The characteristic length, L_c , represents the thickness of this region. In other words, L_c is the maximum thickness of dry material that capillary forces can fill with water. In this region, differences in size between connected pores lead to differences in capillary pressure, which drives the water flow to the surface of the sample. Hence, the pore size distribution has an important effect on the capillary forces. To analyse it, the pore size distribution index (n), has been widely used and related to other water dynamics properties, such as water saturated hydraulic conductivity (K_s) as follows (Lehmann, Assouline and Or, 2008):

$$K_s = k_1 \cdot n^{k_2} \quad (4.1)$$

where k_1 and k_2 are fitting parameters (values proposed in Lehmann, Assouline and Or (2008) as the average of a series of granular materials, such as clays, loams and sands: $k_1 = 0.0077$ and $k_2 = 7.35$).

As explained in the reference (Lehmann, Assouline and Or, 2008), the width of the pore size distribution in porous media can be extracted from the relationship between the capillary pressure and liquid saturation, represented as water retention curves that determine the water saturation depending on the height above the water table (h). According to Lehmann, Assouline and Or (2008), the water retention curves can be linearized as shown in Figure 4.1, h_b being the air-entry value, defined as the head at which the tangent reaches full saturation value, Δh_{cap} is the difference between the capillary pressure needed to drain the largest pores (air-entry value) and the smallest drainable ones, and $h_b + \Delta h_{cap}$ the head at which the tangent saturation becomes 0. Due to the equivalence between head and height above free water level, Δh_{cap} can be estimated as:

$$\Delta h_{cap} (Lc) = \frac{1}{\alpha (n-1)} \left(\frac{2n-1}{n} \right)^{(2n-1)/n} \left(\frac{n-1}{n} \right)^{(1-n)/n} \quad (4.2)$$

where α , extracted from the Van Genuchten parametric model for water retention curves (Van Genuchten, 1980), is the inverse of the air entry suction (1/mm) and can be obtained as follows:

$$\alpha = \alpha_1 (n-1) \quad (4.3)$$

In this equation, α_1 is a fitting parameter (value proposed in Lehmann, Assouline and Or, 2008 as the average of a series of granular materials, such as clays, loams and sands: $\alpha_1 = 0.0087$).

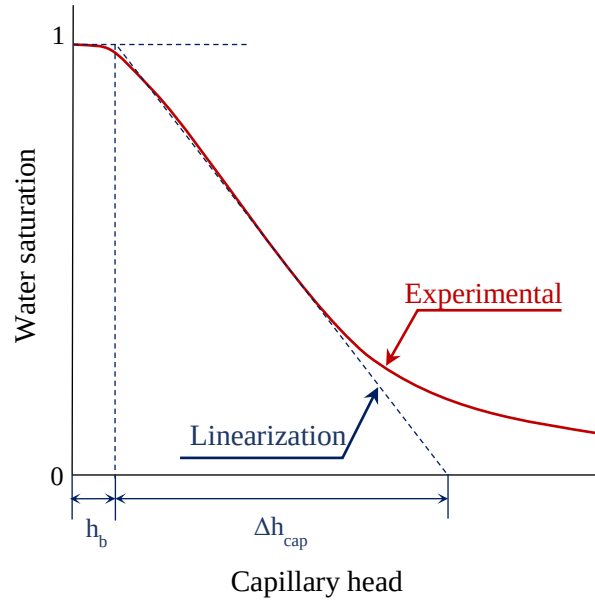


Figure 4.1 Linearization of water retention curve

Finally, for small values of the ratio between the potential evaporation rate and the unsaturated hydraulic conductivity (e_0/K), the viscous dissipation effect during the evaporation can be neglected, considering only the equilibrium between capillarity and gravity (Lehmann, Assouline and Or, 2008). For this reason, it can be assumed that $L_G \approx \Delta h_{cap}$. These correlations allow to obtain not only n as a function of K_s but also L_C as a function of n . As a consequence, L_C can also be obtained as a function of K_s :

$$L_c = f(n) \text{ and } n = f(K_s) \rightarrow L_c = f(K_s) \quad (4.4)$$

As a result, by determining K_s through hydraulic conductivity tests, n and L_C could be easily estimated without the need of drying and monitoring the evolution of the drying front. Moreover, by fitting the estimated L_C -values from the water conductivity measurements to water evaporation tests, k_1 , k_2 and α_1 could be obtained.

4.3 RESULTS

4.3.1 Internal pore size distribution

Changes in the internal pore size distribution of CAM during the curing process were studied through variations of the pore size distribution index, n (Figure 4.2) which presents the ratio between the sizes of the pores. This parameter was constant in time for aggregate samples while variable for CAM over the drying time.

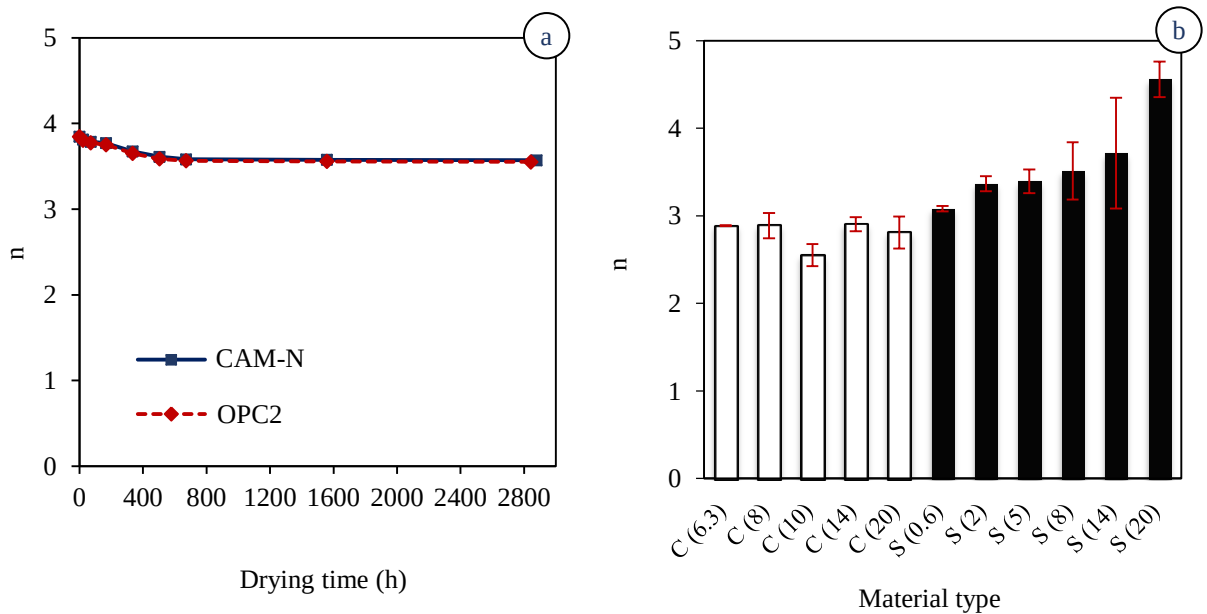


Figure 4.2 Evolution of pore size distribution index (n) with time for cold asphalt without (CAM-N) and with 2% of Portland cement (OPC2) (a) and (b) n -values obtained for aggregate samples with standard deviation (these values were found constant over drying time)

The average n -value obtained for compound aggregate gradations was 2.8 and the standard deviation was 0.1: it did not depend on the maximum size. In contrast, for single-sized aggregates, n increased with the size of the aggregate from 3.0 to 4.5. This shows that the topology of air voids influenced n only when the pore size was above a minimum, as reported in Aboufoul and Garcia (2016). Since it has been reported that

mixtures with higher n need more time to evaporate (Lehmann, Assouline and Or, 2008), it is expected that the time needed to dry single-sized gradations will be longer than for compound aggregate gradations. Furthermore, in CAM, n decreased from 3.8 to 3.6 during the first 2 weeks curing and remained steady afterwards, see Figure 4.2 (a).

In addition, although CAM test samples were made with a compound gradation and 10 mm maximum size, their n -values were between 28% and 37% higher than the average value of 2.8 obtained for other samples with compound aggregate gradation. This means that their hydraulic conductivity is higher, possibly due to the presence of the emulsion and a consequent reduction in mix viscosity and compaction, compared to mixes with only aggregates and water. In addition, as has been reported in Garcia et al. (2013) the presence of bitumen emulsion leads to poor compaction by Marshall method and increased air voids in CAM. It was also found that n can be correlated to time in Figure 4.2 through the empirical equation obtained with the Eureka Nutonian software:

$$n = n_0 + n_1 \exp(n_2 t) \quad (4.5)$$

where n_0 , n_1 and n_2 are material constants. The equation can be read as a first term, n_0 , provided by the aggregate skeleton and a second time-depending term provided by the binder. When there is no emulsion in the samples, $n_1 \rightarrow 0$ and n can be assumed constant over the drying time. By using Excel's Solver tool until the square error reached a minimum, the constants were obtained as $n_0=3.564$ $n_1=0.282$ and $n_2=0.003$ and the correlation coefficient $R^2=0.977$.

4.3.2 Dynamics of water evaporation

Figure 4.3 shows the time required to completely dry the test samples, defined as the time when the evaporation rate became zero.

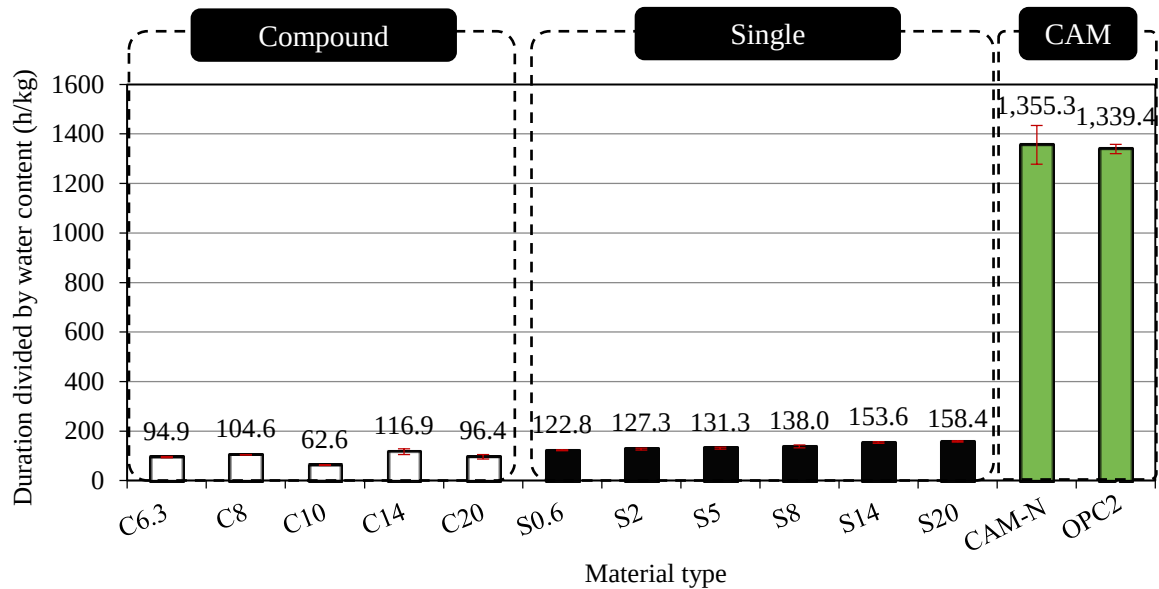


Figure 4.3 Time for fully drying of cold asphalt without (CAM-N) and with 2% cement (OPC2) compared to compound-sized and single-sized aggregate samples

As each material required different amounts of water to be fully saturated, the drying times were normalised by dividing them by the maximum amount of water contained in each specimen. Hence, the evaporation-mass ratio or average time that each material needed to dry a mass unit of water, was obtained. Compound-sized aggregate samples had average evaporation-mass ratio 94.8 h/kg and standard deviation 17.9 h/kg, and the results seem to fluctuate around this average value instead of following a specific trend when varying the maximum size of the aggregate. On the other hand, the time needed to dry single-sized aggregates increased steadily with their size, from 122.9 h/kg to 158.4 h/kg, for aggregates S0.6 and S20, respectively. In Figure 4.2 it was shown that the aggregate size and n are directly correlated for single-sized

aggregates. For this reason, it can be concluded that the time needed to dry this type of aggregate is directly correlated to its n-value. These results contrast with those obtained for CAM with and without cement, 1339.6 h/kg and 1355.3 h/kg respectively, which are 8.6 times higher than S20, the worst case for aggregate samples and 14.3 times higher than the average value obtained for compound-sized aggregates, 94.8 h/kg.

Moreover, the duration of the drying stages was calculated following the recommendations of Shokri and Or (2011): the length of the first stage was determined based on the cumulative mass loss over time (Figure 4.4-b shows the procedure for the example case of sample C8). Since the main factor affecting the water evaporation dynamics during this stage is temperature (Rad, 2014), which was constant after the first 3 h, the cumulative curve showed a quasi-linear increase. Thus, the time when the first stage finished was determined as the moment when the curve deviated from a tangent straight line (Shokri and Or, 2011).

Following the procedure described in Shokri and Or (2011), in order to determine the time when the second stage began, the inverse square of the evaporation ratio was represented on a logarithmic scale versus the curing time (Figure 4.4-c). The curve during the second stage can be approximated to a straight line. The intersection point of the experimental results and this line can be considered the beginning of the second stage.

From these data, it can be concluded that the first stage was shorter and had higher evaporation rate than the transition and second stages. It can be also seen that a sharp and quasi-linear reduction in the evaporation rate happened during the transition

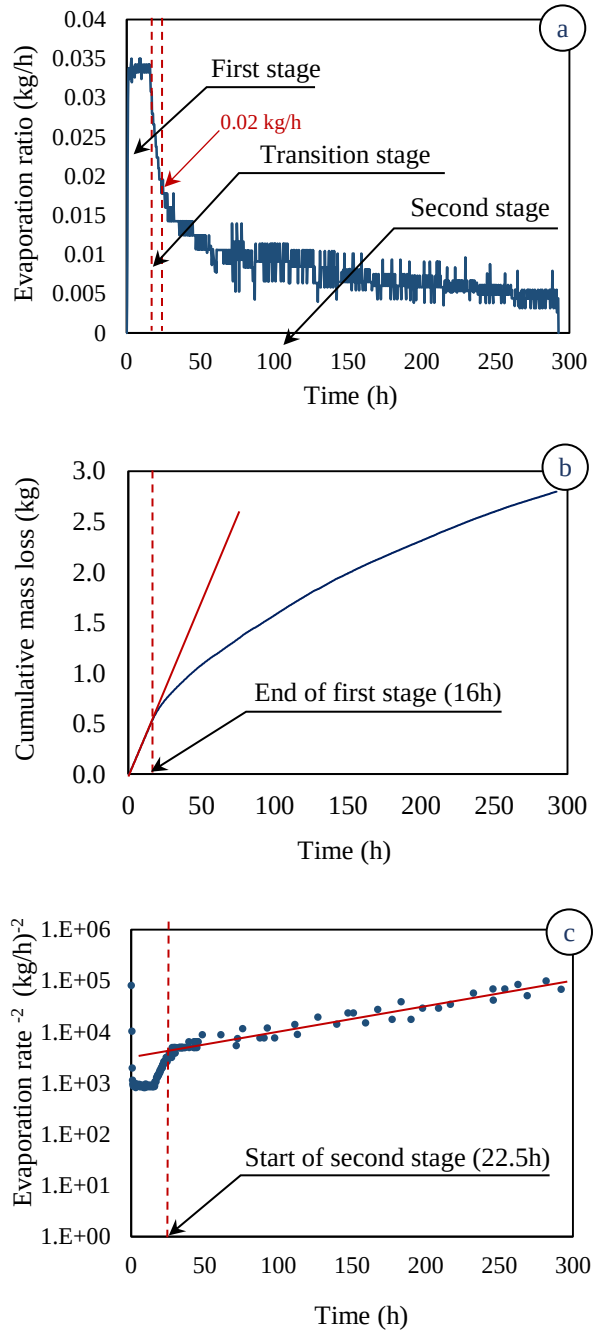


Figure 4.4 Water evaporation curve (a), calculation of end of first stage (b) and beginning of second stage (c). Example case of compound-sized aggregate sample C8

stage, e.g. from 0.034 kg/h to 0.02 kg/h in 6.5 h. Finally, during the second stage, both the evaporation rate and the slope of the evaporation ratio-time curve reduced progressively until both became zero and the material was fully dried. Figure 4.5

shows the duration of the first, transition and second stages for all the materials analysed.

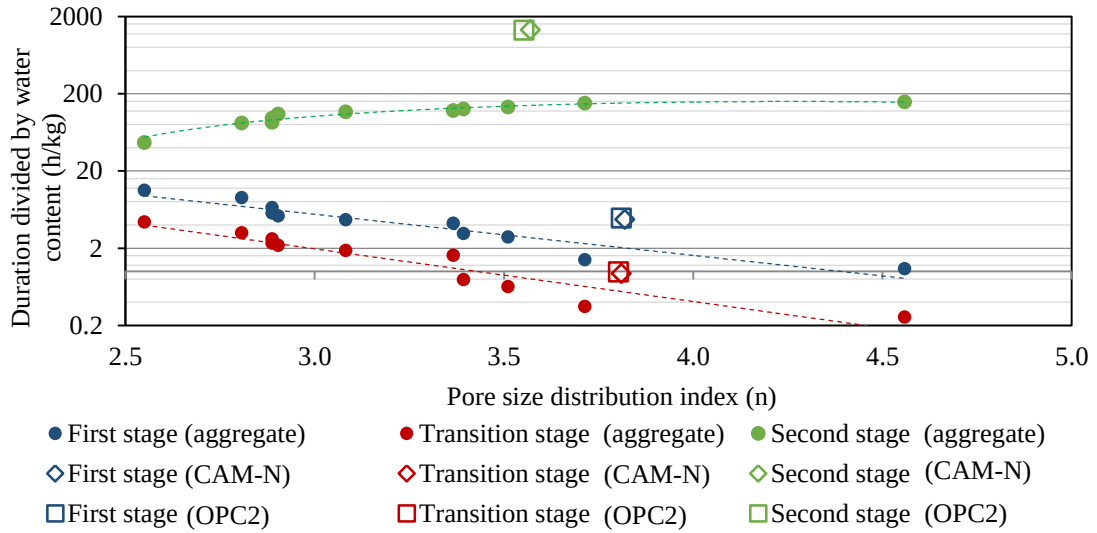


Figure 4.5 Correlation between pore size distribution index (n) and duration of drying stages

It can be seen that the first and transition stages were shorter for higher n values, while the second stage was longer. As has been commented above, the first stage of evaporation is characterised by the formation of a net of capillary water columns that becomes progressively longer with the receding drying front. Eventually, the capillaries collapse due to their own weight during the transition stage. In aggregate media with smaller n values the pore size tends to be smaller, surface tension forces play a strong role and columns are longer. As a consequence the first and transition stages need longer times to complete. In aggregate media with higher n values, capillary forces become weaker and the second stage begins earlier. As a result, water evaporation rates reduce and longer time is needed to dry the material.

In mixtures made with bitumen emulsion, the first and transition stages were respectively 2.4 and 1.9 times longer than in aggregate samples with similar n . Furthermore, the length of the second stage increased from 142 h/kg to 1340 h/kg, almost 10 times longer. In addition, when compared to aggregate samples with the same gradation (sample C10, first values at the right of each curve) it can be seen that the first and transition stages reduced respectively by 56.5% and 77.7% while the second stage increased 27.4 times. In CAM, n became lower with the curing time, not because the pores reduced their diameter, which could accelerate evaporation but because the bitumen emulsion and hydration products blocked the pores during evaporation. As the phenomenon was also observed when no cement was added, it can be concluded that the emulsion by itself can contribute to this effect. As a result, the amount of pores that allowed water evaporation during the first and transition stages reduced and the drying process, especially the second stage, became longer.

In general, it can be observed that the addition of cement did not improve significantly the performance of CAM in terms of internal structure and pore size distribution and that it did not significantly contribute to reduce the drying time. As has been seen in previous studies (Fang et al., 2015), cement improves the strength and stability of CAM but its contribution to accelerate the moisture evaporation was minimal in this study. This could be explained by the fact that the amount of water present in CAM was several times higher than the amount of water required for cement hydration, as has been previously reported by Garcia et al. (2013). In addition, the test samples were fully saturated, which increased the amount of water even further. As explained above, the saturation of specimens was carried out with other purposes different to reaching an optimum mix design. Hence, this non-standard situation might have affected the results.

4.3.3 Evolution of film region

The depths of primary and secondary evaporation surfaces were monitored during the evaporation tests by means of moisture sensors placed at different distances from the surface of the test samples (5, 25, 45, 65 and 85 mm). As an example, Figure 4.6 shows the readings obtained for the mixture S20. As can be seen, the curves of each sensor present three stages. During the first stage, the moisture level was constant and 100%. When the receding drying front reached a given sensor, the moisture level decreased abruptly. Once the section was fully dry, the moisture level became zero.

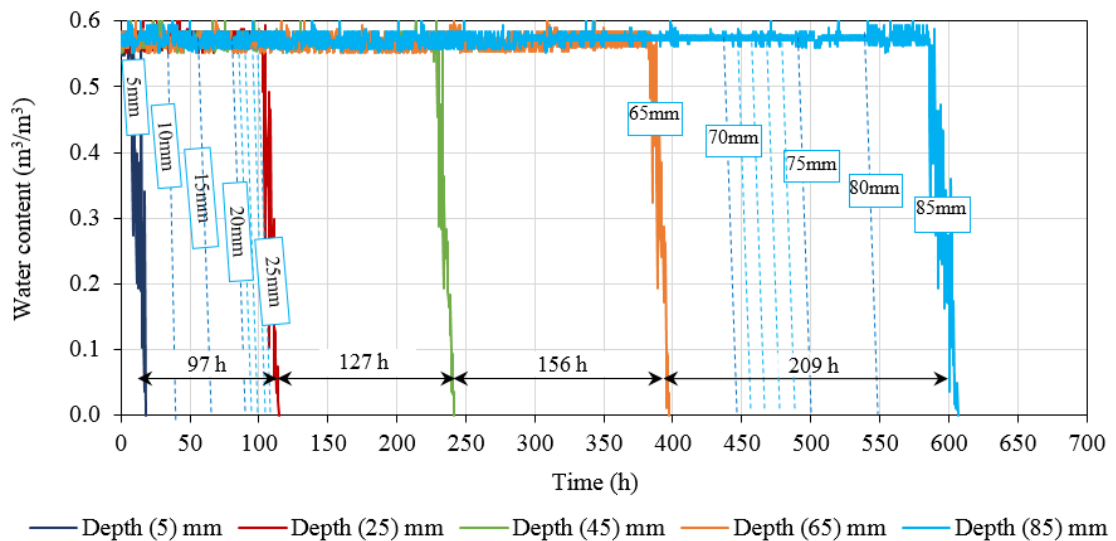


Figure 4.6 Moisture content registered by sensors placed at different depths during drying process. Example case of single-sized aggregate sample S20

In Figure 4.6, the distance between consecutive curves corresponds to the time needed by the water front to travel the vertical distance between sensors. As can be observed, the speed gets progressively slower as the drying front recedes. For example, in Figure 4.6, the drying front moved from 5 mm to 25 mm depth in 97 h but from 65 mm to 85 mm took 209 h. This deceleration indicates that the upper layers of the

material dried faster than those closer to the bottom, as has been mentioned by other authors (Shokri and Or, 2011). Reasons, such as lower temperature and energy dissipation of water travelling through the film and dry regions stand behind this behaviour and highlight the importance of reducing as much as possible the thickness of CAM layers.

In addition, sensors allowed identification of the thickness of the saturated, semi-saturated and dry layers. This was done by interpolating the values measured by the sensors. For example, the sensor placed at 25 mm depth started to measure a decrease in water content after 100 h ; therefore, 100 h was the time needed by the bottom border of the semi-saturated layer to reach that depth. Also, by interpolating the measurements with a linear function in Figure 4.6, it could be deduced that another sensor placed at 22 mm would measure zero moisture content also at 100 h . This means that the thickness of the semi-saturated layer (L_C) between the depths of 22 and 25 mm, after 100 h drying was 2 mm. Repeating the same experiment for a time $t = 500 h$, it can be seen that the thickness of the semi-saturated layer had decreased to 1 mm. In other words, the thickness of the semi-saturated layer reduced the layer moved downwards. The authors believe that the main reason for this behaviour was the lower temperature of the bottom areas, which may have affected the surface tension and capillary forces.

