Universidade do Minho
Escola de Engenharia

Inês Carlos Alves

Biodiesel by-product as an admixture for cement-based materials: an experimental study

July 2013

Universidade do Minho
Escola de Engenharia

Inês Carlos Alves

Biodiesel by-product as an admixture for cement-based materials: an experimental study

Msc Dissertation
Integrated Master in Civil Engineering

Supervised by:
Professor Miguel Azenha
Professor Cândida Lucas

July 2013

To my family.

AKNOWLEDGEMENTS

At the end of the process that led to this work, I would like to express my recognition to all of those who, in a more direct way, have been involved.

First of all, my acknowledge to Professor Miguel Azenha and to Professor Cândida Lucas, on the professionalism, scientific rigor, availability and encouragement that they have demonstrated in the orientation of this work, which have allowed my intellectual growth.

To Professors Aires Camões and José Barroso Aguiar, for having provided all the material and equipment of the Building Materials Laboratory.

To José Granja, for the indispensible help in the treatment of the data related to the EMM-ARM test and to Christoph, by the teachings.

To the lab technicians, for the availability and help that have proved, especially to Engineer Carlos Jesus, without whom the development of the experimental study would have never been possible.

To Engineer Miguel from the Mechanical Department, for the help with handling and setup of the thermostat.

To Pakril, for the availability, to Prio, that provided the crude purified glycerol and to Sika, which has supplied the antifreeze admixture.

To DST, in the person of my dear friend Pedro Teixeira, for the cement.

To my fellows Paula Neto, Vanessa Sequeira and Margarida Vieira.

To all of my friends, remarkably, to Filipa Machado, Isa Ferreira and Catarina Alves for, each one his or her own way, giving me support and for having encouraged me. To Maria João

Freitas, for handing on all the knowledge related to the use of the Photoshop software and, of course, for the friendship.

To Miguel Souto, for the complicity and longstanding friendship and for this five-year *trip*.

At last, but not least

To my parents and sisters, to whom I owe part of what I am, I appreciate the permanent encouragement of my professional and human valorization.

To Mário and Pedro, for making part of my path.

To the Priest Manuel Losa, for being ALWAYS present.

ABSTRACT

The incorporation of admixtures or additions into concrete mixtures is extremely generalized owing to their ability to confer numerous advantageous effects on concrete. However, because admixtures are frequently expensive and may carry relevant ecological footprints, there is an increasingly higher necessity and interest in finding cheaper and more sustainable admixtures in otherwise useless by-products generated by industrial processes.

Biodiesel production in one of such industries, which by-product is the crude glycerol that is produced in a 1:10 mass ratio in relation to biodiesel production, and it generally has 80%-88% of purity, thus containing various impurities, such as ash, soap, chloride and residual methanol. In order to make crude glycerol a useful product for general industry processing, it is necessary to upgrade it to glycerol of high purity. Nonetheless, at intermediate levels of purity, crude glycerol might be usable for concrete industry. In fact, because of its physical-chemical properties and compounds, it is plausible to suspect that there might be a potential synergy between the crude purified glycerol with cement-based materials by applying this treated by-product to the mixture as an admixture. As such evaluation is not yet reported in the literature, the corresponding research opportunity is identified and followed in this work.

Thus, the main objective of this dissertation is to understand the effects of the addition of crude purified glycerol obtained from biodiesel production into cementitious materials. For this purpose, an experimental program has been carried out on several mixtures of cement pastes and mortars regarding the incorporation of crude purified glycerol, but also reference materials such as synthetic glycerol and a commercial antifreeze admixture. The analysis of the obtained results allowed the evaluation of the incorporation of crude purified glycerol over the fresh and hardened properties of cement-based materials. As main conclusions, it is possible to highlight that the inclusion of crude purified glycerol caused a reduction of the initial and final setting times of the cement paste samples and a significant increase in the pace of stiffness/strength evolution in the cement paste samples since early ages. Therefore, there is a strong potential to further study crude purified glycerol as an accelerating admixture.

Keywords: Cement based materials; admixture; biodiesel by-product; glycerol; experimental testing

RESUMO

A incorporação de aditivos ou adições no betão está muito generalizada devido às suas capacidades de conferir diversos efeitos vantajosos no betão. Contudo, as misturas são, por vezes, caras e podem implicar impactos ambientais negativos, pelo que aumenta a necessidade e o interesse em encontrar soluções mais baratas e mais sustentáveis, suportadas no aproveitamento de subprodutos de outras indústrias.

A produção de biodiesel é uma dessas indústrias, cujo subproduto é o glicerol bruto, produzido num rácio de 1:10, em relação à produção de biodiesel e tem, normalmente, um grau de pureza de entre 80%-88%, sendo, portanto, constituído por diversas impurezas, tais como ash, soap and chloride and residual methanol. Para possibilitar a sua utilidade na generalidade das indústrias, é necessário purificá-lo previamente de modo a torna-lo num glicerol com elevado grau de pureza. No entanto, o glicerol bruto purificado a níveis intermédios pode ser útil para a indústria do cimento. De facto, devido à sua composição e às suas propriedades físicas e químicas, é expectável que possa existir uma potencial sinergia entre o glicerol bruto purificado e os materiais cimentícios, quando incorporado na mistura como um aditivo. Face ao exposto, esta investigação constitui uma avaliação desta problemática, que ainda não está reportada na literatura.

Assim, o objetivo principal deste estudo é o de compreender os efeitos da incorporação do glicerol derivado da produção do biodiesel em materiais cimentícios. Para tal, desenvolveu-se um programa experimental a partir da realização de diferentes misturas de pastas de cimento e de argamassas que compreenderam a incorporação não só do glicerol bruto purificado, mas também do glicerol sintético e de uma mistura comercial com propriedades anticongelantes.

A análise dos resultados possibilitou a avaliação dos efeitos da incorporação do glicerol bruto nas propriedades frescas e endurecidas dos materiais cimentícios. Como principais conclusões, é possível afirmar que a incorporação do glicerol provocou uma redução do início e fim de presa e que causou um aumento no grau de aquisição de rigidez/resistência dos referidos materiais. Consequentemente, há um forte potencial para estudar mais aprofundadamente o efeito do glicerol bruto purificado como um aditivo acelerador de presa e endurecimento.

Palavras-chave: Materiais cimentícios; aditivos; sub-produto do biodiesel; glicerol; testes experimentais

LIST OF SYMBOLS AND ABBREVIATIONS

In the name of the intelligibility, the description of each notation or symbol used in the present dissertation is made upon its first appearance in the text.

Roman Letters

a Antifreeze admixture
A Cross section
b Flank of the square section of the prism
d Dimension of the transversal section
d_k Arithmetical mean of the mean carbonation depth of two specimens
$d_{k,\ face}$ Mean depth of carbonation for each exposed face of a specimen
$d_{k,\ spec}$ Mean depth of carbonation for each specimen
d_p Depth of penetration
F Maximum load
F_c Maximum load by the time of the rupture
f_{ct} Tensile splitting strength
F_f Load applied at the center span
g Crude purified glycerol or acceleration of gravity
G Nominal gage length
h Height of water
k_G Permeability
K_w Permeability Coefficient
k_w Permeability coefficient to the water
l Distance between supports
l/c liquid to cement ratio
L is the length of the contact line of specimen; is the change in length at x age, %;
L_3 Thickness of the specimen (m);
L_i Initial comparator reading of specimen minus comparator reading of reference bar at the same time, in mm;

L_x Comparator reading of specimen at x age, minus comparator reading of reference bar at x age, in mm;

m_1 Mass of the specimen saturated in the air;

m_2 Hydrostatic mass of the saturated specimen;

m_3 Mass of the dry specimen;

R_c Compressive strength

R_f Flexural Strength

s Sand

sg Synthetic glycerol

t Length of time it took to penetrate until the d_p depth

w Mass of free water (not chemically bound)

w/c Water to cement ratio

Greek Letters

δ Specimen porosity;

η Dynamic viscosity

η_w Water viscosity at 20ºC

ν Flow of the fluid

ρ Density of water

ρ_1 Inlet gas pressure

ρ_2 Outlet gas pressure

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

1.1 Scope and motivation

The incorporation of admixtures or additions into concrete mixtures is as generalized as the use of hydraulic binders owing to their ability to confer numerous advantageous effects on concrete (Hewlett, 2004a), such as: increased workability, controlled setting, accelerated hardening, reduction of water necessity, improved strength/ductility, damp proofing, permeability reduction, corrosion inhibition, shrinkage reduction, freeze-thaw resistance, reduced carbonation, etc (Ramachandran, 1996). However, because admixtures are often expensive (Lachemi *et al.*, 2004) and may carry relevant ecological footprints, there is an increasing necessity and interest in finding cheaper and more sustainable admixtures in otherwise useless by-products generated by industrial processes. One such type of by-product is ground granulated blast furnace slag (GGBS), which is produced from the blast-furnaces of iron and steel industries, and is very useful in the production of high quality cement paste/mortar and concrete (Siddique and Bennacer, 2012). Several other by-products could be named such as: fly ash, condensed silica fume and rice husk ash (Nagataki, 1994a, Mehta, 1989).

Biodiesel is a clean, non-toxic, biodegradable and renewable burning fuel (Santacesaria *et al.*, 2012). Its worldwide production is rapidly increasing and so is the resulting by-product: crude glycerol, which generally has 80%-88% purity (Ayoub and Abdullah, 2012), and constitutes approximately 10% of the weight of the total biodiesel production. Pure glycerol is a colourless, viscous, and odourless metabolic intermediate and structural component of the major classes of biological lipids, triglycerides and phosphatidyl phospholipids (Rahmat *et al.*, 2010), usually derived from both natural and petrochemical feedstocks (Ayoub and Abdullah, 2012). It is completely soluble in water, in alcohols and hardly at all in many common solvents, with the exception of hydrocarbons (Pagliaro, 2008b). It is a hygroscopic liquid with a high boiling point which is also virtually nontoxic to human health and to the environment (Pagliaro, 2008b). Crude glycerol resulting from biodiesel industry contains various impurities, such as ash, soap and chloride and residual methanol (Ayoub and Abdullah, 2012). Even though pure glycerol has many industrial applications (in areas such as food, livestock feed, biotechnology, pharmaceutical, cosmetics or drug industries (Ayoub and Abdullah, 2012)), the presence of impurities in crude glycerol resulting from biodiesel production render it a low economic value. In fact, in order to purify crude glycerol associated to biodiesel production (80%-88% purity) (Ayoub and Abdullah, 2012) and make it a useful product for general industry processing, it is necessary to upgrade it to highly pure glycerol (up to 98% of purity) (Rahmat *et al.*, 2010). Currently, many processes have been developed to refine/purify crude glycerol and most of them are based on the simple distillation of glycerol, because that can produce a high yield of high-purity glycerol. Other possible processes for crude glycerol purification are based upon chemical and physical treatments and in innovative ion-exchange techniques (Manosak *et al.*, 2011). After being refined, this glycerol finds applications in a broad diversity of end users as mentioned before.

In terms of terminology, it is hereby defined that, in this work, crude glycerol pertains to the glycerol originated from biodiesel production before purification, whereas crude purified glycerol corresponds to the same glycerol with subsequent purification (with a content of glycerol of 90,4%) and synthetic glycerol to the glycerol reagent grade, in its pure form (with a glycerol content of at least 99,5%), produced hydrolytically from fats and oils during soap and fatty acid manufacture (Pagliaro, 2008a).

Studies concerning the incorporation of crude glycerol with 5% of NaCl in clinker during milling have already been performed successfully, with observed improvements of the energy efficiency in handling and grinding processes, thus enhancing cement strength, while the environmental impact was eased (Rossi *et al.*, 2008). Nonetheless, except for this application of crude glycerol in cement production, no other applications were found for this by-product in the industry of cement and concrete.

Because of its physical-chemical properties and compounds, it is plausible to suspect that there might be a potential synergy between the crude purified glycerol with cement-based materials by applying this by-product to the mixture as an admixture. As such evaluation is not yet reported in the literature, the corresponding research opportunity is identified and followed in this work.

1.2 Research objectives and methods

The main objective of this dissertation was to understand the effects of the addition of crude purified glycerol obtained from biodiesel production into cementitious materials. It was further intended to understand if there is an optimum quantity of crude purified glycerol in regard to the benefits that can be harvested from its inclusion in cement-based mixtures. A comparison of performance of crude purified glycerol and synthetic glycerol was also carried out in order to ascertain the influence of impurities. It is finally remarked that the use of crude glycerol was not considered in this research due to its high level of uncontrolled impurities (namely of organic nature) and the results on preliminary tests conducted at the University of Minho that revealed unsatisfactory behaviour (unpublished results).

So that the objectives could be fulfilled, a comprehensive experimental program took place, focusing mainly at the cement paste level. Cement paste specimens containing different percentages of glycerol in two different forms (crude purified and synthetic glycerol) were produced and submitted to tests in their fresh and hardened states, covering the following properties: flowability, set time, compressive, flexural and indirect tensile strengths, shrinkage, elasticity modulus, oxygen and water permeability, water absorption through immersion, carbonation and freezing points. For reference, cement pastes containing a commercial antifreeze admixture were also studied in regard to flexural and compressive strength. In regard to permeability studies, and due to the size of the necessary test specimens, the experiments were carried out in mortars constituted by cement, water, normalized sand and crude purified glycerol.

1.2 Dissertation outline

This dissertation is structured in a total of 6 Chapters, including the present introduction.

The second and third chapters are focused on a literature review. The history and concepts of concrete, cement and admixtures are discussed in the second chapter, followed sequentially, in the third chapter, by a detailed explanation about biodiesel production, as well as the catalysts and feedstock used for its development. The challenges of biodiesel manufacture, concerning the production of crude glycerol are also addressed. Moreover, a review of the aplications of crude glycerol in the manufacture of cement and of synthetic glycerol as an admixture for cement based materials is carried out.

The experimental program is explained in chapter four, through a convenient description of the materials and equipment used, as such as a detailed explanation about each test performed.

The corresponding results are analysed and thoroughly discussed in chapter 5, with inferences being made in regard to the actual behaviour of crude purified glycerol as an admixture for cement-based materials.

At last, a summary of the work developed is presented in chapter six, where the most important conclusions are highlighted. Additionally, in the referred chapter, further developments are suggested to complement the study started in the present dissertation.

2 CONSTRUCTION MATERIALS

2.1 Introduction

Construction materials represent a significant market share in current human commercial activities. Among the construction materials, hydraulic cements, which are produced by calcining a mixture of calcareous and argillaceous materials, are employed in a huge amount and their global consumption is expanding rapidly (Pagliaro, 2008a). It is also stated that, out of the hydraulic binders, the artificial Portland ones are by far the most significant in terms of production volume (Pagliaro, 2008a). In fact, Portland cement has remained a very successful building material since its advent in the nineteenth century (Shi *et al.*, 2011). This type of cement is made by heating a mixture of calcareous materials, such as limestone, and clay or other materials of similar mass composition and plenty reactivity (Taylor, 1990b) ultimately to a temperature of about 1450ºC, which is termed the sintering temperature of cement (Azenha, 2009). At this stage, partial fusion occurs, and ball shaped particles called clinker are produced. Through the addition of a portion of gypsum, which is able to control the rate of set, this clinker is then finely ground to produce cement (Taylor, 1990b). In the anhydrous state, there are four chief minerals present in a Portland cement grain, namely the tricalcium silicate (Ca_3SiO_5), the dicalcium silicate (Ca_2SiO_4), the tricalcium aluminate ($Ca_3Al_2O_6$) and the calcium aluminoferrite (Ca_2AlFeO_5) (Taylor, 1990a). The formula of each of these minerals can be broken down into the basic calcium, silicon, aluminum and iron oxides (Barron, 2010). Hence, traditional cement nomenclature abbreviates each oxide as shown in Table 2.1 (Barron, 2010).

Table 2.1 - Chemical formulae and cement nomenclature for major constituents of Portland cement. Abbreviation notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3 (Barron, 2010)

Mineral	**Chemical formula**	**Oxide composition**	**Abbreviation**
Tricalcium silicate (alite)	Ca_3SiO_5	$3CaO.SiO_2$	C_3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$Ca_3Al_2O_6$	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	Ca_2AlFeO_5	4CaO.Al2O3 Fe2O3	C_4AF

A typical cement contains 50–70% C_3S, 15–30% C_2S, 5–10% C_3A, 5–15% C_4AF, and 3–8% other additives or minerals (such as oxides of calcium and magnesium) (Taylor, 1990b). Figure 2.1 shows a typical cement grain.

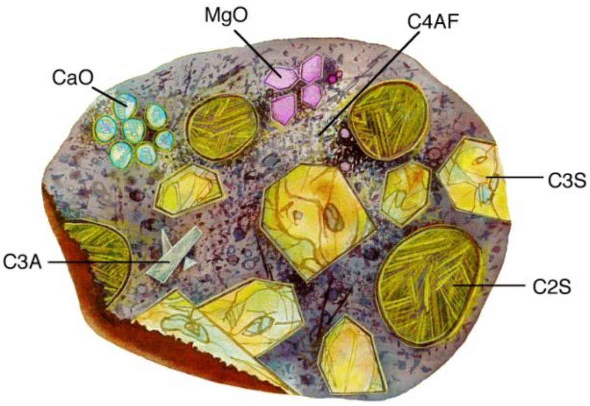


Figure 2.1 - Pictorial representation of a cross-section of a cement grain (Barron, 2010)

The addition of water to dry cement powder, while creating an exothermic reaction, results in a thin cement slurry that sets and develops strength through a series of hydration reactions, which are not linear through time. Instead, cement hydration progresses very slowly at the beginning, allowing the mixture to be appropriately retained before hardening. It is the hydration of the calcium silicate, aluminate and alumina-ferrite minerals the responsible for the hardening of cement (Barron, 2010). The ratio of C_3S to C_2S helps to determine how fast the cement will set, with faster setting occurring with higher C_3S contents. In fact, it is of common knowledge that C_3S is the most important phase in cement for strength development during the first month, while C_2S reacts much more slowly, and contributes to the long-term strength of the cement (Taylor, 1990b). Both the silicate phases react with water to form calcium hydroxide and a rigid calcium-silicate hydrogel, CSH.

The hydration of cement, which may be defined as the combination of all chemical and physical processes that occur after contact of the anhydrous solid with water (Stark, 2011), can be broken down into three distinct stages, known as the early period of hydration, the middle period of hydration and the late period of hydration (Taylor, 1990b), which are schematically represented in Figure 2.2 and whose evolution of hydration products is depicted in Figure 2.3. The process may also be divided into five stages, according to some authors, being them the initial reaction, induction, acceleratory and decelerator periods and the final period of slow reaction.

Stage I – Early period of hydration – Almost immediately after adding water to cement, during the first few minutes of hydration (Figure 2.2(b)), the C_3A phase (the most reactive of the four main clinker minerals) reacts with gypsum and water to form an amorphous, aluminate-rich gel at the surface of the cement grains and small rod-like crystals of ettringite are developed (Winter, 2009). C_3A reaction with water is strongly exothermic but does not last long, typically only a few minutes (five or less) and the heat generation rate curve attains very high values. This initial part of the early period is usually termed as pre-induction and is followed by a period of a few hours of relatively low heat evolution, where cement hydration slows down, that is called the dormant, or induction period. The formation of a protective layer around cement particles, which prevents temporarily further reactions, may be the reason for this dormant period. During this period the material remains workable, i.e., it exhibits negligible mechanical stiffness (Azenha, 2009).

Stage II – Middle period of hydration - During this period, which begins at about 3h (after disruption of the protective layer) and ends at about 24h (Taylor, 1990b), the cement reacts. It coincides with that of strong heat evolution and is characterized by the rapid formation of amorphous calcium silicate hydrate, CSH (Taylor, 1990b) and crystalline calcium hydroxide ($Ca(OH)_2$) (Azenha, 2009). The development of CSH in this period occurs in 2 phases (Barron): After 10 hours of hydration (Figure 2.2 (c)), C_3S has produced CSH, which grows out from the ettringite rods. Therefore, in the initial phase of the reaction, the silicate ions must migrate through the aluminium and iron rich phases to form the CSH. In the latter part of the acceleratory period, after 18 hours of hydration, C_3A continues to react with gypsum, forming longer ettringite rods (Figure 2.2 (d)). This network of ettringite and CSH appears to form a hydrating shell and a small amount of inner CSH forms inside this shell. This coincides with the maximum rate of heat release (Taylor, 1990b) and to a sudden and strong increase in stiffness, with the transition of the material from a fluid-like behaviour to a porous solid, usually attaining stiffness (i.e., Young's modulus, also known as E-modulus) of over 50% of the value at 90 days by the end of this stage (Azenha, 2009). Along with the entire process, porosity of the material begins to diminish in resemblance to the growing formation of solid material (Azenha, 2009).

Stage III - Late period of hydration – After 1-3 days of hydration, reactions slow down and the decelerator period begins (Figure 2.2 (e)). C_3A reacts with ettringite to form some monosulfate and inner CSH continues to grow near the C_3S surface (Barron). In this stage, hydration reactions proceed, but at lower reaction rates owing to the progressive thickening of the hydrated products nearby the cement particles, which strongly reduce the heat generation rate (Azenha, 2009). After 2 weeks of hydration (Figure 2.2 (f)), the gap between the hydrating shell and the grain is totally occupied with CSH and the original outer CSH becomes more fibrous (Barron).

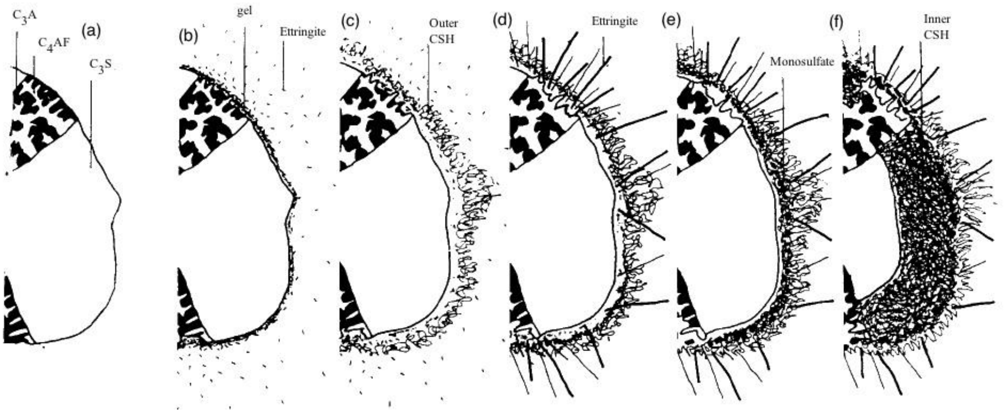


Figure 2.2 - Schematic representation of anhydrous cement (a) and the effect of hydration after (b) 10 minutes, (c) 10 hours, (d) 18 hours, (e) 1-3 days, and (f) 2 weeks. Adapted from Taylor (1990b)

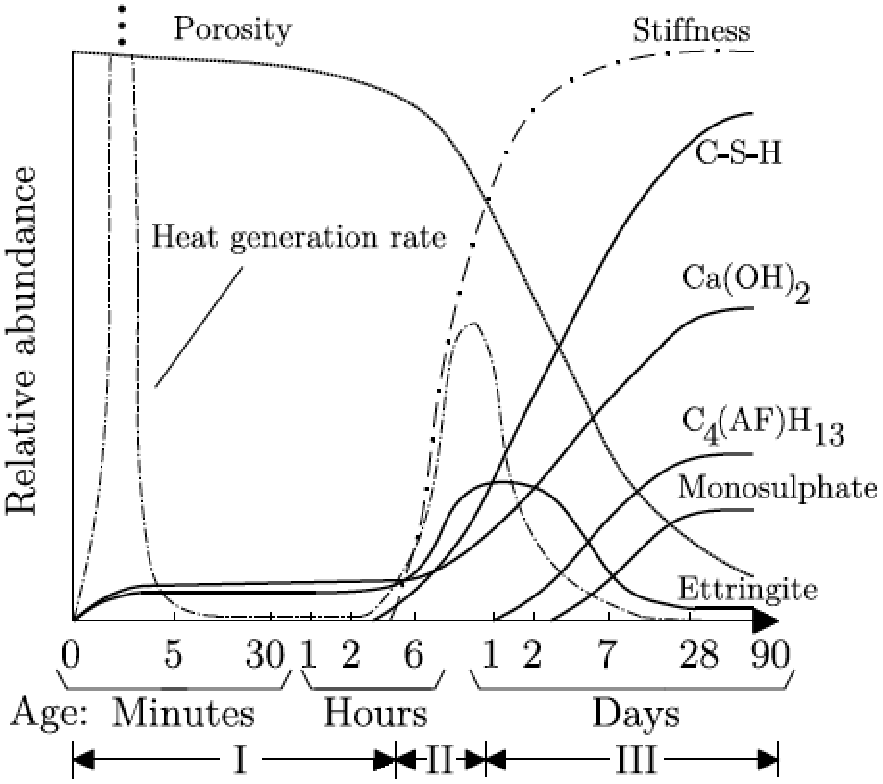


Figure 2.3 - Formation of several hydration products with time, together with porosity and heat generation rate evolution (Azenha, 2009)

One should bear in mind that the set of chemical reactions involved in cement hydration are highly dependent on the composition of the original binder, on the water-to-cement ratio, on the temperature of hydration and on the absence or presence of admixtures (Hewlett, 1987). Therefore, the average timings for the hydration product formation, the heat generation and the porosity evolution illustrated in Figure 2.3 are purely indicative for an ordinary Portland cement at a room temperature of ~20ºC (Azenha, 2009).

By way of conclusion, it is possible to define cement as an adhesive matter, which is proficient in bonding particles of solid substance into an entire compact one, when creased with water (Hewlett, 2004b). The hardening of the paste is due to the chemical reaction between the thin powders that are in their constitution and the water (Ramachandran, 1996), a process that is associated with both chemical and physical-mechanical changes, in particular with setting and hardening, as already mentioned (Hewlett, 2004b).

Concrete is a composite material made up of water and aggregates embedded in a hard matrix of material - the cement or binder - that fills the space between the aggregate particles and glues them together (Mindess, 2003b). The cement paste comprehends the active constituent of concrete, and its properties and performance are fundamentally determined by the properties of the cement paste (Ramachandran, 1996).

2.2 Brief history of cement and concrete

The first calcareous materials to be used as cements in mortars were gypsum and lime. These non-hydraulic materials have been used in Egypt (~3000 B.C.) and even earlier in Crete, Cyprus, Greece and in the Middle East (6000-12000 B.C.) (Mindess, 2003b). Hydraulic limes have also been produced by Greeks and Romans, through calcination of limestone containing argillaceous impurities. It is of common knowledge that Romans used animal fat, milk and blood to improve the quality of their binding mixtures. It is believed that they used this sort of materials to enhance workability, and, in fact, blood is a very efficient air-entraining agent and, moreover, it is able to improve concrete's durability (Hewlett, 2004b). As well as Romans, other civilizations also impregnated admixtures into their mixtures of concrete-like materials: In the middle ages, in Europe, eggs were used; the Chinese made use of Rice paste, lacquer, tung oil, molasses and boiled bananas and in Mesoamerica and Peru, Cactus juice and latex were materials that were commonly used as admixtures for concrete (Mindess, 2003b). Furthermore, these civilizations realized that mixing certain volcanic deposits with lime and sand yielded stronger mortars, which were also resistant to water (Mindess, 2003b). Whereas Greeks used a volcanic ash from the island of Santorini, Romans used a similar one, denominated by them as pozzolana, from the Bay of Naples. In the Middle Ages, the practice of introducing ash was relegated to oblivion and thus, the quality of the cementitious materials declined. High-quality mortars only emerged again by the fourteenth century, when the pozzolans where reintroduced, whereas scientific studies on this subject only started in the eighteenth century (Mindess, 2003b). It was in this epoch that the Portland cement appeared and its usage spread rapidly across Europe and North America (Mindess, 2003b).