In addition, the same procedure to calculate L_C was applied to the rest of the materials, including CAM as can be seen in Figure 4.7. Again, it is clear that the drying process in the single-sized aggregate samples, with shorter L_C , was slower than that of compound-sized aggregate, with higher L_C . Furthermore, the evaporation was significantly slower for the case of CAM, see Figure 4.7 (bottom). The authors

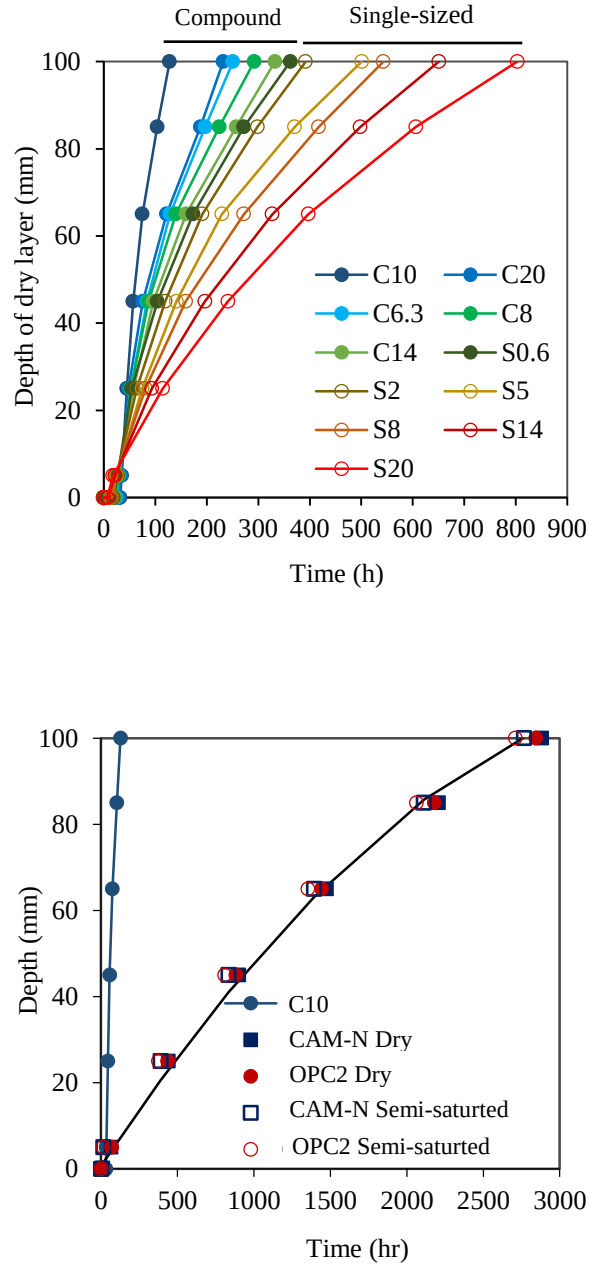


Figure 4.7 (Top) Depth of dry layer over the drying time for aggregate samples. (Down) Depth of dry and semi-saturated layers for CAM with and without cement compared to the aggregate sample with the same gradation, C10

hypothesize that drying in CAM was delayed because a superficial layer with reduced pore size distribution (low n) was produced as soon as the surface got dry, which

limited the transport of moisture to the atmosphere, although this has still to be checked experimentally.

The depth of the film region could be mathematically described by the following empirical relationship obtained using the Eureka Nutonian software:

$$h_d = \frac{k_0 t^{k_1}}{k_2 + t} \quad (4.6)$$

where h_d is the depth of the interface (mm), t is the drying time (sec) and k_0 is a constant that depends on environmental conditions during the drying process, such as temperature and humidity and k_1 and k_2 are material constants which depend on air voids characteristics, such as volume, tortuosity and pore interconnectivity. The model was fitted to the experimental data by Excel's Solver function until the square error between real and predicted data reached a minimum. As a result, the following values for the constants were determined: $k_0=0.634$; $k_1=1.635$ and $k_2=0.020$, obtaining a high-level fitting ($R^2=0.998$).

In Figure 4.8, the L_C values of all the materials analysed, calculated with (i) Equation 4.2 from hydraulic conductivity tests and (ii) data obtained from embedded moisture sensors, have been correlated to the pore size distribution index (n). It can be observed that the L_C - n correlation is independent of the type of material studied. It can be also observed that the addition of cement did not significantly affect L_C of moisture from CAM. Moreover, L_C in CAM is among the lowest of all the material types studied.

Finally, it is remarkable that L_C results are practically identical when they are calculated with Equation 4.2, from hydraulic conductivity results and when they are

directly measured with moisture sensors, demonstrating that hydraulic conductivity can be used to predict L_C of porous materials, including CAM.

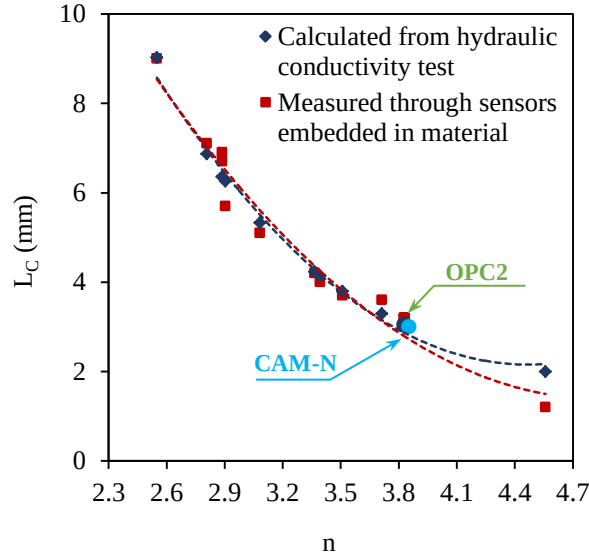


Figure 4.8 Correlation between L_C and n

4.3.4 Calibration of L_C Model

Depending on the n and L_C values in Figure 4.8, the model (Equations 4.1–4.3) of the L_C values were fitted using Excel's Optimization Solver function. Parameters k_1 , k_2 and α_1 were iterated until the sum of the squares of errors was minimised. With the obtained values, Equations 4.1 and 4.3 became as follows:

$$K_s = 0.003 n^{6.493} \quad (4.7)$$

$$\alpha = 0.134 (n - 1) \quad (4.8)$$

Combining Equations 4.2, 4.7 and 4.8, L_C and n could be estimated from the water-saturated hydraulic conductivity (K_s) of the test samples. As can be seen in Figure 4.9, L_C values calculated with Equation 4.2, i.e. calculated from hydraulic conductivity

tests and measured through sensors embedded in the mixture, were strongly correlated ($R^2 = 0.973$).

It is also noticeable that the values obtained for parameters k_1 , k_2 and α_1 , 0.003, 6.493, 0.134 respectively, were significantly different to those proposed by Lehmann, Assouline and Or (2008): 0.0077, 7.35, 0.0087 respectively. The authors have hypothesized that such differences may be caused by different aggregate properties, such as roughness, porosity and aggregate-water affinity, which can affect the water-saturated hydraulic conductivity (K_s) and the inverse of the air entry suction (α).

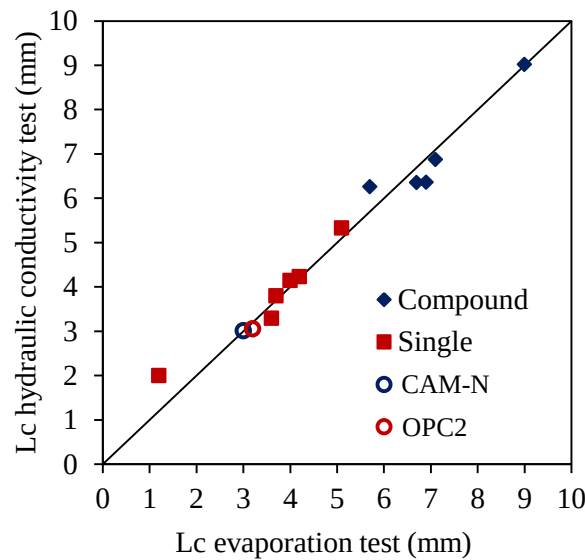


Figure 4.9 Correlation between L_C results obtained from dynamic evaporation and hydraulic conductivity tests

4.4 PREDICTIVE MODEL FOR MECHANICAL PERFORMANCE OVER DRYING TIME

It has been seen above that the thickness of the film region is much lower than that of the dry and saturated layers. In order to develop a semi-empirical predictive model for

the strength evolution of the material, it was assumed that the contribution of the film region is negligible. In addition, the thickness of both dry and saturated layers can be obtained as the distance between the film region and the top or bottom surface respectively, which is given by Equation 4.6 as a function of parameters k_0 , k_1 and k_2 fitted in Section 4.3.3.

To start the model, it has been assumed that the strength of a saturated granular material is F_w , while the strength of the same granular material under dry conditions is F_d . Under the conditions studied in this thesis, the total strength of a drying test sample with thickness, H , is given by the strength of the dry layer, with thickness variable in time, $h_d(t)$, and the strength of the saturated layer, with thickness $H-h_d(t)$.

If bitumen emulsion is added now to the granular material, the emulsion will add an extra strength to the test samples once it breaks and loses water, F_a . The adhesion between aggregate and binder increases as long as the water in between both materials is removed. For this reason, F_a is a parameter variable in time and it has been hypothesized that the adhesion between bitumen and aggregate is linearly correlated to the percentage of dry material in CAM, which can be calculated as the thickness of the dry layer divided by the total thickness of the sample:

$$F_a(t) = \alpha \cdot \frac{h_d(t)}{H} \quad (4.9)$$

where α is the relationship constant that depends on characteristics such as binder-aggregate affinity and the binder content. By combining Equations 4.6 and 4.9, F_a can be obtained as a function of time:

$$F_a(t) = \frac{\alpha}{H} \frac{k_0 t^{k_1}}{(k_2 + t)} \quad (4.10)$$

In addition, if cement is added to CAM, it will add an extra strength F_c , which is a function of time and increases with the progressive hydration of cement. According to (Abd elaty, 2014) for all clinker minerals, the relationship between compressive strength and curing time can be given by a logarithmic function with correlation factors close to 1:

$$F_c(t) = A \ln(t) + B \quad (4.11)$$

where A and B are material coefficients depending on the type and properties of the cement used, such as composition or cement particle size.

With all this in mind, the total strength variable with time, $S(t)$, that will be achieved by a CAM test sample will be:

$$S(t) = \frac{h_d(t)}{H} F_d + \frac{H - h_d(t)}{H} F_w + F_a(t) + F_c(t) \quad (4.12)$$

By substituting Equation 4.10 into Equation 4.12, $S(t)$ can be expressed as a function of h_d and the cement hydration (F_c):

$$S(t) = \frac{h_d(t)}{H} F_d + \frac{H - h_d(t)}{H} F_w + \alpha \cdot \frac{h_d(t)}{H} + F_c(t) \quad (4.13)$$

Grouping variables, Equation 4.13 can be simplified as follows:

$$S(t) = \frac{h_d(t)}{H} (F_d - F_w + \alpha) + F_w + F_c(t) \quad (4.14)$$

The equation shows that the mechanical performance of the material improves when h_d increases, reaching the maximum value when $h_d = H$. In other words, when the section is fully dry.

The strength also increases with α , which is related to the adhesion between binder and aggregates and binder content. As a consequence, the strength can be improved through the use of binders and aggregates with high affinity.

The bearing capacity of the mineral skeleton in both dry and saturated conditions, F_d and F_w , affects positively the total strength of the material. Therefore, the use of aggregates with high angularity and continuous gradations that provide high structural quality and reduce the internal pore size distribution is advisable in terms of strength gain.

If cement is added to the mix, its hydration contributes to increasing the strength of the material, through the growing of hydration products in CAM, see the term F_c . However, as explained in the present chapter, cement hydration will not accelerate the drying process due to the high amount of water contained in CAM.

Finally, Equation 4.5 gives the relationship between n and drying time, t , depending on parameters n_0 , n_1 and n_2 obtained in Section 4.3.1. By combining Equations 4.5 and 4.6, it is possible to obtain the depth h_d as a function of n , as follows:

$$h_d = \frac{\left[\frac{1}{n_2} \ln \left(\frac{n - n_0}{n_1} \right) \right]^{k_1}}{k_2 n_2 + \ln \left(\frac{n - n_0}{n_1} \right)} \cdot k_0 n_2 \quad (4.15)$$

This equation could be introduced in Equation 4.14, obtaining a direct correlation between the mechanical performance, $S(t)$ and n , once the material parameters are fitted as explained in Sections 4.3.1 and 4.3.3 and as shown in Figure 4.10 and 4.11. In other words, the mechanical performance of CAM can be estimated based on the results of quick hydraulic conductivity tests.

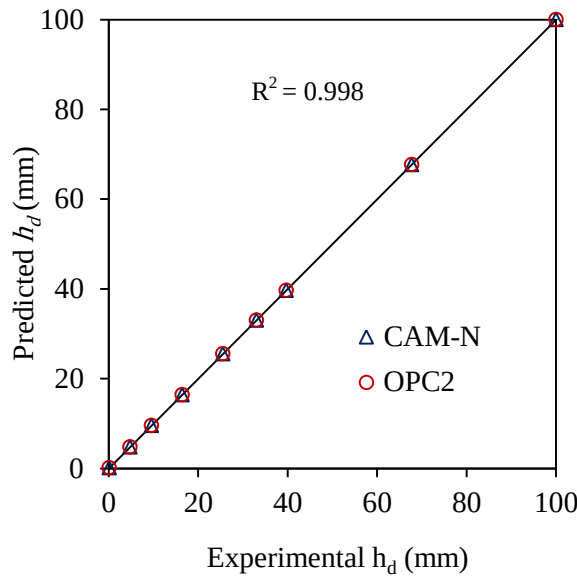


Figure 4.10 Comparison between predicted and experimental results obtained for the depth of semi-saturated interface (h_d)

By calculating the limits in Equation 4.15, it is found that n is maximum when h_d is minimum. This means that the material presents higher pore size distribution, n , when it is wet than when it is dry and the strength improves with the drying level, which matches the observations made in Section 4.3.1. In addition, it has also been seen that n is higher for mixes with emulsion than for aggregate samples. Hence, a contradictory effect is produced: on the one hand, the emulsion provides strength through the term F_a but, on the other hand, the drying process and the increase in $S(t)$

are slower. Depending on the characteristics of the material, one phenomenon will prevail over the other.

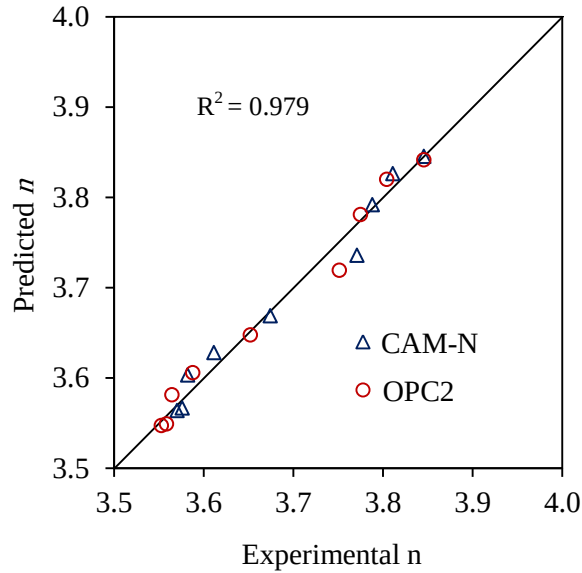


Figure 4.11 Comparison between predicted and experimental results obtained for the pore size distribution index (n)

In Figure 4.12, the results of Marshall stability obtained at different drying times are represented together with the values provided by the model, after fitting the corresponding parameters explained above, see Sections 4.3.1 and 4.3.3. As can be seen, the proposed model can predict the Marshall stability with a very high level of accuracy ($R^2=0.999$) for both mixes with and without cement. In a practical case, the model parameters could be calibrated at early drying stages and the tool could be used to estimate the stability at any time by using the pore size distribution index as input. As n can be directly obtained through quick hydraulic conductivity tests, the proposed tool is not only effective but also easy to use and fast. The on-site applicability should be assessed in future research.

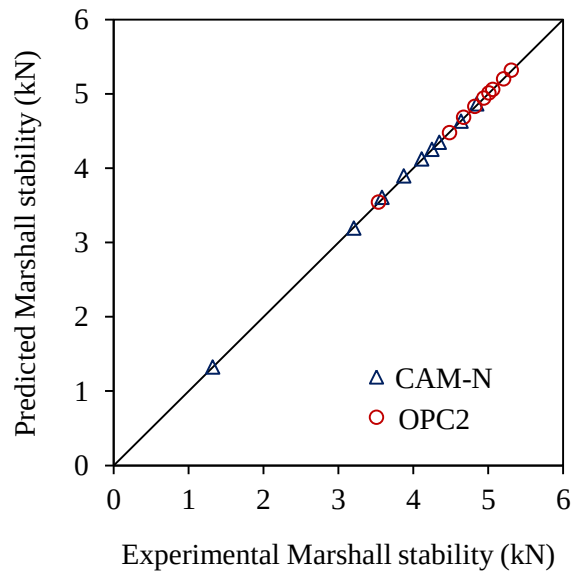
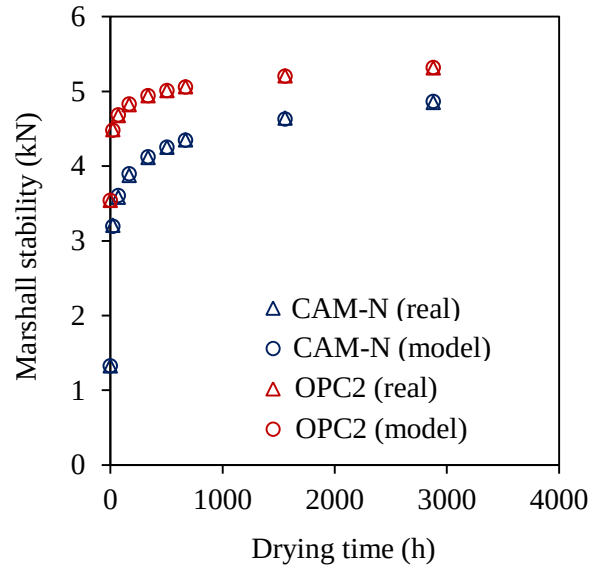


Figure 4.12 (Top & Down) Comparison between predicted and experimental results obtained for Marshall stability of CAM with and without cement

SUMMARY

This part of the research investigates the dynamics of water evaporation in unbound materials and CAM, and how bitumen emulsion relates to these dynamics, through comparison between dynamics in unbound materials and CAM. Moreover, according

to the positive relation between the evaporation (curing) and strength of CAM, the prediction model of the mechanical performance of CAM was developed depending on the contribution of every component of CAM to mechanical performance.

From this experimental work, the most important outcome is the observation that bitumen emulsion is the basic factor in delayed curing and drying in CAM. Moreover, the gradation of aggregate plays an important role in dynamics of water evaporation through its effect on capillary action, then the evaporation of water.

As stated in the literature review (chapter 2), most previous attempts used cement to accelerate and improve CAM performance, while the particular role of cements in water evaporation dynamics remained unclear, thus this research focused on this particular issue in curing. Based on the identified gap in previous literature, this study aims to:

1. Study and understand the effects of cement on the dynamics of water evaporation in CAM.
2. Develop a prediction model for the strength of cement in CAM over time, with reduced time and costs of construction.

These aims are addressed in chapters 5 and 6.

As cement hydration is an exothermic reaction, the concept of activation energy (E_a) is used to determine the minimum energy that cement particles need to trigger the process. In this sense, there are different predictive models of cement strength based on the concept of activation energy (E_a). In addition, in previous sources, there are many previous models to calculate E_a of cement, which are suitable for ordinary

Portland cement (OPC), but they are not appropriate for rapid hardening types, such as calcium aluminate (CAC) and calcium sulfoaluminate cement (CSA).

Accordingly, the next chapter is mainly dedicated to the development of the public model for E_a prediction in cement, which is subsequently deployed to develop a new model to predict the strength of cement in CAM over time (as presented in chapter 6). In addition to that, the next chapter investigates the microstructure of cement. The results of microstructure will be used to explain the strength trend of cement over time in chapters 5 and 6. Moreover, these results will be used to explain the effect of microstructure of cement on the dynamics of water evaporation in CAM in chapter 6.

Chapter Five

New predictive methodology for the apparent activation energy and strength of conventional and rapid hardening concretes

5.1 INTRODUCTION

Ordinary Portland cement (OPC) is commonly used in the manufacture of cement concrete, although hydration reactions of cement can be accelerated by changing its composition. This led to the development of rapid hardening cements, such as calcium aluminate cement (CAC) and calcium sulfoaluminate cement (CSA) (Neville and Brooks, 2010; Winnefeld and Barlag, 2010; Juenger et al., 2011; Winnefeld and Lothenbach, 2012), which reduced the time and costs of construction processes. As these cements also consume more water during hydration reactions (Winnefeld and Barlag, 2010; Juenger et al., 2011; Winnefeld and Lothenbach, 2012), they have great applicability in Cold Asphalt Mixtures (CAM), helping to remove the water contained in CAM, while increasing strength and stiffness (Fang et al., 2015).

As cement hydration is an exothermic reaction (Mehta and Monteiro, 2014), the concept of apparent activation energy (E_a) given by the Arrhenius equation

(Glasstone, Laidler and Eyring, 1941) is used to determine the minimum energy that cement particles need to trigger the process. Hence, it characterises the sensitivity of cement hydration processes to temperature (Mehta and Monteiro, 2014). Such energy is affected by different factors, such as chemical composition, fineness of cement and water/cement ratio (Freiesleben and Pedersen, 1985; Xiong and Van Breugel, 2001; Schindler and Folliard, 2005; Poole, 2007; Neville, 2012). As mechanical properties and hydration rate are strongly correlated, the concept of E_a can be used to predict the maturity level of concrete with time.

Prediction of its mechanical performance during hydration contributes to reduced construction time and costs. In this sense, there are different predictive models based on the concept of apparent activation energy (E_a). However, although these methods are suitable for ordinary Portland cement (OPC), they are not appropriate for rapid hardening types, such as calcium aluminate (CAC) and calcium sulfoaluminate cement (CSA), as the hydration products of CAC are different depending on the curing temperature.

The current investigation aimed to develop a new method based on the apparent activation energy to predict the mechanical performance of both ordinary and rapid hardening cement concretes. It is anticipated that the application of such a model to OPC, normally used in structural applications, would help to reduce construction costs and time as: (1) framework and scaffolding would be removed in an optimal time; (2) the minimum time to start using the structure or infrastructure would be also known; (3) mechanical properties could be predicted avoiding the performance of on-site characterisation tests, and (4) the design of structural reinforcement would be

more accurate. On the other hand, rapid hardening cements are not used that often or are restricted in structural applications. Instead, their use is more common in dry mortar application, rapid repair, special applications where acid resistance is required and refractory applications. Nevertheless, the prediction of the hydration level and strength gain is also important in some other uses, such as additives in CAM, where they play a fundamental role to allows opening of the road in the minimum time possible.

For that, the curing of three types of cement (OPC, CAC and CSA) was studied over a wide range of temperatures, observing different concrete morphologies by scanning electron microscopy (SEM). Mechanical performance was assessed by means of compressive tests, which allowed the determination of the apparent activation energy according to Standard ASTM C1074 (ASTM standard C1074, 2011) and the development of the predictive model.

5.2 THEORETICAL BACKGROUND

5.2.1 Apparent activation energy and strength of cement concrete

Exothermic cement hydration can be defined by the Arrhenius equation (Glasstone, Laidler and Eyring, 1941) as follows in Equation 5.1:

$$k = A * e^{\frac{-E_a}{RT}} \quad (5.1)$$

where, k is the reaction rate ($1/day$), A is the proportionality constant ($1/day$), T is the curing temperature of cement samples (Kelvin), R is the universal gas constant ($8.314 J/mol/K$) and E_a is the apparent activation energy (J/mol) or the minimum quantity of energy that the cement particles must have in order to undergo a hydration reaction

(Glasstone, Laidler and Eyring, 1941). The chemical composition, water/cement ratio (w/c) and particle fineness are the main factors which affect E_a (Freiesleben and Pedersen, 1985; Xiong and Van Breugel, 2001; Schindler and Folliard, 2005; Poole, 2007; Neville, 2012), and can be experimentally determined based on hydration measurements, setting time and mechanical tests (D'Aloia and Chanvillard, 2002; Garcia, Castro-Fresno and Polanco, 2008; ASTM standard C1074, 2011). E_a is commonly used in the literature (Freiesleben and Pedersen, 1985; Xiong and Van Breugel, 2001; Schindler and Folliard, 2005; Poole, 2007; Neville, 2012) as shown in Table 5.1.

Table 5.1 E_a prediction models for cement concrete

Equation	
$E_a = 22100 * P_{C_3A}^{0.30} * P_{C_4AF}^{0.25} * Blaine^{0.35}$	(5.2)
$E_a = 22100 * f_E * P_{C_3A}^{0.30} * P_{C_4AF}^{0.25} * Blaine^{0.35}$	(5.3)
$f_E = 1 - 1.05 \cdot p_{FA} \cdot \left(1 - \frac{p_{FACaO}}{0.40}\right) + 0.40 \cdot p_{SLAG}$	(5.4)
$E_a = 31400 \left((P_{C_3A} + P_{C_4AF}) * P_{gypsum} \right)^{0.13} * Blaine^{-0.07} * \left(\frac{w}{c}\right)^{-0.05}$	(5.5)

P_X = ratio of component X in terms of cement content determined using Bogue estimation (%);
 $Blaine$ = fineness of cement (m^2/kg); f_E = E_a modification factor for supplementary cementitious materials (-); w/c = water to cement ratio of cement paste (-)

Three main types of equation were identified in the literature, hyperbolic (5.6), exponential (5.7) and logarithmic (5.8), to predict the strength of concrete over the curing time as shown in Table 5.2 (Carino, 1984; Freiesleben and Pedersen, 1985; Carino, 1991). If the strength is known, it is possible to use these three equations to obtain the reaction rate (k) and subsequently, E_a .

Table 5.2 Prediction models for strength (S) of cement concrete over curing time

Type	Equation	
Hyperbolic	$S(t_e) = S_u \frac{K (t_e - t_0)}{1 + K (t_e - t_0)}$	(5.6)
Exponential	$S(t_e) = S_u \cdot \exp \left\{ - \left(\frac{\tau_s}{t_e} \right)^{\beta_s} \right\}$	(5.7)
Logarithmic	$S(t_e) = A \cdot \ln(t_e) + B$	(5.8)

S(t_e): the strength at a given time (MPa); S_u: the ultimate strength at infinite time (MPa); K: the reaction rate (1/day); t_e: age for the predicted strength (days); t₀: time at start development of strength (days); τ_s: time constant for strength (days); β_s: shape constant for strength (-); A: fitting parameter (MPa); B: fitting parameter (MPa)

5.2.2 The conversion in the CAC hydration

As summarised in Figure 5.1, based on Odler (2000) and Kirca (2006), CAC cement produces different types of hydration products depending on the curing temperature. Hence, CAH₁₀ is converted to C₂AH₈+AH₃, while C₂AH₈+AH₃ is converted to C₃AH₆+AH₃ when a high temperature (T > 20°C) is applied and enough water is available. Through this conversion, part of the water chemically bonded to hydrated cement is released and CAH₁₀ particles progressively reduce size when converted first to C₂AH₈+AH₃ and then to C₃AH₆+AH₃. Consequently, the porosity of the material increases, while the density and strength decrease.

Although the size of C₃AH₆+AH₃, C₂AH₈+AH₃ and CAH₁₀ is the same, the strength of C₃AH₆+AH₃ is lower than C₂AH₈+AH₃, which is also lower than the strength of CAH₁₀. For this reason, the hydration products will affect the strength of the resulting concrete (Scharf and Odler, 1992).

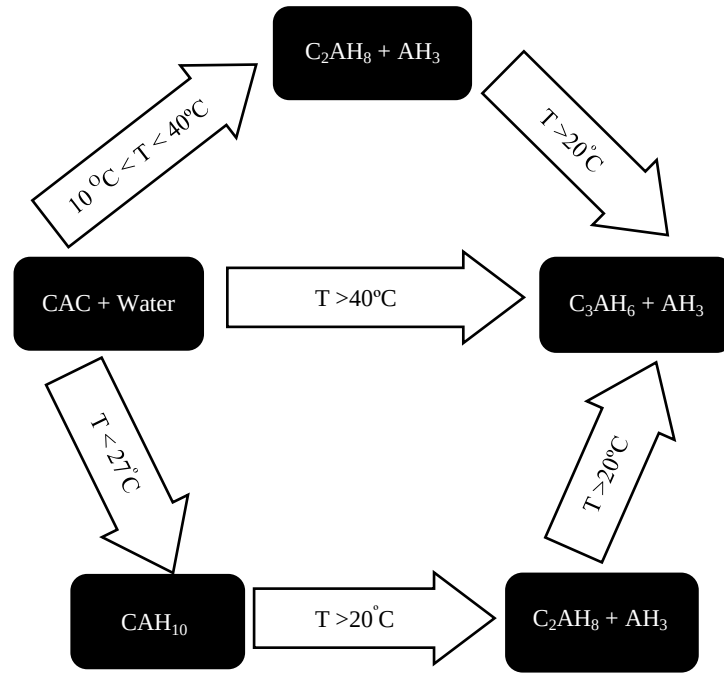


Figure 5.1 Hydration products and conversion behaviour of CAC at different temperatures
(Odler, 2000; Kirca, 2006)

5.3 RESULTS AND DISCUSSION

5.3.1 Morphology of cement concrete

Figures 5.2 to 5.4 show the morphology of hydrated cement products cured at different temperatures. The differences in composition for OPC, CAC and CSA are in accordance with previous publications, such as Del Cura, Garcés and Alcocel (1999), García Alcocel, Garcés and Chinchón (2000), Mehta and Monteiro (2014), Telesca et al. (2014) and Jewell (2015), showing the direct correlation between temperature and degree of hydration.

The OPC microstructure includes three main compounds, calcium silicate hydrates (C-S-H), calcium hydroxide (CH) and ettringite (*E*). It is known that CSH and CH increase over the hydration time (Theconcreteportal.com, 2017), while ettringite is reduced. As the temperature accelerates the hydration process, CSH and CH could be found in OPC samples cured at both 20°C and 50°C, while ettringite was found in OPC samples cured at 20°C, but not in samples cured at 50°C for the same time (Figure 5.2).

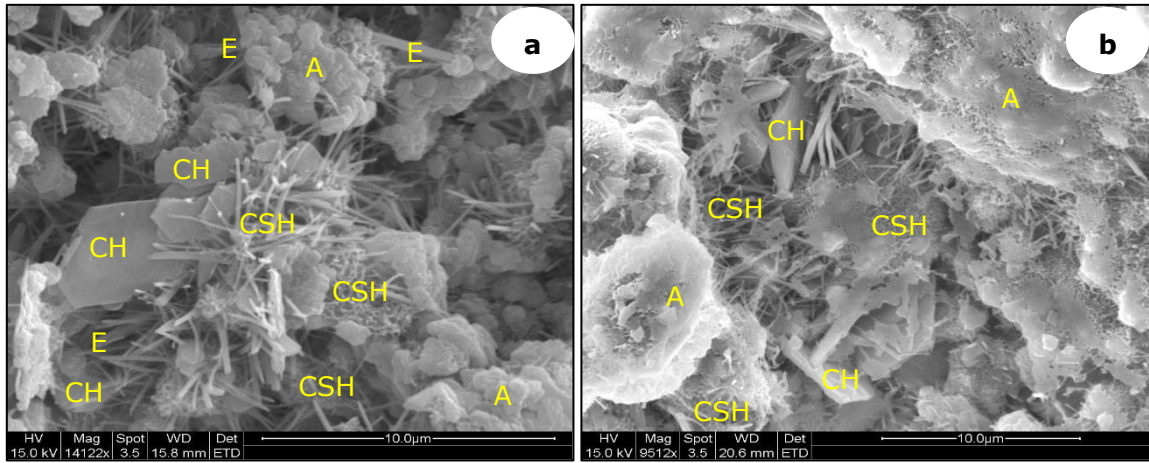


Figure 5.2 Morphology of OPC cured at 20°C (a) and 50°C (b). E – ettringite of OPC; A – aggregate; CH - calcium hydroxide; CSH - calcium silicate hydrate

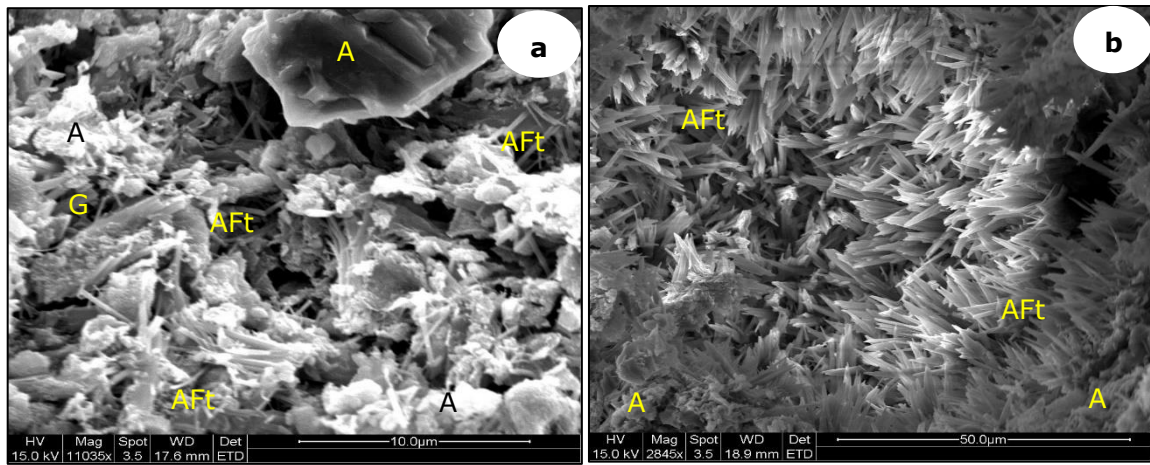


Figure 5.3 Morphology of CSA cured at 20°C (a) and 50°C (b). AFt – ettringite of CSA; A – aggregate; G – gypsum

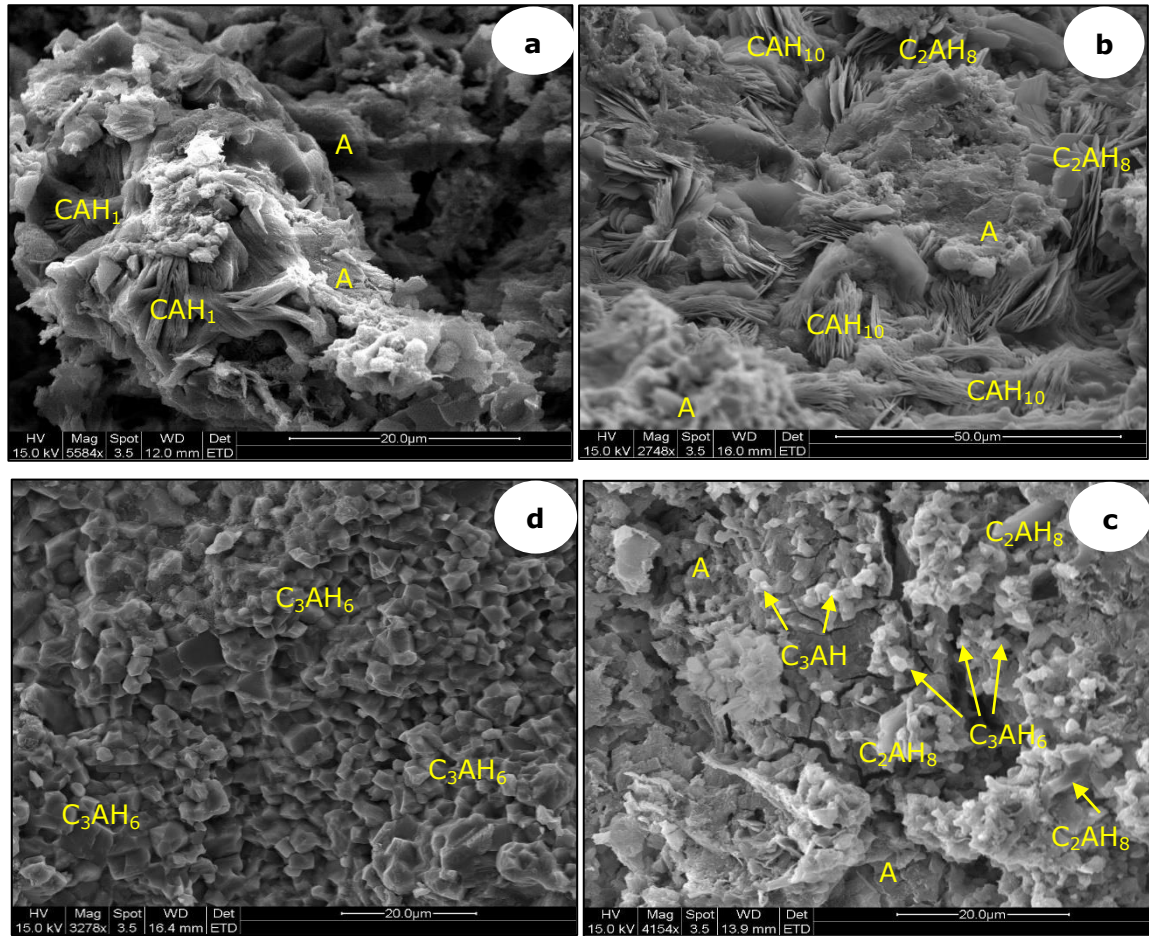


Figure 5.4 Morphology of CAC cured at 4°C (a), 20°C (b), 35°C (c) and 50°C (d). A - aggregate

CSA clinker is commonly mixed with a limited quantity of calcium sulphate (gypsum, G) in order to control the hydration speed, setting time and volume expansion (Glasser and Zhang, 2001). Normally, this gypsum is consumed during CSA hydration, so its content reduces with time. Consequently, and as temperature accelerates the hydration process, it was only found in samples cured at 20°C, but not in samples cured at 50°C (Figure 5.3). The main product resulting from CSA hydration is ettringite, which can be distinguished by its sharp-needle shape. As the

content of this material increases with time, it could be found in greater amounts when samples were cured at 50°C.

As explained in Figure 5.1, hydration of CAC is more complex and the resulting products depend to a large extent on the curing temperature. Thus, CAH_{10} , characterised by a hexagonal shape, could only be found when curing was carried out at 4°C and 20°C (Figure 5.4-a and 5.4-b). In contrast, the cubic-shaped C_3AH_6 was only found in samples cured at 35°C and 50°C (Figures 5.4-c and 5.4-d). Finally, C_2AH_3 was found in samples cured at 20°C and 35°C (Figures 5.4-b and 5.4-c), but at 50°C, all the products were converted to C_3AH_6 (Figure 5.4-d).

5.3.2 Mechanical performance of cement concrete

Figure 5.5 shows how the strength of concrete evolved with time during cement hydration (Neville, 2012). When the temperature of concrete increased, the speed of hydration and strength also increased (Glasstone, Laidler and Eyring, 1941). This is logical; as discussed above, more hydration products can be found at any stage when the temperature is increased.

In general, the strength of CSA is higher than OPC and CAC, while OPC is stronger than CAC only after conversion, agreeing with previously published results (Kirca, 2006; Fang et al., 2015). These differences in strength are due to the different crystalline structures and the strength that each hydration product presents.

For OPC and CSA (Figure 5.5-top), the homogeneity of the hydration products is inversely correlated to temperature (Kjellsen and Detwiler, 1993; Gallucci, Zhang and Scrivener, 2013). Hence, at a high temperature 1) the products of the hydration will be distributed unevenly throughout the sample (Gallucci, Zhang and Scrivener, 2013)

and 2) some solid cement particles will not be reached by water, remaining not hydrated.

Therefore, the final strength is lower compared to samples cured at lower temperatures, as can be seen in Figure 5.5-top.

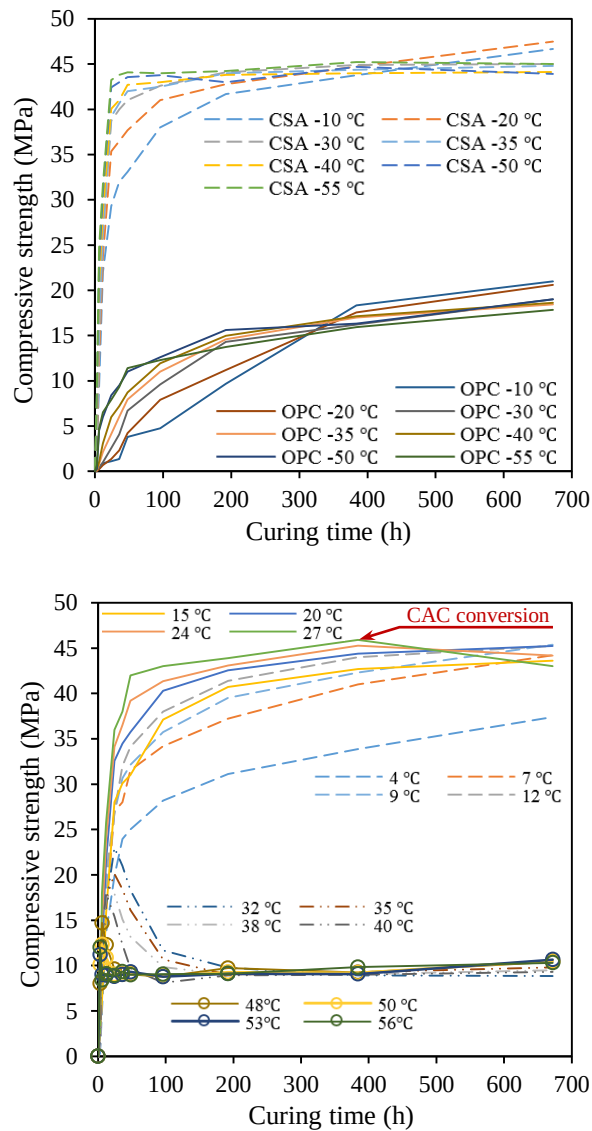


Figure 5.5 Evolution of compressive strength of OPC and CSA (Top) and CAC (Bottom) over curing time at different temperatures

The mix of CSA clinker with calcium sulphate (gypsum) produces expansive hydration products that cause cracks and reduce strength over the hardening stage. It is possible to reduce this expansion and cracking by using a suitable gypsum quantity (commonly lower than 20% of cement) to deplete all gypsum during the plastic stage (Bizzozero, Gosselin and Scrivener, 2011). Expansive stress is not dangerous if, as in the current research, gypsum hydration happens while the material is still plastic; a high w/c ratio, appropriate quantity of gypsum, and high activity gypsum help to achieve this (Odler, 2000; Newman and Choo, 2003; Winnefeld et al., 2017).

For CAC (Figure 5.5-bottom), the strength of samples cured at temperatures higher than 32°C initially increases ($< 25\ h$), but then decreases due to microstructure conversion ($\text{CAH}_{10} + \text{C}_2\text{AH}_8 + \text{AH}_3 \rightarrow \text{C}_3\text{AH}_6 + \text{AH}_3$) (Odler, 2000; Newman and Choo, 2003). After this conversion, all samples have the same microstructure. Consequently, they also present approximately the same steady-state strength of approximately 10 MPa). As temperature accelerates the conversion process, these reductions in strength also occur earlier when the temperature is higher.

In contrast, the strength of CAC samples cured at temperatures lower than 24°C increased over the testing time, as no conversion was produced before 700 h . Nevertheless, according to other authors (Odler, 2000), conversion is expected to occur after longer curing times.

For the intermediate CAC samples cured at 24°C and 27°C, the strength increased initially, but reduced again after approximately 375 h , similar to previous reports (Kirca, 2006).

Due to these sharp changes in composition and strength over the curing time, it is crucial in construction projects using CAC to consider the temperature at which the material will be cured.

5.3.3 Determination of the apparent activation energy (E_a)

Standard specification ASTM C1074 (ASTM standard C1074, 2011) can be used to calculate E_a for the cement, depending on data from the compressive strength test. In order to predict strength, Equations 5.6 (hyperbolic) and 5.8 (logarithmic) were compared, as shown in Figure 5.6 for OPC cured at 10°C. Although both equations fit the experimental results well, the fitting obtained by the hyperbolic equation ($R^2 = 0.993$) is better than that obtained by the logarithmic equation ($R^2 = 0.901$). Table 5.3 shows the results obtained for the other cement types and curing temperatures. In general, it was found that the hyperbolic equation produces better fitting, therefore, Equation 5.6 was selected to calculate the apparent activation energy.

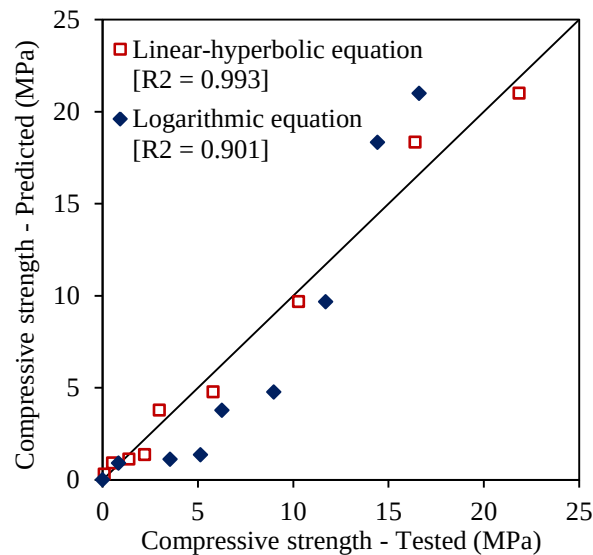


Figure 5.6 Comparison of predicted and tested compressive strength by different strength-maturity relationships for OPC under 10°C

Table 5.3 Determination coefficient R^2 of k (maturity) equation

OPC							
Temperature (°C)	10	20	30	40	50	55	Average
Hyperbolic R^2	0.993	0.998	0.997	0.999	0.988	0.985	0.993
Logarithmic R^2	0.894	0.933	0.968	0.995	0.994	0.991	0.962
CSA							
Temperature (°C)	10	20	30	40	50	55	Average
Hyperbolic R^2	0.992	0.989	0.984	0.985	0.980	0.981	0.985
Logarithmic R^2	0.962	0.926	0.877	0.846	0.810	0.812	0.872
CAC (T < 12°C)							
Temperature (°C)	4	7	12	-	-	-	Average
Hyperbolic R^2	0.992	0.991	0.992	-	-	-	0.991
Logarithmic R^2	0.976	0.968	0.958	-	-	-	0.967
CAC (12°C < T < 27°C)							
Temperature (°C)	15	20	27	-	-	-	Average
Hyperbolic R^2	0.994	0.992	0.984	-	-	-	0.990
Logarithmic R^2	0.962	0.938	0.877	-	-	-	0.925
CAC (27°C < T < 40°C)							
Temperature (°C)	32	35	40	-	-	-	Average
Hyperbolic R^2	0.637	0.671	0.669	-	-	-	0.659
Logarithmic R^2	0.038	0.071	0.198	-	-	-	0.102
CAC (T > 40°C)							
Temperature (°C)	48	53	56	-	-	-	Average
Hyperbolic R^2	0.849	0.963	0.947	-	-	-	0.919
Logarithmic R^2	0.274	0.089	0.096	-	-	-	0.153

Once the compressive strength was determined, the method involves the representation of the Arrhenius plot, which correlates the natural logarithm of k (the reaction rate) and the inverse of the absolute curing temperature. After that, the straight line, which best fits the data is obtained by minimising the square error. The

slope of this line is the ratio between the apparent activation energy and the gas constant, also known as Q-value (see graphical representation in Figure 5.7-top).

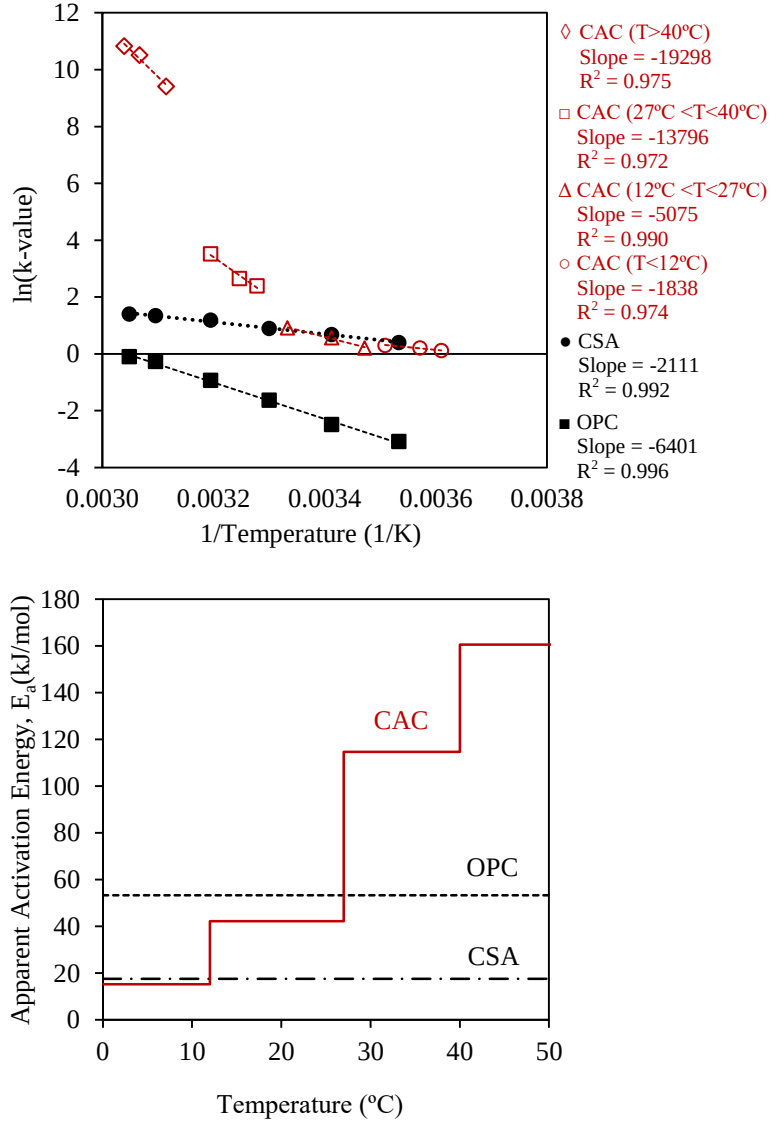


Figure 5.7 Arrhenius plot for OPC, CSA and CAC (Top) and obtained apparent activation energies (Bottom)

The results of OPC and CSA show a linear relationship for the range of temperatures (from 10°C to 55°C). However, CAC shows a non-linear trend, corroborating the findings obtained by previous researchers (Odler, 2000; Dachtar, 2004; Kirca, 2006;

Wang, Li and Xu, 2017). As explained above, this is due to differences in hydration products depending on the curing temperature. Hence, when the series of points are grouped into ranges of temperatures ($T < 12^{\circ}\text{C}$, $12^{\circ}\text{C} < T < 27^{\circ}\text{C}$, $27^{\circ}\text{C} < T < 40^{\circ}\text{C}$ and $T > 40^{\circ}\text{C}$), each of them present a linear relationship with a correlation level R^2 higher than 0.97 in all cases.

Based on the linear trend lines which best fit the points and their slopes, the apparent activation energy could be obtained for each case (Table 5.4). The value of 53.2 kJ/mol obtained for OPC is very similar to others found in the literature, such as 57.5 kJ/mol (Feldman and Beaudoin, 1991). In addition, as can be seen in Figure 5.7 (bottom), E_a of CAC increases with the curing temperature, from 15.3 kJ/mol obtained at temperatures below 12°C to 160.4 kJ/mol at temperatures higher than 40°C . Hence, at temperatures lower than 12°C , E_a for CAC is similar to that obtained for CSA (17.5 kJ/mol). Finally, for higher temperatures E_a is significantly higher for CAC than for the other types of cement.