Mortar and concrete made with Portland cement have been popular constructions materials in the world for the past 170 years or more (Ohama, 1995). The reasons for concrete's supremacy are mostly related to its properties, the economic aspect and the widespread availability of its constituents (Mindess, 2003b).

2.3 From concrete to modern concrete

Concrete and also cement mortar do have some disadvantages, such as delayed hardening, low tensile strength, low ductility, volume instability, low strength-to-weight ratio, large drying shrinkage, and low chemical resistance (Mindess, 2003b). In order to overcome these disadvantages, admixtures can be used. Admixtures can be defined as those ingredients in concrete, other than Portland cement, water and aggregates that are added to the mixture immediately before or during mixing, with the purpose of modifying the properties of mortar or concrete to make them more suitable for a particular work or for economy or for saving energy (Ramachandran, 1996). Admixtures have been used in the production of concrete for at least two millennia (Cheung *et al.*, 2011), but their systematic study for cement-based materials began in the 1930s (Mindess, 2003b) and their application has accelerated greatly in the last four decades (Cheung *et al.*, 2011). Since then, admixtures are widely accepted as materials that contribute to the production of durable and cost-effective concrete structures and, in fact, almost all modern concretes contain one or more admixture in their formulations, as they confer some beneficial effects due to their action on cement (Ramachandran, 1996). Admixtures' contributions include improving the handling properties of fresh concrete and the physic and mechanic properties of the hardened concrete, being the major reasons for using admixtures the following:

i. To reduce the cost of concrete construction (Rixom, 1998);
ii. To achieve certain properties in concrete more effectively than by other means (Mindess, 2003b);
iii. To maintain the quality of concrete during the stages of mixing, transporting, placing, and curing in adverse weather conditions (Mindess, 2003b);
iv. To overcome certain emergencies during concreting operations (Mindess, 2003b).

In fact, "modern concrete" is beyond a mere mixture of cement, water and aggregates; it contains increasingly mineral admixtures that have even extra specific effects, as a result from the development of a new science of concrete and a new science of admixtures (Aïtcin, 2000). In fact, cement and concrete ought to evolve in the regard of the environment within a sustainable development perspective, meaning that more mineral components and chemical admixtures will be combined with clinker and water/cement ratios will be lowered in order to increase the life cycle of concrete structures and reduce as much as possible the use of hydraulic binders and aggregates.

2.4 Admixtures, Additives and Additions

This section begins with a general review of the classification of admixtures with reference to North America and RILEM (Reunion Internationale des laboratoires d'Essais et de Recherches sur les Materiaux et lea Constructions) and to the European Standards. The North American sources include American Concrete Institute (ACI), American Society for Testing Materias (ASTM) and Canadian Standards (CSA). Table 2.2 summarizes the different nomenclatures and corresponding definition in accordance to each institution/standard.

Institution /Standard	Nomenclature	Definition
ACI 116R (2005) and ASTM C 125 (2006)	Admixture	A material other than water, aggregate, hydraulic cement, and fiber reinforcement used as an ingredient of concrete or mortar which is added to the batch immediately before or during its mixing, including both finely divided solids (mineral admixtures) and water-soluble compounds (chemical admixtures).
ASTM C 219 (2007)	Addition	Material that is interground or blended in limited amounts into a hydraulic cement during manufacture either as a processing addition to aid in manufacturing and handling the cement or as a functional addition to modify the properties of the finished product.
RILEM (1992)	Admixture	Inorganic (including minerals) or organic materials in solid or liquid state, added to the normal components of the mixture, in most cases up to a maximum of 5% by weigth of the cement or cementitious materials. Materials such as fly ash, slag, pozzolans or silica fume are not classified as admixtures, although they can be constituents of cement or concrete and also products acting as reinforcement.
BS EN 934-2 (2001)	Admixture	Materials added during the mixing process of concrete in a quantity not more than 5% by mass of the cement content of the concrete, to modify the properties of the mixture in the fresh and/or hardened state
EN 206-1 (2005)	Admixture	Materials added during the mixing process of concrete in small quantities related to the mass of cement to modify the properties of fresh or hardened concrete.
	Addition	Finely divided material used in concrete in order to improve certain properties or to achieve special properties. This standard deals with two types of inorganic additions: – Nearly inert additions (type I); – Pozzolanic or latent hydraulic additions (type II).

Table 2.2 - Nomenclatures and respective definitions according to each institution/standard

Among the scientific world, there is no consensual definition about the terms admixtures, additives and additions. According to Mindess (2003a), the term "additive" lies into a mature phraseology used interchangeably with "admixture". However, concurring to Hewlett (2004a), "admixtures should be distinguished from additives and additions in that these materials (additives and additions) are usually solids and are added to the cement during its manufacturing, (…), or as a major component in the manufacture of concretes and mortars (…)". Besides, according to Coutinho (1988), it is possible to define admixtures as all the substances which are introduced in a percentage less than 5% of the cement weight and which are added during the mixing in order to modify certain properties of the mortars, concrete or cement paste when these materials are in the liquid or solid state and even between the transition of those states. This definition does not encompass grinding mineral substances, such as pozzolans, slags, etc., which are added in larger proportions than 5%. Still according to Coutinho (1988), an additive must be said to be all the substance which is added to cement, in a mortar or concrete, in a higher quantity than 5% of cement weight, or, when added in a smaller quantity, does not perform any action in liquid or solid state or even between the transition of these states (Coutinho, 1988).

In the scope of the present thesis, the adopted definition of admixture is the one embraced by the European Standard BN EN 934-2, i.e., "materials added during the mixing process of concrete in a quantity not more than 5% by mass of the cement content of the concrete, to modify the properties of the mixture in the fresh and/or hardened state" (CEN, 2001). Moreover, fly ash, granulated blast furnace slag and silica fume will be referred as additions, i.e., finely divided inorganic materials used in concrete in order to improve certain properties or to achieve special properties, as this is the accepted definition in Europe. However, a special focus will be given to admixtures, as the aim of the present investigation is to understand the effects of the incorporation of a by-product of an industry as a potential admixture.

Admixtures can be classified by function, as follows (Rixom, 1999, Mehta, 2006, Ramachandran, 1996, Hewlett, 2004b, Hewlett, 1988, Mindess, 2003b):

i. Accelerating admixtures;
ii. Retarding admixtures;

iii. Water-reducing admixtures;
iv. Air-entraining admixtures;
v. Anti-freezing admixtures;
vi. Shrinkage Admixtures;
vii. Corrosion inhibitors;
viii. Multifunction admixtures;
ix. Hydration-control admixtures;
x. Alkali-silica reactivity inhibitors;
xi. Coloring admixtures;
xii. Miscellaneous admixtures, such as waterproofing admixtures, antiwashout admixtures, shotcrete admixtures, flocculating admixtures, pumping aids, damppprofing, foaming admixtures, bonding, permeability reducing, grouting, gas-forming and foaming.

As the aim of this investigation consists in understanding the effects of the incorporation of a industrial by-product (crude purified glycerol) as a potential admixture, a convenient description of some of these types of admixtures follows, focusing particularly on the potentially expectable effects of glycerol.

2.4.1 Accelerators

Accelerator admixtures are used to reduce the setting times and to increase the rate of hardening of cement and concrete mixtures. They comprise chemicals that are capable of affecting the rate of cement hydration, thus decreasing the setting time and, in many cases, increasing the rate of early strength development (Paglia, 2001). According to BS EN 934-2 (CEN, 2001) there are two types of accelerators, namely:

1. Set accelerating admixtures, which constitute those that decrease the time to commencement of transition of the mixture from the plastic to the rigid state;
2. Hardening accelerating admixtures, which increase the rate of development of early strength in concrete, with or without affecting the setting time.

Figure 2.4 shows the different ultimate effects between types 1 and 2 mentioned above.

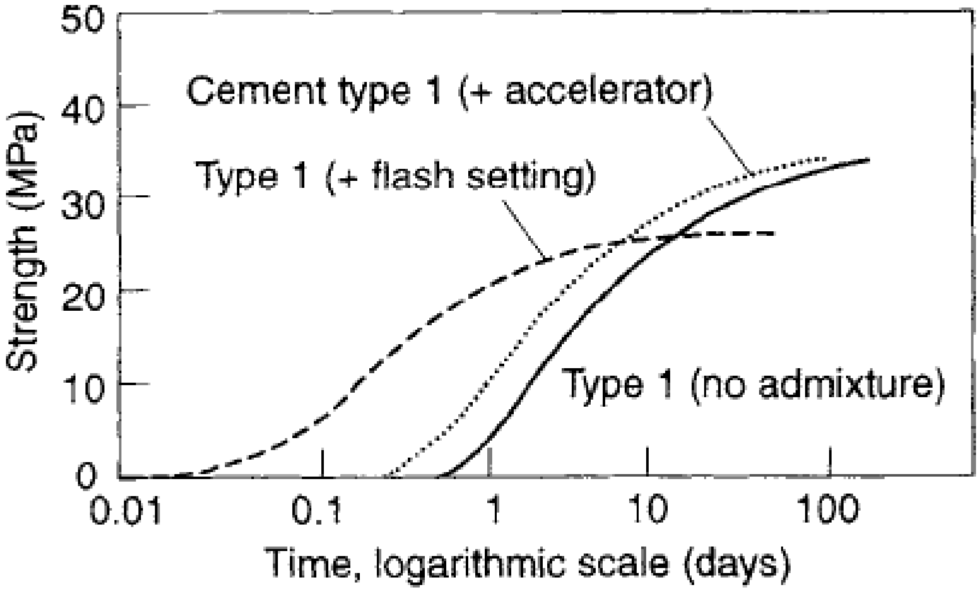


Figure 2.4 – Schematic comparison of strength development with hardening accelerator and flash-setting (set accelerating) admixtures (Hewlett, 1987)

Actually, there might be some overlap between these two main subdivisions, but while the first group affects mainly the tricalcium aluminate phase, the second group acts both in tricalcium aluminate phase and in the tricalcium silicate (alite) phase (Paglia, 2001), but mainly in the last one, resulting in an increase in heat evolution and C-S-H- gel formation at an early age (Hewlett, 1987).

In Figure 2.5 a possible effect of a hardening accelerator admixture on the heat evolution of the mixture is shown. The effect of some hardening accelerator admixtures in the compressive strength of cement pastes is shown in Figure 2.6.

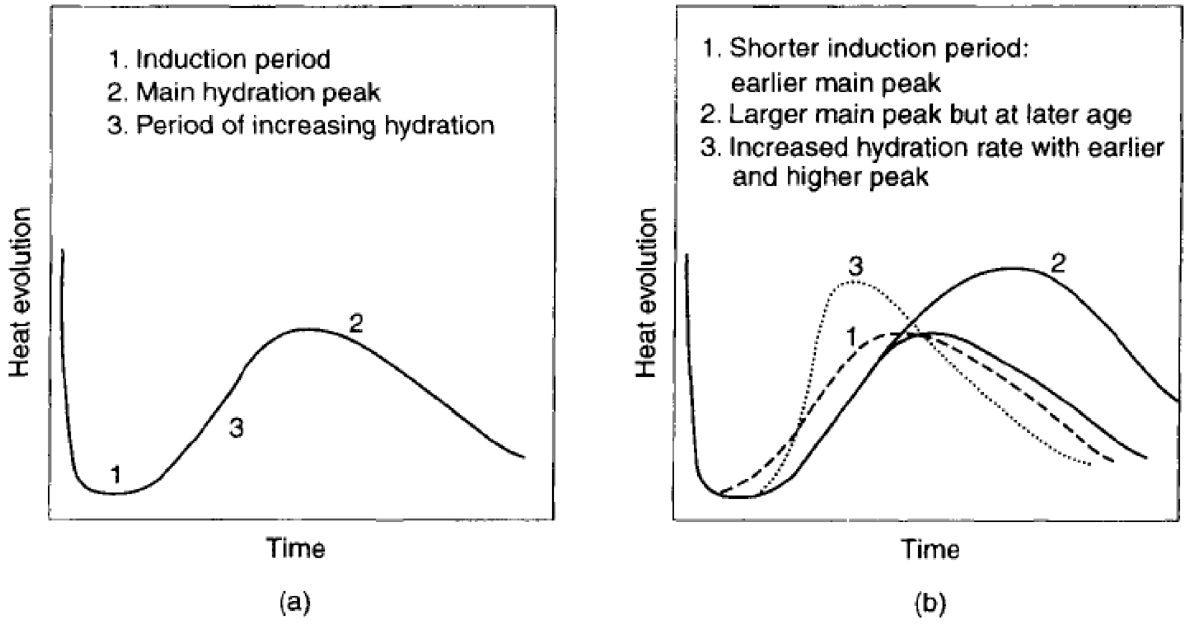


Figure 2.5– (a) General hydration curve from conduction calorimetry and (b) possible accelerative effects on hydration curve (Hewlett, 1988)

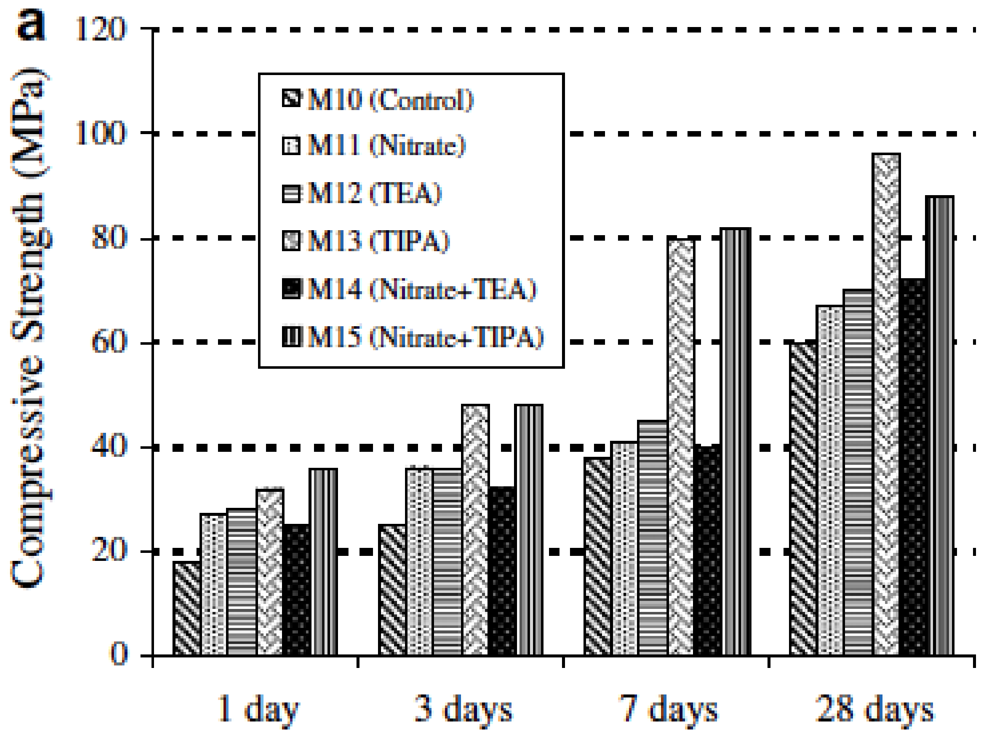


Figure 2.6 – Compressive strength results for control admixtures, admixtures with calcium nitrate (Nitrate), admixtures containing triethanolamine (TEA), admixtures with triisopropanolamine (TIPA), admixtures with Nitrate+TEA and admixtures with Nitrate+TIPA (Aggoun *et al.*, 2008)

In what concerns the set-accelerating group, which may also be referred as flash or false setting admixtures, they are mainly consist of by highly alkaline chemicals, such as carbonates, silicates, aluminates and alkali metal hydroxides. The second group is mostly constituted by soluble salts of alkali and alkaline earth metals, such as halide, nitrate, nitrite, formate, thiosulfate, thiocyanate, calcium, magnesium, barium, ferric, aluminum, sodium, potassium and ammonium (Hewlett, 2004b).

According to their chemical composition, accelerating admixtures for concrete can be split into three major groups, specifically (Mindess, 2003b): i) soluble inorganic salts that include chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates and alkali hydroxides ii) soluble organic compounds that include triethanolamine, calcium formate, calcium acetate, calcium propionate and calcium butyrate; and iii) miscellaneous solid materials as calcium aluminate, seeds of finely divided portland cement, silicate minerals, finely divided magnesium carbonate and calcium carbonate. The performance of accelerators on the effects of the early strength depends fundamentally on their dosage, chemical base, temperature and to the cement employed (chemical composition and fineness) (Prudêncio Jr, 1991).

A study conducted by Heikal (2004), where calcium formate (CF), which is a by-product of the manufacture of polyhydric alcohol, was introduced in normal Portland cement in order to evaluate its effects on the setting times, the compressive strength, between others and he reported that initial and final setting times are accelerated with the addition of CF and that CF increases the early and later strength values and accelerates C-S-H formation (Heikal, 2004).

Various admixtures have been used as set and/or hardening accelerators: calcium chloride was the most widely used set accelerator admixture (Aggoun *et al.*, 2008) owing to its ready availability, low cost, predictable performance characteristics and successful application over several decades. However, one of the limitations to the wider use of calcium chloride in reinforced concrete is the danger of inducing corrosion in reinforced concrete when large quantities of admixture are used (Wise *et al.*, 1995). For this reason, the field of the chloride-free admixtures started being studied and it was found that calcium formate and calcium nitrate gave good results as set accelerators whereas triisopropanolamine proofed to give good results as a hardening accelerator. In some cases, admixture ’ s effectiveness in accelerating/retarding setting depends upon the concentration of the admixture in the cement paste and also on the type of cement used. For example, triethanolamine can produce either set acceleration or retardation, depending on the cement type and addition rate (Aggoun *et al.*, 2008).

These admixtures bring about a number of benefits including reduced bleeding, earlier finishing, improved protection against early exposure to freezing and thawing, earlier use of structure and reduction of protection time to achieve a given quality (ACI, 2003). Besides, accelerators can also play a role as water-reducing admixtures, as actually defined in BSEN 934-2 (CEN, 2001): a set accelerating/water reducing/plasticizing admixture is one that produces the combined effects of water reducing/plasticizing admixture (primary function) and a set accelerating admixture (secondary function). This standard also sets the definition of primary and secondary functions as a single function of a multifunction admixture designated by the manufacturer and a function of a multifunction admixture which is additional to the primary function, respectively.

2.4.2 Retarders

Retarders comprise the admixtures that possess the capability of lengthening the hydration induction period, thus extending the setting times (Ramachandran, 1996). According to BS EN 934-2 (CEN, 2001), set retarding admixtures are those capable of extending the time to commencement of transition of the mixture from the plastic to the rigid state. Some authors refer that there are to types of retarding admixtures. They can either be materials that reduce the solubility of the hydrating components in cement, and so are solubility reducers, as gypsum, for example, or they can be materials that react with a component to form a precipitate on the cement particles, imparting a low-permeability coating on the grains, consequently slowing down the hydration (Hewlett, 1987). The second type of these sort of admixtures generally work by enhancing the early hydration sheath that surrounds cement grains and they can be sugars, heavy metal salts of tin, lead and zinc. Figure 2.7 shows the early hydration reactions of Portland cement with no admixture and in the presence of lignosulfate.

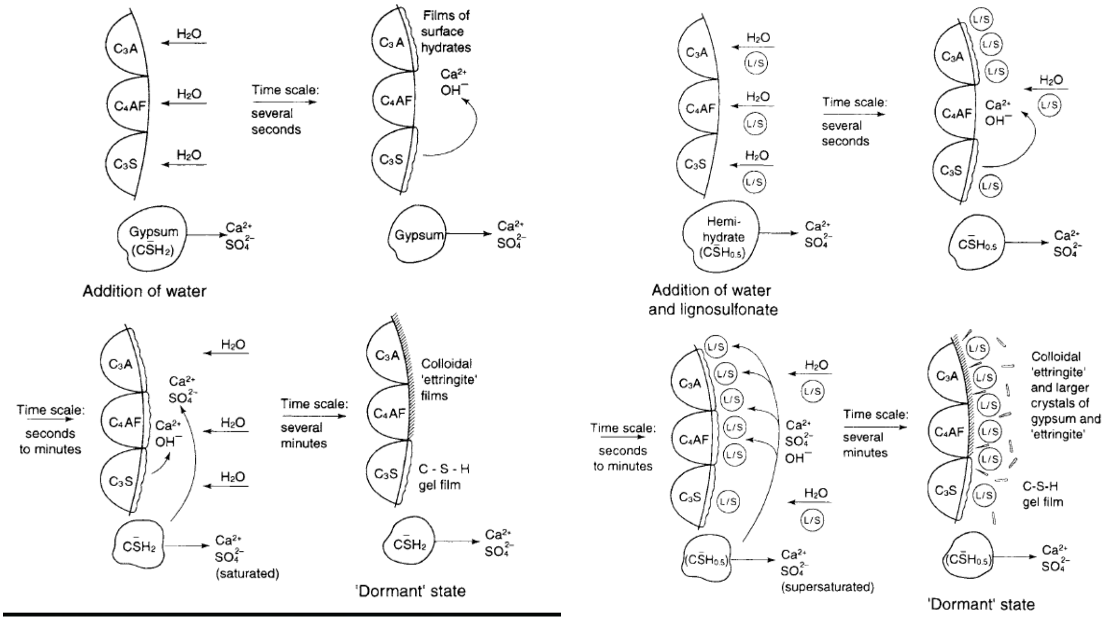


Figure 2.7 – Early hydration reactions of Portland cement: normal behavior with no admixture present (a) and behavior in the presence of lignosulfate (L/S) (Edmeades, 1984)

Retarders can be applied whenever it is desirable to counteract unwanted effects of high temperature that decrease setting times, to retain concrete workable during the placing and consolidation periods, to sidestep complications when some delays may happen between mixing and placing, to resist craking due to form deflection (indeed, if the plastic period is prolonged, concrete can adjust to form deflections without cracking) or even to reduce the 28-day compressive strength (Khan, 2004).

These admixtures can be classified according to their chemical constitution, that is: lignosulfonic acids and their salts; hydroxycarboxylic acids and their salts; sugars and their derivatives; phosphates and organic phosphonate salts and salts of amphoteric metals (zinc, lead and tin); carbohydrates (glucose, sucrose or hydroxylated polymers) and some organic compounds, such as polyvinyl alcohol, sodium aluminomethylsiliconate or sulphanilic acid. Some of these chemicals also own water-reducing capacities and can be classified as water-reducing, set-retarding admixtures (ACI, 2003, Ramachandran, 1996, Mehta, 2006, Mindess, 2003b). Actually, the standard BS EN 934-2 (CEN, 2001) sets out a definition for set retarding/water reducing/plasticizing admixture as one which produces the combined effects of water reducing/plasticizing admixture (primary function) and a set retarding admixture (secondary function). Moreover, it also sets out a definition for set retarding/high range water reducing/superplasticizing admixture as one which produces the combined effects of high range water reducing/superplasticizing admixture (primary function) and a set retarding admixture (secondary function).

2.4.3 Water-reducing/plasticizers admixtures

The water-reducing admixtures, as the name implies, are the group of admixtures which possess as their primary function the capability to produce concrete of a given workability and slump, at a lower water-cement ratio, that is, they reduce the water demand of concrete (Ramachandran, 1996). BS EN 934-2 (CEN, 2001) defines two types of water-reducing admixtures: water reducing/plasticizing admixtures and high range water reducing/superplasticizing admixtures. The first group are those admixtures which without affecting the consistency, permit a reduction in the water content of a given concrete mixture, or which, without affecting the water content increase the slump/flow or produce both effects simultaneously. The second group possesses the exactly same function, but they permit a high reduction in the water content. That said, one may say that this admixture can be hold as a cement saver.

The water reducing/plasticizing admixtures include lignosulfonates acids and their salts, hydroxy-carboxylic acids and their salts and hydroxylated polymers derived from hydrolyzed starch (polysaccharides) (Chan, 1999), while the high range water reducing/superplasticizing admixtures are constituted by low molecular-weight synthetic polymers containing oxyacid groups attached to the carbon backbone at regular intervals and they can be sulfonated naphthalene or melamine formaldehyde condensates, purified lignosulfonates and carboxylated acrylic ester copolymers (polyether-polycarboxylates) (Ramachandran, 1996).

2.4.4 Antifreezing admixtures

Antifreezing admixtures represent those that allow concrete to achieve acceptable strength when cured in cold environments and they can be added to lower the freezing point or to accelerate the release of heat of hydration while giving smaller reductions in the freezing points of water (Mindess, 2003b).

The efficiency of antifreeze admixtures for decreasing the freezing point of water is linked to its eutectic point, which corresponds to lowest temperature below which additional quantities of antifreeze will not depress the freezing point further (Korhoken, 1991). The temperature of the eutectic point varies depending on which compound is used (Karagöl *et al.*, 2013). In Figure 2.8 are represented the freezing points of glycerol-water solutions.

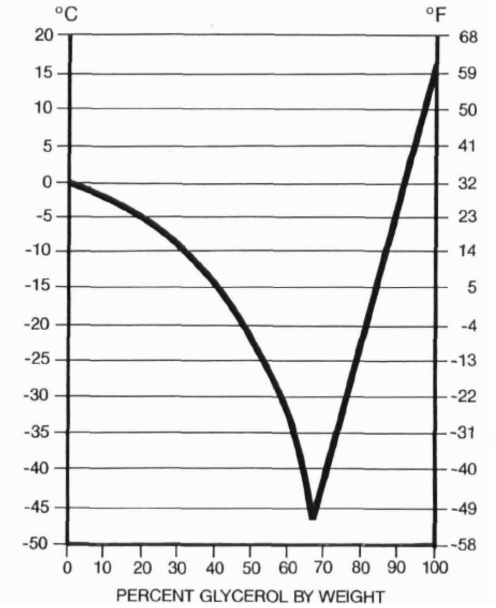


Figure 2.8 – Freezing Points of Glycerol-Water Solutions (Lane, 1925)

Figure 2.9 shows calorimetric curves of solutions containing 0%, 1,5 % and 3% of potassium thiocyanate (KSCN) by weight of cement that were added at a water-to-cement-ratio of 0,25, for the rate of heat development and the total heat evolved at 20ºC and 0ºC, respectively (Wise *et al.*, 1995) and it may be clearly observed that the addition of KSCN the rate of heat evolution at both temperatures.

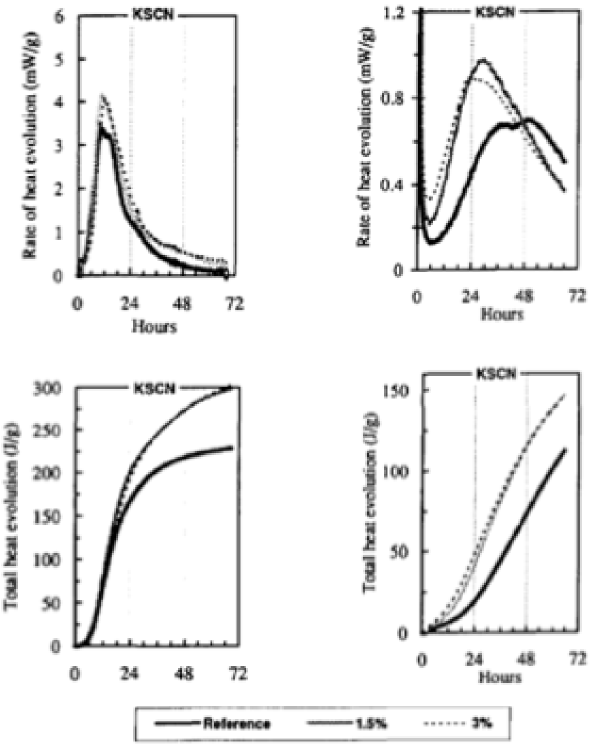


Figure 2.9 - Heat of hydration of cement paste with salts of different concentrations at 20°C and 0ºC, respectively Wise *et al.* (1995)

When temperatures fall below 5ºC, chemical reactions between cement and water drastically decrease, and consequently, the setting time becomes longer. As low hydration speed decelerates the formation of calcium-silicate-hydrate (CSH) gels, which is the most important component of hydration and detains a bonding property, it results in a delayed resistance acquisition, thus affecting the properties of concrete and delaying the time taken for formwork/propping removal (Turkel, 2003). When the water that exists in concrete freezes without setting, there will be not enough water for hydration, as hydration completely stops and concrete volume expands. If temperature rises and the ice inside the concrete melts turning into water, concrete can set and harden. However, since void volume that arises due to melting of ice is quite large, the products of hydration will not be able to fill the voids adequately, causing a reduction in the resistance of the concrete and an increase of water permeability (Turhan, 2003).

Therefore, when concreting is done under cold weather conditions, it is imperative to ensure that it will not freeze while it is in the plastic state (Rixom, 1999).

The chemical materials used with this purpose can be classified into two categories (Ramachandran, 1996). The first ones encompass materials whose freezing points are lower than that of water, thus having negligible effect on hydration kinetics (i.e. nor acceleration, nor retardation effect). This includes sodium nitrite, sodium chloride, weak electrolytes and non-electrolytic organic compounds such as high-molecular-weight alcohols and carbamide. The second category comprises binary or ternary admixture systems that contain potash and additives based on calcium chloride and a mixture between calcium chloride, sodium nitrite, calcium nitrite-nitrate, calcium nitrite-nitrate-urea and other chemicals. These chemicals hold the capability of providing anti-freezing action and of accelerating the set and hardening (Ramachandran, 1996). Some formulations will give protection against freezing to concrete placed in sub-freezing ambient temperatures (ACI, 2003). They contribute to the rapid formation of a dense micro capillary cement structure (Ramachandran, 1996). Conventional non-chloride accelerating admixtures are used in cold weather concreting to offset the retarding effects of slow hydration on the rate of strength development. Such admixtures however do not permit concreting at or below freezing temperatures (Rixom, 1999).

2.4.5 Shrinkage reducing admixtures

Shrinkage admixtures are used to offset shrinkage that may occur in both fresh and hardened concrete (Mindess, 2003b). Some of the procedures adopted to reduce shrinkage cracking are related to the use of high-range water reducers to accomplish very low water-to-cement ratios, the use of expansive admixture, the use of shrinkage compensating cements or the use of admixtures capable of reducing the surface tension effects that contribute to drying shrinkage (Rixom, 1999).

One of the key causes of drying shrinkage is the surface tension developed in the small pores of the cement paste of concrete (Rixom, 1999). When these pores lose moisture, a meniscus forms at the air/water interface, thus creating internal forces that tend to contract the matrix. If the surface tension of water in the capillary pores of concrete is reduced, the tendency to shrink will also be reduced. Figure 2.10 represents a schematic example of the effect of pore meniscus and surface tension on the drying shrinkage of mortar (Balogh, 1996).

Figure 2.10 – Effect of pore meniscus and surface tension on the drying shrinkage of mortar (Balogh, 1996)

Propylene glycol, polyoxyalkylene alkyl ether, glycol ether and calcium sulphoaluminate and lime based materials are also some examples of materials used to offset shrinkage effects (Chan, 1999). Studies concerning the incorporation of ground granulated blast-furnace slag (GGBS) (Li and Yao, 2001), which is a by-product produced from the blast-furnaces of iron and steel industries (Siddique and Bennacer, 2012) have already been performed and it has been realized that GGBS was able to reduce shrinkage (Li and Yao, 2001).

These sort of admixtures hold the purpose of counterweighing the shrinkage of concrete in plastic and hardening states by an expansion yielding effect. The addition of certain water-soluble organic compounds to the fresh concrete decreases the shrinkage by 30-50% (Mindess, 2003a).

In Table 2.3 a summary of the most commonly used admixtures is shown.

Table 2.3 – List of some admixtures and additions for concrete (Chan, 1999, Hewlett, 1988, Hewlett, 2004b, Nagataki, 1994b, Ramachandran, 1996, Rixom, 1999)

	Type of admixture/addition	Desired effect	Typical Chemicals
Admixtures	Accelerators	Accelerate setting and/or early-strength development.	Calcium chloride; Triethanolamine; Sodium thiocyanate; Calcium formate; Calcium nitrite.
	Air-entraining	Improve durability in freeze-thaw, deicer, sulfate, and alkali-reactive environments. Improve workability.	Salts of wood resins; Some synthetic detergents; Salts of sulfonated lignin; Salts of petroleum acids; Salts of proteinaceous material; Fatty and resinous acids and their salts; Alkylbenzene sulfonates; Salts of sulfonated hydrocarbons.
	Anti-freezing	Lower the freezing point of water in concrete, allowing it to obtain the necessary strength to withstand the effects of freezing and accelerates the heat of hydration.	Sodium nitrite; Sodium chloride; Weak electrolytes and non-electrolytic organic compounds (high-molecular-weight alcohols and carbamide); Binary or ternary admixture systems that contain potash; Additives based on calcium chloride and a mixture between calcium chloride, sodium nitrite, calcium nitrite-nitrate, calcium nitrite-nitrate-urea and other chemicals.
	Multi-function	Admixtures that play more than one role.	Plasticizers; Superplasticizers; Water reducers.
	Retarders	Retard setting time.	Lignosulfonic acids and their salts; Hydroxycarboxylic acids and their salts; Borax; Phosphates and organic phosphonate salts and salts of amphoteric metals (zinc, lead and tin); Carbohydrates (glucose, sucrose or hydroxylated polymers) and some organic compounds

				Sugars and their derivatives; Tartaric acid and salts.
	2.4.5.1 Shrinkage admixtures		Offset shrinkage that may occur in both fresh and hardened concrete.	Propylene glycol; Polyoxyalkylene alkyl ether; Glycol ether; Calcium sulphoaluminate and Lime based materials.
	Water-reducers		Reduce water content.	Lignosulfonates acids and their salts; Hydroxy-carboxylic acids and their salts; Hydroxylated polymers derived from hydrolyzed starch (polysaccharides); Sulfonated naphthalene or melamine formaldehyde condensates; Purified lignosulfonate; Carboxylated acrylic ester copolymers (polyether-polycarboxylates).
	Miscellaneous	Waterproofing admixtures	Block or impede the flow of water through the natural capillaries in hardened concrete.	Water repelling materials including soaps and fatty acids and wax emulsions; Methyl siliconates.
		Antiwashout admixtures	Cohesive concrete for underwater placements.	Cellulose; Acrylic polymer.
		Shotcrete admixtures	Reduce/Increase setting; Act as air-entraining agents.	Strong alkalis; Organic bases
		Flocculating admixtures	Reduce the type of bleeding from a destructive form to a more gradual seepage in mixtures.	Polyelectrolytes; Wax emulsions; Aqueous suspensions of clay materials; Natural water soluble gums.
		Pumping aids	Improve pumpability.	Organic and synthetic polymers; Organic flocculents; Hydrated lime; Organic emulsions of paraffin, coal tar, asphalt and acrylics; Bentonite and pyrogenic silicas.
		Damppprofing admixtures	Retard moisture penetration into dry concrete.	Soaps of calcium or ammonium stearate or oleate; Butyl stearate; Petroleum products.
		Foaming admixtures	Produce lightweight, foamed concrete with low density.	Cationic and anionic surfactants; Hydrolized protein.
		Permeability reducing admixtures.	Decrease permeability.	Latex; Calcium stearate.
		Bonding admixtures.	Increase bond strength.	Polyvinyl chloride;

				Polyvinyl acetate; Acrylics; Butadiene-styrene; Copolymers.
		Gas-forming and foaming admixtures.	Cause expansion before setting.	Aluminum powder.
		Grouting	Adjust grout properties for specific applications.	Air-entraining admixtures; Accelerators; Retarders.

3 BIODIESEL

3.1 Introduction

Biodiesel is a cleaner and greener fuel than conventional diesel (Santacesaria *et al.*, 2012). This is primarily due to the fuel properties: low toxicity, biodegradability, less contaminant for the environment as consequence of lower CO2 emissions) (Atadashi *et al.*, 2011). Additionally, also the origin on renewable resources, vegetable oil or animal fats, virgin or recycled from other utilizations (Atadashi *et al.*, 2012) contributes to biodiesel higher level of eco-sustainability. Biodiesel has been gaining more relevance recently, not only because of its environmentally friendly character, but also because of the sharp increase in the prices of petroleum derivatives, and the finite nature of fossil fuels (Marchetti *et al.*, 2007). Besides, it represents a strategic energy resource for the countries which do not possess oil reserves but have large amounts of arable land (Santacesaria *et al.*, 2012). In relation to other petrol-alternative energy sources, biodiesel is a forerunner, with a world production of 16,000 ktonnes in 2009 (Santacesaria *et al.*, 2012). In part this is also due to the absence of technology that can support the utilization of other energy sources with reasonable yield and competitive price. Biodiesel can thus act either as a substitute for petroleum diesel (pure biodiesel - B100) or as an additive to diesel fuel (blended with petroleum diesel in ratios of 2% - B2 -, 5% - B5 - or 20% - B20) (Bozbas, 2008). Nevertheless, and in spite of the raising production, biodiesel cost remains high when comparing with the diesel from petroleum (Balat, 2011). This is due to the fact that many vegetable oils used in the production of biodiesel are edible oils (Balat, 2011). Therefore, the wide utilization of biodiesel faces a major hurdle because it competes directly with land and water resources for food production.

Biodiesel production process yields as by-product glycerol (Abad and Turon, 2012). This compound is traditionally obtained from petroleum refining process, and is widely and extensively used in many industrial processes, which justified an expensive petroleum-based glycerol world market stock exchange. Although the biodiesel-derived glycerol needs treatment to reach the degree of purity that is achieved during petrochemical refining processes, its accumulation destroyed the market, and glycerol passed from high added value product to waste with associated discard costs (Posada *et al.*, 2012).

3.2 Biodiesel production

Biodiesel has a very little amount of sulphur, polycyclic aromatic hydrocarbons and metals (Vasudevan, 2008), and possesses a high flash point. These characteristics make it safe for use, handle, storage and transport (Balat, 2011). Similar to petroleum diesel, biodiesel sets off in compression-ignition engines, which means that this fuel can be used in regular diesel vehicles without the need to make changes in the engine system (Vasudevan, 2008). In addition, as biodiesel is oxygenated, it works better than diesel as a lubricant, increasing the lifetime of the engines (Vasudevan, 2008). This high energy fuel can be defined as an organic compound, a mixture of fatty acids methyl esters (FAME), most commonly obtained by transesterification of vegetable oils, which are composed of triglycerides and fatty acids, with methanol in the presence of alkaline catalysts (NaOH, KOH or related alkoxides) (Tan *et al.*, 2010). Alternatively, there are other methodologies to produce biodiesel, all based on vegetable oils (Atadashi *et al.*, 2011): (i) direct use and blending of; (ii) microemulsions; and (iii) thermal cracking (pyrolysis). A comparison between the main biodiesel production techniques may be seen in Table 3.1.

3.2.1 Direct use and blending

The possibility of directly using vegetable oils as diesel fuel has been considered since the beginning of the diesel engine. In 1893, Rudolf Diesel successfully ran the very first engine using peanut oil (a biomass fuel) (Vivek, 2004). However, the primary concern of the direct use of vegetable oils was their high viscosity (11 to 17 times higher than the one of diesel fuel), (Suwannakarn, 2008) leading to problems in the long run. One problem consists in the polymerization of polyunsaturated fatty acids and gum formation, caused by oxidation during storage as a result of reactivity of C-C double bonds. Another is lower diesel volatility leading to the formation of carbon deposits in engines due to incomplete combustion (Srivastava and Prasad, 2000). Moreover, problems of using vegetable oils also include (Srivastava and Prasad, 2000): (1) coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly; (2) oil ring sticking; (3) carbon deposits, and (4) lubricating oils thickening and gelling as a result of undesirable mixture with the vegetable oils. Despite the practical advantages that the use of these oils would present, such as their liquid nature and portability, high heat content, ready availability and renewability (Vivek, 2004), their prolonged use in modern diesel engine would not be possible due to the decrease in power output and thermal efficiency by carbon deposits (Ma, 1999).

3.2.2 Microemulsions

A microemulsion is technically defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Ma, 1999). Microemulsions with solvents such as methanol, ethanol and 1-butanol have been studied for biodiesel production in order to solve the problem of the high viscosity of vegetable oils (Schwab *et al.*, 1987). They are able to improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984). However, the significant injector needle sticking, the carbon deposits, the incomplete combustion and the increase in the viscosity of lubricating oils are reported for utilizing the fuel produced from this process in long term run (Ma, 1999).

3.2.3 Thermal cracking (pyrolysis)

Pyrolysis is defined as the conversion of one substance into another by means of heat in the absence of air (or oxygen) (Demirbas, 2008) at temperatures ranging from 450 °C to 850 °C, or by heat with the aid of a Lewis acid catalyst (Suwannakarn, 2008), and cleavage of chemical bonds to yield small molecules (Weisz, 1979). The type of acid catalysts used in this process may be zeolites, montmorillonite clay, aluminium chloride, aluminium bromide, ferrous chloride and ferrous bromide (Suwannakarn, 2008). However, the equipment for pyrolysis is expensive and, in addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also eliminates the environmental benefits associated with using an oxygenated fuel (Ma, 1999).

3.2.4 Transesterification

As mentioned above, transesterification of vegetable oils is the most common way to produce biodiesel. This reaction transforms triglycerides molecules into fatty acid alkyl esters (the desired fuel) and glycerol, in the presence of a short-chain alcohol, such as methanol, ethanol, butanol or propanol (Borges and Díaz, 2012). Most preferably, methanol or ethanol are used. The reaction needs a catalyst, as may be seen in Figure 3.1. The overall process is normally a sequence of three successive chemical steps: triglycerides are transformed into diglycerides, these are transformed into monoglycerides, and glycerol and esters are formed from monoglycerides. In all these reactions esters are produced (Chouhan and Sarma, 2011), as represented in Figure 3.1. Although the equilibrium lies towards the production of fatty acid esters and glycerol, all of these steps are theoretically reversible reactions (Marchetti *et al.*, 2007).

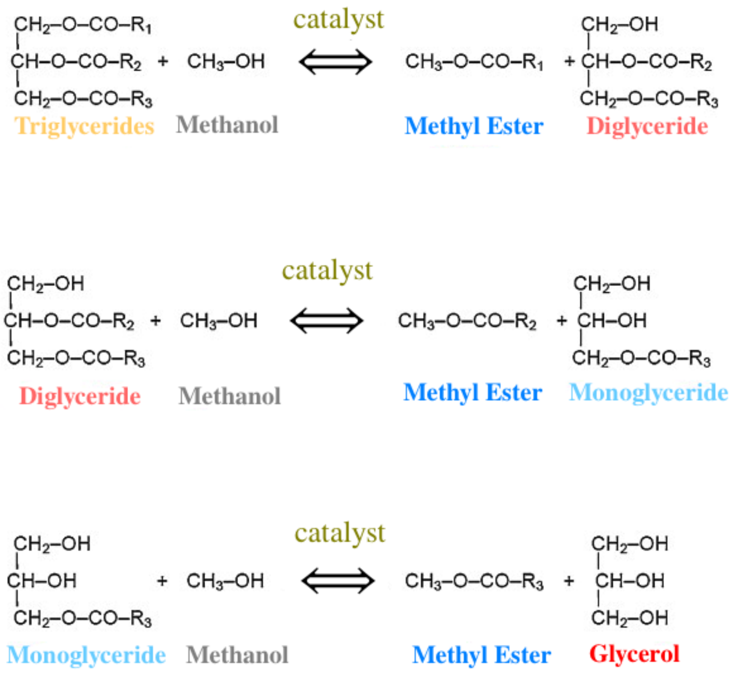


Figure 3.1 - Transesterification Reactions

Table 3.1 - Biodiesel production Techniques

Technologies	**Advantages**	**Disadvantages**
Direct use	1. Liquid nature and portability 2. High heat content 3. Ready availability 4. Renewability	1. High viscosity 2. Bad volatility 3. Bad stability
Microemulsion	1. Simple process 2. Improve spray characteristics	1. Incomplete combustion 2. Carbon deposits 3. Injector needle sticking

Pyrolysis	1. Simple process	1. High temperature is required 2. Equipment is expensive 3. Low purity
Transesterification	1.Fuel properties are closer to diesel 2.High conversion efficiency 3. Low cost 4. It is suitable for industrialized production	1. Low free fatty acid and water content are required (for base catalyst) 2. Pollutants will be produced because products must be neutralized and washed 3. Accompanied by side reactions 4. Difficult reaction products separation

3.3 Catalysts

There are several types of catalysts, chemical catalysts - alkali or acid - that can be homogeneous or heterogeneous, and biocatalysts - enzyme based (Meher, 2006). If the catalyst remains in the same phase as the reactants during transesterification (liquid phase), it is called an homogeneous catalytic. Conversely, if the catalyst gets into different phase (solid, immiscible liquid or gaseous), it is called heterogeneous catalytic (Chouhan and Sarma, 2011). The heterogeneous catalytic transesterification possesses some advantages over the homogeneous one (Kiss *et al.*, 2010): higher yields due to absence of soap and fatty acid formation (Bloch, 2008); simpler design due to no requirements for purification and separation steps (Di Serio, 2007); high glycerine purity with very low water content (Bloch, 2008) and no salt contaminants (Bournay, 2005); the catalyst can be reused (Sarma, 2008); there is no, or very less amount of waste water produced during the process; and the separation of glycerol from biodiesel is much easier (Lee, 2010). A single drawback relates to high energy consumption as a result of higher reaction temperatures due to lower activity of the solid catalyst (Kiss *et al.*, 2010). In fact, the glycerol produced by homogeneous catalytic transesterification is of low quality (Canakci, 2001a), and requires prolonged process and distillation for purification (Grandos, 2007), which increases the cost of both end products (biodiesel and glycerol) (Ji, 2006). Heterogeneous catalytic transesterification process overcomes these problems, as the alcohol is unmixable with solid heterogeneous catalyst (Chouhan and Sarma, 2011). Furthermore, in the end of the transesterification process, it is considerably easy to separate the catalyst from biodiesel and glycerol (Chouhan and Sarma, 2011).

Alkali-catalysed transesterification is faster than acid-catalysed (Borges and Díaz, 2012). Besides, alkaline catalysts are less corrosive than acidic compounds. Because of these facts, industrial processes usually incline towards base catalysts (Borges and Díaz, 2012). However, if a glyceride has a higher free fatty acid content and more water, acid-catalysed transesterification is preferable (Refaat, 2009). Homogeneous and heterogeneous catalysts are listed in Table 3.2**.**

Biocatalysts are naturally occurring lipases (enzymes), which have the ability to perform the transesterification reactions (Sheedlo, 2008) and they have been gaining more importance in biodiesel's preparation lately owing to their ready availability, biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure (Marchetti *et al.*, 2007). Moreover, these enzymes may have the potential to outperform chemical catalysts (Sulaiman, 2007). Lipases can be found in a vast number of microbial species: the bacteria *Pseudomonas fluorescens (Iso, 2001)* and *P. cepacia (Deng, 2005),* the yeasts *Candida antarctica (Kinney A.J., 2005) and C. rugosa (Chen, 2003),* and the fungi *Rhizomucor miehei (Soumanou, 2003), R. oryzae (Matsumoto, 2001), and Thermomyces lanuginosus (Xu, 2004).*

Table 3.2 - Catalysts Categories

Categories			**Name**
Chemical	Homogeneous	Alkali	- Sodium hydroxide; - Sodium methoxide; - Potassium hydroxide; - Potassium methoxide; -Sodium amide; - Sodium hydride; -Potassium amide; - Potassium hydride
		Acid	- Sulphuric acid; - Phosphoric acid; - Hydrochloric acid; - Organic sulfonic acid

Categories		Name
Heterogenous	Alkali	- Waste material based catalyst; - Boron group based catalyst; - Transition metal oxides and derivatives; - Alkali metal oxides and derivatives; - Mixed metal oxides and derivatives ; - Carbon group based catalyst
	Acid	-Ion-exchange resins

3.4 Feedstock of biodiesel

Biodiesel feedstock can be categorized into three groups: vegetable oils (edible or non-edible), animal fats, and waste cooking oil including triglycerides (Borugadda and Goud, 2012). Among all groups, production from edible vegetable oils is the most popular one, as currently more than 95% of the world biodiesel is produced from edible vegetable oils such as rapeseed, soybean, sunflower and palm (Borugadda and Goud, 2012). This may be explained because of these cultures availability, portability, renewability, high heat content (about 88% of D2 fuel), low sulfur and aromatic compounds content, and biodegradability. The drawback is however that a continuous and large-scale production of biodiesel from edible oils competes with food supply in the long term (Gui, 2008). This causes the inflation of edible oils prices and causes serious food supply problems, in particular in developing countries where most of these plants are produced. Additionally and importantly, the increasing demand for extensive use of land for the production of oleaginous plants causes massive deforestation, with long-term consequences in biodiversity and climate (Borugadda and Goud, 2012). Therefore, the rapidly growing world population and rising consumption of biofuels, increasingly demand for more food and biofuels (Balat, 2011). Based on the above, one may say that the price of biodiesel mostly depends on the price of the feedstock. In fact, the cost of feedstocks is revealed to account for 60 - 75% of the total cost of biodiesel fuel production (Huang, 2010b), and that the economic viability of the biodiesel industry in the near future is compromised by economical and environmental factors, biodiesel predictably loosing competitiveness to the petrol-derived diesel.

In order to try to overcome these disadvantages, one area of research is the search for efficient non-edible oil sources, which are not suitable for human consumption. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel: besides being unsafe to eat, in contrast to the edible oils, non-edible oil crops can be grown in wastelands which are unsuitable for food crops and which cost of cultivation is minor (Borugadda and Goud, 2012). The disadvantage of using these oils is that most non-edible oils contain high free fatty acids, a fact that may lead to the need of multiple chemical steps or alternate approaches to produce biodiesel (Canakci, 2001b). Thus, the production cost may be increased and the ester yield may lower. Throughout the world, large amounts of non-edible oil plants are available in nature, some of which already used in edible and non-edible oil production. The types of vegetable oils used are listed in Table 3.3**.**

New generation feedstocks of biodiesel include microalgae. Microalgae are photosynthetic (Chisti, 2008, Balat, 2011), therefore able to grow on minimal amounts and variety of nutrients, and like all microorganisms, can be multiplied very fast in small spaces (Huang, 2010a). This does not mean that the technology for the multiplication of photosynthetic microalgae is inexpensive or energy free. Quite the opposite, cultivating large amounts of algae is expensive and technologically defying. Anyway, microalgae have long been recognized as potentially good source for biofuel production because of their high oil content and rapid biomass production (Sharma, 2008), and it appears to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels (Balat, 2011).

Table 3.3 - Types of Vegetable Oils used in biodiesel production

Categories		**Name**
Vegetable Oils	Edible	*- Apeseed;* *- Soybean;* *- Sunflower and palm*
	Non-edible	*- Jatropha tree (J. curcas);* *Karanja (P. pinnata);* *- Tobacco seed (N. tabacum L.);* *- Rice bran;* *- Mahua (M. indica);* *- Neem (A. indica);* *- Rubber plant (H. brasiliensis);* *- Castor;* *- Linseed;* *- Microalgae*

The fats derived from animals include tallow (Oner, 2009), white grease or lard (Lu, 2007) and chicken fat (Guru M, 2010). They are low in FFAs and water, they are clean and renewable (Sheedlo, 2008) and they offer an economic advantage because they are often priced favorably for conversion into biodiesel (Wen Z, 2009). However, their availability is a limited, meaning these would hardly satisfy the fuel needs of the world.

Waste cooking oils (WCO) also offer a significant potential as low-cost raw material for biodiesel production. The price of waste cooking oil is 2–3 times cheaper when compared with virgin vegetable oils (Phan, 2008), which turns this feedstock into a promising alternative. In fact, a massive amount of WCOs is being generated all over the world, and its management is tough, causing disposal problems and wide contamination of the ground water and land. Due to legislation gaps, and/or absent police supervision, or simple by ignorance, large amounts of waste cooking oil are discharged into rivers and landfills (Balat, 2011). This way the use of waste cooking oil to produce biodiesel offers significant advantages because of the reduction in environmental pollution (Balat, 2008). Despite being a virtually inexhaustible source of energy, the disadvantage of the use of this feedstock consists in the presence of undesirable components such as FFAs and water (Jacobson, 2008).

3.5 Challenges of biodiesel production

Apart from the sustainability challenges raised by the environmental and politic-economical problems posed by the use of fertile arable land to produce vegetal species for fuel, there are several technical challenges that need to be attended in order to make biodiesel profitable (Ma, 1999). First and foremost, to lower production costs, low-cost fats and oils should be used as raw materials. Nevertheless, one of the major problems associated with these is the presence of water and free fatty acids in solution that can lead into the formation of soap during the transesterification of the triglyceride in the presence of some catalysts, diminishing the yield, and requiring refining to remove the soap. This is because FFA’s are a potential contaminant in oils and fats (Van Gerpen, 2008). Therefore, the quality of the feedstock used in the transesterification process, which is directly linked to the formation of soap, is determinant.

The second pressing issue in biodiesel production process is the inevitable production of large amounts of raw glycerol (De Torres *et al.*, 2012) in a 1:10 ratio (Posada *et al.*, 2012). For every 45.3 kg of biodiesel produced, 4.53 kg of crude glycerol are created (Cardona C, 2007). Approximately, it constitutes about 10 % (wt/wt) of the total product, and presents a 80%-88% purity (Ayoub and Abdullah, 2012, Nitayavardhana and Khanal, 2011). As the biodiesel industry is rapidly expanding, a world-wide glut of crude glycerol is being created (Yazdani, 2007). Raw glycerol comes in uneven and variable mixture with contaminants and therefore, it requires expensive purification in order to become, at least, ready for use in the food, pharmaceutical, or cosmetics industries (Nitayavardhana). This way, biodiesel producers must seek for large volume alternative methods for its disposal, as the valorisation of glycerol, turning it into added-value products, has a potential to improve the profitability of biodiesel in a broader bio refinery scenario (Abad and Turon, 2012).

3.6 Glycerol

The concept of the words ‘glycerine’ and ‘glycerol’ are often misunderstood. Generally, the word ‘glycerine’ refers to purified commercial products containing more than 95% of glycerol, whereas the word ‘glycerol’ specifically refers to the chemical compound (Table 3.4) (Ayoub and Abdullah, 2012). Glycerol is the simplest trihydric alcohol there is (Ayoub and Abdullah, 2012). It is a colourless fluid with sweetish taste, viscous at room temperature, and odourless (Pagliaro, 2008a), which is virtually nontoxic to human health and to the environment (Administration, 1979). Glycerol is non-inflammable due to a high boiling point. It is hygroscopic and therefore soluble in water (owing to its three hydrophilic hydroxyl groups) and alcohols, and hardly at all in many common solvents, with the exception of hydrocarbons (Ayoub and Abdullah, 2012). Glycerol is the metabolic intermediate and structural component of the major classes of biological lipids, triglycerides and phosphatidyl phospholipids from all range of cells from bacteria to man (Pagliaro, 2008a). At low temperatures, glycerol tends to supercool instead of crystallizing (SDA., 1990). Water solutions of glycerol resist freezing, a property responsible for glycerol's use as an antifreeze in cooling clear liquid systems, such as automobile radiator cooling systems. Because of that, glycerol was the first type of antifreeze used in automobile radiator cooling systems. Though later replaced by ethylene glycol for the mentioned purpose, combinations of an alcohol or a glycol and glycerol are still employed for that application. Glycerol-water and glycerol-alcohol solutions are used in some refrigeration systems and in quick freezing of foods (SDA., 1990). Glycerol is also a usual element of solvents for enzymatic reagents stored at temperatures below 0 °C and it also works as a cryoprotectant of some cells and biological tissues to reduce damage by ice crystals in freezing environments up to -80°C (Miner, 1953).