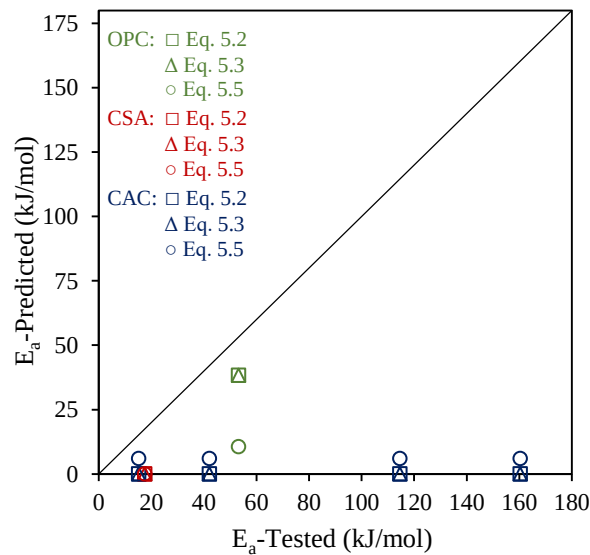


Figure 5.8 Comparison between predicted and tested E_a results obtained by Equations 5.2, 5.3 and 5.5

Table 5.4 Temperature, apparent activation energies, and parameters by regression analysis of the hyperbolic equation for different cement types

OPC							E_a (kJ/mol)	R^2
Temperature (°C)	10	20	30	40	50	55		
S_u (MPa)	38.98	29.87	22.35	20.00	18.35	16.98	53.2	0.996
K (1/day)	0.045	0.083	0.194	0.392	0.761	0.901		
t_0 (day)	0.188	0.178	0.140	0.050	-0.013	-0.016		
CSA							E_a (kJ/mol)	R^2
Temperature (°C)	10	20	30	40	50	55		
S_u (MPa)	46.08	47.39	47.62	46.73	46.98	47.64	17.5	0.992
K (1/day)	1.488	1.959	2.443	3.281	3.823	4.039		
t_0 (day)	0.031	0.031	0.026	0.014	0.012	0.010		
CAC ($T < 12^\circ\text{C}$)							E_a (kJ/mol)	R^2
Temperature (°C)	4	7	12	-	-	-		
S_u (MPa)	36.44	43.42	46.23	-	-	-	15.2	0.974
K (1/day)	1.115	1.232	1.349	-	-	-		
t_0 (day)	0.049	0.046	0.045	-	-	-		
CAC ($12^\circ\text{C} < T < 27^\circ\text{C}$)							E_a (kJ/mol)	R^2
Temperature (°C)	15	20	27	-	-	-		
S_u (MPa)	45.12	46.41	47.03	-	-	-	42.2	0.990
K (1/day)	1.227	1.767	2.449	-	-	-		
t_0 (day)	0.040	0.031	0.024	-	-	-		
CAC ($27^\circ\text{C} < T < 40^\circ\text{C}$)							E_a (kJ/mol)	R^2
Temperature (°C)	32	35	40	-	-	-		
S_u (MPa)	14.74	13.82	11.29	-	-	-	114.7	0.972
K (1/day)	10.92	14.14	33.78	-	-	-		
t_0 (day)	0.005	0.002	0.000	-	-	-		
CAC ($T > 40^\circ\text{C}$)							E_a (kJ/mol)	R^2
Temperature (°C)	48	53	56	-	-	-		
S_u (MPa)	10.07	9.381	9.501	-	-	-	160.4	0.975
K (1/day)	1214	3668	5061	-	-	-		
t_0 (day)	0.000	0.000	0.000	-	-	-		

5.4 PREDICTIVE MODELS

5.4.1 E_a prediction model for cement concrete

Equations 5.2, 5.3 and 5.5 presented in Table 5.1 were used to compare their capacity to predict E_a . In Figure 5.8, predicted and measured experimental results are graphically compared. These models fit better the results obtained for OPC, as they were designed for this type of cement, but they are not suitable for rapid hardening cements (CSA and CAC). For this reason, a new model was developed for these types of cement in the present investigation. As the best results were obtained by Equations 5.2 and 5.3, and Equation 5.2 is simpler than Equation 5.3, the new model was obtained based on Equation 5.2, as follows:

$$E_a = b \cdot Blaine^\delta \cdot \prod_{x=1}^n P_x^{\gamma_x} \quad (5.9)$$

where b , δ and γ are fitting parameters (-). In order to make the model more versatile and suitable for a wider range of cements, such as CAC and CSA, now, not only C_3A and C_4AF components were considered (Equation 5.2), but a generic number (n) of compounds (x), P_x being the content of each of them (%). In the present research, the following compounds were included: C_3S , C_2S , C_3A , C_4AF , MgO , C_4A_3S , CT , C_2AS , CA , CA_2 , MA , Cs , $C_{12}A_7$, C_3FT , Ff , $MA_{0.1}F_{0.9}$ and $C_{20}A_{13}M_3S$.

In addition, as the water/cement ratio has significant effect on the apparent activation energy (Carino, 1991), a parameter $(w/c)^\beta$ was added, as follows:

$$E_a = b \cdot Blaine^\delta \cdot \left(\frac{w}{c}\right)^\beta \cdot \prod_{x=1}^n P_x^{\gamma_x} \quad (5.10)$$

Finally, for CAC, as discussed above, the curing temperature significantly affects the hydration products and consequently, also the apparent activation energy. So a new factor (a), multiplied by the curing temperature (T) was added. As this effect is only produced in CAC, a factor k , whose value is 1 for CAC and 0 for any other type of cement, was also added:

$$E_a = k \cdot a \cdot T^\alpha + b \cdot Blaine^\delta \cdot \left(\frac{w}{c}\right)^\beta \cdot \prod_{x=1}^n P_x^{\gamma_x} \quad (5.11)$$

By fitting experimental data by Excel's Solver tool and the minimum square error method, the following fitting parameters were obtained:

$$\begin{aligned} \bullet k &= \begin{cases} 1 & \text{if CAC is used} \\ 0 & \text{if other cement types are used} \end{cases} & \bullet \alpha &= 0.001 \\ & & \bullet \beta &= -0.104 \\ \bullet a &= \begin{cases} -49.100 & \text{if } T < 12^\circ\text{C} \\ -22.223 & \text{if } 12^\circ\text{C} \leq T \leq 27^\circ\text{C} \\ 50.053 & \text{if } 27^\circ\text{C} < T \leq 40^\circ\text{C} \\ 95.612 & \text{if } T > 40^\circ\text{C} \end{cases} & \bullet \delta &= -0.046 \\ & & \bullet b &= 198.07 \\ \bullet Q_x &= C_3S^{0.175} \cdot C_2S^{0.121} \cdot C_3A^{0.093} \cdot C_4AF^{0.106} \cdot MgO^{0.051} \cdot C_4A_3S^{0.229} \cdot CT^{-0.148} \cdot \\ & C_2AS^{0.290} \cdot CA^{-0.076} \cdot CA_2^{-0.068} \cdot MA^{-0.065} \cdot CS^{0.460} \cdot C_{12}A_7^{0.044} \cdot C_3FT^{0.014} \cdot Ff^{-0.130} \cdot \\ & MA_{0.1}F_{0.9}^{0.011} \cdot C_{20}A_{13}M_3S_3^{0.021} \end{aligned}$$

Figure 5.9 shows the comparison between the experimental E_a results and those predicted by Equation 5.11. Two sets of data were used for this validation, results of experimental tests performed at temperatures not used previously for the fitting and calibration of the model (1°C, 8°C, 12°C, 14°C, 21°C, 27°C, 28°C, 36°C, 40°C, 42°C, 53°C and 60°C for CAC, and 35°C for OPC and CSA), as well as published data

(Schindler, Dossey and McCullough, 2002; Bien-Aimé, 2013) which included the composition of cements used and the experimental results.

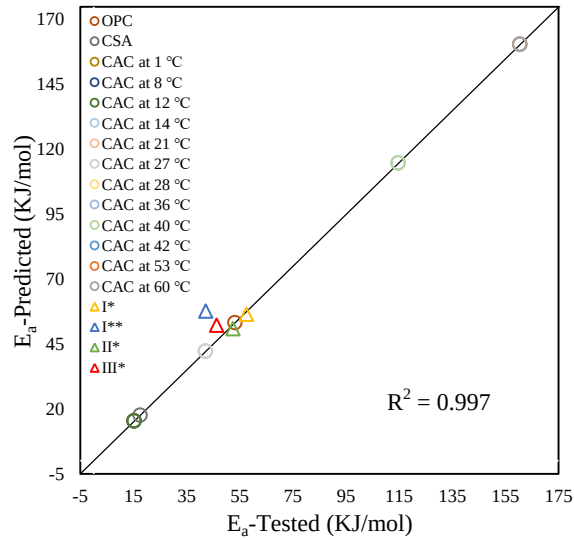


Figure 5.9 Comparison between predicted and tested results obtained for E_a by Equation 5.11. Ordinary Portland Cement (I), Modified Portland Cement (II), Rapid-Hardening Portland Cement (III). (*A. Bien-Aimé, 2013; ** A. Schindler, T. Dossey, B. McCullough, 2002)

The prediction level was high for OPC and CSA, as well as CAC at a wide range of temperatures ($R^2 = 0.997$). The model also presented high accuracy when compared with the predicted results of other authors and the fitting is significantly better than current methods as shown in Figure 5.9. Therefore, the validation of the model can be considered satisfactory.

5.4.2 Predictive model for the strength of cement concrete

As explained above, the hyperbolic equation (Equation 5.6) was used to predict the strength of the cement concrete with time. In this equation, the K -value was calculated

by Equation 5.1, t_0 was considered equal to zero and S_u was obtained using Equation 5.6 and measuring experimentally the strength of samples at a curing time of 3 days.

The validation of the model (Figure 5.10) was undertaken by using compressive strength data of OPC and CSA samples cured at 35°C and CAC at 9°C, 24°C, 38°C, and 50°C for different curing times (0.50, 1.0, 1.5, 2, 4, 8, 16 and 28 days). Hence, these values were not used for the initial calibration of the model and can be considered as independent data.

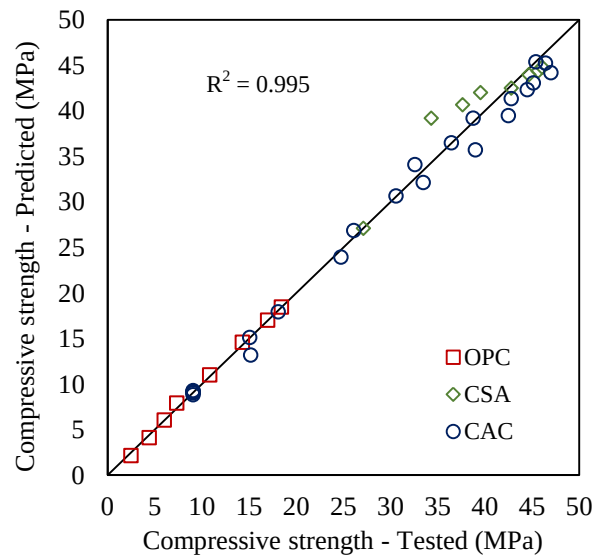


Figure 5.10 Comparison between predicted and experimental compressive strength results

As can be seen in Figure 5.10, a very high correlation ($R^2 = 0.995$) was obtained for the range of different types of cement and curing temperatures, which proves that it is possible to predict the strength of cement concrete, including rapid hardening at any curing temperature using the E_a -based model proposed in the present investigation.

SUMMARY

It is clear that the curing temperature has a major impact on the hydration products of CAC cement. Moreover, the addition of gypsum to CSA can lead to expansive phenomena. Consequently, it was found that apparent activation energy and concrete strength are also affected by these factors, and that conventional models commonly used for OPC are not suitable for rapid hardening concrete.

The present chapter proposes a new methodology to predict both apparent activation energy and strength for these types of cement at any curing temperature. For the case of apparent activation energy, it was found that the model can accurately fit the experimental data ($R^2 = 0.997$). In same sense, high accuracy ($R^2 = 0.995$) was found for strength prediction model.

As stated in the summary of chapter 4, chapters 5 and 6 address the fundamental aim of studying the effect of cement on the dynamics of water evaporation in CAM. Moreover, the prediction model of the strength of cement in CAM over time is developed to reduce the time and costs of the construction processes.

Chapter 6 presents the achievement of this aim with regard to a thorough investigation of the effects of cement on dynamics of water evaporation in CAM and the results pertaining to the microstructure presented in chapter 5 as an ancillary factor to explain the results of the investigation. In addition, models to predict strength of cement in CAM are developed depending on the prediction model, with the apparent activation energy (E_a) addressed in the current chapter.

Chapter Six

Prediction of water evaporation and stability of cold asphalt mixtures containing different types of cement

6.1 INTRODUCTION

Over recent decades, many studies have attempted to improve the mechanical performance of CAM during the early curing stages by adding cement (Terrell and Wang, 1971; Nassar et al., 2016). The process can also be accelerated by using rapid hardening cements, such as calcium aluminate cements (CAC) and calcium sulphate (or calcium sulphoaluminate) cements (CSA) (Fang et al., 2015; Nassar et al., 2016). In comparison to ordinary Portland cement (OPC), these types of cement (especially CSA) improve performance, especially during the first days, as they have a faster hydration process, and consume more water during this time.

Although the mechanical performance of cold asphalt mixtures (CAM) can be improved by using cement additions, it is unclear how this affects the dynamics of water evaporation during drying. This chapter investigates CAM samples with different contents and types of cement (ordinary Portland, calcium aluminate and

calcium sulfoaluminate), tested by dynamic evaporation, hydraulic conductivity and Marshall stability tests. Finally, a new predictive model will be obtained to estimate the contribution of cement hydration products to the total stability of CAM.

6.2 THEORETICAL CONSIDERATIONS

6.2.1 Prediction model for CAM stability

Predicting the mechanical properties of CAM with different types and quantities of cement has great importance to accurately design the mix and predict its performance under traffic loads at any stage of the curing/drying process. For this reason, the following semi-empirical model has been developed (Saadoon, Garcia and Gómez-Meijide, 2017) by considering that the total stability of the mix is the sum of the stability provided by the mineral skeleton (aggregates), plus the broken bituminous emulsion and the products of cement hydration, acting on the three sources independently, as follows:

$$S(t) = \frac{h_d(t)}{H} (S_d - S_w + \alpha) + S_w + S_c(t) \quad (4.14)$$

where $h_d(t)$ is the thickness of the dry layer at a given time (t); H is the total thickness of the material; S_d is the strength of the granular material under dry conditions; S_w is the strength of the granular material under saturated conditions; α is a relationship constant depending on characteristics, such as binder-aggregate affinity and binder content; and $S_c(t)$ is the strength provided by the products of cement hydration at a given time (t).

The following equation was also proposed (Saadoon, Garcia and Gómez-Meijide, 2017), which allows the prediction of the thickness of the dry layer (h_d) as a function of the pore size distribution (n), which changes with time in CAM:

$$h_d = \frac{\left[\frac{1}{n_2} \ln \left(\frac{n - n_0}{n_1} \right) \right]^{k_1}}{k_2 n_2 + \ln \left(\frac{n - n_0}{n_1} \right)} \cdot k_0 n \quad (4.15)$$

where n_0 , n_1 , n_2 , k_0 , k_1 and k_2 are different material constants related to binder content, air void characteristics (such as tortuosity and pore interconnectivity), and environmental conditions during the drying process, such as temperature and humidity.

However, this model was only validated for granular materials and conventional CAM. Hence, the evolution of n over the curing/drying process might be affected by the simultaneous reactions of water with cement and the precipitation of hydration products within the internal pore network. In addition, the contribution of cement to the total stability of CAM (term $S(t)$ in Equation 4.14) has not been ascertained, thus the model is not yet suitable for application in CAM containing cement. Hence, the present investigation aims to develop and validate a predictive model for this term.

6.2.2 Water dynamics in CAM

As seen in Equation 4.14, n is a fundamental parameter of CAM, related to the speed of water evaporation, which can be divided into three stages, first, transition and second (Graham, 2004). As the evaporation rate decreases from the first to the second stage, in order to accelerate drying, it is important to prolong the first stage, which depends on capillarity (Graham, 2004), as much as possible.

The duration of the first stage of water evaporation in a porous material is strongly related to the maximum height of capillary action (L_C) that the internal pore network can provide (Graham, 2004). Such upwards capillary action decreases when the pore size distribution (n) increases in the material (Saadoon, Garcia and Gómez-Meijide, 2017) and it is also opposed by the opposite downwards action of gravity (L_G) and viscous forces (L_V), as described in Equation 6.1.

$$L_C = L_G + L_V \quad (6.1)$$

Where L_C is maximum capillary rise, L_G and L_V represent reductions due to gravity and viscous forces respectively.

When the material has very dense porous texture (e.g. clays), the effect of viscous forces is important. However, in other materials, such as CAM, the effect of viscous forces is practically negligible (Lehmann, Assouline and Or, 2008). Consequently, for these materials, Equation 6.1 is commonly simplified, as follows:

$$L_C \approx L_G \quad (6.2)$$

Based on the Van Genuchten expression for the water retention curve (Van Genuchten, 1980), Lehmann, Assouline and Or (2008) proposed the following equation to calculate L_G :

$$L_G = \frac{1}{\alpha (n-1)} \left(\frac{2n-1}{n} \right)^{(2n-1)/n} \left(\frac{n-1}{n} \right)^{(1-n)/n} \quad (4.2)$$

where α (1/cm) is a parameter related to the inverse of the air entry suction that can be calculated as a function of the pore size distribution index (n) and parameter α_1 , which

was found in the literature review with different values, such as 0.134 (Saadoon, Garcia and Gómez-Meijide, 2017) or 0.0087 (Lehmann, Assouline and Or, 2008) depending on the studied material:

$$\alpha = \alpha_1(n - 1) \quad (4.3)$$

At the same time, it is known that the pore size distribution is related to the water-saturated hydraulic conductivity of porous material (K_s), making it possible to calculate n by Equation 4.1, proposed by Lehmann, Assouline and Or (2008) and also used by Saadoon, Garcia and Gómez-Meijide (2017):

$$K_s = k_1 \cdot n^{k_2} \quad (4.1)$$

where k_1 and k_2 were 0.0077 and 7.35 respectively in Lehmann, Assouline and Or (2008), while they were 0.003 and 6.493 respectively in Saadoon, Garcia and Gómez-Meijide (2017).

By applying Equations 4.1–4.3, L_C can be easily obtained by carrying out quick hydraulic conductivity tests, instead of by monitoring the material over the whole evaporation process. However, this was not yet proven for CAM containing cement (CAM-C), as the cement-water reaction and the precipitation of hydration products might change the hydraulic characteristics of the mix during the process. Hence, the present study investigates how the addition of cement affects the dynamics of water evaporation in CAM.

As previously stated, there are three stages of evaporation during the drying process of a porous material. In order to see how the pore size distribution of CAM-C affects

the duration of these, methods to definition of these stages used in previous studies were followed (Shokri and Or, 2011; Saadoon, Garcia and Gómez-Meijide, 2017), as explained in section 4.3.2.

6.3 RESULTS AND DISCUSSION

6.3.1 Effect of the temperature on L_C in CAM -C

The effect of temperature on L_C was investigated by placing moisture sensors in the material and by the estimations given by the hydraulic conductivity tests. The tests were carried out at different ambient temperatures: 35°C, 40°C, 45°C, 50°C, 55°C, 60°C, and 65±3°C.

The results are shown in Table 6.1. It can be seen that L_C only decreased by 0.042 mm and 0.021 mm (depending on the test) when the temperature increased by 30°C, from 35°C to 65°C. These results agree with those published in Neriah et al. (2014) and lead to the conclusion that the curing temperature produces no significant effect on L_C . Consequently, it is possible to compare the dynamics of water evaporation in two different materials heated differently.

6.3.2 Internal pore size distribution of CAM-C

Figure 6.1-top shows how n decreases in CAM over the curing time. As reported in Saadoon, Garcia and Gómez-Meijide (2017), this is related to the progress of emulsion breaking and cement hydration processes, which leads to reduced permeability of the material. It can be also seen that n reduced more when cement was used (compared to control mixes without cement), especially when rapid hardening cements (CAC and CSA) were selected. In addition, Figure 6.1-bottom also shows how n decreases more

as long as the content of cement in the mix increases. For these reasons, it can be concluded that the products of cement hydration contribute to fill and/or block cavities of the internal pore network.

Table 6.1 Effect of temperatures on L_C obtained by different methods

Temperatures (°C)	L_C (mm)	
	Sensor	Hydraulic conductivity
35	3.025	3.010
40	3.000	3.010
45	2.996	3.005
50	2.990	3.004
55	2.987	3.000
60	2.985	2.990
65	2.983	2.989

It can also be seen that, in general, n tends to sharply decrease during the first days, after which the decreasing rate is much lower. This first period is significantly shorter when rapid hardening cements are used, but there is no substantive difference between the cases of mixes without cement and mixes with OPC. Hence, the duration measured for these cases was around 3 days, while for the cases of mixes containing conventional cements, it was around 28 days. This difference also comes from the higher water consumption of CAC and CSA cements during the first hydration days (Fang et al., 2015), producing more hydration products inside the pore network and facilitating the breaking of emulsion.

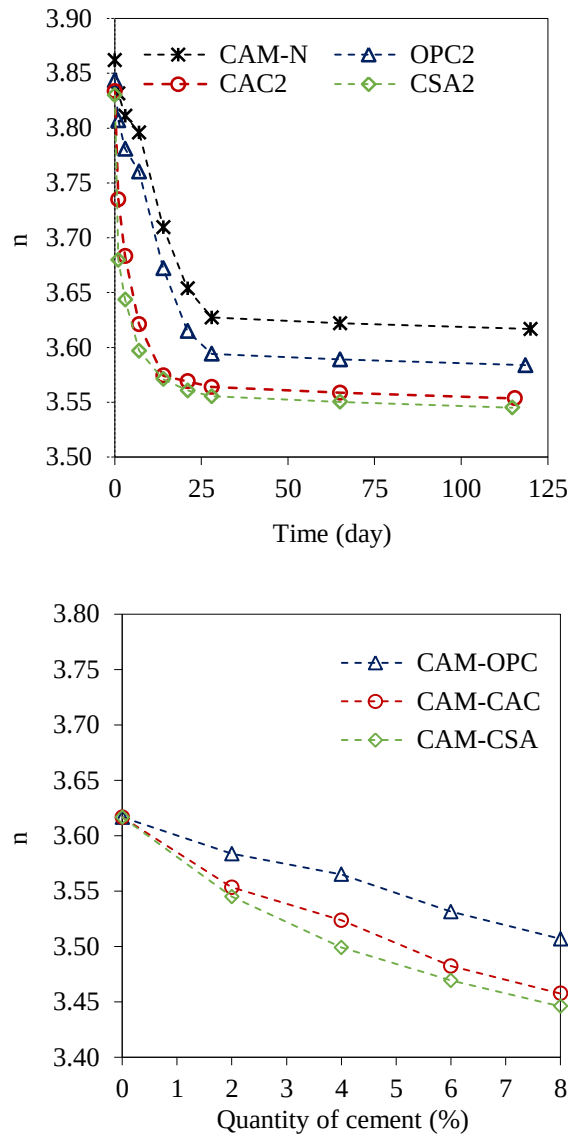


Figure 6.1 Evolution of pore size distribution index (n) with time for the case of mixes with 2% cement content (Top) and effect of the type and quantity of cement on n (Bottom)

The decrease of n in CAM might be understood as a positive effect, as it would contribute to increase capillary action (L_C) (Lehmann, Assouline and Or, 2008) and therefore contribute to reduce the drying time. However, besides this effect, reductions of n in CAM are mainly related to blocked and/or filled cavities of the internal pore

network by residual bitumen after the breaking of the emulsion and hydration products of cement (Saadoon, Garcia and Gómez-Meijide, 2017). This reduces the permeability of the material, and consequently the time to dry mixes with emulsion and cement is actually longer than for samples of aggregate with identical gradation and n but without any of these binders.

6.3.3 The dynamic of water evaporation in CAM-C

CAM samples were considered fully dry when the change in mass became lower than 0.5% of total mass per day. Figure 6.2 shows such duration for CAM samples containing different types and amounts of cement.

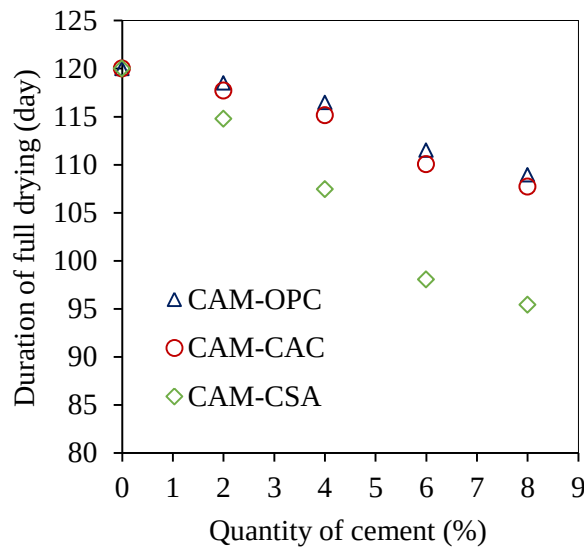


Figure 6.2 Time for full drying and cement (quantity and type)

It can be seen that the time for full drying reduces when the amount of cement increases, and also when rapid hardening cements (CAC and CSA) are used. This is

produced by the higher amount of water that these cements need for hydration, and their higher hydration rate that makes them consume this water faster.

When comparing between both rapid hardening cements, it can be seen that drying is faster when using CSA rather than CAC. This might be related to the fact that CAC needs lower w/c ratio to reach full hydration. In addition, it has an internal structure that changes over the course of the hydration process, releasing part of the chemically bonded water that had been reacted in earlier stages (Odler, 2000).

The relationship between the duration of the evaporation and n is shown in Figure 6.3. It can be seen that while the duration of the first and transition stages tends to decrease when n increases, the duration of the second stage tends to increase. Taking into account that the first stage is characterised by the formation of a network of growing capillary water columns that progressively collapse during the transition stage, it is expected that the longer these columns are, the longer the first and transition stages are too. With a high pore size (high n), capillary forces become weaker. Hence, first and transition stages end earlier and the second stage also begins earlier. However, this does not mean that more water has been evaporated, nor that during the second stage the drying is faster. Subsequently, the second stage is prolonged due to the weaker capillary effect.

Considering this and the previous observation on reductions in n when cements (especially rapid hardening cements) are used, it is expected that when cement content is increased or when rapid hardening cements are used, the first and transition stages become longer while the second stage becomes shorter.

6.3.4 Evolution of the moisture region in CAM-C

The evolution of the depth of the dry layer over time in CAM containing different types and contents of cement was measured by moisture sensors; the results are shown in Figure 6.4.

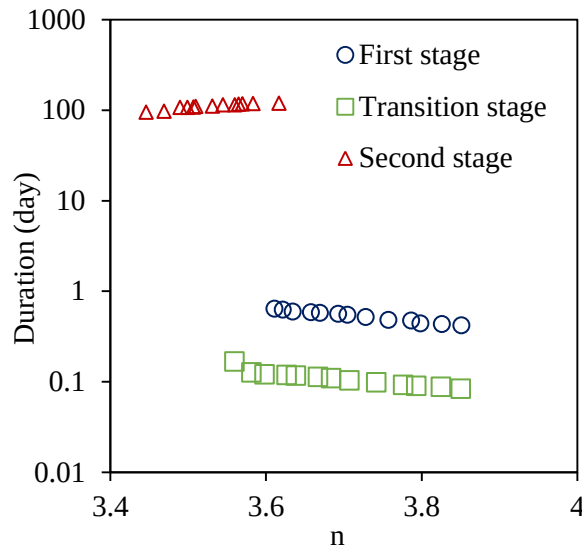


Figure 6.3 Correlation between pore size distribution index (n) and duration of drying stages

It can be seen that the drying process starts from the upper region of the sample and moves toward the bottom surface. As concluded in other studies (Yiotis et al., 2004; Saadoon, Garcia and Gómez-Meijide, 2017), it was found that the distance travelled by the dry layer in a given time interval reduces progressively, as it gets further from the surface (drying deceleration). The evaporated water must travel further upwards through the sample to reach the environment, producing energy losses, which reduces the rate of water evaporation (Saadoon, Garcia and Gómez-Meijide, 2017). As a

consequence, small increases in pavement thickness can involve great increases in drying time.

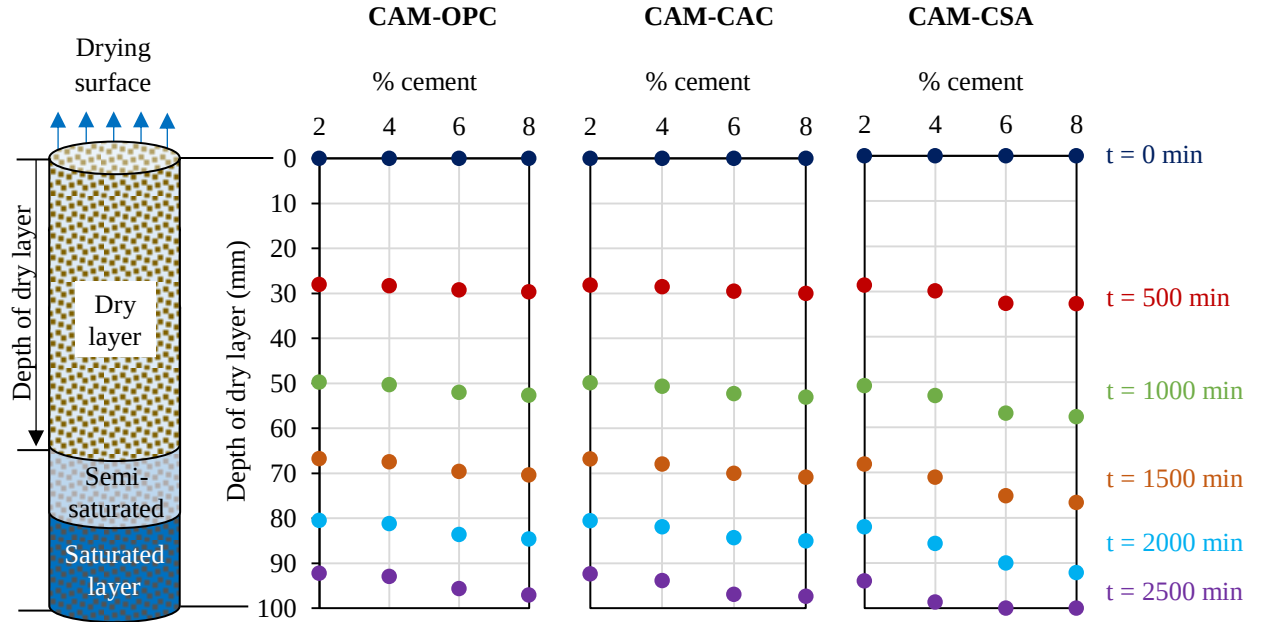


Figure 6.4 Evolution of depth of dry layer over drying time in samples with different cement types and compositions

It can be also seen that increases in cement content produce a slight acceleration of the dry layer while travelling downwards. At the same time, the use of CSA also produces slightly higher drying speeds, while the behaviours obtained by OPC and CAC are practically identical. This is related to the explanations given before about the higher amount of water that CSA cement absorbs during its hydration.

6.3.5 Prediction of L_C in CAM -C based on hydraulic conductivity

Two groups of L_C values of the CAM-C have been measured in the current chapter. The first group was measured in the laboratory via the sensor, as explained in the previous section (6.3.4); whereas, the second group of L_C values were measured depending on the n values, which were measured via the hydraulic conductivity test

(see Figure 6.3). Subsequently, according to Equations 4.1–4.3, these two groups of L_C data were both fitted using Excel's Optimization Solver function.

The constants α_1 , k_1 and k_2 after the fitting were 0.133, 0.003 and 6.50 respectively. Due to differences in the materials used, these values are different from those published in Lehmann, Assouline and Or (2008), but approximately the same as those published in Saadoon, Garcia and Gómez-Meijide (2017). Figure 6.5 shows a strong correlation ($R^2 = 0.964$) between L_C calculated by the hydraulic conductivity test and by sensors embedded in the material. The good fitting results indicate that Equations 4.1 to 4.3 are reliable tools to compare water dynamics properties, such as L_C , requiring little time and effort, not only for CAM-N (as demonstrated in (Saadoon, Garcia and Gómez-Meijide, 2017)) but also for CAM containing cement.

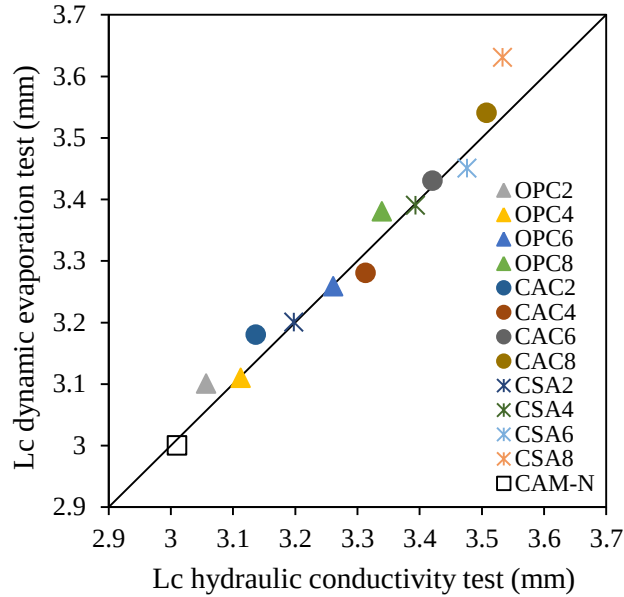


Figure 6.5 Correlation between L_C results obtained from dynamic evaporation test and hydraulic conductivity test

6.3.6 Degree of hydration of cement in CAM-C

The hydration degree of cement in CAM with different types and quantities of cement is shown in Figure 6.6.

It can be seen that the hydration rates of rapid hardening cements are higher than OPC. Hence, for the specific case of CAM containing 2% cement, during the first 24 *h* of curing, the hydration degrees for OPC2, CAC2 and CSA2 were 74%, 90% and 91% respectively. However, when enough drying time was given, the hydration degree became approximately 100% for all samples. In general, all the samples with CSA reached full hydration after 115 days, while samples with CAC needed 118 days. On the other hand, some specimens containing OPC did not reach full hydration even after the maximum tested duration of 125 days.

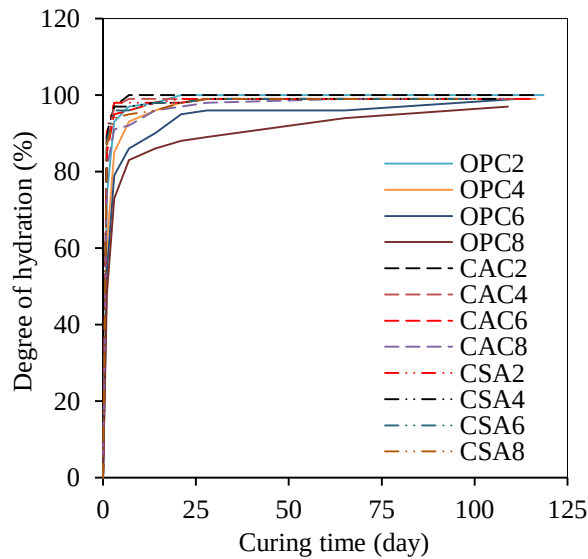


Figure 6.6 Evolution of hydration degree of cement in CAM containing cement over drying time

Although with enough time all samples can reach full hydration, in some cases the evaporation of water can be faster than the cement hydration, consequently cement in

the areas closest to a specimens' surface could remain non-hydrated at the end of the process. This is especially likely when high quantities of slow-hardening cement are added, such as OPC6 and OPC8, as shown in Figure 6.6.

These results confirm the findings of a previous investigation (Fang et al., 2015) in that: (i) the bitumen emulsion has no effect on the final hydration degree of cement; (ii) most cement finished its hydration completely during the first days; and (iii) hydration of OPC is slower than CAC and CSA.

6.3.7 Mechanical performance of CAM-C

The evolution of Marshall stability over drying time for CAM samples containing different types and percentages of cement can be seen in Figure 6.7-top.

It can be seen that the stability of cement increases with time. This is attributable to two actions: the breaking of asphalt emulsion and the hydration of cement. In order to quantify both, Figure 6.7-bottom represents the contribution of hydrated cement to the total stability. The stability of CAM samples tends to be higher as the cement content increases in the mix. In addition, CSA produces larger quantities of binder during hydration than CAC and OPC (Fang et al., 2015). Thus, it is possible to determine how mixes with CSA actually obtained greater stability.

When comparing CAC and OPC, it can be seen that despite the former consuming more water, mixes containing this type generally obtained lower stability than mixes containing OPC. This matches the observations of Kirca (2006), attributed to the conversion of CAH_{10} into C_2AH_8 and C_3AH_6 during CAC hydration, which leads to increased material porosity and reduced linkages among the mineral fractions (Odler, 2000). Moreover, the load capacity of CAH_{10} is lower than C_2AH_8 and C_3AH_6 . High

temperature and w/c accelerate this conversion (Odler, 2000). In the current work, due to the test condition, the conversion of CAC happened very quickly at the beginning of the process (in fact it was so rapid it was difficult to identify).

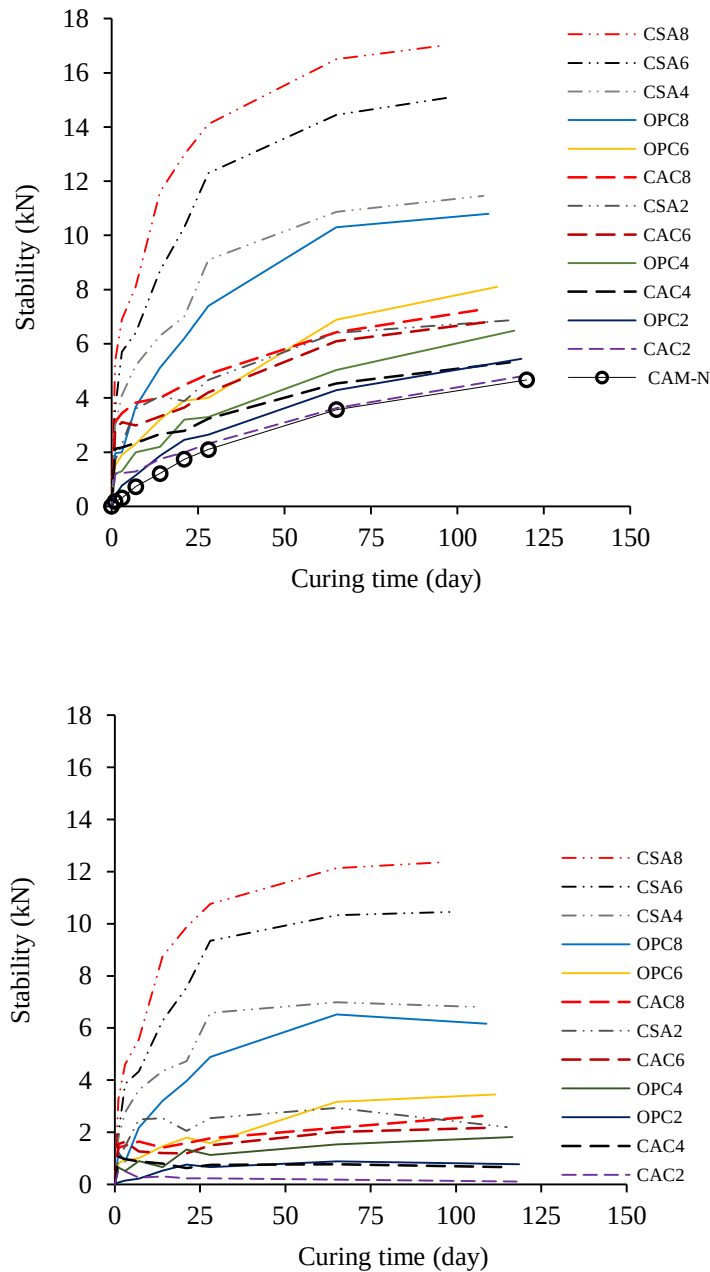


Figure 6.7 Evolution the stability of CAM over drying time (Top), Evolution the stability of cement in CAM contain cement over drying time (Bottom)

In Fang et al. (2015) and Nassar (2016) it is explained that the addition of cement does not affect the mechanical performance provided by the asphalt emulsion to the mix. Hence, it can be assumed that the differences observed in Figure 6.7 are produced by the different types and amounts of cement. The average contribution of cement hydration products to the total stability of CAM was 39.61% for OPC, 22.98% for CAC, and 63.05% for CSA cement.

6.3.8 Apparent Activation energy of cement in CAM-C

Equation 5.11 (Saadoon, Garcia and Gómez-Meijide, 2018 b) was used in the present investigation to predict the apparent activation energy (E_a) of the three different types of cement according to their composition:

$$E_a = k \cdot a \cdot T^\alpha + b \cdot Blaine^\delta \cdot \left(\frac{w}{c}\right)^\beta \cdot \prod_{x=1}^n P_x^{\gamma_x} \quad (5.11)$$

Where:

$$\begin{aligned} \bullet k &= \begin{cases} 1 & \text{if CAC is used} \\ 0 & \text{if other cement types are used} \end{cases} & \bullet \alpha = 0.001 \\ & & \bullet \beta = -0.104 \\ \bullet a &= \begin{cases} -49.100 & \text{if } T < 12^\circ\text{C} \\ -22.223 & \text{if } 12^\circ\text{C} \leq T \leq 27^\circ\text{C} \\ 50.053 & \text{if } 27^\circ\text{C} < T \leq 40^\circ\text{C} \\ 95.612 & \text{if } T > 40^\circ\text{C} \end{cases} & \bullet \delta = -0.046 \\ & & \bullet b = 198.07 \\ \bullet Q_x &= C_3S^{0.175} \cdot C_2S^{0.121} \cdot C_3A^{0.093} \cdot C_4AF^{0.106} \cdot MgO^{0.051} \cdot C_4A_3S^{0.229} \cdot CT^{-0.148} \cdot \\ & C_2AS^{0.290} \cdot CA^{-0.076} \cdot CA_2^{-0.068} \cdot MA^{-0.065} \cdot CS^{0.460} \cdot C_{12}A_7^{0.044} \cdot C_3FT^{0.014} \cdot Ff^{-0.130} \cdot \\ & MA_{0.1}F_{0.9}^{0.011} \cdot C_{20}A_{13}M_3S_3^{0.021} \end{aligned}$$

To measure the effect of w/c ratio on the apparent activation energy, tests were undertaken with CAM containing three types of cement (CSA, CAC and OPC) and four different percentages (2%, 4% 6% and 8%), maintaining the same water content (19 g/100 g of total mix).

Figure 6.8 shows the results of apparent activation energy of CSA, CAC and OPC cement in CAM samples with different w/c ratios. It can be seen that the apparent activation energy generally tends to slightly decrease when the w/c ratio increases, corroborating previous studies (Poole, 2007). This is because when there is more water covering the cement particles, slightly lower energy is necessary to trigger the hydration reactions.

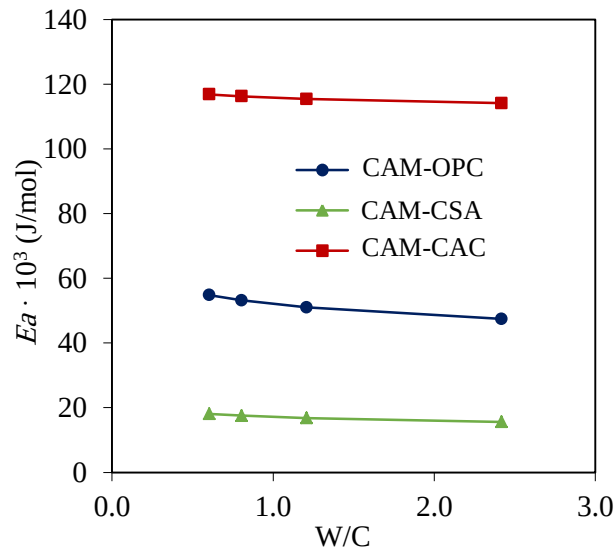


Figure 6.8 Effect water/cement ratio on E_a

It can also be seen that, compared to mixes containing OPC ($E_a \approx 50 \cdot 10^3$ J/mol), the apparent activation energy of mixes with CAC was more than double ($E_a \approx 115 \cdot 10^3$ J/mol) while for mixes with CSA the apparent activation energy was less than half ($E_a \approx 15 \cdot 10^3$ J/mol). The author consider that these behaviours must be related to the

different chemical compositions and subsequent reactions during the hydration process, but further investigation is necessary to fully understand these, as the tests carried out for the present investigation do not allow any further analysis in this regard.

6.4 PREDICTIVE MODEL FOR THE STABILITY PROVIDED BY CEMENT

To calculate the stability provided by the cement during and after hydration, cement concrete samples were manufactured with the same types and quantities of materials, method of manufacture, compaction and curing as previous CAM samples, but without any addition of bituminous emulsion to the mix. Moreover, different cement contents were used (2%, 4% and 8%) leaving the content of 6% for the post-validation of the model once it was calibrated with previous results. Different equations were found in the literature to predict the development of strength in concrete, such as hyperbolic (Equation 5.6) (Carino, 1984), exponential (Equation 5.7) (Freiesleben and Pedersen, 1985) and logarithmic (Equation 5.8) (Carino, 1991) (Table 5.2).

Table 5.2 Strength prediction models for cement concrete

Type	Equation	
Hyperbolic	$S(t_e) = S_u \frac{K (t_e - t_0)}{1 + K (t_e - t_0)}$	(5.6)
Exponential	$S(t_e) = S_u \cdot \exp \left\{ - \left(\frac{\tau_s}{t_e} \right)^{\beta_s} \right\}$	(5.7)
Logarithmic	$S(t_e) = A \cdot \ln(t_e) + B$	(5.8)

S(t_e): the strength at a given time (MPa); S_u: the ultimate strength at infinite time (MPa); K: the reaction rate (1/day); t_e: age for the predicted strength (days); t₀: time at start development of strength (days); τ_s: time constant for strength (days); β_s: shape constant for strength (-); A: fitting parameter (MPa); B: fitting parameter (MPa)

Equation 5.6 has been found to be the most accurate (Schindler, Dossey and McCullough, 2002; Saadoon, Garcia and Gómez-Meijide, 2018 b), thus it was selected for the present study.

In this equation, t_0 is the time at which the cement hydration starts, considered zero for the present investigation. S_u is the ultimate strength that the samples will achieve if enough curing time is elapses. It is dependent on different factors, such as w/c ratio, characteristics of cement and aggregate, type of curing and weather conditions. As the hydration develops much faster during the first days and can be accelerated by increasing the curing temperature (Neville and Brooks, 2010; Fang et al., 2015), S_u was experimentally estimated by curing a series of samples (with cement and no emulsion) for 7 days at 70°C. However, in the present investigation the tests were carried out at 40°C, with the expectation of slower curing. In order to estimate the necessary time (t_e) to achieve at 40°C the same curing level as for 7 days at 70°C (Δt), the Arrhenius equation was developed as follows:

$$\frac{1}{t} = A * e^{\frac{-E_a}{RT}} \rightarrow t_e = \sum_0^{t_0} \exp\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \Delta t \quad (6.3)$$

where A is the material proportionality constant (1/day); R is the universal gas constant (8.314 J/mol/K); T is 313 K (40°C); and T_{ref} is 343 K (70°C). The apparent activation energy (E_a) was calculated based on the composition of cement, according to Equation 5.11. Finally, once t_e and $S(t_e) \approx S_u$, are known, Equation 5.6 can be applied to obtain the reaction rate (K).

Once K was obtained, Equation 5.6 was used to predict the stability provided by cement in samples containing not only cement but also bitumen emulsion. Figure 6.9-

top shows that Equation 5.6 was not accurate enough to predict this contribution, with the predicted stability being greater than the real. As explained above, the final stability provided by cement, if enough curing/drying time is given, will be the same (Fang et al., 2015). However, the presence of bituminous emulsion acts as a retardant, as it is more difficult for the water to reach the cement particles (Fang et al., 2015). This effect was taken into account and Equation 5.6 was modified by adding a factor

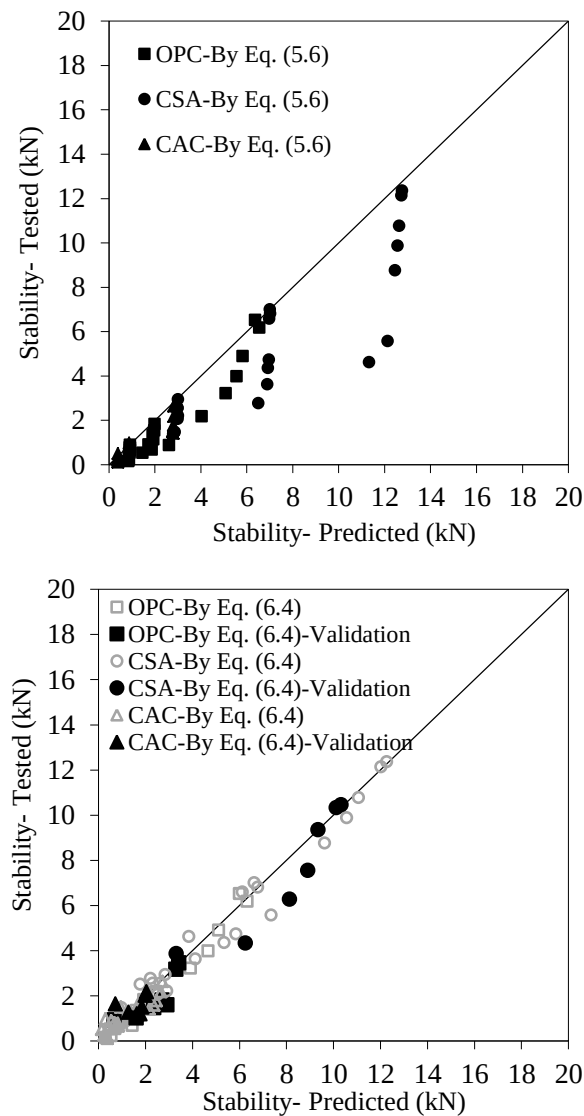


Figure 6.9 Comparison between stability of cement in CAM tested and predicted by Equation 5.6 (Top) and Equation 6.4 (Bottom)

$(t_e/t_{0+1})^\gamma$, which reduces the predicted stability at early curing/drying stages, but whose effect is practically negligible at the end of the process. This factor was obtained based on the scientific background of the authors and by using *Eureqa Nutonian Mathematical Software*, which iterated different possibilities until the one with minimum error was obtained. Hence, Equation 5.6 was developed, as follows:

$$S_c(t_e) = S_u \frac{K(t_e - t_0)}{1 + K(t_e - t_0)} \cdot \left(\frac{t_e}{t_e + 1}\right)^\gamma \quad (6.4)$$

where γ is a fitting parameter, whose value was obtained by minimising the square error between experimental and predicted data. In this case, this value resulted in $\gamma = 3.75$, with which the correlation between real and predicted values ($R^2=0.984$) improved significantly, as shown in Figure 6.9-bottom.

Once the model was calibrated, its validation was carried out by testing a new series samples with 6% cement content, which had not been used before for the model calibration (as explained above, for model calibration only samples with 2%, 4% and 8% were used). The same steps described above were followed to predict S_c and the predicted results for this new series of samples were also added to Figure 6.9-bottom. It can be seen that a high-quality prediction was achieved ($R^2 = 0.972$), which proves that the model has consistency and effectiveness for both conventional OPC and rapid hardening cements (CAC and CSA).

SUMMARY

Three types of cement (one normal and two rapid hardening cements) were investigated in terms of their effect on the performance of cold asphalt mixture

(CAM). This investigation has studied the dynamics of water evaporation and mechanical performance of CAM mixed with different types and quantities of cement.

The salient point of this part of the investigation is that, according to types and quantities of cement used, cement does not make an important contribution to accelerate the dynamics of water evaporation, although it consumes a substantial amount of water in its reaction (hydration). Therefore, the benefit of using cement in CAM is increased strength, without a clear role in accelerating the curing of CAM.