Crude glycerol is the co-product of biodiesel production. While the pure glycerol has thousands of technological and industrial applications, biodiesel glycerol does not possess a high economic value owing to the presence of a variety of impurities, such as moisture, ash, soap and chloride contents (Ayoub and Abdullah, 2012). It becomes imperative to find new convenient uses for glycerol also in the perspective of reducing the cost of biodiesel production (C.-H. Zhou, 2008). When the alcohol used to operate the transesterification reaction is not totally recovered, these impurities can also include residual methanol. As stated by some reports, crude glycerol from biodiesel industry comprises carbon at about 25%, a small quantity of metals such as Na, Ca, K, Mg, Na, P, and S, a small amount of proteins, fats and carbohydrates (Ayoub and Abdullah, 2012). The refining process of glycerol implies the removal of residual contaminant organic matters, water, salt and odours, so that the refined glycerol becomes with up to 99,5% purity, depending this value upon the purification method used and the initial feedstock's chosen for biodiesel production (Singhabhandhu A, 2010). In Table 3.4 may be seen the specifications of each type of glycerol.

Table 3.4 - Quality parameters of different categories of glycerol (partially based in Hazimah AH (2003) and in Mohtar Y (2001))

Parameter	Crude Glycerol	Purified Glycerol	Commercial glycerol
Glycerol content (%)	60-80	80-99,8	99,2-99,98
Moisture contents (%)	1,5-6,5	0,11-0,8	0,14-0,29
Ash (%)	1,5-2,5	0,054	<0,002
Soap (%)	3,0-5,0	0,56	N/A
pH	0,7-1,3	0,10-0,16	0,04-0,07
Chloride (ppm)	ND(*)	1,0	0,6-9,5
Colour (APHA)	Dark	-	-

*not demonstrated

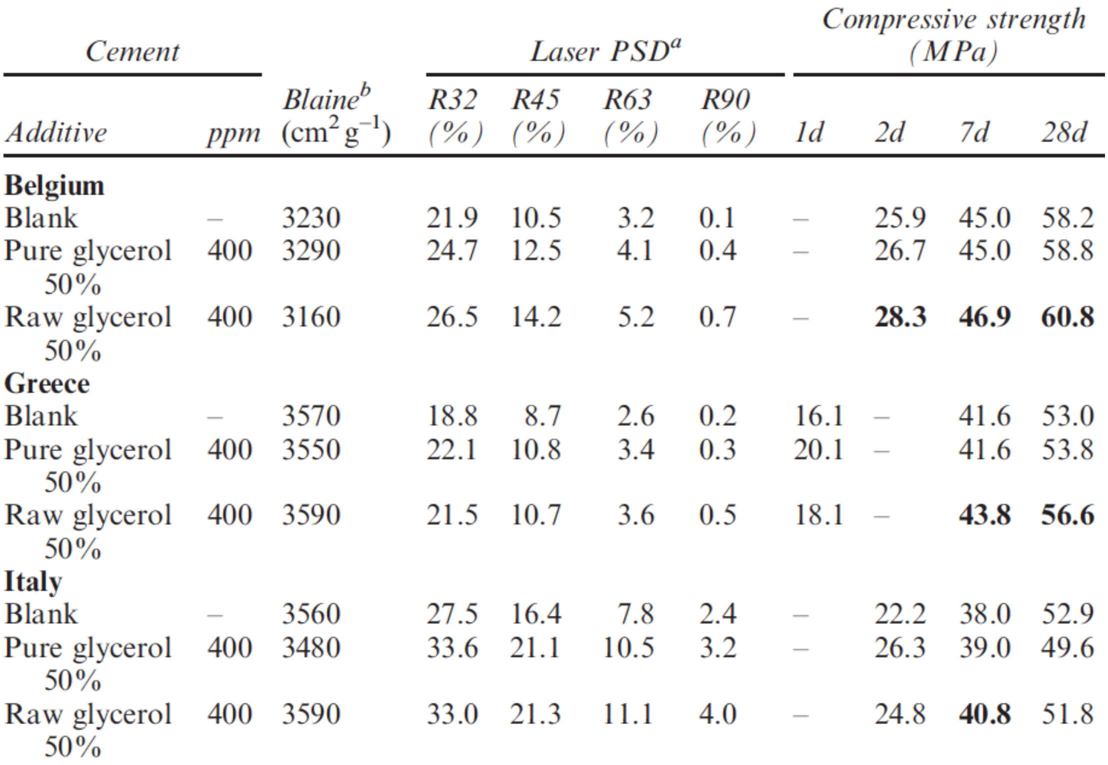
After being refined, glycerol finds applications in a broad diversity of end users. In fact, glycerol is a material of great utility in many areas, as listed in Table 3.5**.**

Table 3.5 - List of currently available and predicted outlets for crude glycerol (Ayoub and Abdullah, 2012)

Field of Application	**New applications of glycerol**
Chemical Industry	Textile industry, plastic industry, explosives industry, polymer industry.
Commodity Chemicals	Natural organic building blocks.
Pharmaceutical industry	Drugs administration adjuvants~~,~~ health supplements
Biotechnology	Cryopreservation of biological materials and cells
	Organic acid, Omega-3, succinic acid by fermentation, EPA by fungus.
Cosmetic industry and oral care	Cosmetics, skin care and renewal, tanning agents, shampoos and hair softeners; tooth paste
Cleaning agents	Softeners, liquid detergents adjuvant
Food	Safe sweeteners, food products preservation, thickening agent.
Livestock feed	Cow and other animals' feed, pigs diet, poultry feed.
Miscellaneous	Basic materials, hydraulic and fire-resistance fluid, de-icing aircraft, thermo-chemical products.
Energy as fossil fuel substitution and biogas	Liquid fuel, conversion into ethanol or hydrogen, burning as fuel pellets, combustion in incinerators, combustion as boiler fuel.

3.7 Crude glycerol as a by-product and an admixture for cement

It has already been shown that pure glycerol has good performance in improving compression strength and that it also works as an anticracking, when combined with a film-forming polymeric material (Pagliaro, 2008a). Besides, small quantities of glycerol (0,5%) can be employed in an additive in order to improve concrete's waterproofing. However, the use of glycerol in cement industry has in the past been precluded by its very high cost (Pagliaro, 2008a), which is not the case of crude biodiesel-derived glycerol. Studies concerning the incorporation of crude glycerol in clinker during milling have taken place (Rossi *et al.*, 2008). Results suggest that crude glycerol from biodiesel can be used as an excellent quality additive for cement because it enhances compression strength and aids grinding and handling properties (Pagliaro, 2008a). According to the authors, tests were carried out concerning the international standards in Belgium, Italy and Greece on three types of clinker, in which pure and crude glycerol from biodiesel production have been added in amounts similar to those used with standard additives, in a water-to-cement ratio of 0,5. The results showed that, in all cases, glycerol in the crude form, containing 5% NaCl and with a slightly orange colour (due to the presence of natural dyes) was found to produce similar or even improved mechanical and chemical properties to those produced by three other additives, including pure glycerol itself**, as demonstrated in** Figure 3.2 (Pagliaro, 2008a).



Cement			*Laser PSD*^{a}				*Compressive strength (MPa)*			
Additive	*ppm*	*Blaine*^{b} ($cm^2 g^{-1}$)	*R32* (%)	*R45* (%)	*R63* (%)	*R90* (%)	*1d*	*2d*	*7d*	*28d*
Belgium										
Blank	–	3230	21.9	10.5	3.2	0.1	–	25.9	45.0	58.2
Pure glycerol 50%	400	3290	24.7	12.5	4.1	0.4	–	26.7	45.0	58.8
Raw glycerol 50%	400	3160	26.5	14.2	5.2	0.7	–	**28.3**	**46.9**	**60.8**
Greece										
Blank	–	3570	18.8	8.7	2.6	0.2	16.1	–	41.6	53.0
Pure glycerol 50%	400	3550	22.1	10.8	3.4	0.3	20.1	–	41.6	53.8
Raw glycerol 50%	400	3590	21.5	10.7	3.6	0.5	18.1	–	**43.8**	**56.6**
Italy										
Blank	–	3560	27.5	16.4	7.8	2.4	–	22.2	38.0	52.9
Pure glycerol 50%	400	3480	33.6	21.1	10.5	3.2	–	26.3	39.0	49.6
Raw glycerol 50%	400	3590	33.0	21.3	11.1	4.0	–	24.8	**40.8**	51.8

Figure 3.2 - Granulometry and performance properties of three cement clinkers with addition of pure or raw glycerol (Pagliaro, 2008a)

The results are surprising and may be explained by an existent synergy between glycerol and the inorganic salts present (Rossi *et al.*, 2008). Moreover, a second major benefit of glycerol as a cement additive comes from its use in grinding and handling technologies. Its use in low levels, either in pure or raw form, leads to significant improvements in the morphologic and rheological properties after the milling step of different cement clinkers (Rossi *et al.*, 2008). In fact, a similar or better performance was obtained in comparison to the typical grinding additives (Rossi *et al.*, 2008).

4 EXPERIMENTAL PROGRAM

4.1 Introduction

In the present chapter, the materials used in the experimental program, as well as the tests and procedures are described.

It is remarked that, as a principle, most of the experiments reported in this dissertation were preceded by trial tests in order to ensure the proper use of equipments and methods, especially in the cases where standards are applied. In particular concern to the tested materials, care was also taken to assure the quality and uniformity of mixtures throughout the experimental program.

The present chapter aims to present the experimental program conducted in the scope of this dissertation, with detailed explanation of the general intents, materials, mixtures, procedures and testing techniques. The experiments took place at the Professor Júlio Barreiros Martins laboratory, situated in the Civil Engineering Department of the University of Minho.

4.2 Overview

The research program consisted in the study of different admixtures, with the main purpose of determining wether the introduction of crude purified glycerol from biodiesel production into cement based materials (cement paste, mortar or concrete) could be beneficial or not. Another important intent was to determine the difference in behaviour of cement-based materials when synthetic glycerol is used, as opposed to the partially purified glycerol obtained from biodiesel production, which is much cheaper and sustainable. It was chosen not to study the performance of cement based materials with incorporation of crude glycerol arising from biodiesel production without any purification, because it would be difficult to guarantee uniformity quality standards, owing to the presence of a variety of impurities, such as moisture, ash, soap and chloride contents (Ayoub and Abdullah, 2012) in that glycerol, as may be seen in Table 3.4 (chapter 3). For that reason, as already stated, it was decided to study the incorporation of the purified one, which has the composition that follows in section 4.3.4.

The study of concrete mixtures and specimens with analysis of their properties would be particular lengthy and expensive when considering the quantity of feedstock required and all the laboratory resources associated (e.g. space to storage feedstock and samples, the occupation time of equipments, and the human resources necessary). Assuming that concrete is a biphasic material, that is, granular skeleton embedded into an agglomerating matrix, it was intended to characterize the behaviour of its agglomerating phase. Therefore, the matrix has been simulated through the fulfilment of cement pastes and mortars, which have been made with part of concrete constituents.

In order to accomplish the aims, it was decided to study admixtures with crude purified glycerol (g), with synthetic glycerol (sg) and with a commercial antifreeze (a). The dosage of g (or sg) was considered within the overall liquid content (i.e. the crude glycerol solution was considered as a partial substitute of water in the dosage). By default, all mixtures had a liquid to cement ratio (l/c) of 0,5. The inclusion of glycerol was made into the liquid, i.e. l=w+g or l=w+sg.

The overall strategy of experiments in the fresh and hardened state is outlined in Figure 4.1. With regard to the fresh state tests, flowability and set time determination tests were performed. In what concerns the hardened state ones, several campaigns have been conducted in order to evaluate the mechanical and the durability properties of admixtures containing crude purified glycerol, such as compressive, flexural and splitting tensile strengths, shrinkage, and elasticity modulus evaluation.

In what concerns the shrinkage tests, this investigation has focused on the drying shrinkage only, which is by far the most relevant cause of shrinkage in regular concretes applied in Portugal. It occurs in hardened concrete as a result of evaporation of internal water (Li and Yao, 2001).

After analysing the results of the set-time tests and also of the compressive and flexural strengths tests, it was decided to perform an elasticity modulus determination test, through the EMM-ARM methodology, which is capable of analysing the kinetics of the elasticity modulus evolution since the instant of casting.

Several testing methods exist for evaluating the durability (or durability indexes) of concrete and various quantitative measures are used to describe progressive damage. In the present research, the following tests were selected: carbonation test, the oxygen and water permeability tests and the water absorption through immersion test.

As already reported in chapter 3 of the present document, glycerol was the first type of antifreeze used in automobile radiator cooling systems and, besides, it also works as a cryoprotectant to reduce damage by ice crystals in some organisms (Miner, 1953). That said, it was intended to understand if crude purified glycerol could lower the freezing point of the water.

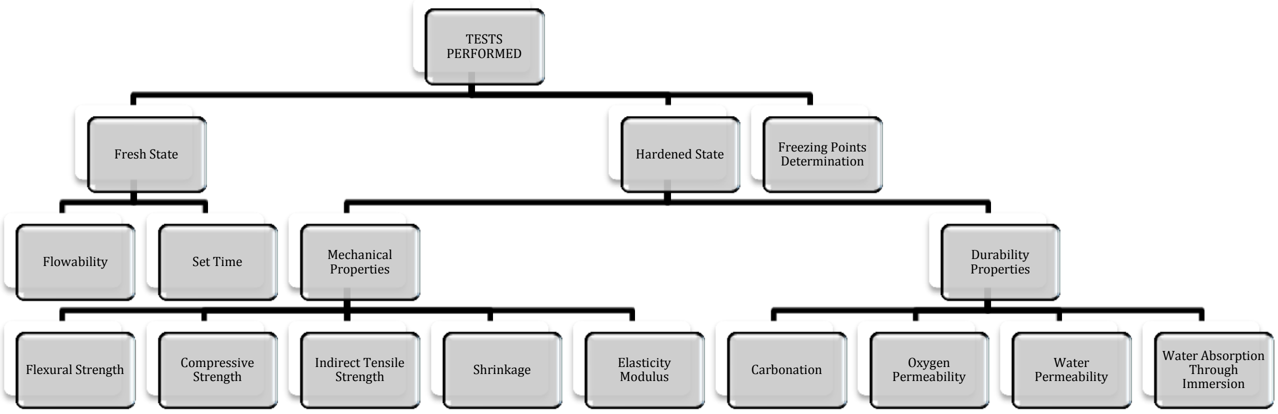


Figure 4.1 Overview of the experimental program

Different admixtures regarding different substitution amounts of incorporation of the already mentioned materials were prepared and casted into different types of specimens. The strategy of testing in terms of specimen size, ages of testing and number of specimens per kind of test is shown in

Table 4.1. It should be noted that all the experiments were performed on cement paste specimens, except for the case of permeability and water absorption through immersion tests.

Table 4.1- Specimens used in this research

Test	Specimen	Age (days)	Number of specimen per test
Flowability	-	0	-
Vicat Needle	-	0	-
Flexural Strength	3 prims (4x4x16 cm^3)	3 7 28	3 3 3
Compressive Strength	*	3 7 28	3 3 3
Indirect Tensile Strength	ϕ5cm x 50 cm^3	28	4
Shrinkage	2,5x2,5x25 cm^3	0-28; 56; 84	3
EMM-ARM	ϕ2cm x 55 cm^3	0-7	1
Porosity	ϕ5cm x 40 cm^3	28	2
Oxygen Permeability	ϕ5cm x 40 cm^3	28	2
Water Permeability	ϕ5cm x 40 cm^3	29	2
Carbonation	4x4x16 cm^3	56 63 70	3 3 3

- Specimens used in the compressive tests are the two halves that result from the flexural one.

4.3 Materials

4.3.1 Ordinary Portland cement

Portland Cement type I, 42.5R was used in accordance to EN 197-1 (CEN, 2000a) specification. All the cement used in this experimental program was supplied by SECIL in a single remittance, thus minimizing the effects of variability in cement properties. Ordinary Portland Cement type I was chosen in order to simplify the interpretation of results, avoiding the necessity of evaluation of interactions with supplementary materials that would possibly occur in other types of cement.

The physical and mechanical properties of the cement are presented in Table 4.2 whereas the chemical composition and fineness of the cement is shown in Table 4.3. Both these tables present information regarding the same type of cement provided by the same supplier, tested respectively in 2004 and 2009.

Table 4.2 - Physical and mechanical properties of CEM I 42,5R (SECIL, 2004)

Physical Properties		**Mechanical Properties**	
Initial Setting time	≥ 60 min	**Compressive Strength (MPa)**	
Expandability	≥ 10 mm	**2 days**	≥ 20
		7 days	-
		28 days	≥ 42,5 and ≤ 62,5

Table 4.3 - Chemical Composition (%) and fineness of CEM I 42,5R (Azenha, 2009)

SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO (Total)**	**MgO**	**SO_3**	**K_2O**	**Free CaO**	**Loss on Ignition**	**Blaine (cm^2/g)**
19,82	4,22	3,4	62,66	2,21	3,47	-	-	-	4112

4.3.2 Sand

The fine aggregate used to perform mortars was Standard Sand certified in accordance with NP EN 196-1 (CEN, 2006a). In Table 4.4 is shown the physical and chemical properties of this sand.

Table 4.4 - Physical and chemical properties of the Standard Sand (SNL, 2007)

Product Name	**Standard Sand**
Chemical Characteristics	Quartz - Also known as Silica sand (SiO_2)
Physical state	Solid
Form	Crystallized
Form of grains	Sub angular
Colour	White
Smell	Odourless
pH	7
Fusion temperature	1610° C
Boiling temperature	2230°C
Decomposition temperature	None
Mass volume	Absolute: 2,63 g/m^3; Apparent: 1,6 g/cm^3
Flash point, self-inflammation temperature and explosive characteristics	Not applicable
Solubility	Insoluble in water, soluble in hydro-fluoric acid

4.3.3 Synthetic glycerol

The synthetic glycerol, Glycerol A.R., was supplied by HIMEDIA. Its main properties are shown in Table 4.5.

Table 4.5 - Synthetic glycerol properties (HIMEDIA, 2013)

Product Name	Glycerol, A.R.
Synonym	Glycerin; 1,2,3-Propanetriol, Glycerin
Molecular Formula	$C_3H_8O_3$
Molecular Weight	92.09
Shelf Life	4 years
Appearance	Colorless to faint yellow syrupy, very hygroscopic liquid
Solubility	1 mL miscible in 1 mL of water
Chloride (Cl)	≤ 0.0025%
Heavy metals (as Pb)	≤ 0.0005%
Iron (Fe)	≤ 0.0004%
Sulphate (SO4)	≤ 0.0030%
Sulphated ash	≤ 0.01%
Water (K.F.)	≤ 2.00%
Assay (NaOH Titration/GC)	min. 99.50 % max. 101.00 %
Flash Point (°C)	160 °C (320ºF)
Storage Temperature (°C)	Store below 30°C

4.3.4 Crude purified glycerol

The crude purified glycerol used in the research program was supplied by Prio Energy enterprise, in a quantity of 100L. It possesses a yellowish colour, as observable in Figure 4.2. The main properties of this product, according to information provided by the supplier, are shown in

Table 4.6. This biodiesel was produced from genetically modified raw materials, which can either be vegetable oils or animal fats, and short chain alcohols, and without the use of Jatropha oil or used vegetable oils (PRIO, 2012).

Figure 4.2 - Sample of Crude Purified Glycerol

Table 4.6 – Crude Purified Glycerol Analysis Report (PRIO, 2012)

Parameter/Units	Method	Limits	Results
Density of Glycerol (kg/m^3) at 20ºC – water solutions		≥ 1208	1264,0
pH			6,5
Water Content [%wt]	Karl Fisher Tiration	8 to 13	9,0
Sodium Chloride [%wt]	AOC Ea 2-38	≤ 5	4,9
Glycerol Content [%wt]	AOC Ea 6-51	> 80	90,4
Methanol Content [%wt]	EN 14110	≤ 0,1	< 0,001
Matter organic non glycerol (MONG) [%wt]	NF T60 368	≤ 2,0	< 0,5

As this analysis bulletin provided by Prio states out that the crude purified glycerol contains 4,9% of sodium chloride, it was decided to request for a salinity analysis of a sample of this glycerol. The analysis took place in LabMinho – Water and Industrial Effluents Analysis, Lda. and the results showed that the content of sodium chloride was of 132mg/L (0,132g/L). In fact, the quantity of salt that is present is very small, which sustains the idea that the sodium chloride does not have relevant effect in the results of this research. A work conducted by Griffin and Henry (1964) regarding the incorporation of sodium chloride into concrete reported that at a mixing-water salinity of approximately 25 g/L, strength is improved and corrosion of mild steel is negligible (Griffin and Henry, 1964). Many other works regarding the incorporation of sodium chloride or of sea water in concrete mixtures are addressed in literature (Emmanuel *et al.*, 2012, Har *et al.*, 2010), but none of them focuses on such a small quantity of sodium chloride as the one that actually occurs in the specimens of this experimental program. Therefore, the quantity of NaCl can be considered negligible.

4.3.5 Antifreeze

An antifreeze admixture (a), Sika Antigel, which is suitable to produce cement-based materials that are meant to be exposed to temperatures until -6 to -8ºC during their curing period, was provided by Sika. The main properties of this product are listed in Table 4.7.

Table 4.7– Sika Antigel properties (SIKA, 2011)

Product Name	Sika Antigel
Description	Liquid admixture used to produce cement-based materials at low temperatures. It is free from chlorides.
Uses	Antifreeze admixture used to protect concrete that may be exposed to temperatures from –6 °C to –8 °C during their curing period. It is used in all works where temperatures are low during the day and very low during the night.
Characteristics	Improves workability; Reduces the need of water, for the same workability; Improves concrete strength when placed at low temperatures; Improves concrete permeability.
Appearance/Colour	Colourless
Density (20ºC)	Approx. 1,25 kg/l
pH	Approx. 7
Solids content	Approx. 35%
Recommended Dosage	1%

4.3.6 Water

The water used to prepare the cement paste and mortars in this research program was collected from the public water supply of the city of Guimarães (tap water), according to the standard EN 206-1 (CEN, 2000b) and also fulfilling the specification E 372 (LNEC, 1993a). In fact, according to this specification, if the water is drinkable, it is also adequate for the production of cement-based materials.

4.4 Mixes and general procedure

4.4.1 Compositions of cement pastes and mortars under study

Mixture 1 is considered the reference one (termed P_R), solely composed of CEM I 42.5 (c) and water (w), with a w/c ratio of 0,5. Such elevated w/c ratio was related to the intention of assuring a large extension of the hydration reactions, without any kind of hindering associated to water shortage in the pore network. The summary of the mortar/cement paste mixtures studied is shown in Table 4.8.

The influence of introducing crude purified glycerol solution (g) into cement paste was investigated through mixtures 2-5, in which the percentage of crude purified glycerol solution ranges the values: 0.5%; 1%; 3% and 20%. Nonetheless, the liquid (w or w+g) to cement (c) ratio was kept constant and equal to 0,5. The four selected percentages for crude purified glycerol solution were related to the evaluation of its performance as an admixture, with typical admixture dosage (usually below 3%), following a strategy of partial replacement of the water in the mixture. The nomenclature of mixtures 2 to 5 is made in accordance to the percentage of crude purified glycerol solution: P_0,5%g, P_1%g, P_3%g and P_20%g. It should be noted however that the glycerol content of the crude purified glycerol solution is of approximately 90% (according to Table 4.6). Therefore, as an example, in order to assure 1% of glycerol in overall mass, a slightly higher percentage of crude purified glycerol solution would have been necessary: 1,11%.

Regarding the synthetic glycerol, two substitution ratios are considered in mixtures 6-7, with sg/w equal to 1% and 20%, respectively (mixtures P_1%sg and P_20%sg), while the influence of the antifreeze admixture was evaluated through accomplishment of mixture 8, P_1%a, through the incorporation of 1% of the antifreeze.

In addition to this, a reference mortar and three other mortars containing 0,5%, 1% and 3% of crude purified glycerol, hereby denominated as M_R, M_0,5%g, M_1%g and M_3%g, were also performed.

Table 4.8 - Mixtures Performed

	Name	**c (g)**	**w (g)**	**s (g)**	**g (g) ***	**sg (g)**	**a (g)**	**l/c**
1	P_R	10000	5000					0,5
2	P_0,5% g	10000	4944,69		55,31			0,5
3	P_1% g	10000	4889,38		110,62			0,5
4	P_3% g	10000	4668,14		331,86			0,5
5	P_20% g	3000	836,28		663,72			0,5
6	P_1% sg	3000	1470			30		0,5
7	P_20% sg	3000	900			600		0,5
8	P_1% a	5000	2450				50	0,5
9	M_R	450	225	1350				0,5
10	M_0.5% g	450	223,98	1350	1,02			0,5
11	M_1% g	450	222,51	1350	2,49			0,5
12	M_3% g	450	217,53	1350	7,47			0,5

Despite the diversity of tests that have been executed, they were not all intended to be accomplished among all the admixtures performed. Table 4.9 shows which mixtures were subjected to each test.

Table 4.9 – List of mixtures submitted to the different tests

Test **Mixture**	1	2	3	4	5	6	7	8	9	10	11	12
Flowability	X	X	X	X		X		X				
Set Time	X	X	X	X		X		X				
Compressive Strength	X	X	X	X		X		X				
Flexural Strength	X	X	X	X		X		X				
Tensile Splitting Strength	X	X	X	X								
Shrinkage	X	X	X	X								
EMM-ARM	X		X	X		X						
Carbonation	X	X	X	X								
Oxygen Permeability									X	X	X	X
Water Permeability									X	X	X	X
Water Absorption Through Immersion									X	X	X	X

The compressive and flexural strength tests were meant to be accomplished in mixtures 1-8. However, as mixtures 5 and 7 revealed extensive cracking upon unmoulding, as shown in Figure 4.3, they were rendered unusable for experimenting. Such large quantity of glycerol in the mixture (20%) is therefore considered unfeasible.

Tensile splitting strength was performed only with mixtures 1-4 in order to check if it was observed the same tendency of the one that was occurring in relation the to flexural strength tests. Shrinkage tests were performed among mixtures 1-4, in order to understand if crude purified glycerol could act as a shrinkage reducer. The EMM-ARM methodology was only applied to mixtures 1, 3, 4 and 6 due to equipment availability limitations.

Figure 4.3 - Photo of specimens from mixtures 5 and 7 upon unmoulding after 20h

In order to accomplish the oxygen and water permeability tests, mortars have been produced. The necessity of producing mortars instead of cement pastes to perform these tests is justified by the following reasons:

- A trial test was previously performed in cement pastes and it was concluded that it was not possible to perform these tests in cement pastes, owing to the cracks that occur at the final drying stage.

- The procedure adopted required the use of mortars.

In summary, permeability and water absorption tests were performed in mixtures 9, 10, 11 and 12. Carbonation tests were just accomplished in mixtures 1-4, thus covering all the range of mixtures with g, together with the reference mixture.

Bearing in mind that glycerol is used in refrigeration systems and in quick freezing of foods (SDA., 1990) and that it works as a cryoprotector of cells and biological tissues (Miner, 1953), it was of primordial importance to figure out if the incorporation of crude purified glycerol could lower the freezing point of water solutions. Therefore, five water solutions were prepared, all of them with a content of 150g of water, and submitted to a freezing point determination test. The admixtures were composed by: a) water; b) water with 1% of crude purified glycerol; c) water with 3% of crude purified glycerol; d) water with 1% of synthetic glycerol; and d) water with 1% of the commercial antifreeze admixture.

A summary of the standards and/or procedures that have been followed in the scope of this dissertation is shown in Table 4.10.