Based on the analysis presented in this chapter and the outcomes of previous chapters, it can be concluded that bitumen emulsion delays curing; cement has no fingerprint in accelerating curing; and gradation of aggregate affects the capillary action of CAM, and its consequent curing. Therefore, it is very important to investment effect of the gradation of aggregate on the evaporation boogie accelerate development the performance of CAM. Thus the following part of the thesis presents a detailed investigation of the effect of gradation of aggregate on curing, while subsequent discussion explains the prediction of the dynamics of evaporation, and the time taken to open the road to traffic.

Chapter 7

A general model to predict the time required to open road surfaces built of cold asphalt mix

7.1 INTRODUCTION

As is known, approximately 90% of CAM weight is composed of aggregates (Virginiadot, 2018) and the binder is bitumen emulsion, which is normally composed of 60% of bitumen and 40% of water. In the previous chapters, the effect of binder materials (bitumen emulsion, cement) on dynamics of water evaporation was investigated and understood. Depending on that, it is interested to investigate and understanding effect this component on dynamic of water evaporation.

In unbound granular materials, it has been observed that the gradation and geometry of the aggregates is one of the main factors affecting the topology of the pores (Saadoon, Garcia and Gómez-Meijide, 2017). Such topology is the main factor that affects the hydraulic properties (Aboufoul and Garcia, 2016; Saadoon, Garcia and Gómez-Meijide, 2017) and dynamics of water evaporation of the porous materials (Lehmann, Assouline and Or, 2008; Saadoon, Garcia and Gómez-Meijide, 2017). As

will be extensively explained in the following section, Theoretical Considerations, it is possible to find a correlation between the gradation of the aggregates and the dynamics of water evaporation, such as time to full drying.

Because aggregates represent more than 90% of total weight in CAM, it is expected that their gradation will affect the water evaporation dynamics and curing period of CAM. By developing a relationship between the aggregate gradation and evaporation properties of water in CAM, it will be possible to: (a) to select the optimum aggregates that will minimise the duration of the curing stage, (b) estimate the curing time of pavements built with this material. Consequently, it will be possible to predict the time required to open roads to traffic, when they are built of CAM.

Hence, in the present chapter, the correlation between CAM's properties related to material gradation, microstructure and hydraulic behaviour will be correlated to the dynamics of water evaporation in (i) unbound granular materials, (ii) samples of CAM with no cement addition and (iii) with the addition of three different types of cement. The evaporation rate, during the first and secondary stages of the drying process, will be modelled numerically and, a general model to predict the time required to open a road made of CAM to traffic will be developed in this part of thesis.

7.2 THEORETICAL CONSIDERATION

7.2.1 Aggregate gradation and topology of voids

The gradation of an aggregate and the air void structure within an unbound material can be described through different parameters, which have effect on other different

properties of an unbound material or an asphalt mixture, such as hydraulic conductivity (Aboufoul and Garcia, 2016; Horiba, 2018). These are:

1. Characteristics related to aggregate gradation: mean (M) and standard deviation (S) of aggregate size, uniformity coefficient (C_u), and coefficient of gradation (C_c), which can be calculated as shown in Table 7.1.

Table 7.1 Parameters of the aggregate gradation and voids topology (*Lehmann, Assouline and Or, 2008; Norhidayah et al., 2014; Aboufoul and Garcia, 2016; Saadoon, Garcia, and Gómez-Meijide, 2017; Horiba, 2018; Texto, 2018*)

Parameter	Formula	No.
Mean size	$M = \frac{\Phi_{16} + \Phi_{50} + \Phi_{84}}{3}$	(7.1)
Standard deviation	$\sigma = \frac{\Phi_{84} - \Phi_{16}}{4} + \frac{\Phi_{95} - \Phi_5}{6.6}$	(7.2)
Phi-value	$\Phi_x = -\log_2 d_x$	(7.3)
Uniformity coefficient	$C_u = \frac{d_{60}}{d_{10}}$	(7.4)
Coefficient of gradation	$C_c = \frac{d_{30}^2}{d_{60} * d_{10}}$	(7.5)
Pore size distribution index	$n = \left(\frac{K_s}{0.003} \right)^{0.154}$	(7.6)
Air voids content	$A_v = \frac{\text{Total air voids area}}{\text{Total image area}} * 100$	(7.7)
Circularity	$C_i = \frac{4 \pi * \text{area of void}}{(\text{Perimeter of void})^2}$	(7.8)
Roundness	$R = \frac{4 * \text{area of void}}{\pi * (\text{major axis of void})^2}$	(7.9)
Aspect ratio	$AR = \frac{\text{Longer dimension}}{\text{Shorter dimension}}$	(7.10)
Tortuosity	$T = \frac{\text{Length of pore}}{\text{Shortest distance between pore ends}}$	(7.11)

$d_x = d_5, d_{10}, d_{16}, d_{30}, d_{50}, d_{60}, d_{84}$ and d_{95} .

$d_5, d_{10}, d_{16}, d_{30}, d_{50}, d_{60}, d_{84}$ and d_{95} : the diameter at which 5, 10, 16, 30, 50, 60, 84 and 95% of the sample's mass is comprised of particles with a diameter less than this value.

As an example, when C_u is greater than 6, it can be determined that the unbound granular material is well-graded, while if it is lower than 4, the granular material is poorly-graded or close to uniformly graded, which means that the particles have almost identical size (Texto, 2018).

2. Characteristics related to the topology of voids structure: Tortuosity, circularity, roundness, aspect ratio, surface area, number of voids, voids class and pore size distribution index. These characteristics can be calculated as shown in Table 7.1, based on measures obtained by X-ray CT scans. When the circularity, roundness and aspect ratio of air voids are close to 1, the shape of the voids is similar to a sphere, while if the aspect ratio is higher and the value of circularity and roundness are close to zero, the voids have elongated shape, as shown in Figure 7.1 (Norhidayah et al., 2014).

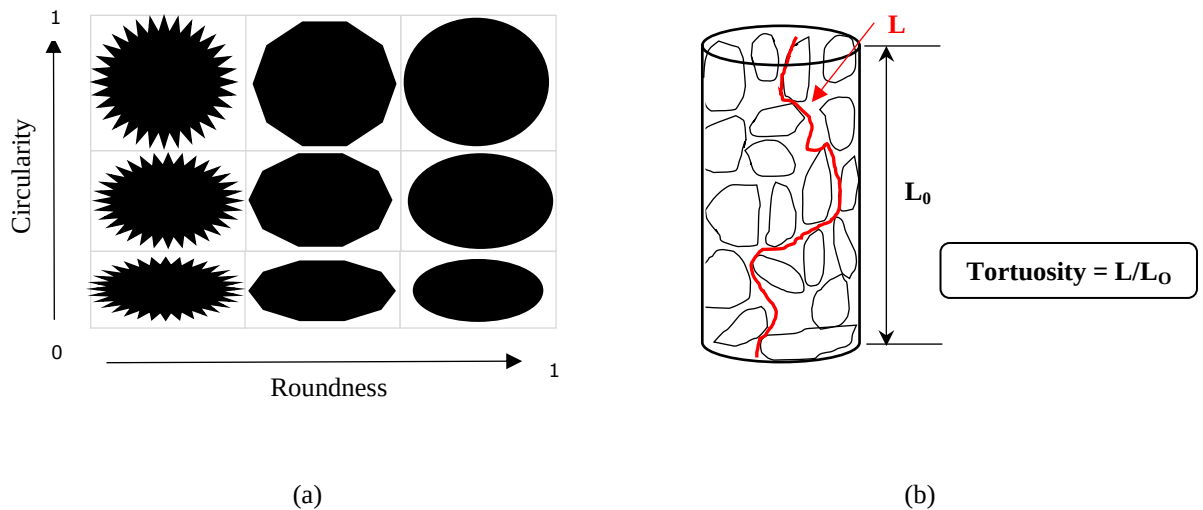


Figure 7.1 Visual description of properties related to pore topology: roundness, circularity (a), and tortuosity (b)

7.3 OVERVIEW OF THE METHODOLOGY FOLLOWED IN THE PRESENT CHAPTER

According to previous publications (Lehmann, Assouline and Or, 2008; Saadoon, Garcia and Gómez-Meijide, 2017), aggregate gradation is an important factor, which conditions the structure of air voids in a porous material. At the same time, this structure affects the hydraulic behaviour, which determines the time needed to fully dry interstitial water present inside porous materials. These correlations lead to the conclusion that aggregate gradation has an effect on the dynamics of water evaporation of porous materials, and consequently, on the time needed to fully dry them. Therefore, it might be possible to estimate, based on its gradation, its drying rate. Figure 7.2 shows schematically such correlations and the main parameters involved in each of them (Lehmann, Assouline and Or, 2008; Norhidayah et al., 2014; Saadoon, Garcia and Gómez-Meijide, 2017; Brocku, 2018; Texto, 2018). These parameters will be taken into account during the present research.

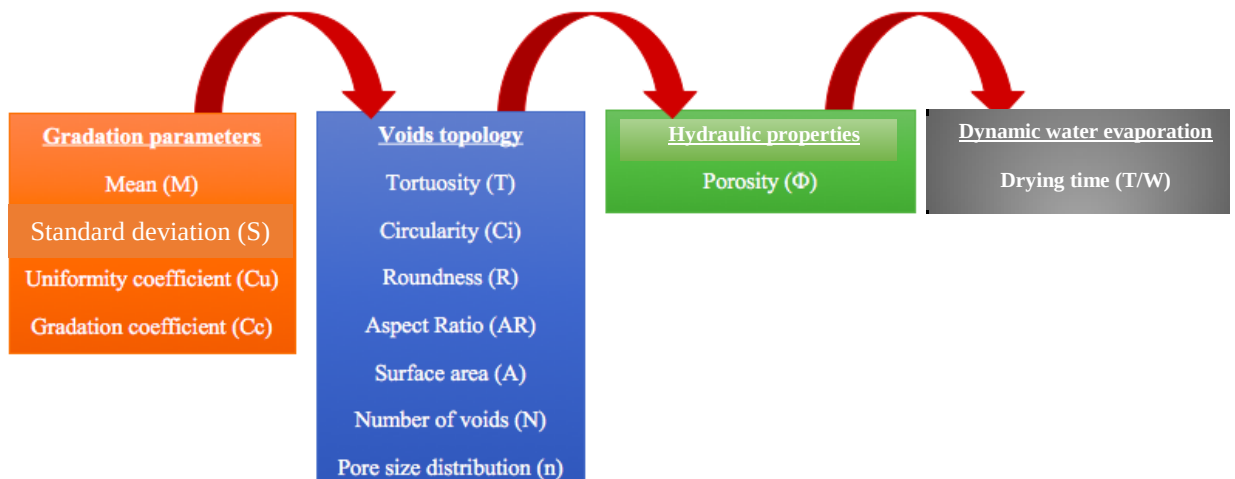


Figure 7.2 Correlations between different characteristics of porous materials followed in this thesis in order to obtain a prediction model of drying time based on aggregate gradation

In order to obtain a predictive model of the drying time of CAM based on its aggregate gradation, the following steps were followed:

- Identification of gradation characteristics, which mostly affect the parameters related to voids topology.
- Identification of parameters related to voids topology, which produce the highest effect on the hydraulic properties of the material.
- Definition of the relationship between time of full drying and hydraulic properties of the material.

7.4 PEARSON'S CORRELATION ANALYSIS

The correlation between the various parameters studied was analysed with linear regression and described by using Pearson's correlation coefficients (R^2). This correlation coefficient can rank between 0 and 1. When it is between 0 and 0.4, the correlation can be considered very low; from 0.4 to 0.7, there is a moderate correlation and from 0.7 to 1, there is a high or very high correlation (Garcia et al., 2015).

7.5 RESULTS AND DISCUSSION

7.5.1 Test results

In Table 7.2 it is possible to see the results of all the properties tested, regarding dynamics of water evaporation, hydraulic behaviour, voids topology and aggregate gradation. These parameters were determined as follows:

- Dynamics of water evaporation: as explained in Chapters 3 & 4 (sections 3.5.1 and 4.3.2 respectively)
- Hydraulic behaviour (porosity): calculated from the porosity test as described in Chapter 3 (section 3.5.2)
- Voids topology: depending on CT-scan images taken through the aggregate samples (see Figure 7.4 for example) (see section 3.5.5); using 7.7-7.11 in Table 7.1, ImageJ software calculated the voids parameters automatically. The parameter (n) is calculated according to the relation between these parameters and hydraulic conductivity of materials as explained in section 4.2.
- Aggregate gradation: equations 7.1 to 7.5 were used in calculation of the aggregate parameters in Table 7.2 depending on the gradations of aggregate in Figure 3.3.

Table 7.2 The Hydraulic properties, and dynamics of water evaporation that experimentally measured. Topological constants of aggregate measured by CT scan test. Gradation parameters.

Sample	Dynamics of water evap.	Porosity	Topological constants							Gradation parameters			
	T^*/W (h/kg)	Φ (%)	T (-)	Ci (-)	R (-)	AR (-)	A (mm ²)	N (-)	n (-)	M (mm)	S (mm)	Cu (-)	Cc (-)
C6.3	94.78	29.41	3.70	0.828	0.557	1.80	6.41	358	2.887	1.38	0.14	235.71	26.19
C8	104.62	31.06	3.62	0.824	0.557	1.80	7.04	342	2.888	1.74	0.15	63.33	9.87
C10	62.58	22.72	4.03	0.835	0.559	1.79	4.23	409	2.550	1.95	0.14	59.29	7.75
C14	116.26	31.79	3.73	0.828	0.543	1.84	6.90	358	2.904	4.09	0.26	17.50	3.89
C20	95.71	26.94	3.73	0.830	0.547	1.83	6.10	337	2.808	3.29	0.13	40.00	5.38
S2	127.25	34.23	2.74	0.795	0.552	1.81	6.78	384	3.366	2.00	0.00	1.00	1.00
S14	153.45	47.14	3.18	0.883	0.685	1.48	10.63	344	3.714	14.0	0.00	1.00	1.00
S20	158.35	56.34	3.60	0.877	0.713	1.42	15.15	290	4.559	20.0	0.00	1.00	1.00

*Time of full drying/water content (T/W), Porosity (Φ), Tortuosity (T), Circularity (Ci), Roundness (R), Aspect ratio (AR), Surface area (A), Number of voids (N), Pore size distribution index classes (n), Mean size of aggregate (M), Standard deviation of aggregate (S), uniformity coefficient of aggregate (Cu), Coefficient of gradation (Cc). *The time when the evaporation rate became 0 kg/h.*

The correlations between each pair of properties were studied through a Pearson's statistical analysis. The obtained Pearson's coefficients can be seen in Figure 7.3.

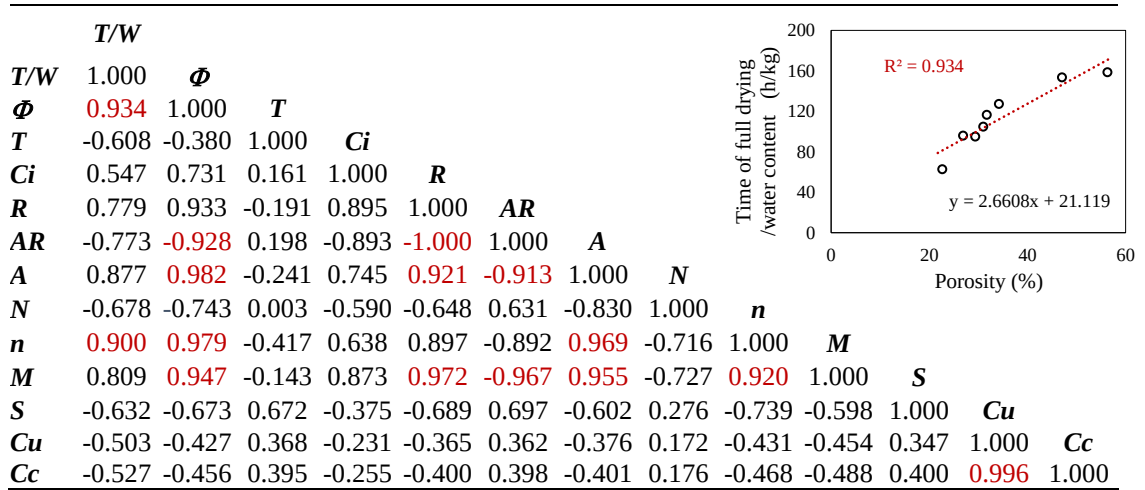


Figure 7.3 Results of Pearson's correlation test

7.5.2 Homogeneity of microstructure of air voids

Figure 7.4 includes some X-ray images of aggregate samples.

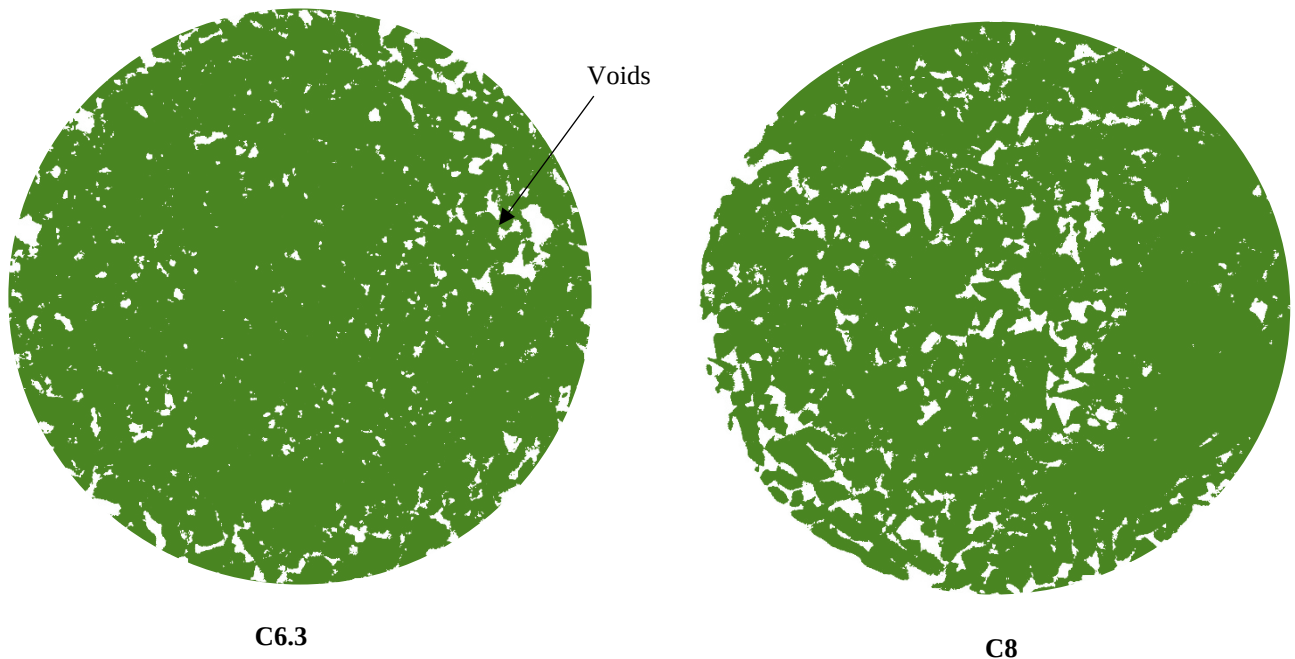


Figure 7.4 Continues below

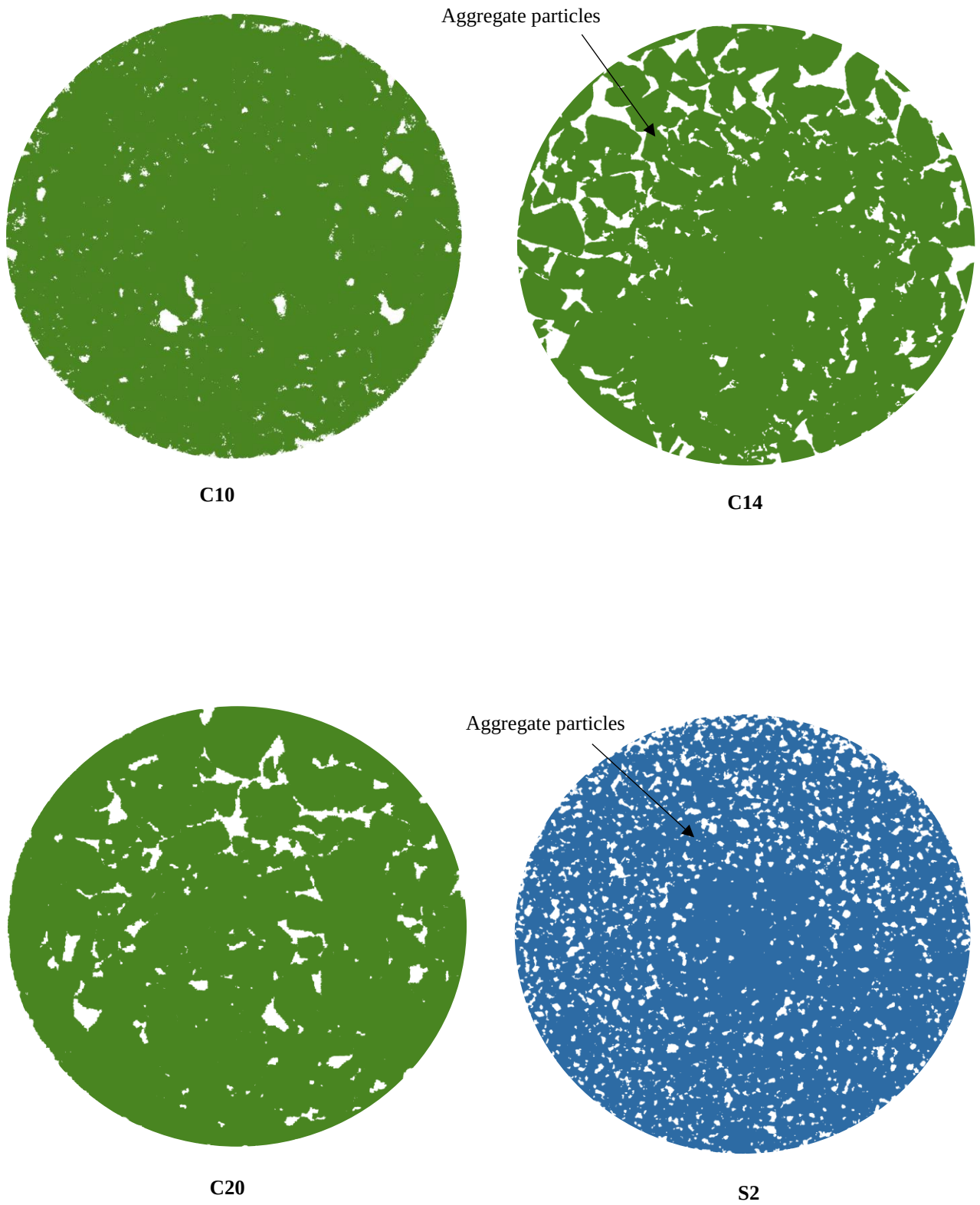


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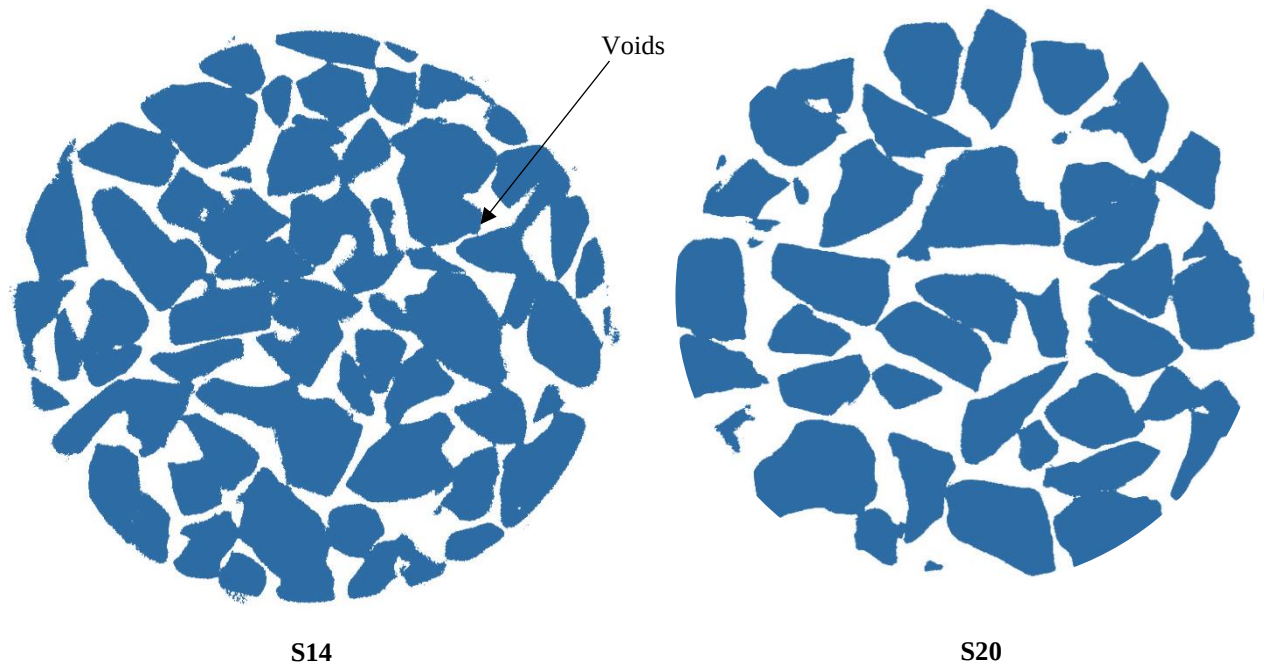


Figure 7.4 Includes some X-ray images of aggregate

The vertical profile of air voids can be seen in in Figure 7.5 and the standard deviation from the average can be seen in Table 7.3.

Table 7.3 Variation of air voids content of the aggregate through vertical sample profile

Type of sample	Compound aggregate					Single aggregate		
	C6.3	C8	C10	C14	C20	S2	S14	S20
Standard deviation	5.47	5.98	3.98	6.87	5.00	8.74	6.75	5.56

In general, all samples have air voids profiles with homogenous distribution. For this reason, the adopted method for sample manufacturing can be considered appropriate. In addition, it can be determined that the properties (i.e. dynamics of water evaporation, hydraulic conductivity and microstructure characteristics) measured in a specific region of the samples are representative of the whole material.

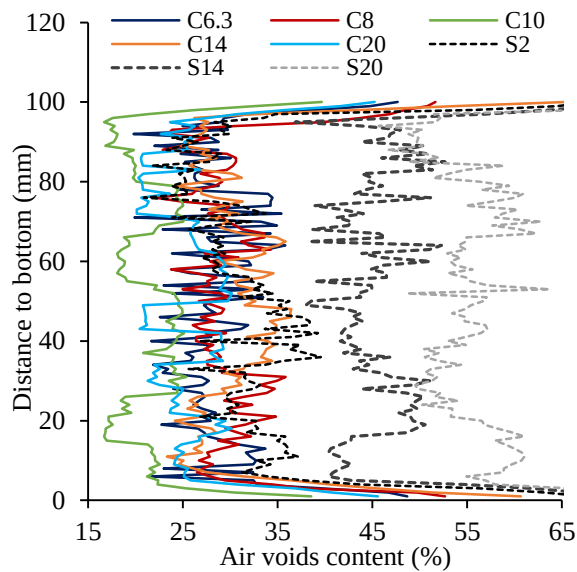


Figure 7.5 Vertical profile of air voids content in aggregate samples

As can be seen, the maximum size of compound aggregate samples has no clear correlation with the air voids content, all the lines oscillating around very similar values. However, the size in single aggregate samples has a clear effect on their air voids content, being higher as long as the size increases.

7.5.3 Correlations between properties obtained for unbound granular materials

According to previous research in the area (Aboufoul and Garcia, 2016; Saadoon, Garcia and Gómez-Meijide, 2017), the porosity of porous materials is strongly correlated with most of the other hydraulic properties such as the hydraulic conductivity. In addition, it can be determined fast and easily through a simple volumetric test (Aboufoul and Garcia, 2016). As it can be seen in Figure 7.3, this property (the porosity) has, indeed, very high positive correlation with the time to full drying ($R^2=0.934$). Hence, increases in porosity can be translated into extensions of

time required to reach full drying. This phenomenon is related to the stronger capillary action happening when the porosity is reduced because increased porosity implies higher air void size. For this reason, when the goal is to accelerate the curing/drying time of CAM or unbound granular materials, the porosity needs to be minimised.

Furthermore, among all topological constants, the surface area of air voids has the highest correlation with porosity ($R^2=0.982$). As it has been found that the surface area of air voids increases with porosity, it can be expected that increases in air voids surface area will lead to longer times for full drying. In Figure 7.3 it can be seen how, indeed, the correlation coefficient obtained between the voids surface area and time for full drying is high ($R^2 = 0.877$). Similarly, when the surface area of air voids increases, the capillary action of the material reduces and, consequently, the drying time will be longer (Lehmann, Assouline and Or, 2008; Saadoon, Garcia and Gómez-Meijide, 2017).

Moreover, it has been found that the mean size of aggregate has a strong correlation to the surface area of air voids ($R^2 = 0.955$), while all the other parameters of aggregate gradation, such as standard deviation of aggregate size, uniformity coefficient of aggregate, coefficient of gradation have lower correlation with this parameter (see Figure 7.3). According to this, reductions in the average size of the aggregate will contribute to reduce the surface area of voids and, as a result, increase the capillary action, which will accelerate the drying of the material (Lehmann, Assouline and Or, 2008; Saadoon, Garcia and Gómez-Meijide, 2017). Due to the high positive correlation between time of full drying and the mean size of aggregate ($R^2 = 0.809$), it

would be useful to reduce the latter in CAM in order to accelerate the curing or drying process.

7.6 Predictive model of evaporation rate in cold mix asphalt or unbound layer

The model will be divided in two parts, depending on whether the material is on the first or the second evaporation stage (as was described in Section 2.9.3 and Figure 2.17). According to the literature (Lehmann, Assouline and Or, 2008; Or et al., 2013), the transition stage, happening between the two main phases, lasts for a negligible time compared to the duration of the whole drying process. For this reason, it will not be included in the model.

7.6.1 Predictive model of evaporation rate for the first stage of evaporation

As stated in section 2.9.3, during the first stage the water loss is mainly due to the evaporation of free water from the surface. Hence, the rate of evaporation $e_I(t)$ depends practically only on the environmental conditions surrounding the material (Lehmann, Assouline and Or, 2008; Or et al., 2013; Saadoon, Garcia and Gómez-Meijide, 2017). For this reason, it can be calculated as the evaporation rate of free water (E_F) multiplied by the surface area of water exposed to the environment (A_S) and the temperature ($T(t)$), which depends on the heating time (NALDC, 2018).

$$e_I(t) = E_F \cdot A_S \cdot T(t) \quad (7.12)$$

where $e_I(t)$ is measured in kg h^{-1} , E_F in $(\text{kg m}^{-2} \text{ h}^{-1} \text{ }^{\circ}\text{C}^{-1})$, A_S in m^2 and $T(t)$ in $^{\circ}\text{C}$. In addition, due to the configuration of the test in the current investigation, the evaporation is only happening from the upper surface of the material, whose area is

A_{us} . Thus the surface of free water can be calculated by multiplying this by the porosity (Φ) as:

$$A_S = A_{us} \cdot \Phi \quad (7.13)$$

According to previous publications (Aboufoul and Garcia, 2016), it is possible to estimate the porosity of a porous material based on the results of the hydraulic conductivity test, as follows:

$$\Phi = \frac{b}{K_s - a} + c \quad (7.14)$$

where K_s is the hydraulic conductivity (m/h), Φ is the porosity and a , b and c are fitting parameters depending on material characteristics. By replacing Equation 7.14 in Equation 7.13, the area of exposed water is:

$$A_S = A_{us} \left(\frac{b}{K_s - a} + c \right) \quad (7.15)$$

At the beginning of the test, the surface temperature of the material was 20°C. After the heating started, the temperature of the surface gradually increased during first stage until a steady-state temperature was reached (Figure 7.6). The analytical relationship between temperature and heating time can be calculated by the Newton's law of heat transfer (García et al., 2013):

$$mc \frac{dT}{dt} = -k A (T - T_{ss}) \quad (7.16)$$

where k is a heat transfer coefficient (s^{-1}), which depends of the area of the materials exposed to the environment, mass of the test samples and specific heat capacity. $T(t)$ is the temperature of the material and $T_{ss}(t)$ is the steady-state temperature that the material reaches when the energy input balances the energy losses.

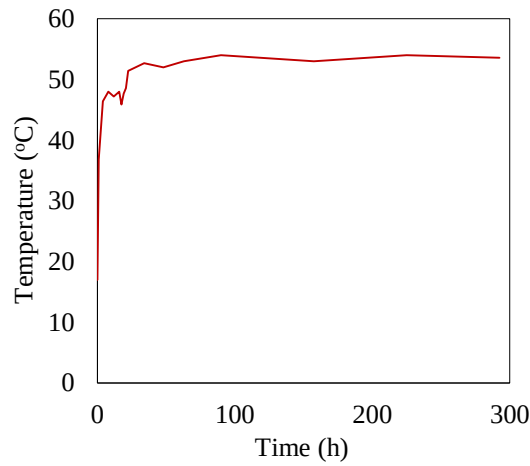


Figure 7.6 Temperature of material with time. Example cases to C8

After integration, Equation 7.17 was obtained:

$$T(t) = T_{ss} - (T_{ss} - T_{air}) e^{-kt} \quad (7.17)$$

Parameter k can be obtained by fitting the experimental temperature-time curves to this equation. By replacing Equations 7.15 and 7.17 in Equation 7.12, the following equation was obtained.

$$e_I(t) = E_F \left(A_{us} \cdot \left(\frac{b}{K_s + a} + c \right) \right) (T_{ss} - (T_{ss} - T_{air}) e^{-kt}) \quad (7.18)$$

In this equation, the first term is constant, which just depends on the material and the configuration of the test. Therefore:

$$\alpha = E_F A_{us} \left(\frac{b}{K_s + a} + c \right) \quad (7.19)$$

The difference between the steady-state temperature (T_{ss}) and the air temperature (T_{air}) is also a constant that can be named ΔT . With these simplifications, Equation 7.18 can be rewritten, as follows:

$$e_I(t) = \alpha (T_{ss} - \Delta T e^{-kt}) \quad (7.20)$$

This equation can be further simplified, by taking into account the following constants:

$$A = \alpha T_{ss} \quad (7.21)$$

$$B = \alpha \Delta T \quad (7.22)$$

This leads to the final shape of the equation, as follows:

$$e_I(t) = A - B e^{-kt} \quad (7.23)$$

where A is the maximum evaporation rate during the first stage which happens at the end of this (kg h^{-1}). B is the difference between the initial and final evaporation rate happening in the first stage (Kg h^{-1}). At time $t = 0$, the difference ($A-B$) gives the

value of the initial evaporation rate. From this value, the rate increases with time according to the exponential relationship.

As it can be seen in Figure 7.7, the porosity of CAM (in this case CAM-N) remains practically constant over the first and second stages. For this reason, the average value of the porosity over these stages can be assumed equal to the porosity value measured at the beginning of each of them. This phenomenon happened for all the studied materials, including both CAM (Figure 7.7). Note that in unbound granular materials, the porosity remains constant over time.

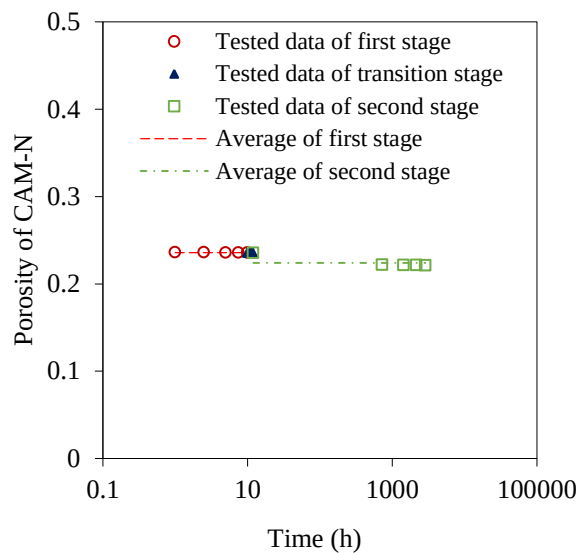


Figure 7.7 As a example to change porosity with time (CAM-N)

By using Excel Solver tool and the method of minimum square error, Equation 7.23 was fitted to experimental data obtained for all the studied materials. Hence, parameters A , B and k were obtained, as shown in Table 7.4.

Table 7.4 Fitting parameters to first stage of evaporation rate to unbound materials and CAM

	<i>A</i>	<i>B</i>	<i>k</i>
Unbound Granular Material			
C6.3	3.37×10^{-2}	5.54×10^{-3}	5.91×10^{-1}
C8	3.40×10^{-2}	5.57×10^{-3}	5.90×10^{-1}
C10	2.99×10^{-2}	2.49×10^{-3}	6.03×10^{-1}
C14	3.41×10^{-2}	6.07×10^{-3}	5.89×10^{-1}
C20	3.19×10^{-2}	2.50×10^{-3}	5.98×10^{-1}
S0.6	3.41×10^{-2}	6.31×10^{-3}	5.78×10^{-1}
S2	3.98×10^{-2}	6.89×10^{-3}	5.67×10^{-1}
S5	4.03×10^{-2}	6.91×10^{-3}	3.68×10^{-1}
S8	4.06×10^{-2}	7.54×10^{-3}	3.38×10^{-1}
S14	4.26×10^{-2}	8.17×10^{-3}	3.32×10^{-1}
S20	4.85×10^{-2}	9.18×10^{-3}	2.28×10^{-1}
Cold Mix Asphalt			
CAM-N	2.85×10^{-3}	7.72×10^{-4}	0.60×10^{-1}
OPC2	0.99×10^{-3}	3.73×10^{-4}	0.60×10^{-1}
OPC4	0.89×10^{-3}	2.80×10^{-4}	0.60×10^{-1}
OPC6	0.87×10^{-3}	2.10×10^{-4}	0.60×10^{-1}
OPC8	0.85×10^{-3}	2.00×10^{-4}	0.60×10^{-1}
CAC2	0.93×10^{-3}	3.04×10^{-4}	0.60×10^{-1}
CAC4	0.87×10^{-3}	2.18×10^{-4}	0.60×10^{-1}
CAC6	0.86×10^{-3}	2.18×10^{-4}	0.60×10^{-1}
CAC8	0.83×10^{-3}	1.90×10^{-4}	0.60×10^{-1}
CSA2	0.88×10^{-3}	2.70×10^{-4}	0.60×10^{-1}
CSA4	0.81×10^{-3}	1.82×10^{-4}	0.60×10^{-1}
CSA6	0.78×10^{-3}	1.47×10^{-4}	0.60×10^{-1}
CSA8	0.75×10^{-3}	0.90×10^{-4}	0.60×10^{-1}

As can be seen, these parameters are lower for CAM than for granular materials, which indicates that the evaporation rate is also lower. This happens even for samples with approximately the same porosity and gradation. Hence, it can be said that the fact of adding bitumen emulsion, reduces the drying capacity of the material (Saadoon,

Garcia and Gómez-Meijide, 2017). The cement addition also produces a detrimental effect. Thus, when this increases, porosity and evaporation rate reduce.

For all the samples, there is also a positive correlation between porosity and evaporation rate during the first stage. This is due to the fact that higher porosity produces a larger water surface in contact with the atmosphere, the key factor for the development of the first stage.

The heat transfer coefficient (k) is related to how fast the heating energy travels through the material. Hence, it is related to density and porosity. All CAM samples have approximately the same porosity (23%); therefore, the k -values were also approximately the same. This porosity is more than the porosity of CAM in practice, which ranges from 6–15% (Muncy, 1990; Davidson, 2005; Khalid and Monney, 2009; Redelius, Östlund and Soenen, 2016; Lundberg et al., 2016). This difference in porosity can be attributed to the manual compaction used in the current project.

For the case of unbound aggregate, compound gradation samples (lower porosity) have higher k than samples with single size gradation (higher porosity). For example, S20 has a low k -value (0.18) due to its great porosity (56.34%). This correlation between porosity and k is also compatible with the results found in the literature (García et al., 2013).

Finally, Figure 7.8-top shows the comparison between predicted and experimental results obtained for an example of unbound granular material (S0.6) and an example of CAM (OPC4). As can be seen, the correlation level in both cases ($R^2=0.974$ and $R^2=0.955$) is noticeably high. The comparison for all the samples tested at different times of first stage can be seen in Figure 7.8-bottom. Again, the general correlation

level for unbound materials and CAM ($R^2=0.995$ and $R^2=0.989$) was very high, which proves that the model has great accuracy and applicability during the first stage.

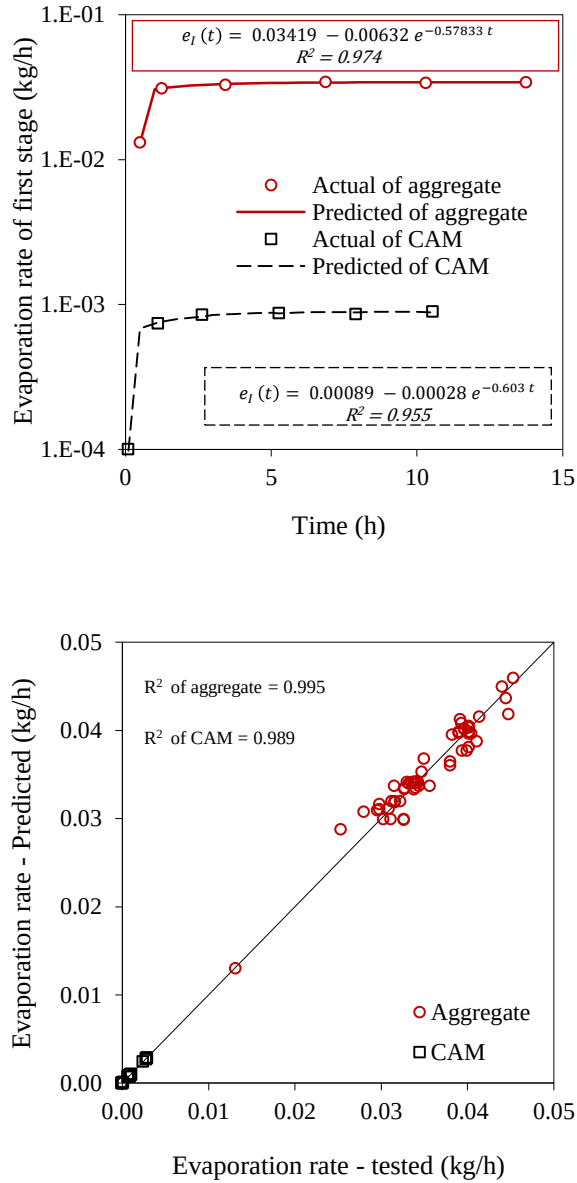


Figure 7.8 Comparison between predicted and experimental evaporation rates obtained for samples S0.6 and OPC4 (Top), and for the rest of the cases (Bottom)

7.6.2 Predictive model of evaporation rate for the second stage of evaporation

Unlike the previous case, during the second stage the dynamics of water evaporation depend mainly on the diffusion properties (Shokri, Lehmann and Or, 2009). During this stage, the evaporation rate, $e_{II}(t)$, can be estimated by applying the following modification of Fick's law (Shokri, Lehmann and Or, 2009):

$$e_{II}(t) = D_p \frac{C_{sat} - C_{\infty}}{L_{diff}(t)} \quad (7.24)$$

where $e_{II}(t)$ is obtained in kg h^{-1} , D_p is the gas (water vapour) diffusion coefficient ($\text{m}^3 \text{ soil air m}^{-1} \text{ soil h}^{-1}$), C_{sat} is the saturated water vapour density (kg m^{-3}) at the secondary drying front (surface between semi-saturated and dry layer), C_{∞} is the water vapour density at the surface (kg m^{-3}) and L_{diff} is the length for vapor diffusion (thickness of dry layer) (m).

According to Shokri, Lehmann and Or (2009), D_p can be calculated by the equation proposed by Moldrup et al. (2000):

$$D_p = D_0 \frac{\varepsilon^{2.5}}{\Phi} \quad (7.25)$$

Furthermore, according to Shokri, Lehmann and Or (2009), the air-filled porosity (ε) can be assumed equal to the total porosity of the material (Φ). Therefore:

$$D_p = D_0 \Phi^{1.5} \quad (7.26)$$

As in the present investigation the drying is produced only from the upper surface of the material, the depth of the dry layer over the drying time (Figures 4.8 and 6.5) can be mathematically described by the following empirical relationship proposed in by Saadoon, Garcia and Gómez-Meijide (2017):

$$L_{diff.} = \frac{k_0 t^{k_1}}{k_2 + t} \quad (4.8)$$

where L_{diff} is the depth of the film region (dry layer) (m), t the drying time (h) and k_0 , k_1 , and k_2 are material constants. By substituting, Equations 7.26 and 4.8 into Equation 7.24, the following equation for the evaporation rate of water during the second stage could be obtained:

$$e_{II}(t) = (D_0 \Phi^{1.5}) (C_{sat} - C_{\infty}) \frac{k_2 + t}{k_0 t^{k_1}} \quad (7.27)$$

In this equation, the following constants can be defined:

$$\alpha = \frac{(D_0 \Phi^{1.5}) (C_{sat} - C_{\infty}) k_2}{k_0} \quad (7.28)$$

$$\beta = \frac{(D_0 \Phi^{1.5}) (C_{sat} - C_{\infty})}{k_0} \quad (7.29)$$

Hence, Equation 7.27 can be rewritten as:

$$e_{II}(t) = (\alpha + \beta t) t^{-k_1} \quad (7.30)$$

According to this equation, the evaporation rate tends to zero with time. As has been explained before in section 7.6.1, the porosity of CAM reduces over the drying time until it becomes steady at full drying. Nevertheless, and as in the first stage, these changes are not significant to produce accurate predictions. Therefore, the porosity will be assumed constant during the second stage, as stated in Figure 7.7, and used in Equation 7.30 to predict the evaporation rate of CAM.

The constants α , β , and k_1 , were calculated by fitting Equation 7.30 to the evaporation rate, obtained for all the studied materials, using the method of minimum square errors. This values can be found in Table 7.5. As these parameters depend on the porosity, they were practically constant for the case of CAM: approximately, $\alpha = 1$, $\beta=0.60$, $k_1= -1.96$, see Table 7.5, because the gradation and binder content used was the same for every material studied. On the contrary, for the case of unbound granular samples, these had different gradations and porosities. Consequently, significant differences in the material parameters could be observed.

Once the values of Table 7.5 were obtained, the evolution of the evaporation rates over the second stage can be estimated as shown in Figure 7.9-top for the example cases of samples C8 (unbound granular material) and OPC6 (CAM with 6% of ordinary Portland cement). As it can be seen, the correlation rates ($R^2= 0.999$ and $R^2=0.911$) are very high. For the rest of the samples, correlation results can be seen in Figure 7.9-bottom. As can be seen, the general correlation obtained for unbound granular samples and CAM was respectively $R^2= 0.954$ and $R^2=0.877$, which proves that the model can produce, in general, very accurate predictions.

Table 7.5 Fitting parameters to second stage of evaporation rate to aggregate and CAM

	α	β	$-k_1$
Unbound Granular Material			
C6.3	0.825	0.005	-1.190
C8	0.940	0.008	-1.210
C10	0.132	0.005	-1.127
C14	0.946	0.096	-1.574
C20	0.739	0.005	-1.183
S0.6	0.994	0.112	-1.583
S2	1.000	0.157	-1.609
S5	1.000	0.430	-1.765
S8	1.045	0.548	-1.774
S14	1.056	0.674	-1.781
S20	1.149	0.996	-1.797
Cold Mix Asphalt			
CAM-N	1.000	0.676	-1.969
OPC2	1.000	0.597	-1.960
OPC4	1.000	0.596	-1.958
OPC6	1.000	0.594	-1.947
OPC8	1.000	0.592	-1.937
CAC2	1.000	0.597	-1.968
CAC4	1.000	0.597	-1.947
CAC6	1.000	0.593	-1.934
CAC8	1.000	0.592	-1.933
CSA2	1.000	0.595	-2.010
CSA4	1.000	0.592	-2.010
CSA6	1.000	0.586	-2.005
CSA8	1.000	0.584	-2.001

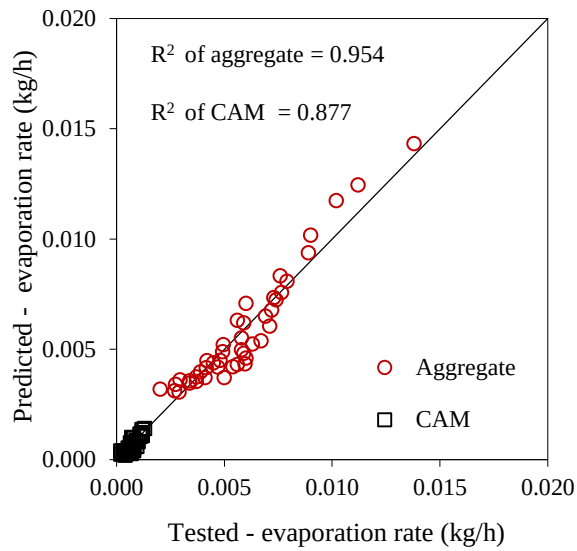
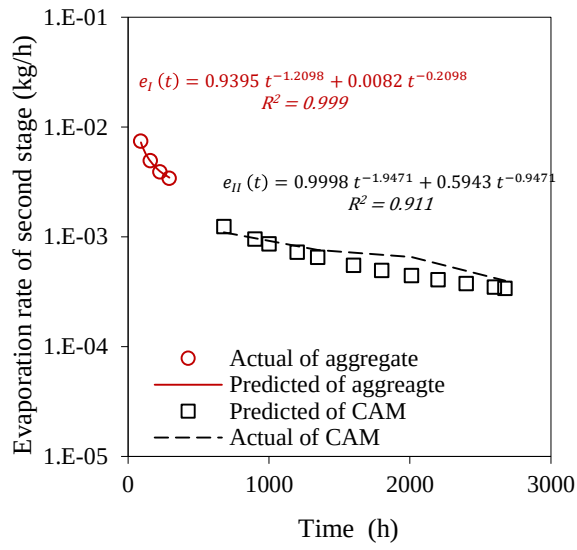


Figure 7.9 Comparison between predicted and tested evaporation rates obtained for samples C8 and OPC6 (Top), and for the rest of the cases (Bottom)

7.7 Predictive model for the minimum time required to open the road to traffic loads

According to standard specifications (SSRB, 2003), a road can be opened to traffic when a Marshall stability of at least 5 kN is reached. By carrying out Marshall tests on the studied CAM samples after different curing times, it was possible to determine the time needed for each of them to reach the reference stability. Then, assuming that within the whole drying/curing process, the length of the first stage is negligible and, by applying Equation 7.30, it was possible to obtain the evaporation rate at the moment when the Marshall stability was 5 kN, as is shown in Figure 7.10-top.

Afterwards, the time to reach 5 kN was correlated with the type and content of cement in the samples, as it can be seen in Figure 7.10-top. In this paper, the type of cement used was classified according to the maximum amount of water absorb during hydration reactions (0.42 g/g for OPC, 0.45 g/g for CAC and 0.75 g/g for CSA) (Odler, 2000; Neville, 2012; Fang et al., 2015). As can be observed in Figure 7.10-top, an exponential relationship could be obtained with a high correlation level ($R^2=0.90$), being practically independent of the type of cement that was used. Hence, the evaporation rate at the time when the road can be opened to traffic, can be defined as:

$$e_v = 0.0001 e^{0.9113 W P_c} \quad (7.31)$$

where W is the hydration water required by the cement type used and P_c is the cement content in the material.