Table 4.10 - Tests and Standards

Test	**Standard/Methodology**
Flowability	NF EN P18-358 (CEN, 1985)
Set Time	NP EN 196-3
Freezing Points Determination	Korhonen (2011)
Compressive Strength	NPEN 196-3 (CEN, 2006b)
Flexural Strength	NPEN 196-3 (CEN, 2006b)
Indirect Tensile Strength	NP EN 12390-6 (CEN, 2003)
Elasticity modulus	Azenha *et al.* (2011)
Shrinkage	C490-04 (ASTM, 2004)
Porosity	E 394 (LNEC, 1993c)
Oxygen permeability	Grube (1984)
Water permeability	Cabrera (1999)
Carbonation	E 391 (LNEC, 1993b) Fpr 12390-12 (CEN, 2010)

4.4.2 Mixing, casting and curing

Cement pastes

Mixes were prepared in metal containers using a vertical paddle, with a capacity of 15L. According to the standard NPEN 196-3 (2006), the materials have been added in the container according to the following sequence of procedures: i) cement was placed; ii) water was added to the cement (such instant is designated by “t=0”); iii) mixing started at 60 rpm and extended for 90 seconds; iv) mixing stopped for 30 seconds and glycerol (or antifreeze) was incorporated when applicable and v) mixing resumed at 60 rpm for another 90 seconds.

Mortars

Mortars were prepared in a metal container, with a maximum capacity of 5L. With respect to the standard NPEN 196-1 (2006), the materials have been added in the tub according to the following sequence of procedures: i) cement was placed; ii) water was added to the cement (such instant is designated by “t=0”); iii) mixing started at 60 rpm and extended for 30 seconds; iv) while mixing continued at 60 rpm for another 30 seconds, sand was added; v) mixing stopped for 90 seconds and glycerol was introduced when applicable and vi) mixing resumed at 120 rpm for 60 seconds. The water content in sand was measured, according to NPEN 196-1 (2006), and mortars were only produced when the water content and was found to be less than 0,2%.

After this procedure, cement pastes and mortars have been placed in the respective moulds (when applicable), which had been previously oiled.

Overall information about the specimens that were cast, in terms of geometry, number of specimens, and corresponding ages of testing (when applicable) was already shown in Table 4.1.

Before submitting the specimens produced to perform the oxygen and water permeability tests to them, they have been wet cut to obtain the required dimensions (ϕ5cm x 40 cm^3).

The different tests performed required different curing conditions that may be analysed in Table 4.11. That follows:

Table 4.11 - Curing Conditions in compliance with each test performed

Test	Curing Conditions	Further Clarification
Flowability	-	Test performed immediately after the production of pastes.
Set Time	Specimens were immersed into a container full of water at 20±1ºC until the first measure and, since then, they were held in the wet chamber (20±1ºC) outside the water.	Specimens were not demoulded until the instant of measuring the final set.
Compressive Strength	Curing at 20ºC: After demoulded, specimens were held in the wet chamber inside water, until the age of test.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1ºC and, after 20h, they were demoulded.
	Curing at -1ºC: After demoulded, specimens were held in the deepfreeze at -1ºC, until the age of test.	
Flexural Strength	Curing at -1ºC: After demoulded, specimens were held in the deepfreeze at -1ºC, until the age of test. Curing at 20ºC: After demoulded, specimens were hold in the wet chamber inside water, until the age of test.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
Tensile Splitting Strength	After demoulded, specimens were held in the wet chamber inside water, until the age of test.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
Shrinkage	After demoulded, they were hold in a chamber with controlled temperature and humidity (23±1ºC and 61±5%) were length change has been measured.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
EMM-ARM	Specimens were cured with a sealing cap.	Specimens were not demoulded.
Oxygen Permeability	After demoulded, specimens were kept in the wet chamber until the age of test, covered with cling film in order to halt water loss.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
Water Permeability	After demoulded, specimens were kept in the wet chamber until the age of test, covered with cling film in order to halt water loss.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and,

		after 20h, they were demoulded.
Water Absorption Through Immersion	After demoulded, specimens were kept 14 days in the wet chamber inside water and another 14 days outside water in the wet chamber. After this, they were located into the carbonation chamber until the age of test.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
Carbonation	After demoulded, specimens were kept 14 days in the wet chamber inside water and another 14 days outside water in the wet chamber. After this, they were located into the carbonation chamber (HR, TEMP) until the age of test.	Immediately after placement in the mould, specimens were placed into the wet chamber (RH above 95%) at a temperature of 20±1C and, after 20h, they were demoulded.
Freezing Points	-	Water solutions were immediately placed in the deepfreeze at -20ºC.

4.5 Experimental techniques

The present section presents the description of the experimental techniques and procedures applied during this research. The description encompasses the following techniques: flowability, set time, compressive and flexural strengths, indirect tensile strength, shrinkage, elasticity modulus, water and oxygen permeabilities, carbonation and freezing points determination.

4.5.1 Marsh Cone – flowability determination

This test may be divided into two distinct phases: the first one consists in the manufacture of the paste; and the second one in the gauging of time (fluidity time or drain time) that a certain volume of that paste takes to flow through the orifice of the cone. The equipment used and the procedure adoptive to the production of the pastes and to the execution of the test, were based in French standard NF P18-358 (CEN, 1985). Tests were carried out so that to produce 1200 cm^3 of cement paste, considered the volume sufficient to the accomplishment of this test.

After the production of each mixture, cement paste was spilled into the cone while its outlet, with an inside diameter of 8.3 mm, was integrally wrapped, until bringing a volume of 1300 cm^3. The distance between the lower extremity of the pump discharge and the bottom of the measure pan was set in 30 cm. Subsequently, in order to allow the draining, the pump discharger was uncovered. At that moment, the measurement of flow time started.

Test result consists in the determination of the indispensable time to allow the flow of 800 cm^3 of cement paste. The test is concluded when the volume of cement paste deposited in the measurement pan reaches the referred volume. Flow times have been measured after 6 minutes since the addition of water to cement.

4.5.2 Vicat's needle – set time determination

The Vicat test is a standard test for measuring the setting times of cement paste (CEN, 2006b). The initial set defines the onset of rigidity, when bleed water disappears and finishing can begin, whereas final set approaches the time when finishing becomes impossible, when measurable strength development begins. The physical contextual of the test is founded on the resistance of a paste to dynamic penetration by a needle with (shear strain), obtaining information about the initial and final set time, which is very useful to compare cement setting properties.

In order to perform this test, it was followed the standard NP EN 196-3 (CEN, 2006b).

4.5.3 Flexural strength

Flexural strength tests have been fulfilled according to the procedure described in NP EN 196-1 (CEN, 2006a). Upon rupture, the halves of the specimen were re-used for compressive strength testing. Two campaigns of flexural strength tests have been performed: one after curing at 20ºC and another after curing at -1ºC. At the prescribed time, specimens were transported out of their cold rooms and allowed to thaw up to a controlled temperature of about 20° C at their center of mass (which took at about half an hour). This consisted in a necessary precaution to avoid testing frozen specimens, which could yield false high strengths that vanish upon thawing.

Tests have been performed in three prismatic specimens of each mixture and the centre-point load has been applied at the centre span at a constant velocity of 50±10 N/s until rupture. After rupture, the semi-prisms have been covered with a wet rag, until the moment of the compressive strength testing.

In Figure 4.4 a photo of a cracked specimen can be observed, highlighting the two halves to be used for compressive strength testing.

Figure 4.4 - Two halves of the specimen to be used for compressive strength testing after the flexural strength procedure

Flexural strength is determined by the following formula (CEN, 2006a):

$$R_f = \frac{1{,}5 \times F_f \times l}{b^3} \qquad [4.1]$$

Where:

R_f is the flexural strength, in MPa;

F_f is the load applied at the center span, by the time of the rupture, in N;

l is the distance between supports, in mm;

b is the flank of the square section of the prism, in mm.

The value of the flexural strength, in each age, results from the average of the values obtained for three specimens.

4.5.4 Compressive strength

Compressive tests have been carried out according to the procedure described in standard NP

EN 196-1 (CEN, 2006a). Two campaigns of compressive strength tests have been performed: one after curing at 20ºC and another after curing at -1ºC.

Tests have been performed in the two halves of the three cracked prismatic specimens of each mixture and the compressive load has been applied at a constant velocity of 2400±200 N/s until rupture.

Compressive strength is determined as follows (CEN, 2006a):

$$R_c = \frac{F_c}{1600} \qquad [4.2]$$

Where:

R_c is the compressive strength, in MPa;
F_c is the maximum load by the time of the rupture, in N;
1600 is the area of the auxiliary load transmission boards (40mm x 40mm), in mm^2.

The value of the compressive strength, in each age, results from the average of the values obtained for three specimens.

4.5.5 Tensile splitting strength

One of the methodologies used to characterize the behaviour to tensile strength consists of subjecting cylindrical specimens to the indirect tensile strength test, also known as Brazilian test.

The methodology used to perform these tests was adapted from NP EN 12390-6 (CEN, 2003) that describes the methodology used to test concrete specimens. Regarding this methodology, specimens were removed from water and the excess of moisture was eliminated before placing them in the test machine. Stripes of pressed board were also prepared and stowed between the specimen and the steel component, over the entire length of the bottom and top lines of contact of the specimen. The overall test setup is shown in Figure 4.5.

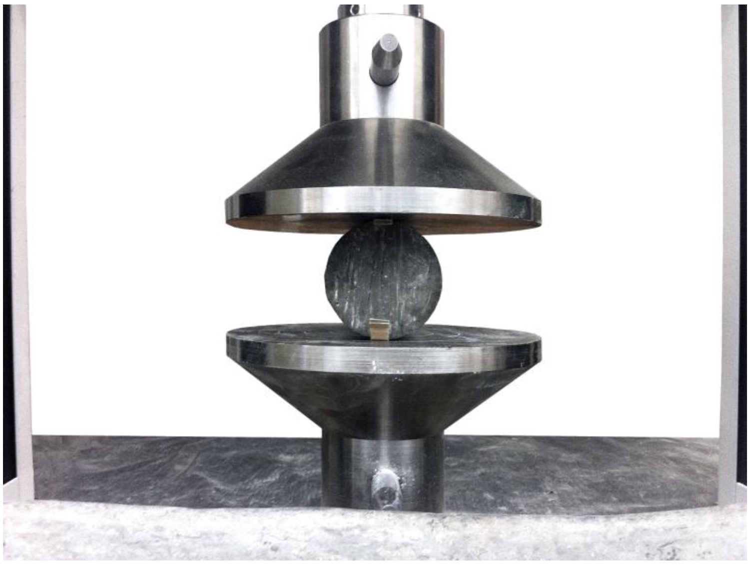


Figure 4.5 - Indirect Tensile Strength Procedure

Tensile splitting strength is determined as follows:

$$f_{ct} = \frac{2\times F}{\pi\times L\times d} \qquad [4.3]$$

where:

f_{ct} is the tensile splitting strength, in MPa;
F is the maximum load, in N;
L_1 is the length of the contact line of specimen, in mm;
d is the dimension of the transversal section, in mm.

The value of the tensile splitting strength results from the average of the values obtained for three specimens.

4.5.6 Shrinkage

Concerning the procedure, the standard C490-04 (ASTM, 2004) was followed. It is of remarkably importance to state that, before filling the specimens with cement paste, a plug in each extremity of the mould has been placed, as highlighted in Figure 4.6, in order to allow the specimen to fit in the length comparator.

Figure 4.6 – Detail of the plug embedded in each extremity of the specimen

The measurement procedure involves a reference frame and analogical indicator that is calibrated at every measurement with a known length invar rod. The measurement of the specimen’s length is made immediately after calibration - see Figure 4.7.

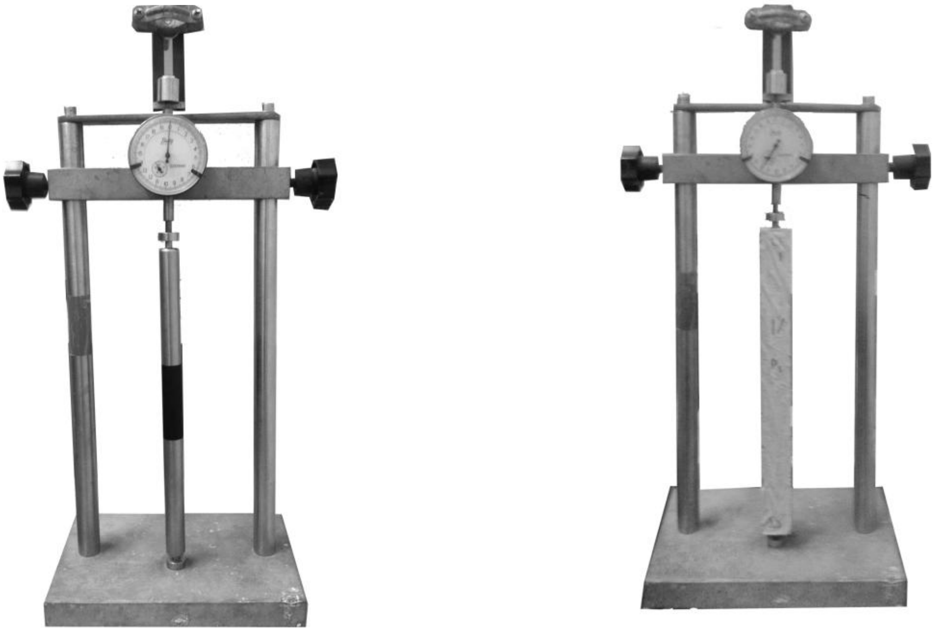


Figure 4.7 – (a) Measure of the length change of the reference bar; (b) Measure of the length change of the specimen

Length change was measured on the four sides of the specimen, upside and upside down, and an average of the results was taken as the comparator reading of the specimen. Weight losses of the admixtures during the 28-days drying period have also been monitored.

Length change is calculated as follows:

$$L = \frac{(L_x - L_i)}{G} \times 100 \qquad [4.4]$$

Where,

L is the change in length at age x, %;
L_x is the comparator reading of specimen at age x, minus comparator reading of reference bar at age x, in mm;
L_i is the initial comparator reading of specimen minus comparator reading of reference bar in mm;
G is the nominal gage length (250mm).

4.5.7 Elasticity modulus evaluation - EMM-ARM methodology

The EMM-ARM methodology consists in measuring the E-modulus through principles that are conceptually similar to the ones adopted in resonant frequency-based methodologies (Azenha *et al.*, 2011). The material to be tested (cement paste) is placed into a mould of known dimensions, stiffness and weight (e.g. acrylic tube), which is in turn placed into known support conditions (e.g. cantilever). An accelerometer is placed at the resulting composite beam, and the monitored accelerations allow identification of the 1st flexural mode of vibration. The method relates the first resonant frequency acquired to the evolving elasticity modulus of the tested specimen (Maia, 2013) using the ambient vibration as excitation to the composite cantilever (Azenha *et al.*, 2011). The main advantages of this method consist in its ability to provide a continuous measurement of the paste or mortar E-modulus, starting right after casting (Azenha *et al.*, 2011) and also in the possibility of extracting quantitative information about the ‘structural setting time’, as well as the changes in the reaction kinetics from a macroscopic point of view caused by the use of admixtures and partial substitutions of cement (Azenha *et al.*, 2010). An example of the results obtained for a plain cement paste and the corresponding cement pastes containing an accelerator and a retarder may be seen in Figure 4.8.

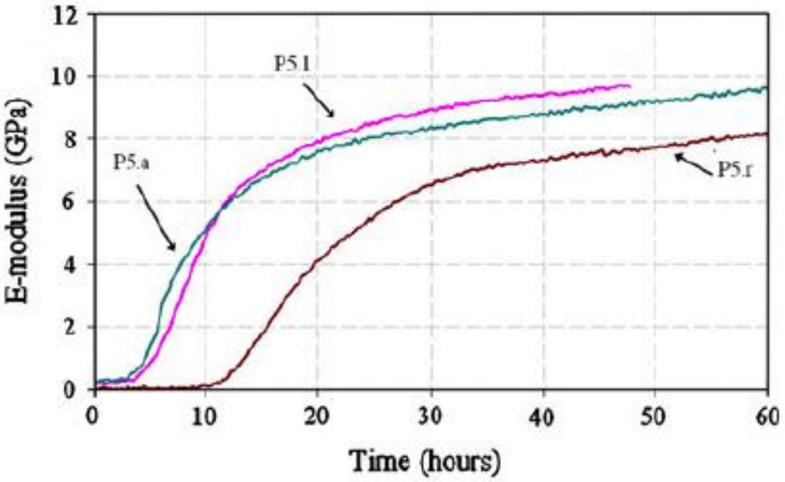


Figure 4.8 - Estimated Ec for plain pastes (P5.1), and for pastes with retarding (P5.r) or accelerating (P5.a) admixtures (Azenha *et al.*, 2011)

The methodology applied in the context of this dissertation consists in casting the cement paste into acrylic tubular moulds - Figure 4.9 a)-, with length is of 550 mm and the inner and outer diameters of 16 and 20 mm, respectively, being one of the extremities closed with a lid - Figure 4.9 b) - before the introduction of the cement paste. After filling the mould, the other extremity of the mould is properly closed. Then, the acrylic tube is fixed through a rigid support, simulating the structural behaviour of a horizontal composite beam - Figure 4.9 d).

In order to monitor the accelerations in the vertical direction induced merely by ambient excitation, an accelerometer is placed at the free extremity of the mould - Figure 4.9 c).

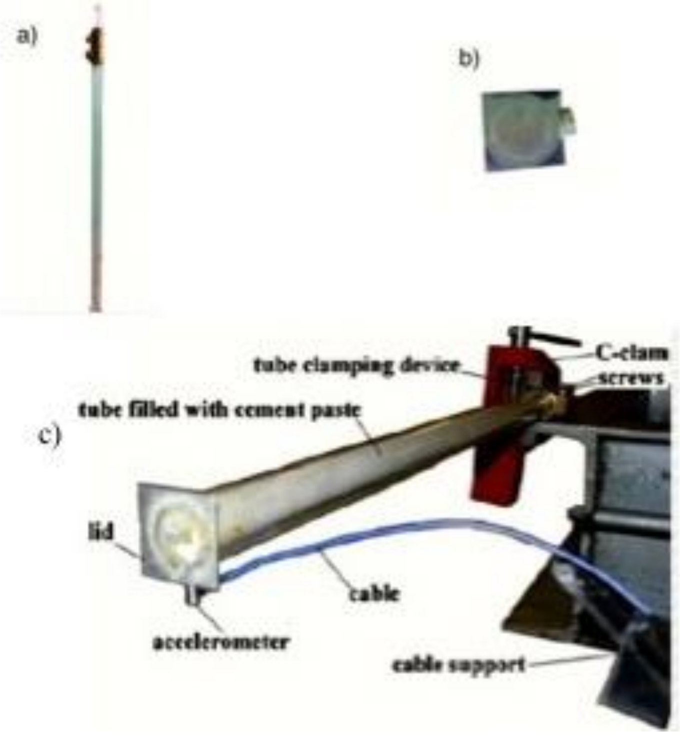


Figure 4.9 – a) Acrylic tube; b) Detail of the lid; and c) Experimental setup in the measuring position for the EMM-ARM and the accelerometer (Azenha *et al.*, 2011)

To facilitate a better understanding of this procedure, a plan view of the scheme of the experimental setup may be seen in Figure 4.10.

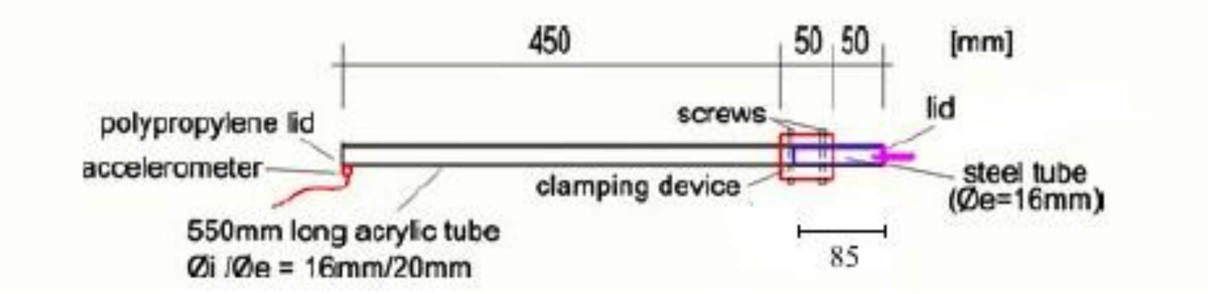


Figure 4.10 - Scheme of the experimental setup (plan view) (adapted from (Azenha *et al.*, 2011))

4.5.8 Carbonation

The procedure adopted followed the standard E 391 (LNEC, 1993b) and the technical specification Fpr 12390-12 (CEN, 2010).

At each testing age, one end of each specimen was sliced to make a 5 cm thick tile to measure the carbonation depth. The newly made end surface of the prism specimen was sealed again and returned to the curing condition. The carbonation depth, which corresponds to the thickness of the unmodified colours layer, was measured after spraying phenolphthalein–alcohol solution onto the sliced surface. In Figure 4.11 may be seen a generic example of a carbonated specimen.

According to these documents, it shall be recorded the mean depth of carbonation for each exposed face of a specimen ($d_{k,\ face}$), the mean depth of carbonation for each specimen ($d_{k,\ spec}$) and calculated the arithmetical mean of the mean carbonation depth of two specimens (d_k).

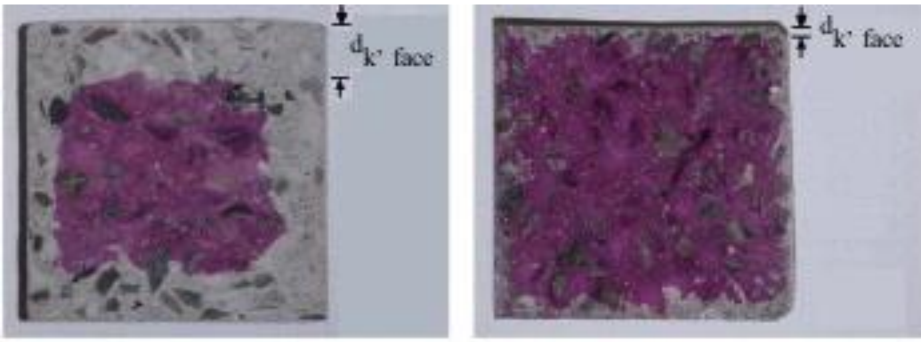


Figure 4.11 – Example of a typical result of a carbonated specimen adapted from (Kim *et al.*, 2009)

4.5.9 Water absorption through immersion

The methodology was adapted from the standard E 394 (LNEC, 1993c), which consists in the determination of water absorption by immersion. Essentially, this test consists in two chief steps: saturating the specimens followed by drying. First, mortars are immersed in water at 20±3 ºC until the change in mass during 24 hours is less than 0,1%, being its saturated mass called as m_2. Subsequently, mortars are dried in a ventilated oven at a temperature of 105±5 ºC, until the difference in mass during 24 hours is less than 0,1%. The dry mass is named m_3.

Porosity is determined as follows:

$$A_i = \frac{m_1 - m_3}{m_1 - m_2} \times 100 \qquad [4.5]$$

Where,

m_1 is the mass of the specimen saturated in the air (g);
m_2 is the hydrostatic mass of the saturated specimen (g);
m_3 is the mass of the dry specimen (g).

The value of the water absorption results from the average of the values obtained for two specimens.

4.5.10 Permeability

In order to determine oxygen and water permeabilities, it was used Leeds' unit permeameter, which was developed in Leeds University (UK) and that has been widely used to determine water and oxygen permeability of concrete and mortars (J.P.C.Gomes *et al.*, ?).

Leeds' unit permeameter was firstly developed with the purpose of determine the permeability to the gas (Grube, 1984) and later, it has been modified in order to allow the measurement of the permeability to the water as well (Cabrera, 1999). This cell is constituted for:

- A compartment to the specimen (**FIGURE 4.12** (a));
- A manometer of pressure with precision (**FIGURE 4.12**(b));
- A supply of stable gas (**FIGURE 4.12** (c));
- Bubble flow meters (**FIGURE 4.12** (d)).

Oxygen Permeability
To measure specimen' oxygen permeability, it was adopted the procedure developed by the Civil Engineer Department of the University of Beira Interior.

Concerning the methodology, after drying specimens in the stove at 110°C for 24 hours, their sides were waterproofed with a thin coat of paraffin, so to ensure that the uniaxial penetration only occurred through the top of the specimens, and then they were left in a desiccator for another 24 hours to allow the tightening of paraffin. Subsequently, each specimen was placed in a cylinder inside a PVC sleeve, under pressure, and then inside the test cell. All the valves were kept closed and then it was opened the oxygen valve and the intermediate valve.

Oxygen was putted down at 3-bar pressure, being the flux of gas measured in the downstream extremity thru a capillary tube. The diameter of the capillary tube was of 2,5mm. Three flux measures were done after 30 minutes, once constant flux was achieved.

Oxygen permeability is determined by the following equation:

$$k_G = \frac{2\nu.L.\eta.\rho_2}{A.(\rho_1^2 - \rho_2^2)} \qquad [4.6]$$

Where,
k_G is the permeability (m^2);
ν is the flow of the fluid (m^3/s);
η is the dynamic viscosity (Ns/m^2);
L_3 is the thickness of the specimen (m);
A is the cross section (m^2);
ρ_1 is the inlet gas pressure (N/m^2);
ρ_2 is the outlet gas pressure (N/m^2).

In the knowledge that oxygen viscosity at 20°C is of 2.02 x 10^{-6} N.s/m^2, the oxygen apparent permeability may be calculated according to the equation:

$$k_0 = \frac{4.04.10^{-5}.\upsilon.L}{A.(\rho_1^2 - 1)} \qquad [4.7]$$

The value of the oxygen permeability results from the average of the values obtained for two specimens.

Water Permeability

Water permeability was measured similarly to the oxygen permeability, also following the procedure developed by the Civil Engineering Department of the University of Beira Interior.

After concluding the oxygen permeability test, a solution of alcohol, phenolphthalein and water was introduced in the valve of the cell. After this, all the valves were kept closed and then it was opened the oxygen valve and the intermediate valve. Oxygen was putted down at 3-bar pressure for three hours. After that, specimens were broken in two halves and the depth of penetration of the solution was measured in five points.

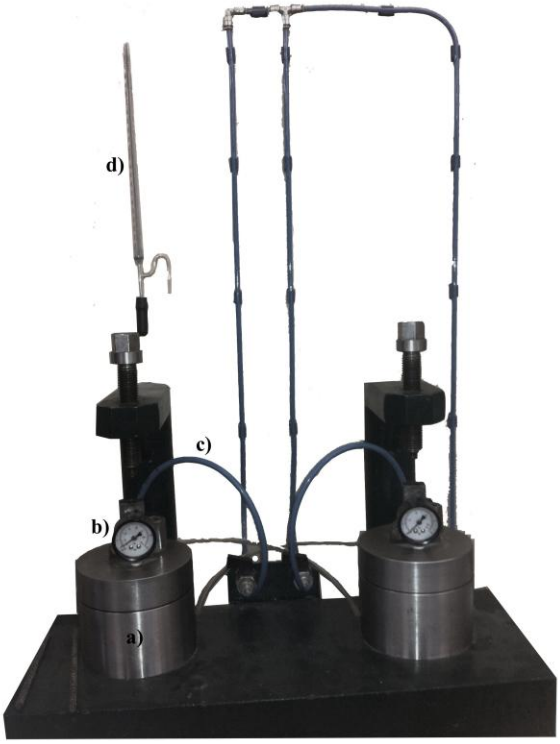


Figure 4.12 - Leeds unit permeability and its constituents

Water permeability is determined by the following formulas:

$$k_w = \frac{d_p^2 \times \delta}{2 \times h \times t} \qquad [4.8]$$

Where,

k_w is the permeability coefficient to the water (m^2);
d_p is the depth of penetration (m);
δ is the specimen porosity;

t is the length of time it took to penetrate until the d_p depth (s);
h is the height of water (mH_2O).

$$K_w = k_w \times \frac{\eta}{\rho \times g} = k_w \times 1{,}3 \times 10^{-7}$$

[4.9]

Where,

K_w is the permeability coefficient (m^2);
η_w is the water viscosity at 20ºC;
ρ is the density of water (1000kg/m^3);
g' is the gravity (9,81 m/s^2).

The value of the water permeability results from the average of the values obtained for two specimens.

4.5.11 Freezing points determination

Freezing points were obtained by recording the temperature along time through temperatures sensors, PT-100, which were embedded into different cups, each one containing the water solutions mentioned in section 4.4.1. Each glass of water solution was placed in the deepfreeze at a temperature of -20ºC – see Figure 4.13 (a). In order to ensure that the fridge kept a constant temperature, a thermostat was installed in the fridge and monitored through a probe that contained a PT-100, as illustrated in Figure 4.13 (b).

Figure 4.13 – Deepfreeze used (a) and detail of thermostat with the probe (b)

5 TESTS RESULTS AND DISCUSSION

5.1 Introduction

The analysis and discussion of test results regarding the experimental programme shown in Chapter 4 are thoroughly discussed in the present chapter. The results are presented in a sequential manner according to each of the adopted experimental techniques, starting with fresh properties, then covering mechanical properties (short term) and finally evaluating durability indexes. Nonetheless, whenever applicable, cross-comparisons among distinct experimental methods are made to support observed evidence/tendencies.

It is remarked that results pertaining to mixtures P_20%g and P_20%sg (5 and 7, respectively) are not shown in this chapter as the corresponding specimens revealed extensive cracking upon unmoulding, as already stated in section 4.4.1.

5.2 Presentation and analysis of the results

5.2.1 Flowability

Figure 5.1 and Table 5.1 (where is represented the average of the three tests – T1, T2 and T3 – performed for each mixture) compare the influence of different dosages of crude purified glycerol, synthetic glycerol and also of the antifreeze admixture in fluidity of cement pastes, as compared to the reference one. There is a slight improvement of the fluidity of the mixtures P_1%g, P_1%sg and P_1%a, when compared to the reference mixture. Mixes containing 0,5% and 3% of crude purified glycerol showed a higher flow time when compared to the reference mixture, although the difference was relatively small.

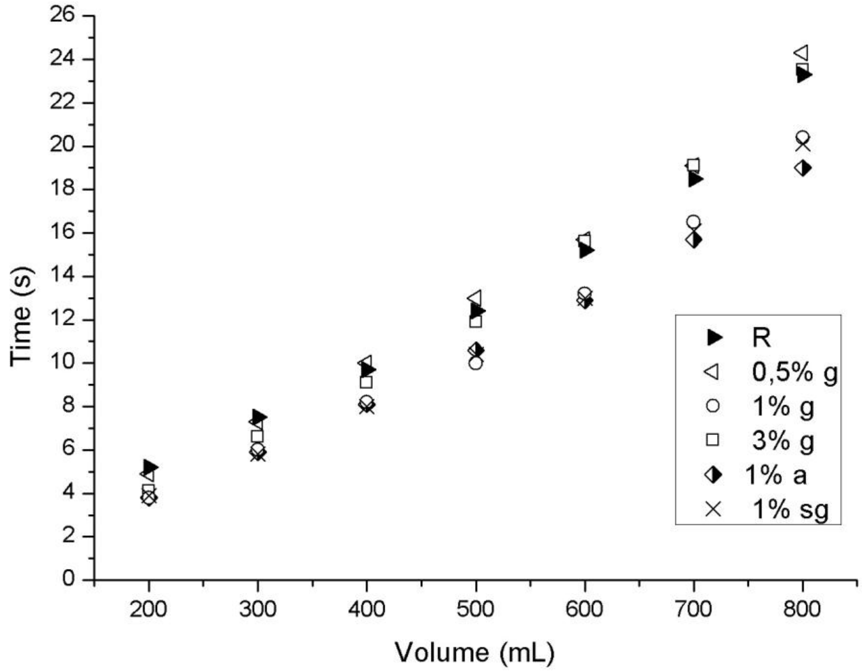


Figure 5.1 - Flowability results of cement pastes (each result corresponds to the average of 3 tests)

Table 5.1 - Overall results of flowability, including average flow time, standard deviation and coefficient of variation

Mixture	Time,$_{avg}$ [s]	s/ Cv
P_R	23,33	0,47 2,03%
P_0,5%g	24,33	0,45 1,85%
P_1%g	20,4	0,44 2,14%
P_3%g	23,5	0,4 1,70%
P_1%sg	20,07	0,38 1,89%
P_1%a	19,03	0,4 2,12%

5.2.2 Setting time

The observed initial and final setting times are reported in Table 5.2, where it can be seen that crude purified glycerol, synthetic glycerol and also the antifreeze admixture favour a significant setting time reduction of the cement paste samples. In order to better understand the relative changes in setting times, Table 5.2 also presents the percentage difference of setting time of all mixtures in regard to the reference mixture.

By observation of the table it may be seen that the shortest initial and final setting times were achieved by mixture P_1%g, after 3h50m and after 6h45m, respectively (all instants are relative to the instant of addition of the water to the cement in the mixer). When compared to the initial and final setting times of the reference mixture, which were found after 8h00m and 11h50m, respectively, it corresponds to a decrease of over 52% of the initial setting time and of over 43% of the final setting time. An almost identical effect was observed for mixture P_1%sg, with initial and final setting times of 4h00m and of 6h50m, respectively. In what concerns mixtures P_0,5%g, P_3%g and P_1%a, they also contributed to a reduction of the initial and final setting times, although in a less percentage, as may be seen in Table 5.2.

Therefore, if glycerol is seen as a setting accelerating admixture, two main conclusions are withdrawn: (i) the optimum percentage for use is 1%; (ii) the purified glycerol shows the same performance as the synthetic glycerol.

Table 5.2 - Initial and Final Setting Times

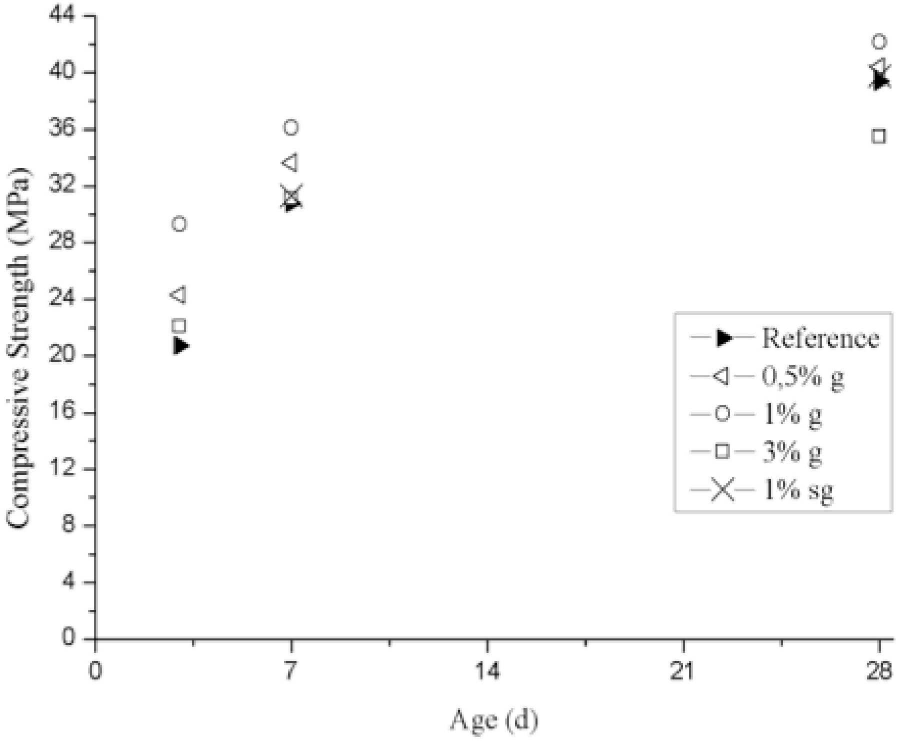
	P_R	**P_0,5%g**	**P_1%g**	**P_3%g**	**P_1%sg**	**P_1%a**
Initial Setting	08h00	05:30:00	03h50	06h05	04h00	05h30
Difference (%)	-	-31%	-52%	-24%	-50%	-31%
Final Setting	11h55	09h20	06h45	10h20	06h50	09h00
Difference (%)	-	-22%	-43%	-13%	-43%	-24%

5.2.3 Compressive Strength

Compressive strength evaluation after 3, 7 and 28 days curing at 20ºC± 1

The data concerning the compressive strength development for cement pastes incorporating crude purified glycerol (g) and synthetic glycerol (sg) is presented in Figure 5.2 together with the corresponding average values and the percentage differences, with regard to the reference mixture. The average compressive strength obtained among all tested specimens at each corresponding age, together with the standard deviation and the coefficient of variation, is shown in Table 5.3.

Age (d) / Admixture	P_0,5%g	P_1%g	P_3%g	P_1%sg
3	17%	41%	6%	n/a
7	9%	17%	1%	2%
28	3%	7%	-10%	1%



*n/a – not applicable. Test hasn't been performed

Figure 5.2 - Compressive strength results of pastes cured at room temperature (each result corresponds to the average of 3 specimens) and percentage differences of average compressive strength, in regard to the reference mixture

In what respects the incorporation of crude purified glycerol, it may be stated that, in a dosage of 1%, it affected significantly the evolution in the early age compressive strengths, as it increased compressive strength by 41% and 17%, at 3 and 7 days, respectively, when compared to control mixture values. By the age of 28 days, the increase in compressive strength was not as significant (only of 7%). Considering the incorporation of 0,5% g, increases of compressive strength in regard to the reference mixture were also observed, but in smaller percentage differences (17%, 9% and 3%, for 3, 7 and 28 days, respectively). In what concerns the maximum glycerol amount, 3%, it produced a slight improvement in compressive strength by the age of 3 days (a gain of 6%), but then, by the age of 7 days, it did not develop any significant difference in the value of the compressive strength, when compared to the reference mixture. As a matter of fact, a difference of 1% in the results lies within the effects of experimental error and specimen dispersion. By the age of 28 days, the reference mixture achieved even a better compressive strength than the one containing 3% of crude purified glycerol. Concerning the mixture with 1% of sg, and considering that it contains the same quantity of glycerol as P_1%g, it would be expectable that, by the age of 7 days, it would achieve a similar compressive strength to P_1%g. However, the results show that compressive strength for admixtures containing 1%sg is similar to the one obtained with reference mixtures.

Table 5.3 - Average compressive strength, standard deviation and coefficient of variation at each corresponding age, of pastes cured at room temperature

Age	**P_R**		**P_0,5%g**		**P_1%g**		**P_3%g**		**P_1%sg**	
[d]	**Rc,avg**	**s/Cv**	**Rc,avg**	**s/Cv**	**Rc,avg**	**s/Cv**	**Rc,avg**	**s/Cv**	**Rc,avg**	**s/Cv**
3	20,74	1,23 5,93%	24,31	1,11 4,57%	29,3	1,48 5,06%	22,12	1,44 6,53%	n/a	n/a n/a
7	30,78	0,98 3,18%	33,65	2,66 7,90%	36,13	1,14 3,15%	31,1	0,78 2,49%	31,31	1,15 3,66%
28	39,41	0,50 1,27%	40,41	1,11 2,74%	42,17	0,79 1,86%	35,46	1,09 3,07%	39,78	0,95 2,38%

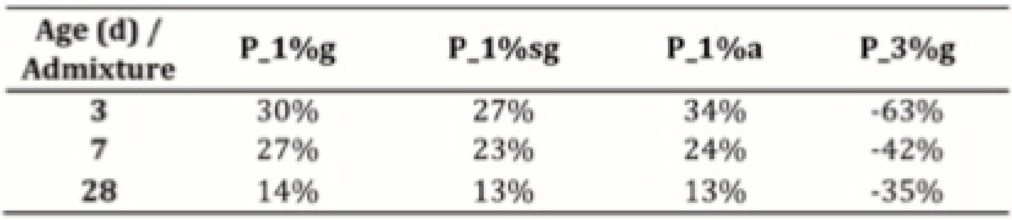
*n/a – not applicable. Test hasn't been performed

From the table, one can unmistakeably state that mixture sample P_1% g, with crude purified glycerol dosage of 1%, exhibits highest compressive strength at all days of testing as compared to the other mixtures that have crude purified glycerol dosage of 0%, 0,5% and 3% and also to the one that has 1% of synthetic glycerol.

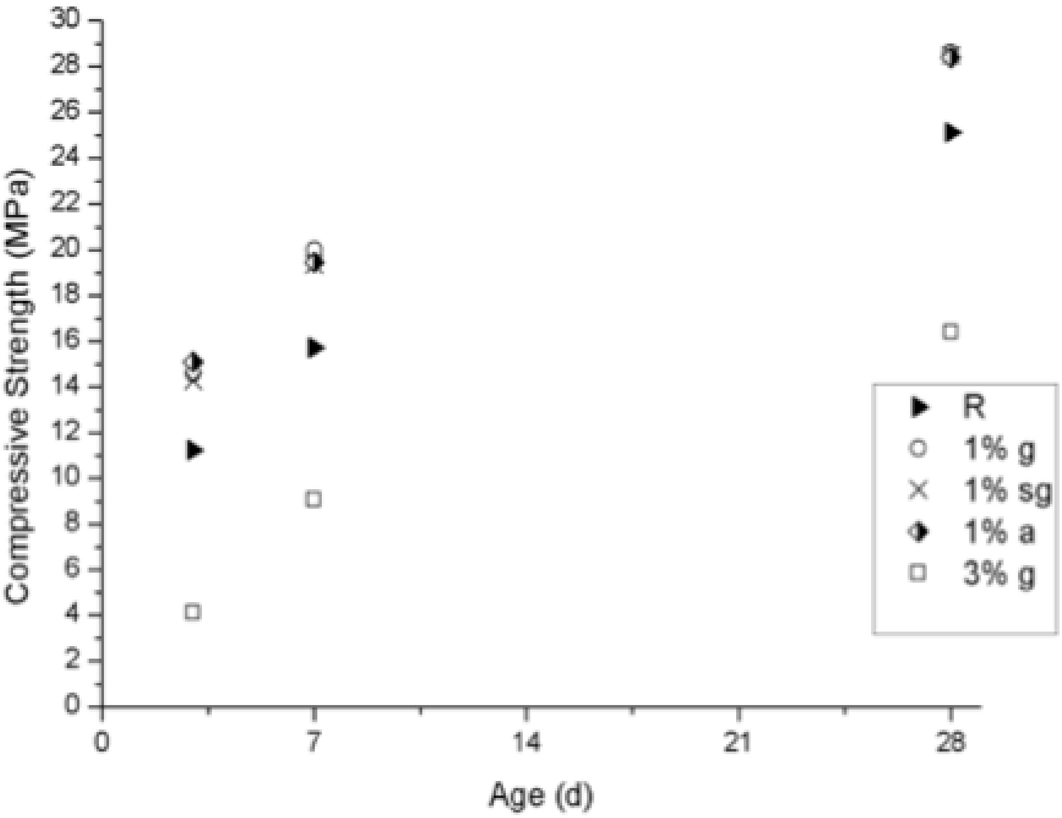
Considering the results, it is believed that there might be a synergy between glycerol's molecule and cement paste and that the optimum value of incorporation crude purified glycerol is of 1%, beyond which saturation seems to occur.

Compressive strength evaluation after 3, 7 and 28 days under curing at -1ºC

Figure 5.3 shows the results of the compressive strength of samples exposed to -1ºC for 3, 7 and 28 days (after initial curing at 20ºC for 18 hours) and the corresponding average values and the percentage differences, with regard to the reference mixture.



Age (d) / Admixture	P_1%g	P_1%sg	P_1%a	P_3%g
3	30%	27%	34%	-63%
7	27%	23%	24%	-42%
28	14%	13%	13%	-35%



*n/a – not applicable. Test hasn’t been performed

Figure 5.3 - Compressive strength results of pastes cured at -1ºC (each result corresponds to the average of 3 specimens) and percentage differences of average compressive strength, in regard to the reference mixture

Adding 1% of crude purified glycerol caused an increment in the compressive strength of about 30%, 27% and 14%, for 3, 7 and 28 days, respectively, when compared to the compressive strength of reference sample that was exposed to the same conditions. The addition of 1% of synthetic glycerol also conferred good results: it improved cement pastes' compressive strength by 27%, 23% and 13%, when compared to the reference mixture, by the ages of 3, 7 and 28 days, respectively. These results may be compared with the ones obtained by adding 1% of the commercial antifreeze: it improved the compressive strength by 34%, 24% and 13%, when compared to the reference mixture, by the age of 3, 7 and 28 days. On the other side, the incorporation of 3%g caused an antagonistic effect, with decreases of 63%, 42% and 35% of the compressive strength, in relation to the reference mixture.

The average compressive strength obtained among all tested specimens at each corresponding age, together with the standard deviation and the coefficient of variation, is shown in Table 5.4.

Table 5.4 - Average compressive strength, standard deviation and coefficient of variation at each corresponding age, of pastes cured at -1ºC

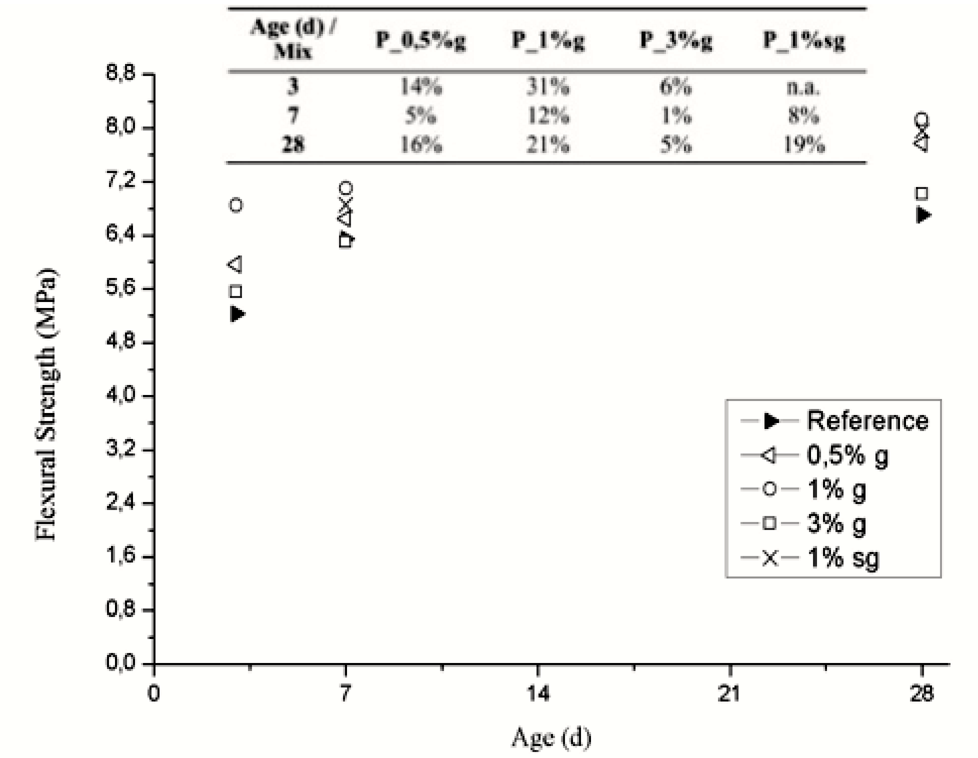
Age [d]	**P_R**		**P_1%g**		**P_1%sg**		**P_1%a**		**P_3%g**	
	Rc$_{,avg}$	**s/Cv**	**Rc$_{,avg}$**	**s/Cv**	**Rc$_{,avg}$**	**s/Cv**	**Rc$_{,avg}$**	**s/Cv**	**Rc$_{,avg}$**	**s/Cv**
3	11,25	0,56 4,95%	14,59	0,56 3,81%	14,28	0,70 4,91%	15,11	0,89 5,90%	4,13	0,53 12,90%
7	15,72	0,70 4,45%	19,99	0,80 3,99%	19,37	0,45 2,32%	19,46	0,38 1,95%	9,07	0,36 4,01%
28	25,14	0,57 2,28%	28,60	1,02 3,55%	28,50	1,33 4,67%	28,39	1,19 4,19%	16,40	1,08 6,58%

The effect of the crude purified glycerol on the cold weather concreting seems to be reasonable as the goal in proportioning mixtures for cold weather is to achieve a concrete that cures rapidly, that is, one that sets more quickly and gains strength more rapidly than it ordinarily would (Korhonen, 2011). In fact, the performance of adding 1% g to the mixture was quite similar to the one obtained with a commercial antifreeze product. It is also interesting to notice that, unlike the case of specimens cured at room temperature, the use of synthetic glycerol conducted to similar performance as that which was obtained with crude purified glycerol.

5.2.4 Flexural Strength

Flexural strength evaluation after 3, 7 and 28 days curing at 20ºC± 1

The flexural strengths of cement pastes with various levels of replacement of crude purified glycerol and synthetic glycerol, as well as those of the reference mixture are presented in Figure 5.4.



Age (d) / Mix	P_0,5%g	P_1%g	P_3%g	P_1%sg
3	14%	31%	6%	n.a.
7	5%	12%	1%	8%
28	16%	21%	5%	19%

*n/a – not applicable. Test hasn't been performed

Figure 5.4 - Flexural strength results of pastes cured at room temperature (each result corresponds to the average of 3 specimens) and percentage differences of average compressive strength, in regard to the reference mixture

At an early age of 3 days, all cement pastes with crude purified glycerol exhibited a higher flexural strength when compared to the reference mixture. At the age of 7 days, although less pronounced, the very same tendency was turned out regarding 0,5% and 1% substitution amounts, as may be observed in the figure. Cement paste containing a level of replacement of 3% exhibited a similar flexural strength to the reference one. At the age of 28 days, all cement pastes containing crude purified glycerol exhibited a higher flexural strength, when compared to the reference cement paste, as shown in Figure 5.4.

In what concerns the incorporation of synthetic glycerol, with a substitution amount of 1%, it is clearly observable that it also shows a higher flexural strength when compared to the reference mixture, similarly to the mixture with 1% of crude purified glycerol, as displayed in

Figure 5.4.

The average flexural strength obtained among all tested specimens at each corresponding age, together with the standard deviation and the coefficient of variation, is shown in Table 5.5.

Table 5.5 - Average flexural strength, standard deviation and coefficient of variation at each corresponding age, of pastes cured at 20ºC

Age [d]	**P_R**		**P_0,5%g**		**P_1%g**		**P_3%g**		**P_1%sg**	
	$Rf_{,avg}$	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**
3	5,23	0,37 7,02%	5,97	0,42 6,99%	6,85	0,24 3,54%	5,55	0,18 3,29%	n/a	n/a n/a
7	6,35	0,54 8,57%	6,65	0,39 5,91%	7,1	0,53 7,41%	6,3	0,49 7,82%	6,86	0,44 6,46%
28	6,71	0,18 2,75%	7,77	0,11 1,44%	8,13	0,34 4,12%	7,02	0,21 2,99%	7,96	0,13 1,62%

*n/a – not applicable. Test hasn't been performed

For all curing periods, cement paste with a crude purified glycerol content of 1% consistently exhibited the highest flexural strength relatively to that of the control cement paste, as can be seen in Table 5.5, which means that it once again corresponds to the optimum level of cement replacement using crude purified glycerol.

As already stated in section 5.2.2, when compared initial and final setting times of cement pastes containing crude purified glycerol with control mixture, it may be seen that the presence of 1% of this glycerol strongly reduces them. That said, and also considering the results of the compressive and flexural strengths, this crude purified glycerol can be classified as a hardening accelerator.

Regarding the incorporation of 1% of synthetic glycerol, although it yields similar effects to the ones produced by the incorporation of 1% of crude purified glycerol in what respects the results obtained from the set time test and also from the flexural one, when analysing the compressive strength, the corresponding results surprisingly seem to be more similar to the reference mixture (without any admixture) than to those of the mixture containing 1% of crude purified glycerol, thus revealing an opposite conclusion to the one obtained for setting time and flexural strength tests.

Flexural strength evaluation after 3, 7 and 28 days under curing at -1ºC

The flexural strength of specimens cured at -1ºC for 3, 7 and 28 days (after 18h at 20ºC) may be seen Figure 5.5.

Age (d) / Admixture	P_1%g	P_1%sg	P_1%a	P_3%g
3	34%	19%	31%	-60%
7	21%	18%	15%	-42%
28	17%	11%	14%	-23%

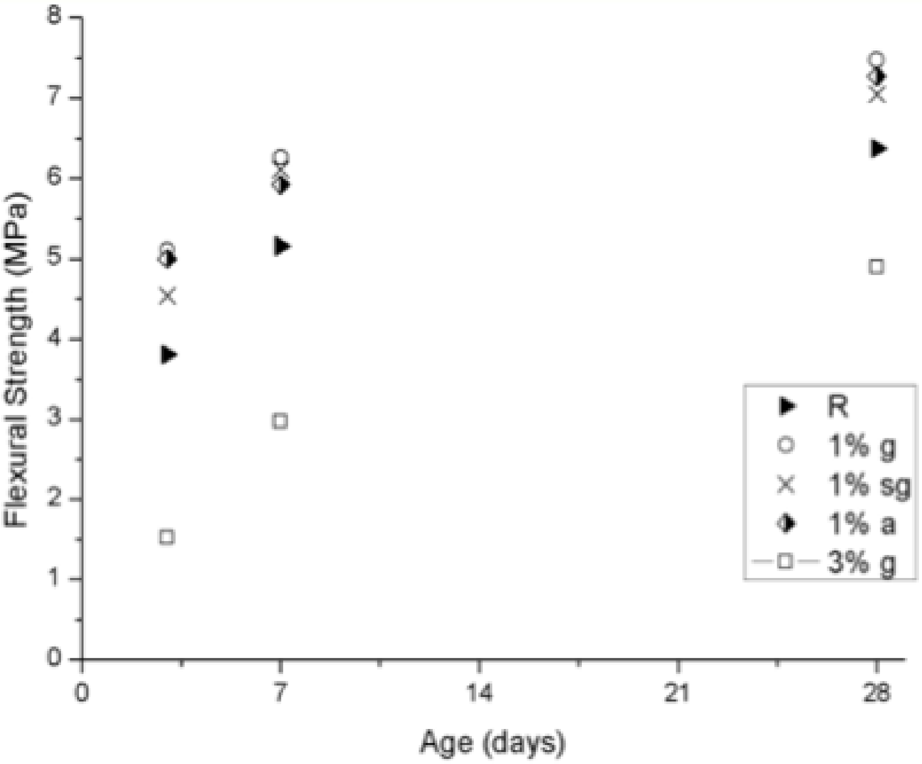


Figure 5.5 - Flexural strength results of pastes cured at -1ºC (each result corresponds to the average of 3 specimens) and percentage differences of average compressive strength, in regard to the reference mixture

Similarly to the results obtained for the compressive strength, the performance of specimens containing crude purified glycerol at 1% of cement weight was also found to be better than the reference mixture and comparable with specimens containing the antifreeze admixture.

The gains of flexural strength of mixtures containing 1% of crude purified glycerol were of about 34%, 21% and 17%, when compared to the reference mixture, by the age of 3, 7 and 28 days, as shown in Table 5.6. In what concerns the incorporation of 1% sg, the improvements were of 19%, 18%, 11%, as compared with the reference mixture, also by the ages of 3, 7 and

28 days. The incorporation of the commercial antifreeze brought about very similar results, with gains of 31%, 15% and 14%, by the age of 3, 7 and 28 days, also in relation to the reference mixture. Also analogously to the compressive strength results, the incorporation of 3%g also decreased the flexural strength values in relation to the reference mixture at about 60%, 42% and 23%, by the age of 3, 7 and 28 days, as stated in Table 5.6.