Finally, by introducing Equation 7.31 into Equation 7.30, the model which gives the time needed to open the road to traffic (τ) could be found. As was stated in section 7.6.2

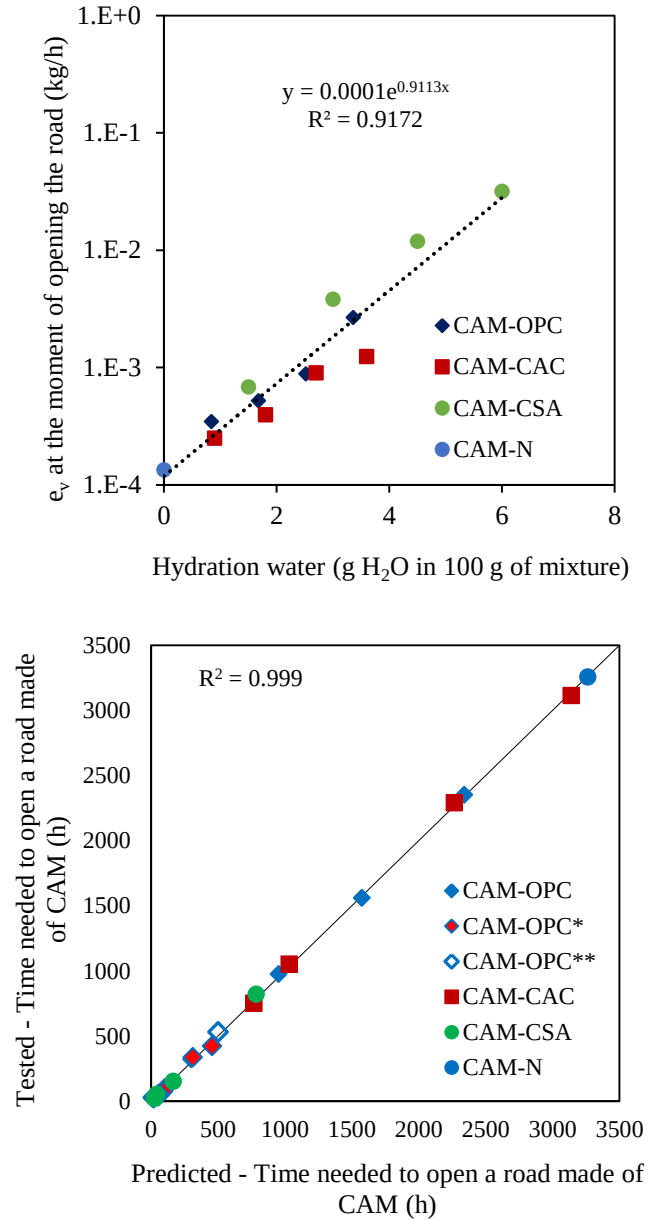


Figure 7.10 Relationship between the evaporation rate at the moment of opening the road and hydration water (Top). Correlation between predicted and tested data according to proposed model (Bottom).
(*Garcia et al., 2013; ** Fang et al., 2015)

(Table 7.5), the parameters of Equation 7.30 are approximately constant for all tested CAM samples. Therefore, the average of these parameters can be replaced in equation 7.30 to predict the minimum time required by a road to reach 5 kN, to open a road to traffic loads, as follows:

$$(1 + 0.6 \tau) \tau^{-1.96} = 0.0001 e^{0.9113 W P c} \quad (7.32)$$

Finally, in Figure 7.10-bottom, the terms at both sides of the equality of Equation 7.32 were correlated. Although the using of data from previous work in Figure 7.10-bottom, obtaining, as can be seen, a high correlation of $R^2=0.999$. This high value shows that the proposed model can predict the time needed to open a road made of CAM with great accuracy.

SUMMARY

According to the investigation carried out in the current chapter, among other conclusions, it was found that porosity, surface area of voids, and the mean size of particles of unbound materials produced a highly positive impact on the time of full drying. Therefore, reducing any one of those parameters (porosity, surface area of voids, and mean size of particles) would lead to reduced time of full drying to unbound materials or CAM, and vice-versa. In addition, a predictive model was obtained, able to fit the rate of water evaporation in these materials, with which, based on simple and quick evaporate rate tests, another model was made for the prediction of the necessary time to open a road to traffic.

Chapter Eight

Conclusions and Recommendations for Further Research

8.1 PREFACE

This project has sought to understand and predict the curing process of CAM without cement and with varying cement additions, and to compare these mixes with soil/granular materials without binder. Tests were performed on samples to study the dynamics of water evaporation, hydraulics, and microstructure, and the results were correlated to the mechanical performance through a statistical model. Based on that, models were developed in order to predict the evaporation and mechanical properties of CAM.

8.2 CONCLUSION

According to experimental work of the current research, the key conclusions were as follows.

Dynamics of water evaporation in cold asphalt mixtures

1. The evaporation of moisture in CAM follows three stages: (i) first, (ii) transition, and (iii) second. In the first stage, the material is fully saturated; in

the transition stage, the capillaries connecting the saturated region and the material surface progressively collapse; and in the second stage a superficial dry layer is formed and the remaining water is evaporated from inside the material.

2. The partially-saturated area that constitutes the film region travels from top to bottom, at a decreasing speed, which implies that the drying process slows down with time.
3. The thickness of the partially-saturated layer can be measured both through sensors embedded in the material and through evaporation dynamics theory, which depends only on the hydraulic conductivity and pore size distribution of the material. This allows prediction of the thickness of the partially-saturated layer in a much faster way than through sensors embedded in the material.
4. The drying started from the upper side of the sample, moving downwards, and the drying rate decreased as the level of water was closer to the bottom. Hence, small increases in pavement thickness can lead to big increases in drying time.
5. Aggregates compacted without emulsion present constant pore size distribution when the gradation is composed of multiple sizes. On the other hand, when the gradation is single-sized, the pore size distribution index (n) is higher and grows with the size the aggregates.
6. There is a relationship between the pore size distribution index (n) and water dynamics during drying. The test results showed that n and the time for drying the specimens are directly correlated. The drying process took longer in granular materials with higher pore size distribution index. In general, in order to shorten the drying time of a layer of aggregate or cold asphalt mixture, the

pore size distribution and the layer thickness has to be reduced. In both cases, the mechanical performance can be affected.

7. The permeability test is a reliable method to investigate the pore size distribution (n) of CAM/ granular materials, making it possible to optimise the material to be faster drying in less time and with less effort.
8. In cold asphalt mixes, the pore size distribution index is not constant and decreases over the curing time, taking longer to fully dry. Consequently, hydraulic conductivity decreases with time. This reflects the fact that the emulsion is a component that delays the water evaporation, progressively reducing hydraulic conductivity over time.
9. Depending on the strength of every component in CAM, a model to predict the mechanical performance of cold asphalt mixes over the drying time was developed, which predicted the mechanical performance of cold asphalt mixes with good accuracy of fit.

New predictive methodology for the apparent activation energy and strength of conventional and rapid hardening concretes

- The hydration products of CAC depend on the curing temperature.
- Models of prediction of the apparent activation energy developed in previous research accurately fit the results of apparent activation energy for OPC, but were not suitable for the rapid hardening cements studied in this research (CSA and CAC).
- This project proposed a new methodology to predict activation energy for different types of cement (OPC, CAC and CSA), and found that the model accurately fitted the experimental data.

Prediction of water evaporation and stability of cold asphalt mixtures containing different types of cement

- The curing rates of CAM made with bitumen emulsion cannot be significantly improved by the addition of the types and quantities of cement studied. This is because the amount of water present in CAM is several times higher than that needed for cement hydration.
- When using bituminous emulsion, the reaction level of water with cement at the end of the curing/drying process is the same as without emulsion. However, the bitumen slightly delays these reactions.
- Cement hydration products fill and/or close pores during curing, as does the bituminous binder. Consequently, n of CAM without cement is higher than CAM containing cement. As the hydraulic conductivity reduces, the time for full drying is actually shorter.
- Rapid hardening cements (CAC and CSA) produce a greater volume of hydration products than OPC. Therefore, CAM containing rapid hardening cements presents lower n than CAM containing OPC.
- Even though cement hydration consumes water, a large amount of water still remained in CAM with cement after 28 days, which contributed to the later development of the internal structure. At the same time, when using a high quantity of OPC, it is possible that some cement remains non-hydrated as a solid powder, especially in the upper parts of specimens. Consequently, this cement does not contribute to the mechanical performance of CAM.
- CAM with CSA obtained higher stability than CAM with OPC and CAC, as CSA consumes more water during hydration. Despite this, mixes with

CAC have lower final stability than mixes with OPC due to the conversion of hydration products that increases mix porosity.

- A new model was proposed to predict the contribution of cement hydration products to the total stability of CAM. The prediction of the model was found to be very accurate.
- It was seen that the temperature of the material does not affect the capillary action relative to this process.

A general model to predict the time required to open road surfaces built of cold asphalt mix

- The evaporation rate during the first stage can be modelled based on free water evaporation phenomena, while during the second stage, it can be modelled based on diffusion phenomena, which mainly depend on the porosity of the material. The time required for a CAM pavement to reach suitable stability to bear traffic loads can be predicted based on the accurate modeling of water evaporation rate developed and validated in this study.
- The topological parameters of air voids (i.e. circularity, roundness, aspect ratio, surface area, number of voids, and pore size distribution index) in granular materials are inter-correlated among themselves, and with the hydraulic properties and aggregate gradation.
- When porosity, circularity, roundness, surface area, pore size distribution index, and mean size of aggregate increase, (1) tortuosity, aspect ratio, number of voids, standard deviation of aggregate size, uniformity

coefficient of aggregate and coefficient of gradation decrease; and (2) the time of full drying increases, because the capillary action decreases.

- All of the aggregate properties studied in the present research are correlated to the maximum size of the aggregate when the gradation is single-sized, but no correlation was found when the samples were continuously-graded.
- Porosity plays a key role in the evaporation process. When it increases, the evaporation rate also increases, thus the time to dry a given amount of water decreases.

8.3 RECOMMENDATIONS FOR FURTHER RESEARCH

This study achieved more in-depth understanding of the dynamics of water evaporation in CAM, particularly by investigating mechanical performance relative to the impacts of water evaporation dynamics and different CAM compositions and ingredients. Specifically, this study has identified specifications of aggregate gradation to accelerate water evaporation in CAM and improve its mechanical performance.

There are many different areas and points that could be researched further in order to support and validate the findings of the present study. Therefore, based on the work presented in this study, the following suggestions are made.

1. This research only investigated the effects of different types of cement on dynamics of water evaporation. Although pozzolanic and cementitious materials manifest similar final characteristics of cement, their particular impacts on the dynamics of water evaporation should be investigated in order

to gather data on the hydraulic effects of materials on the dynamics of water evaporation. This could help in making decisions about the use of materials in cold asphalt mixtures.

2. This study considered the hydraulic properties and mechanisms of internal transport during evaporation and their impacts on the rate of evaporation under constant weather conditions. However, in real-life applications, weather conditions vary greatly (e.g. in terms of temperature, relative humidity, wind and rain, and solar radiation), having fundamental impacts on water evaporation and the structural and mechanical performance of CAM pavements. It is necessary to investigate the affects of different weather conditions on the rate of evaporation in porous materials in order to have a fuller understanding of the dynamics of water evaporation and how this is linked to other properties (e.g. the relations between hydraulic properties, the mechanisms of internal transport, and weather conditions). In addition, different weather conditions should be explored to determine whether various CAM mixes will dry faster or slower.
3. Most previous researchers used and suggested using more cement in order to accelerate the dynamics of water evaporation in CAM, but the current results stated that cement does not have significant effects on this dynamic. Therefore, the impacts of other techniques and materials should be investigated, including RAP, healing, SBR, and steel aggregate.
4. Mechanical performance was only investigated using the Marshall stability test, which is linked with the subsequent dynamics of water evaporation of CAM. However, resistance to permanent deformation, fatigue, durability, moisture susceptibility, resistance to ravelling, ageing damage, and skid

resistance etc. effect cold asphalt performance too, and future study is needed to explore these impacts.

5. This work concluded that bitumen emulsion is the main factor delaying the drying of CAM, but only one type of cationic bitumen emulsion was investigated. Therefore, future study is needed to characterize the affects of different types of bitumen emulsion (i.e. different quantities of bitumen) on the curing of CAM.
6. The thickness of a cold asphalt layer affects the speed of CAM drying. Therefore, more investigation is need concerning the relationship between thickness and drying.
7. The correlation between the dynamics of water evaporation in CAM on site and in laboratory conditions has not been adequately researched, which is a major shortcoming in existing research. It is necessary to study this in order to link the performance of CAM in real applications to theoretical laboratory investigations, in order to improve understanding of CAM performance and the accuracy of current academic models.
8. Depending on hydraulic properties and other factors, CAM microstructure changes with time. Potential changes due to this were investigated in this study, but more accurate results would be obtained in relation to evaporation and the microstructure of CAM using nanoscale and macroscale tests such as SEM and MIP test.
9. Aggregate is the greatest component in the bitumen mixture, comprising 95% of its mass, therefore this work investigated the effect of the gradation of aggregate on the dynamics of water evaporation in CAM. However, other

characteristics of aggregate like type and smoothness of surface should be investigated to determine their impacts on the dynamics of water evaporation.

10. The roles of compaction method and compaction energy on the performance of CAM are important during curing, and should be studied in terms of the CAM microstructure and the dynamics of water evaporation.
11. Previous studies (Fang, 2016) stated that with the same quantity and specifications of bitumen, there is approximately the same bonding strength in normal bitumen and bitumen of emulsion. However, more investigation is needed to investigate the bonding of bitumen of the emulsion, and the relationship between the dynamics of water evaporation and the bonding of bitumen emulsion.

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Appendix

A1: Previous studies to develop the CAM by the cementitious and/or pozzolanic materials

Filler		Plasticizing agent	The effect of filler on the properties	References
Type	Quantity (%)			
OPC	0, 1, 2, 3	Water	• Flow (Reduce) • Curing rate (Increase) • Resilient modulus (Increase)	Terrell and Wang, 1971
OPC	0, 1.3, 3	Water	• Resilient modulus (Increase) • Resistance to water damage (Increase)	Schmidt, Santucci and Coyne, 1973
OPC	0, 1, 2, 3	Water	• Stability (Increase) • Resistance to water damage (Increase)	Head, 1974
OPC	1, 2	Water	• Flow (Reduce) • Dry stability (Increase) • Soaked stability (Increase) • Stability loss (Reduce)	Arora and Arabiat, 1986
OPC	0, 2	Water	• Mechanical strength (Increase)	Giuliani and Rastelli, 1996
OPC	0, 1, 2, 3, 4	Water	• Stiffness modulus (Increase) • Resistance to permanent deformation (Increase) • Durability (Increase)	James, Needham and Brown, 1996
OPC	0, 1, 2, 3, 4	Water	• Curing rate (Increase) • Ultimate stiffness modulus (Increase) • Resistance to permanent deformation (Increase) • Resistance to fatigue cracking (Increase) • Resistance to water damage (Increase) • Viscosity (Increase) • The rate of coalescence of the bitumen emulsion (Increase)	Needham, 1996

Table A1 Continue

Appendices

OPC	0, 1, 2, 3, 4	Water	• Resistance to permanent deformation (Increase) • Fatigue strength (Increase) • Resistance to water damage (Increase) • The viscosity of binder (Increase) • Stiffness modulus (Increase)	Brown, and Needham, 2000
HL	1 (of emulsion)			
CaCl ₂	1			
OPC	0, 1, 2	Water	• Early life strength (Increase)	Thanaya, 2003
RSC				
Natural Cement				
OPC	2	Water	• Enhance stiffness and strength development	Ellis et al., 2004
GGBS	2, 4			
OPC	1.5			
OPC + FA	1.23 (OPC) + 0.27 (FA) 1.25 (OPC) + 0.25 (FA)	Water	• Dry indirect tensile strength (Increase) • Soaked indirect tensile strength (Increase)	Hodgkinson and Visser, 2004
Limestone	11.35 (OPC) + 0.15 (Limestone)			
GGBS	1.5			
Rock flour	1.5	Water	• Resilient modulus (Increase) • Resistance to water damage (Increase) • Resistance to permanent deformation (Increase) • Resistance to creep (Increase)	Orue, Celik and Akosy, 2006
OPC	0, 1, 2, 3, 4, 5, 6			
OPC	2			
FA	5	Water	• Indirect tensile strength (Increase) • Resilient modulus (Increase) • Resistance to permanent deformation (Increase)	Kishore Kumar et al., 2008
Lime	2			
OPC + FA	2 (OPC) + 5 (FA)			
Lime + FA	2 (Lime) + 5 (FA)	Water	• Indirect tensile strength (Increase) • Resilient modulus (Increase) • Resistance to permanent deformation (Increase) • Resistance to water damage (Increase)	Halles and Thenoux, 2009
Portland Cement (II)	0, 1, 2, 3			
Cement Kiln Dust	0, 1, 2, 3			
HL	0, 1, 2, 3			
FA	0, 1, 2, 3			

Table A1 Continue

Appendices

OPC	0, 0.5, 1, 1.5, 2	Water	• Flow (Reduce) • Marshall stability (Increase) • Resilient modulus (Increase) • Tensile strength (Increase) • Resistance to moisture damage (Increase) • Resistance to permanent deformation (Increase)	Niazi and Jalili, 2009
HL	0, 0.5, 1, 1.5, 2			
Lime slurry	0, 0.5, 1, 1.5, 2			
RSC	0, 1, 2	Water	• Stiffness (Increase) • Fatigue strength (Increase) • Resistance to creep (Increase)	Thamaya, Forth and Zoorob, 2009
FA	4			
OPC	0, 1.375, 2.75, 4.125, 5.5	Water	• Stiffness modulus (Increase) • Creep modulus (Increase) • Resistance to water damage (Increase)	Al Nageim et al., 2012
FA	0, 1.375, 2.75, 4.125, 5.5			
OPC	1.5, 3, 4.5, 6	Water	• Stiffness modulus (Increase) • Resistance to permanent deformation (Increase) • Creep modulus (Increase)	Al-Hdabi et al., 2013a
OPC	6	Water	• Stiffness modulus (Increase) • Creep modulus (Increase) • Resistance to permanent deformation (Increase) • Resistance to water damage (Increase)	Al-Hdabi et al., 2013b
WFA1	6			
WFA1	6			
OPC	2	Water	• The mechanical properties (Increase)	Khan et al., 2013
OPC	0, 3, 6	Water	• Significantly contributes to the hardening	Fang et al., 2014
OPC	2, 3, 4	Water	• Viscosity (Increase) • Indirect tensile strength (Increase) • Dynamic stability (Increase) • Indirect tensile strength at low temperature (Increase) • Dry shrinkage (Increase)	Wang, Wang and Ali, 2014
OPC	0, 3, 6	Water	• The early strength (Increase) • Stiffness (Increase) • Stability (Increase)	Fang et al., 2015
CSA	0, 3, 6			
CAC	0, 3, 6			
OPC	5	Water	• Ultimate stiffness modulus (Increase)	Nassar et al., 2016
OPC + FA	OPC (1) + FA (4)		• Resistance to permanent deformation (Reduce)	
OPC + GGBS	OPC (1) + GGBS (4)		• Resistance to water damage (Increase)	
OPC + FA + SF	OPC (1) + FA (4) + SF (1)			

Table A1 Continue

Appendices

OPC +	OPC (1) +
GGBS +	GGBS (4) +
SF	SF (1)
OPC + FA	OPC (1) + FA
+ SF	(4) + SF (2)
OPC +	OPC (1) +
GGBS +	GGBS (4) +
SF	SF (2)

A2: Previous studies to develop the cold bitumen mixture by compaction

Types of compaction machine	The method of compaction	References
Gyratory	200 revolutions	Jnr, 2002
Marshall hammer	100 Blows (50 blows/end)	Thanaya, 2007
	150 Blows (75 blows/end)	
Gyratory	80 revolutions	Dash, 2013
	120 revolutions	
Marshall hammer	100 Blows (50 blows/end)	Dash, 2013
	150 Blows (75 blows/end)	
Gyratory	40 revolutions	
	80 revolutions	
	100 revolutions	
	120 revolutions	

A3: Previous studies to develop CAM by curing

No.	The Method of curing	References
1	- Firstly, the specimen was unsealed for 20 h @ 30°C - Secondly, the specimen was placed in a plastic bag and sealed for 24 h @ 40°C - Thirdly, after the 24 h the specimens were removed from the plastic bag, weighed and placed in another dry plastic bag and re-sealed. The sealed specimens were put in the oven for another 24 h @ 40°C - Fourthly, after the last 24 h the specimens were removed from the plastic bag and weighed. - Fifthly, the specimens were immediately placed in a dry placed bag, sealed after the specimen cooled down to room temperature (approximately one hour). - Sixthly, after curing the specimens were kept sealed in plastic bags at room temperature.	Jan Ebels, 2008
2	- Firstly, the slab, while still in the mould, was placed in an oven for 72 h @ 40°C - After 24 hours the side frames of the mould were removed and the slab remained on the base plate - After the 72 h curing period the slab was left to cool at ambient temperature and sealed prior to the beam cutting process.	Müller, 2012
3	6 h @ 60°C 24 h @ 60°C 6 h @ 25°C 24 h @ 25°C	
4	72 h in mould @ 40 °C 21 days @ room temperature	Dash, 2013
5	72 h in mould @ 60 °C + 24 h @ambient temperature 6 h @ 60 °C 24 h @ 60 °C 72 h @ 60 °C	Ling, 2013
6	14 days @ 35°C + 20% humidity	Serfass et al., 2004

A4: The more countries production of bitumen emulsion in the world (Le Coroller, 1999)

No.	Country	The consumption of bitumen every year (Ton) * (10³)	The quantity of bitumen used in the emulsion (%)
1	Italy	100	3
2	Germany	130	3
3	UK	160	5
4	Thailand	300	24
5	Japan	316	5
6	Spain	350	18
7	Brazil	400	5
8	Mexico	515	34
9	France	1.010	25
10	USA	2.300	5

No.	Country	The quantity of emulsion every year (Ton) * (10³)
1	Denmark	20
2	Belgium	20
3	Austria	23
4	Netherlands	30
5	Sweden	70
6	Turkey	85
7	Portugal	86

A5: The different uses into the bitumen emulsion (James, 2006)

Type of construction	Anionic			Cationic		
	RS	MS	SS	RS	MS	SS
Plant mixes						
Open-graded		X ^a			X ^a	
Dense-graded			X			X
Reclaimed asphalt pavement (RAP)		X				X
Stockpile mix		X ^a			X ^a	
Pre-coated chips					X	X
Mix paving						
Open-graded					X ^a	
Slurry			X			X ^b
Slurry for cape seal			X			X ^b
Microsurfacing						X ^b
In-place mixes						
RAP		X ^a			X ^a	X
Dense-graded			X			X
Soil stabilization			X			X
Spray applications						
Chipseal	X			X		
Fog seal–cement curing		X		X	X	
Tack coat		X ^a	X		X ^a	X
Prime			X ^a			X ^a
Dust palliative			X			X
Mulch			X			
Penetration macadam				X		
Other						
Waterproofing coatings			X ^c			
Driveway and footpath sealers			X ^c			X ^c

^a May contain solvent, ^b Need not pass cement mix test, ^c May contain clay

A6: The famous tests of the bitumen emulsion and bitumen residue (AEMA, 2004)

No.	Test	Standard specifications
Bitumen emulsion tests		
1	Particle charge test	ASTM D 244
2	Identification test for cationic rapid-setting emulsion	ASTM D 244
3	Identification of cationic slow-set emulsions	ASTM D 244
4	Viscosity	ASTM D 244
5	Demulsibility	ASTM D 244, D 6936
6	Settlement and storage stability tests	ASTM D 244, D 6930
7	Cement mixing	ASTM D 244, D 6935
8	Oversized particles or sieve test	ASTM D 244, D 6933
9	Coating ability and water resistance	ASTM D 244
10	Field coating test	NS*
11	Unit weight of bitumen emulsion	ASTM D 244, D 6937
12	Residue and oil distillate by distillation	ASTM D 244, D 6997
13	Residue by evaporation	ASTM D 244, D 6934
14	Breaking index	NS
15	Vialit test	NS
16	Zeta potential	NS
Bitumen residue tests		
17	Specific gravity	ASTM D 70 AASHTO T 228
18	Solubility in Trichloroethylene	ASTM D 2042 AASHTO T 44
19	Penetration	ASTM D 5 AASHTO T 49
20	Ductility	ASTM D 113 AASHTO T 51

Table A6 Continue

Appendices

21	Float	ASTM D 139 AASHTO T 50
22	Elastic recovery after ductility	ASTM D 6084 AASHTO T 301
23	Force ductility	AASHTO T 300
24	Ring and ball softening point	ASTM D 36 AASHTO T 53
25	Tensile strength (stress)	NS
26	Torsional recovery	California test 332
27	Toughness and tenacity	NS
28	Absolute viscosity	ASTM D 4957 AASHTO T 202

* Not standard

A7: The chemical composition of Portland cement (Neville and Brooks, 2010)

Oxide		Typical Composition (%)	
	CaO		63
	SiO ₂		20
	Al ₂ O ₃		6
	Fe ₂ O ₃		3
	MgO		1.5
	SO ₃		2
	K ₂ O		1
	Na ₂ O		
	Other		1
	Loss on ignition		2
	Insoluble residue		0.5

Main Compounds in Portland cement			
Groups	Name of compound	Oxide composition	Abbreviation
Silicates	Tricalcium silicate	3CaO.SiO ₂	C ₃ S
	Dicalcium silicate	2CaO.SiO ₂	C ₂ S
Aluminates	Tricalcium aluminate	3CaO.Al ₂ O ₃	C ₃ A
	Tetracalcium aluminoferrite	4Cao.Al ₂ O ₃ .Fe ₂ .O ₃	C ₄ AF