Table 5.6 - Average flexural strength, standard deviation and coefficient of variation at each corresponding age, of pastes cured at -1ºC

Age	**P_R**		**P_1%g**		**P_1%sg**		**P_1%a**		**P_3%g**	
[d]	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**	**$Rf_{,avg}$**	**s/Cv**
3	3,81	0,26 6,78%	5,11	0,29 5,73%	4,54	0,15 3,26%	5,00	0,33 6,53%	1,52	0,12 7,99%
7	5,16	0,23 4,42%	6,26	0,61 9,81%	6,11	0,30 4,93%	5,92	0,32 5,48%	2,97	0,22 7,50%
28	6,37	0,20 3,16%	7,47	0,09 1,24%	7,05	0,20 2,79%	7,27	0,22 3,05%	4,89	0,21 4,28%

Therefore, in view of the similitude of improved behaviour associated to mixtures including 1% of crude purified glycerol in terms of flexural strength (associated to tensile rupture) and compressive strength, it can be argued that the basic improvement mechanism is being the same in both cases (tension and compression).

5.2.5 Tensile Splitting Strength

The tensile strength of cement pastes measured by splitting test at 28 days is shown in Table 5.7, where may be seen the results regarding the three specimens that have been considered, termed S1, S2 and S3, the average tensile splitting strength, the standard deviation, the coefficient of variation at each corresponding age, and also the percentage differences of average tensile splitting strength, in regard to the reference mixture. It was expect that results regarding the splitting tensile strength test would be similar to the ones obtained through the flexural strength test, because in theory, these tests are conduct by the same tensile rupture mechanism. However, within the analyses of the table, it is possible to conclude that this test yielded similar results among all mixtures. In fact, these results are not consubstantiated by the flexural strength results..

Table 5.7 - Overall results of tensile splitting strength, including the value obtained for each specimen, average, standard deviation and coefficient of variation

Mixture	**Age [d]**	**Specimen**	**F [N]**	**fct, $_{avg}$ [MPa]**	**s/Cv**	**Difference [%]**
P_R	28	S1	17230,32	2,39	0,09	-
		S2	19020,36			
		S3	17038,58		3,62%	
P_0,5%g	28	S1	21203,18	2,26	0,14	-6%
		S2	20759,49			
		S3	22176,56		6,15%	
P_1%g	28	S1	18080,11	2,72	0,09	14%
		S2	17105,72			
		S3	16516,92		3,39%	
P_3%g	28	S1	19393,48	2,19	0,10	-8%
		S2	18059,90			
		S3	18965,17		4,58%	

5.2.6 Shrinkage

By observation of the plotted curves in Figure 5.6, which correspond to the average drying shrinkage results of three replicate specimens for each mixture, it appears that the shrinkage strains slightly diminish among mixtures P_0,5%g and P_1%g, when compared to the reference mixture. However, by increasing the quantity of glycerol until 3%, shrinkage is increased. This behaviour can be explained as inter-related to the one observed for the compressive strength: the mixtures with higher compressive strength are bound to correspond to a denser cementitious matrix, which is probably less permeable and thus limits the rate of water loss to the surrounding environment, which is in turn directly related to the development of drying shrinkage.

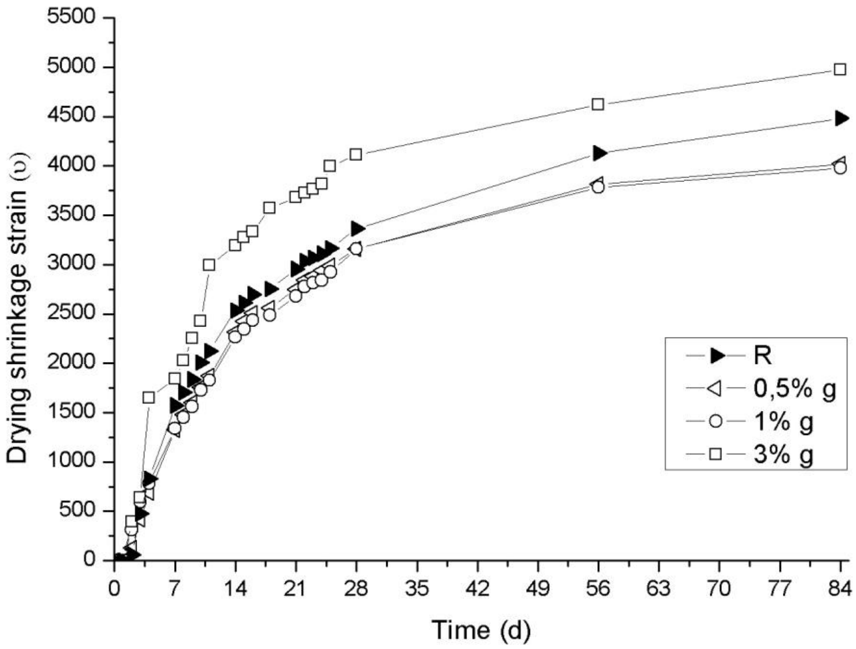


Figure 5.6 – Average cumulative drying shrinkage results of three replicate specimens for each mixture

5.2.7 Elasticity Modulus

The effect of crude purified glycerol on the E-modulus evolution may be analysed in Figure 5.7, where mixtures P_R, P_1%g, P_3%g and P_1%sg are involved.

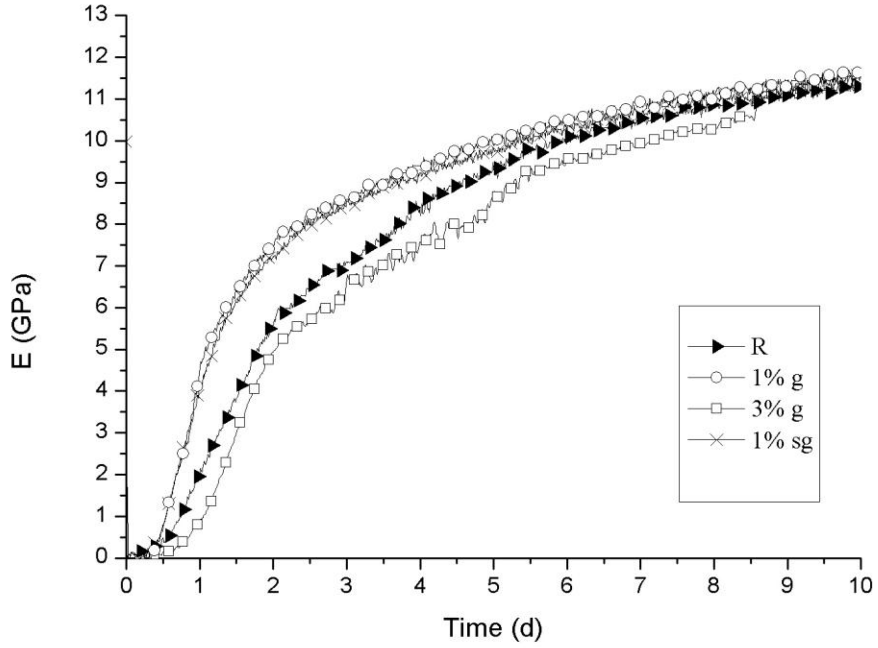


Figure 5.7 – E-modulus evolution for mixtures P_R, P_1%g, P_3%g and P_1%sg, regarding the EMM-ARM methodology

By observation of Figure 5.7, it is possible to confirm that all pastes exhibit almost zero E-modulus after casting, which, as a matter of fact, corroborates their fluid-like behaviour (Azenha, 2009). In addition, it is possible to identify the end of the dormant stage, after which pastes start to exhibit structural stiffness. From the Figure 5.7, it is also perceptible that mixtures P_1%g and P_1%sg develop stiffness in a faster way than the reference one. Regarding these mixtures, it is possible to state that crude purified glycerol and synthetic glycerol had their strongest effect between 0 and 3 days, as illustrated in Table 5.8. From the age of 6 days until the age of 10 days, which corresponds to the end of the test, the difference in E-modulus values of the different mixtures was almost negligible: 11,6 GPa concerning the reference admixture, 11,8 GPa regarding admixture with 1% of crude purified glycerol, 11,8 GPa in respect to admixture containing 1% of synthetic glycerol and 11,7 GPa considering admixture with 3% of crude purified glycerol.

Table 5.8 - Compressive strength regarding mixtures P_1%g, P_3%g and P_1%sg, comparatively to the reference mixture, together with the values obtained for the elasticity modulus

Test	Age (d) / Mixture	P_1%g	P_3%g	P_1%sg	P_R
Compressive Strength	**3**	29,3	22,12	n/a	-
	7	36,13	31,1	31,31	-
	28	42,17	35,46	39,78	-
EMM-ARM	**1**	4,58 GPa	0,89 GPa	4,19 GPa	2,13 GPa
	3	8,59 GPa	6,68 GPa	8,33 GPa	7,08 GPa
	7	10,92 GPa	9,95 GPa	10,63 GPa	10,51 GPa
	10	11,79 GPa	11,76 GPa	11,72 GPa	11,58 GPa

*n/a – not applicable. Test hasn't been performed

Analysing the Table 5.8, it is possible to infer that incorporation of 1%g, in terms of compressive strength, had its strongest effects by the age of 3 days. Bearing in mind that evolution kinetics of elastic modulus occurs in a faster way than the evolution kinetics of the compressive strength, this result is actually corroborated by the EMM-ARM results, which show a higher difference in terms of elasticity modulus by the age of 1 day, until the age of 3 days, when comparing P_1%g with P_R.

Regarding mixture P_1%sg, by analysing the table, it is possible to conclude that results between compressive strength and elasticity modulus development are not consistent. Actually, this fact has already been reported along the present chapter, as compressive strength results concerning admixture P_1%sg are not either consistent with the ones obtained through the flexural strength test and do not corroborate the set time result.

Concerning mixture P_3%g, it is possible to assure that results regarding compressive strength and E-modulus development are also consistent: it is observable that mixture P_3%g takes longer time to gain stiffness when compared to all mixtures involved and that it also attains a smaller early-age compressive strength than mixture P_1%g. Although by the age of 28 days it is possible to observe a decrease in terms of compressive strength of mixture P_3%g when compared to the reference mixture and that such decrease of stiffness is not noticeable at later ages (10 days), it is not proper to state that results are contradictory: in fact, as already mentioned, evolution kinetics of elastic modulus occurs in a faster way than the evolution kinetics of the compressive strength and perhaps, if mixture P_3%g was tested for its compressive strength at later ages, a similar performance to the one obtained by reference mixture would be achieved.

Moreover, it is also important to state that, when comparing the effect of incorporation of 1% of crude purified glycerol (and also of 1% of synthetic glycerol) with results obtained through the introduction of an accelerator admixture (see figure 4.8), the behaviour of the mentioned products as accelerators is more pronounced.

In Figure 5.8 is schematised an overlapping of the results from the EMM-ARM and from the set time test and it is observable that the results correlate well: P_1%g and P_1%sg were the mixtures that gained set more quickly, according to the set time test; they were also the ones that gained stiffness more quick, according to the EMM-ARM procedure. In what concerns P_R and P_3%g, there is a little discrepancy between the two tests, which may be explained due to the lack of resolution of the EMM-ARM methodology in very early age.

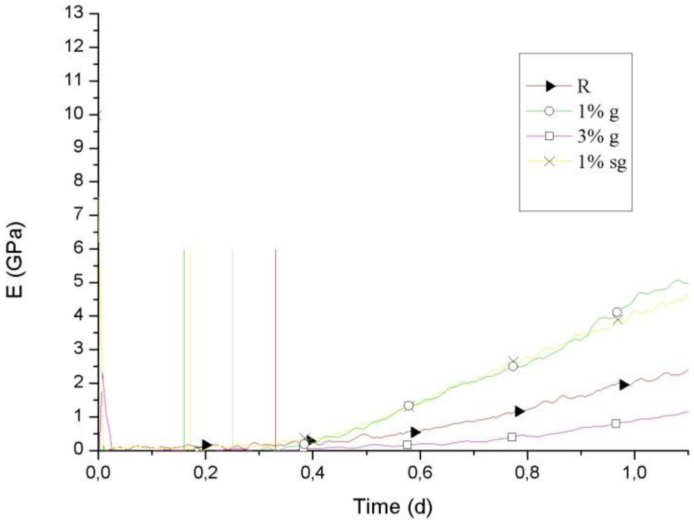


Figure 5.8 – Overlapped results of EMM-ARM and set time tests

5.2.8 Water absorption through immersion

Water absorption results of mortar at 28 days are shown in Figure 5.9, where can be observed the results regarding the two specimens that have been considered, termed S1, S2. This figure indicates that the incorporation of crude purified glycerol had a small influence on water absorption. Average values of water absorption were of 16,27% for reference mortar, 15,76% for M_3%g and of 15,15% and 15,01% for M_0,5%g and M_1%g, respectively, as indicated in Table 5.9, together with the results for both specimens tested, average, standard deviation and coefficient of variation.

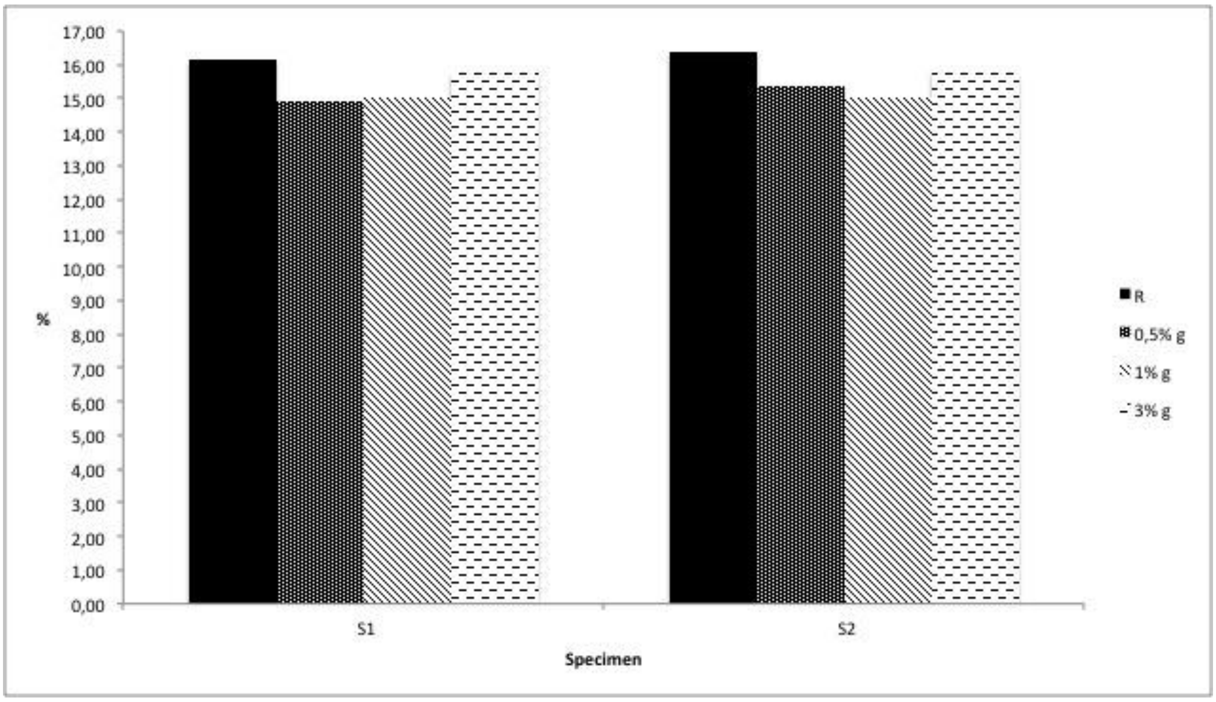


Figure 5.9 - Water absorption results obtained for the both tested specimens, by the age of 28 days

Table 5.9 – Water absorption results for both specimens tested, together with the average, standard deviation and coefficient of variation

Mixture	Specimen	Water absorption [%]	$Kw_{médio}$ (m^2)	s/Cv
M_R	S1	16,27	33,55	0,180
	S2	16,40		0,54%
M_0,5%g	S1	14,91	15,15	0,34
	S2	15,39		2,24%
M_1%g	S1	15,00	15,01	0,01
	S2	15,02		0,07%
M_3%g	S1	15,74	15,76	0,03
	S2	15,78		0,19%

It is evident that the incorporation of 0,5%g and of 1%g gave the optimum performance, resulting in the lowest water absorption values, although little pronounced.

5.2.9 Oxygen and Water Permeability

The results obtained for oxygen and water permeability in mortars by the age of 28 days, for the two specimens that have been considered, termed S1, S2, are shown in Figure 5.10 and in Figure 5.11, respectively.

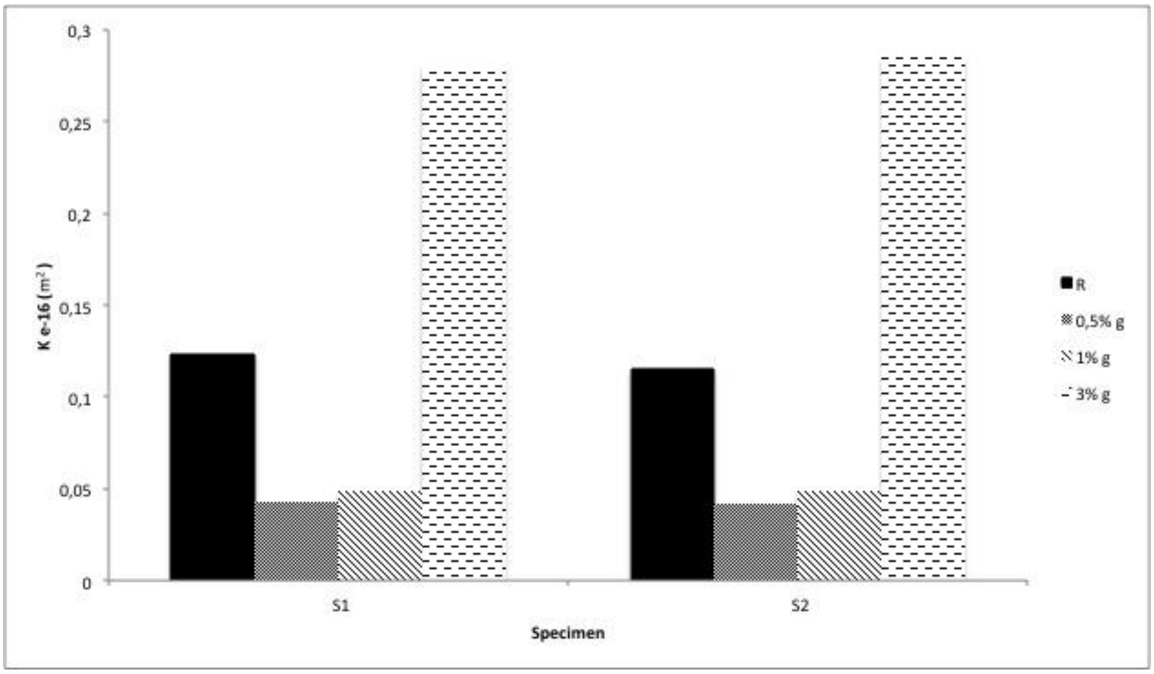


Figure 5.10 – Oxygen permeability results obtained for the both tested specimens, by the age of 28 days

The permeability of mortars that contain 0,5% and 1% of crude purified glycerol was found to be much lower than that of the reference mortar. The average oxygen permeability of M_0,5%g and M_1%g was about 0,043 × 10^{-16} m^2 and 0,049 × 10^{-16} m^2, respectively, by the age of 28 days. The one of the unmodified reference mortar was about 0,119 × 10^{-16} m^2, while the one of the mixture containing 3% of crude purified glycerol was about 0,282 × 10^{-16} m^2. In Table 5.10 are shown the results for both specimens tested, together with the average, standard deviation and coefficient of variation.

Table 5.10 – Oxygen permeability results for both specimens tested, together with the average, standard deviation and coefficient of variation

Mixture	**Specimen**	**K e^{-16}(m^2)**	**$K_{médio}e^{-16}$ (m^2)**	**s/Cv**
M_R	S1	0,123	0,119	0,005

	S2	0,115		4,54%
M_0,5%g	S1	0,043	0,043	0,001
	S2	0,042		2,34%
M_1%g	S1	0,049	0,049	0,0001
	S2	0,049		0,20%
M_3%g	S1	0,280	0,282	0,004
	S2	0,285		1,42%

By observation of Figure 5.11, it may be concluded that water permeability results corroborated the same tendency of the oxygen permeability ones.

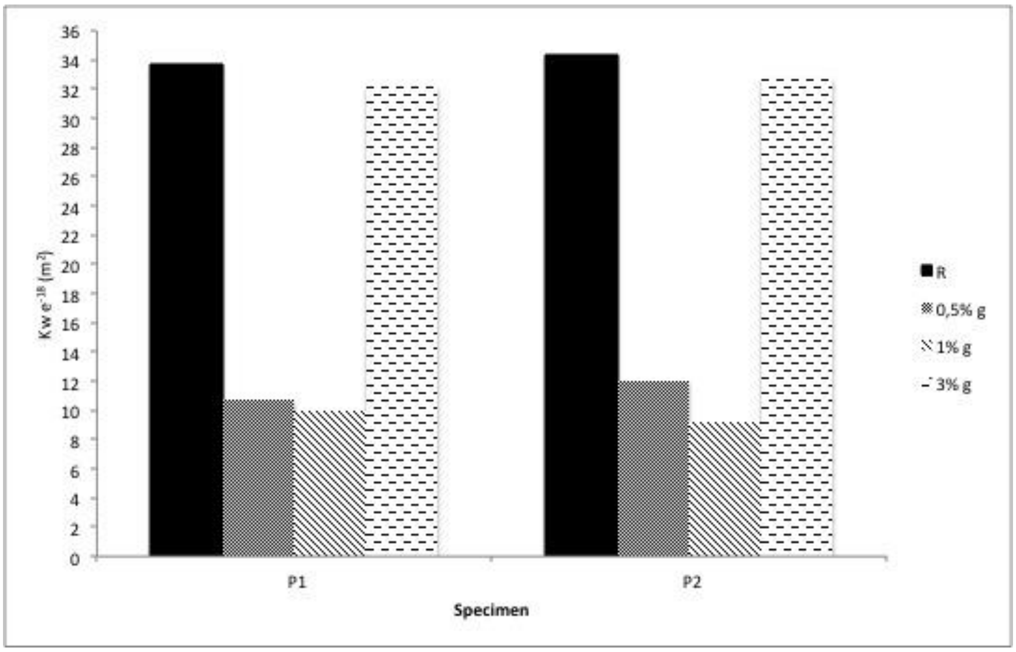


Figure 5.11 - Water permeability results obtained for the both tested specimens, by the age of 28 days

The reference mortar mixtures were the ones which exhibit the higher water permeability value, with an average of 33,55 × 10^{-18} m^2, followed by the mortars containing 3% of crude purified glycerol, which showed a water permeability average value of 32,45 × 10^{-18} m^2. Mortars with 0,5%g and 1%g were the ones that conducted to the best results: an average of 11,4 × 10^{-18} m^2 and of 9,57 × 10^{-18} m^2, respectively. In Table 5.11, the results for both specimens tested, together with the average, standard deviation and coefficient of variation are shown.

Table 5.11 - Water permeability results for both specimens tested, together with the average, standard deviation and coefficient of variation

Mixture	Specimen	Kw e^{-18} (m^2)	Kw$_{\text{médio}}$ (m^2)	s/Cv
M_R	S1	32,72	33,55	1,170
	S2	34,38		3,49%
M_0,5%g	S1	10,74	11,40	0,94
	S2	12,06		8,25%
M_1%g	S1	9,95	9,57	0,54
	S2	9,19		5,64%
M_3%g	S1	32,17	32,45	0,39
	S2	32,73		1,20%

It is worth noting here that, in this investigation, the incorporation of 0,5%g and 1%g yielded the optimum performance, resulting in the lowest permeability and water absorption values.

5.2.10 Carbonation

With regard to the carbonation tests, it is of primordial importance to primary clarify that cement pastes contained several cracks that have developed along the curing period, as may be seen in Figure 5.12.

Figure 5.12 – Specimen after the curing period

Owing to that, it was not possible to take measurements in all faces of all specimens, thus creating the unusual configuration of specimens after the vaporization of the phenolphthalein solution, as shown in Figure 5.13.

Figure 5.13 – Specimen appearance after vaporization of phenolphthalein solution

By observation of Figure 5.14, it may be stated that admixtures containing 3% of glycerol exhibited lower carbonation depths in all ages. However, it may be seen that the carbonation depth of these mixtures was higher by the age of 56 days than by the age of 63 days, which is the opposite of what was expected and of what happens between the other mixtures. Actually, as by the age of 63 days specimens have been exposed for a longer time to the action of the CO_2 in the same conditions, it was almost imperative that the carbonation depth would have to increase. Concerning the reference mixture, it showed a lower carbonation depth by the age of 56 days, when compared to mixtures with 0,5%g and 1%g, but, by the ages of 63 and 70 days it did not turned out the same tendency. Mixes containing 0,5%g and 1%g showed similar carbonation depths by the ages of 56 and 63 days, but, by the age of 70 days, mixture containing 1%g exhibited the highest carbonation depth of all mixtures while mixture containing 0,5%g revealed a carbonation depth similar to the one of the mixtures containing 3%g.

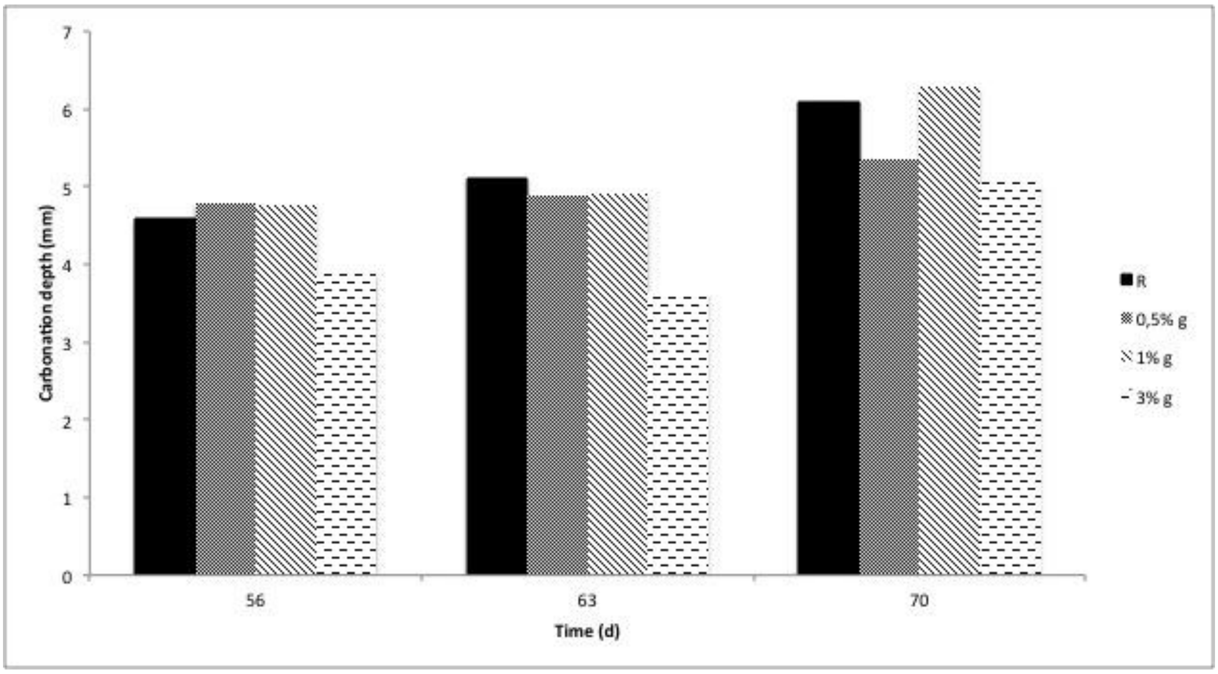


Figure 5.14 – Average carbonation results of three tested specimens by 56, 63 and 70 days

By way of conclusion, it is possible to state that carbonation results did not lead to any solid conclusions because it has not been verified any tendency of reduction or increase of the carbonation depth in none of the mixtures down through the age.

5.2.11 Freezing points evaluation

As the incorporation of crude purified glycerol, synthetic glycerol and of the commercial antifreeze admixture yielded better results in terms of compressive and flexural strength, with regard to the reference mixture, it was expected that the freezing points results would show a reduction of the eutectic point of water when the referred products were introduced. However, as may be seen in Figure 5.15, results were found to be inconclusive. Actually, it is very difficult to calculate the freezing point of cement pastes by eutectic point of mixtures containing water and crude purified glycerol, synthetic glycerol or the antifreeze admixture because the temperature of the other ingredients that are present in cement pastes also affect the temperature of the mixtures, especially the hydration of the cement with water during the mixing period of hydration of cement, the freezing point of the mixture cannot be done on a precise estimation.

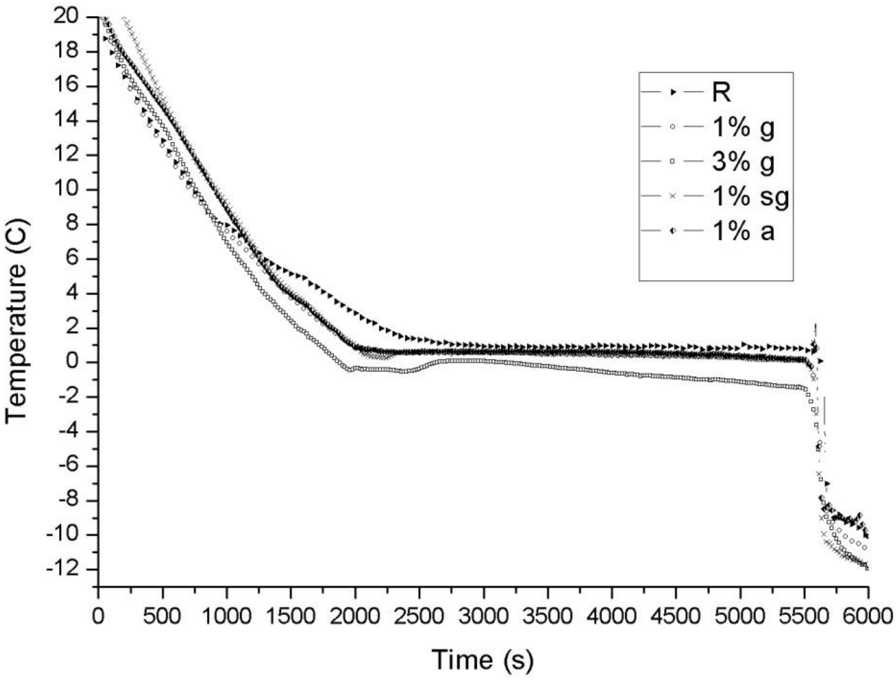


Figure 5.15 – Freezing points water-glycerol (in crude an synthetic form) and water-antifreeze admixtures solutions

6 CONCLUSION

6.1 General remarks

In the present dissertation, the incorporation of crude purified glycerol into cement-based materials has been studied, in order to evaluate its application as a cheaper yet effective alternative admixture to those that are nowadays used. For such purpose, an experimental program has been deployed, comprising several mixtures: reference mixtures; mixtures that contained various crude purified glycerol contents; mixtures based on the use of synthetic glycerol; mixtures with antifreeze admixture. The analysis of the results allowed the evaluation of the respective effects over the fresh and hardened properties of cement based materials, including some durability related properties.

In what concerns the collected data and results obtained regarding the incorporation of crude purified glycerol, two main observations can be highlighted:

- The inclusion of crude purified glycerol caused the reduction of the initial and final setting times of the cement paste samples;
- Crude purified glycerol caused a significant increase in the pace of stiffness/strength evolution in the cement paste samples since early ages.

Considering the above observations, it may be stated that crude purified glycerol acts as an accelerator admixture, both for setting and general hydration kinetics. This conclusion is based on set-time tests, EMM-ARM testing for continuous stiffness evaluation since casting, and tests on compressive and flexural strength.

All the performed tests show that, among the studied percentages of incorporation of crude purified glycerol, the optimum percentage is 1%, value beyond which saturation seems to occur. In fact, within the studied percentages of dosage (0,5%, 1% and 3%) the accelerating behaviour of glycerol was most significant for 1% dosage, followed by 0,5% and the worst performance happened for 3%. This indicates that the optimum dosage should rely somewhere between 0,5% and 3%.

Regarding the incorporation of 1% of synthetic glycerol, it can be said that it yields similar effects to the ones produced by the incorporation of 1% of crude purified glycerol in what respects the results obtained from the set time test, from the flexural test and also from the EMM-ARM test. However, when analysing the compressive strength obtained for 1% incorporation of synthetic glycerol, the corresponding results surprisingly seem to be more similar to the reference mixture (without any admixture) than to those of the mixture containing 1% of crude purified glycerol, thus revealing an opposite conclusion to the one obtained for setting time, flexural strength and E-modulus evolution. This topic needs further study as mentioned in the next section (prospects for future research).

Moreover, it is also possible to state that the incorporation of crude purified glycerol contributes to a reduction of permeability properties in mortars (both to water and oxygen). Permeability tests showed decreased oxygen permeability of the mortars containing 0,5% and 1% of crude purified glycerol (as compared to the reference mixture without admixture) in a percentage of 64% and 59%, respectively, and decreased water permeability of 66% and 71%, for P_0,5%g and P_1%g, respectively, whereas the mixtures containing 3% glycerol exhibit opposite trends with increased oxygen permeability in a percentage of 137% and similar water permeability when compared to the reference mixture. These trends in permeability results have also been confirmed by the drying shrinkage tests, as a slight reduction of shrinkage of cement pastes containing 0,5% and 1% of crude purified glycerol has been verified (in a percentage of 10% and 11% when compared to the reference mixture, respectively), as opposed to the results regarding the incorporation of 3% of crude purified glycerol, in which case, shrinkage was even increased in a percentage of 12%. It may be argued that crude purified glycerol may have created conditions to reduce permeability in mortars containing 0,5% and 1% of crude purified glycerol. One possible explanation for such reduction could be the partial occlusion of cement micro pores induced by the presence of glycerol. Nonetheless, further studies would be necessary to establish the actual reasons.

Although the results of the freezing points of solutions containing glycerol (crude purified and synthetic) were found to be inconclusive, the flexural/compressive strength tests for specimens cured at -1ºC (after initial curing at 20ºC for 18 hours) showed that the inclusion of 1% crude purified glycerol improved strength gains during the low temperature curing period, as compared to the reference mixture. In fact, the strength reductions at the reference ages of 3, 7 and 27 days for mixtures containing 1% of crude purified glycerol, when compared to curing at 20ºC, were respectively of 30%, 35% and 27%, which is lower to what occurred for the reference samples without admixture (reduction of 46%, 49% and 36%) and similar to those obtained for mixtures containing a commercial antifreeze admixture (27%, 37% and 28%).

As a final remark, it can be said that the present research allowed unveiling the potential of using crude purified glycerol as an admixture for cement-based materials with comparable behaviour to commercial accelerating admixtures and antifreezing admixtures. These findings are of particular importance because of the relatively low cost of crude purified glycerol and the fact that this is a quite sustainable by-product that results from a renewable resource (Rossi *et al.*, 2008).

6.2 Prospects for future developments

In conscience of the limitations of the work conducted in the scope of this dissertation, some ideas are forwarded to continue pursuing proof of the feasibility of adopting crude purified glycerol as an admixture for cement-based materials:

- Repetition of the compressive and flexural strength tests regarding cement pastes with 1% of synthetic glycerol due to the apparently contradictory results, in order to rule out the hypothesis that an experimental problem might have occurred or to better interpret the reason for distinct tendencies for compressive and flexural strength;
- Assess if the same type of conclusions obtained in this dissertation would have been obtained in the case of distinct w/c ratios (e.g. 0.3 and 0.6) and distinct types of cement (e.g. type II and type IV);
- Evaluate more percentages of crude purified glycerol dosage between 0.5% and 3% as to infer the optimum recommendable value;
- Infer if the dosage of glycerol should be expressed as a function of cement content, rather than as a function of water content, with relevant consequences on the definition of optimum dosages;
- Accomplishment of carbonation tests among mortars instead of cement pastes, as the results obtained towards this test revealed to be inconclusive mainly due to the amount of cracks originated in the cement paste specimens (not bound to occur in mortar specimens);

- Performance of freezing points determination in fresh cement pastes, instead of in glycerol-water and commercial antifreeze-water solutions, as the behaviour of freezing temperature might be affected by interactions between the cementitious mixture and the admixture (crude purified glycerol or commercial antifreeze);
- Fulfilment of flexural and compressive strength tests in cement pastes with the same substitution amounts of crude purified glycerol, of synthetic glycerol and of the antifreeze admixtures at lower temperature curing conditions such as -5ºC.
- Testing the effects of the crude purified glycerol in concrete as to verify if there is any scale effect, or if the conclusions remain the same that were obtained for cement pastes/mortars;
- Execution of EMM-ARM tests at an extreme scenarios where temperatures right after casting are as low as -1ºC or -5ºC to continuously assess hydration kinetics in mixtures containing crude purified glycerol, antifreeze admixture or no admixture at al.

7 REFERENCES

ABAD, S. & TURON, X. 2012. Valorization of biodiesel derived glycerol as a carbon source to obtain added-value metabolites: Focus on polyunsaturated fatty acids. *Biotechnol Adv,* 30**,** 733-41.

ACI 2003. E4-03 - Chemical Admixtures for Concrete.

ADMINISTRATION, U. S. F. A. D. 1979. Glycerin; GRAS status as a direct human food ingredient. . *Federal Register* 48(27): 5759–60.

AGGOUN, S., CHEIKH-ZOUAOUI, M., CHIKH, N. & DUVAL, R. 2008. Effect of some admixtures on the setting time and strength evolution of cement pastes at early ages. *Construction and Building Materials,* 22**,** 106-110.

AÏTCIN, P.-C. 2000. Cements of yesterday and today: Concrete of tomorrow. *Cement and Concrete Research,* 30**,** 1349-1359.

ASTM 2004. C490-04 - Standard Practice for Use of Apparatus for the Determination of Length Chanfe of Hardened Cement Paste, Mortar and Concrete. ASTM.

ATADASHI, I. M., AROUA, M. K., ABDUL AZIZ, A. R. & SULAIMAN, N. M. N. 2011. Membrane biodiesel production and refining technology: A critical review. *Renewable and Sustainable Energy Reviews,* 15**,** 5051-5062.

ATADASHI, I. M., AROUA, M. K., ABDUL AZIZ, A. R. & SULAIMAN, N. M. N. 2012. The effects of water on biodiesel production and refining technologies: A review. *Renewable and Sustainable Energy Reviews,* 16**,** 3456-3470.

AYOUB, M. & ABDULLAH, A. Z. 2012. Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. *Renewable and Sustainable Energy Reviews,* 16**,** 2671-2686.

AZENHA, M. 2009. *Numerical Simulation of the structural behaviour of concrete since its early ages.* PhD PhD, Faculty of Engineering of the University of Porto.

AZENHA, M., FARIA, R., MAGALHA, AMP, X, ES, F., RAMOS, L., CUNHA, A., AMP & X 2011. Measurement of E-modulus of cement pastes and mortars since casting, using a vibration based techinique. *Mater Struct,* 9**,** 1-12.

AZENHA, M., MAGALHÃES, F., FARIA, R. & CUNHA, Á. 2010. Measurement of concrete E-modulus evolution since casting: A novel method based on ambient vibration. *Cement and Concrete Research,* 40**,** 1096-1105.

BALAT, M. 2011. Potential alternatives to edible oils for biodiesel production – A review of current work. *Energy Conversion and Management,* 52**,** 1479-1492.

BALAT, M., BALAT, H. 2008. A critical review of biodiesel as a vehicular fuel. *Energy Convers Manage* 49**,** 2727-41.

BALOGH, A. 1996. Concrete Construction. 546-51.

BARRON, A. R. Hydration of Portland Cement. *Connexions Project*.

BARRON, A. T. 2010. *RE: Chemical Composition of Portland Cement.* Type to RESOURCE, O. E.

BLOCH, M., BOURNAY, L., CASANAVE, D., CHODORGE, J.A., COUPARD, V., HILLION, G., LORNE, D. 2008. Fatty acid esters in Europe: market trends and technological perspectives. *Oil&Gas Science and Technology***,** 405-417.

BORGES, M. E. & DÍAZ, L. 2012. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renewable and Sustainable Energy Reviews,* 16**,** 2839-2849.

BORUGADDA, V. B. & GOUD, V. V. 2012. Biodiesel production from renewable feedstocks: Status and opportunities. *Renewable and Sustainable Energy Reviews,* 16**,** 4763-4784.

BOURNAY, L., CASANAVE, D., DELFORT, B., HILLION, G., CHODORGE, J.A. 2005. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerol produced by biodiesel plants. *Catalysis Today***,** 190-192.

BOZBAS, K. 2008. Biodiesel as an alternative motor fuel: Production and policies in the European Union. *Renewable and Sustainable Energy Reviews,* 12**,** 542-552.

C.-H. ZHOU, J. N. B., Y.-X. FAN, G.Q. LU 2008. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chemical Society Reviews* 35**,** 527-549.

CABRERA, J. G. 1999. Design and production of high performance concrete. *Proceedings of International Conference: Infrastructure Regenaration and Rehabilitation Improving the Quality of Life Through Better Construction***,** 1-14.

CANAKCI, M., VAN, GERPAN. J. 2001a. Biodiesel production from oils and fats with high free fatty acids. *Trans ASAE 44***,** 1429–1436.

CANAKCI, M., VAN, GERPEN, J. 2001b. Biodiesel production from oils and fats with high free fatty acids. . *Trans ASAE* 44**,** 1429-36.

CARDONA C, P. J., MONTOYA M. 2007. Use of glycerol from biodiesel production: conversion to added value products. *In: Proceedings of European Congress of Chemical Engineering (ECCE-6).* 16-20.

CEN 1985. NF EN P18-358 - Admixtures for concretes, mortars and grouts. Routine grouts for prestressing ducts. Measurement of fluidity and water reduction.: Francaise de Normalisation (NF).

CEN 2000a. EN 197-1 - Cement - Composition, specifications and conformity criteria - Part 1: Common cements.

CEN 2000b. EN 206-1 - Concrete. *Part 1: Specification, performance, production and conformity*. CEN.

CEN 2001. BS EN 934-2. Admixtures for concrete, mortar and grout. . *Part 2: Concrete admixtures - definitions, requirements, conformity, marking and labelling.*

CEN 2003. NP EN 12390-6 - Ensaios do betão endurecido. Parte 6: Resistência à tracção por compressão de provetes. Lisboa: Instituto Português da Qualidade.

CEN 2006a. NP EN 196-1. Métodos de ensaios de cimento. Parte 1: Determinação das resistências mecânicas. Caparica: Instituto Português da Qualidade.

CEN 2006b. NP EN 196-3 - Métodos de ensaio de cimentos. Parte 3: Determinação do tempo de presa e da expansibilidade. Caparica: Instituto Português da Qualidade.

CEN 2010. 12390-12. Testing Hardened Concrete - Part 12: Determination of the potential carbonation resistance of concrete: Accelerated carbonation method.

CHAN, R. W. M., HO, P. N. L., CHAN, E. P. W. 1999. Report on Concrete Admixtures for Waterproofing Construction. *Structural Engineering Branch - Architectural Services Department*.

CHEN, J. W., WU, W.T. 2003. Regeneration of immobilized Candida Antarctica lipase for transesterification. *J Biosci Bioeng 92(2)***,** 231-237.

CHEUNG, J., JEKNAVORIAN, A., ROBERTS, L. & SILVA, D. 2011. Impact of admixtures on the hydration kinetics of Portland cement. *Cement and Concrete Research,* 41**,** 1289-1309.

CHISTI, Y. 2008. Biodiesel from microalgae beats bioethanol *Trends Biotechnol,* 26**,** 126-31.

CHOUHAN, A. P. S. & SARMA, A. K. 2011. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and Sustainable Energy Reviews,* 15**,** 4378-4399.

COUTINHO, A. S. G., A. 1988. Capítulo 4 - Adjuvantes. *Fabrico e Propriedades do Betão - Volume I.* II ed. Lisboa: LNEC.

DE TORRES, M., JIMÉNEZ-OSÉS, G., MAYORAL, J. A., PIRES, E. & DE LOS SANTOS, M. 2012. Glycerol ketals: Synthesis and profits in biodiesel blends. *Fuel,* 94**,** 614-616.

DEMIRBAS, A. 2008. *Biodiesel: A Realistic Fuel Alternative for Diesel Engines,* Springer-Verlag London Limited.

DENG, L., XU, X.B., HARALDSSON, G.G., TAN, T.W., WANG, F. 2005. Enzymatic production of alkyl esters through alcoholysis: A critical evaluation of lipases and alcohols. *J Am Chem Soc 82(5)***,** 341-347.

DI SERIO, M., COZZOLINO, M., GIORDANO, M., TESSER, R., PATRONO, P., SANTACESARIA, E. 2007. From homogeneous to heterogeneous catalysts in biodiesel production. *Industrial & Engineering Chemistry Research***,** 6379-6384.

EDMEADES, R. M., HEWLETT, P.C. THOMAS, R.E. 1984. An explanation of some anomalous admixture behaviour. *Building Research Establishment*.

EMMANUEL, A. O., OLADIPO, F. A. & OGUNSANMI, O. E. 2012. Investigation of salinity effect on compressive strength of reinforced concrete. *Journal of Sustainable Development,* 5.

GRANDOS, M. L., POVES, M.D., ALONSO, D., MARISCAL, R., GALISTEO, F.C., MORENO-TOST, R., ET AL. 2007. Biodiesel from sunflower oil by using activated calcium oxide. *Appl Catal B: Environ 73***,** 317–326.

GRIFFIN, D. F. & HENRY, R. L. 1964. The effect of salt in concrete on compressive strength, water vapor transmission and corrosion of reinforcing steel. California: U.S. Naval Civil Engineering Laboratory.

GRUBE, H., LAWRENCE, C.D. 1984. Permeability of concrete to oxygen. *Proc. RILEM Seminar on Durability of Concrete Structures under normal outdoor exposure.***,** 68-79.

GUI, M. M., LEE, K.T., BHATIA, S. 2008. Feasibility of edible oil vs non-edible oil vs. waste edible oil as biodiesel feedstock. . *Energy* 33**,** 1646-53.

GURU M, K. A., CAN O, CINAR C, SAHIN F. 2010. Biodiesel production from waste chicken fat based sources and evaluation with Mg based additive in a diesel engine. *Renew Energy* 35**,** 637-43.

HAR, H. B. M., HUSSIAN, N. N. B. H. & MISWAN, M. R. B. 2010. The effect of salinity on the concrete and reinforcementbar.

HAZIMAH AH, O. T., SALMIAH A. 2003. Recovery of glycerol and diglycerol from glycerol pitch. . *J Oil Palm Res 2003,* 15**,** 1-5.

HEIKAL, M. 2004. Effect of calcium formate as an accelerator on the physicochemical and mechanical properties of pozzolanic cement pastes. *Cement and Concrete Research,* 34**,** 1051-1056.

HEWLETT, P. C. 1988. *Cement admixtures: uses and applications*.

HEWLETT, P. C., EDMEADES, R.M. 2004a. Chapter 15 - Cement Admixtures. *In:* HEWLETT, P. C. (ed.) *Lea's Chemistry of Cement and Concrete.* Fourth ed. London: Elsevier Science & Technology Books.

HEWLETT, P. C., EDMEADES, R.M. 2004b. *Lea's Chemistry of Cement and Concrete,* London, Elsevier Science & Technology Books.

HEWLETT, P. C., YOUNG, J.F. 1987. Physico-chemical interactions between chemical admixtures and Portland cement. *Journal of materials Education,* 9(4)**,** 395-435.

HIMEDIA. 2013. *Material Sfaety Data Sheet* [Online]. Available: http://himediadownloads.com/MSDS/RM1027.pdf [Accessed 10/2/2013.

HUANG, G., CHEN, F., WEI, D., ZHANG, X., CHEN, G. 2010a. Biodiesel production by microalgal biotechnology *Appl Energy* 87**,** 38-46.

HUANG, G., CHEN, F., WEI, D., ZHANG, X.W., CHEN, G. 2010b. Biodiesel production by microalgal biotechnology. *Appl Energy,* 87**,** 38-46.

ISO, M., CHEN, B.X., EGUCHI, M., KUDO, T., SHRESTHA, S. 2001. Production of biodiesel fuel from triglycerides and alcohol using immobilized lipase. *J Mol Catal B Enzym 16(1)***,** 53-58.

J.P.C.GOMES, OLIVEIRA, L. A. P., PEREIRA, C. N. G. & TORGAL, F. P.? Ensaios de absorção e permeabilidade em agregados.

JACOBSON, K., GOPINATH, R., MEHER, L.C., DALAI, A.K. 2008. Solid acid catalyzed biodiesel production from waste cooking oil. *Appl Catal B Environ* 85**,** 86-91.

JI, J., WANG, J., LI, Y., YU, Y., XU, Z. 2006. Preparation of biodiesel with the help of ultrasonic and hydrodynamic caviation. *Ultrasonics 2006* 44**,** 411–4.

KARAGÖL, F., DEMIRBOĞA, R., KAYGUSUZ, M. A., YADOLLAHI, M. M. & POLAT, R. 2013. The influence of calcium nitrate as antifreeze admixture on the compressive strength of concrete exposed to low temperatures. *Cold Regions Science and Technology*.

KHAN, B., ULLAH, M. 2004. Effect of a retarding admixture on the setting time of cement pastes in hot weather. *Eng. Sci.,* 15**,** 63-79.

KIM, J.-K., KIM, C.-Y., YI, S.-T. & LEE, Y. 2009. Effect of carbonation on the rebound number and compressive strength of concrete. *Cement and Concrete Composites,* 31**,** 139-144.

KINNEY A.J., C. T. E. 2005. Modifying soybean oil for enhanced performance in biodiesel blends. *Fuel Process Technology 86(10)***,** 1137-1147.

KISS, F. E., JOVANOVIĆ, M. & BOŠKOVIĆ, G. C. 2010. Economic and ecological aspects of biodiesel production over homogeneous and heterogeneous catalysts. *Fuel Processing Technology,* 91**,** 1316-1320.

KORHOKEN, C., CORTEZ, E. 1991. Antifreeze Admixtures for Cold Weather Concreting. *ACI***,** 1-4.

KORHONEN, C. J., ORCHINO, S.A. 2011. Off-the-Shelf Antifreeze Admixture for Concrete. *Technical Report TR02-07. US Army Corps of Engineers.*

LACHEMI, M., HOSSAIN, K. M. A., LAMBROS, V., NKINAMUBANZI, P. C. & BOUZOUBAÂ, N. 2004. Self-consolidating concrete incorporating new viscosity modifying admixtures. *Cement and Concrete Research,* 34**,** 917-926.

LANE, L. B. 1925. Freezing Points of Glycerol and Its Aqueous Solutions. *Ind. Eng. cHEM.,* 17 (9)**,** 924.

LEE, J. S., SAKA, S. 2010. Biodiesel production by heterogeneous catalysts and supercritical technologies: review. *Bioresour Technol 101:7191–200.*

LI, J. & YAO, Y. 2001. A study on creep and drying shrinkage of high performance concrete. *Cement and Concrete Research,* 31**,** 1203-1206.

LNEC 1993a. E372 - Água de amassadura para betões: Caraterísticas e verificação da conformidade.

LNEC 1993b. E391 - Betões: Determinação da resistência à carbonatação. *Documentação Normativa, Especificação LNEC.* Lisboa: Laboratório Nacional de Engenharia Ciivl.

LNEC 1993c. E394 - Determinação da Absorção de Água por Imersão.

LU, J., NIE, K., XIE, F., WANG, F., TAN, T. 2007. Enzymatic synthesis of fatty acid methyl esters from lard with immobilized Candida *Process Biochem,* 42**,** 1367-70.

MA, F., HANNA, M.A. 1999. Biodiesel production: a review. *Bioresource Technology 70***,** 1-15.

MAIA, L. A., M., FARIA, R. FIGUEIRAS, J. 2013. Elasticity Modulus Monitoring Through an Ambiente Vibration Response Method - Application to Cement Based-Pastes. *Materials and Structures,* 6**,** 453-458.

MANOSAK, R., LIMPATTAYANATE, S. & HUNSOM, M. 2011. Sequential-refining of crude glycerol derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption. *Fuel Processing Technology,* 92**,** 92-99.

MARCHETTI, J. M., MIGUEL, V. U. & ERRAZU, A. F. 2007. Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews,* 11**,** 1300-1311.

MATSUMOTO, T., TAKAHASHI, S., KAIEDA, M., UEDA, M., TANAKA, A., FUKUDA, H., KONDO, A. 2001. Yeast whole-cell biocatalysts constructed by intracellular overproduction of Rhizopus oryzae lipase is applicable to biodiesel fuel production. *Appl Microbiol Biotechnol 57(4)***,** 515-520.

MEHER, L. C., SAGAR, D.V., NAIK, S.N. 2006. Technical aspects of biodiesel production by transesterification: a review. *Renew Sustain Energy Rev,* 10**,** 248-268.

MEHTA, P. K. 1989. Pozzolanic and Cementitious by-Products in Concrete - Another Look. *ACI,* 114**,** 1-44.

MEHTA, P. K., MONTEIRO, P.J.M. 2006. *Concrete: Microstructure, Properties and Materials,* McGraw-Hill.

MINDESS, S., YOUNG, J.F., DARWIN, D. 2003a. Chapter 8 - Chemical Admixtures. *Concrete* Second ed. Upper Saddle River, New Jersey: Pearson Education, Inc.

MINDESS, S., YOUNG, J.F., DARWIN, D. 2003b. *Concrete,* Upper Saddle River, New Jersey.

MINER, C. S., DALTON, N.N. 1953. *Glycerol,* New York.

MOHTAR Y, T. T., SALMIAH A. 2001. Quality of basic oleochemicals produced in Malaysia. . *Informatics* 12**,** 529-36.

NAGATAKI, S. 1994a. Mineral Admixtures in Concrete: State of the Art and Trends. *ACI,* 144**,** 447-482.

NAGATAKI, S. 1994b. Mineral Admixtures in Concrete: State of the Art and Trends. *American Concrete Institute*.

NITAYAVARDHANA, S. & KHANAL, S. K. 2011. Biodiesel-derived crude glycerol bioconversion to animal feed: a sustainable option for a biodiesel refinery. *Bioresour Technol,* 102**,** 5808-14.

NITAYAVARDHANA, S., KHANAL, S.K., Biofuel residues/wastes: ban or boon? . *Crit. Rev. Environ. Sci. Technol.*

OHAMA, Y. 1995. Introduction. *Handbook of Polymer-Modified Concrete* Park Ridge, New Jersey, U.S.A.: Noyes Publications.

ONER, C., ALTUN, S. 2009. Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. *Appl Energy* 86**,** 2114–20.

PAGLIA, C. W., F., BOHNI, H. 2001. The influence of alkali-free and alkaline shotcrete accelerators within cement systems. I. Characterization of the setting behaviour. *Cement and Concrete Research,* 31**,** 913-918.

PAGLIARO, M., ROSSI, M. 2008a. *The Future of Glyverol: New Usages for a Versatile Raw Material,* University of Milan, The Royal Society of Chemistry.

PAGLIARO, M., ROSSI, M. 2008b. Glycerol: Properties and Production. *The Future of Glycerol. New uses of a versatile raw material.* RSCPublishing.

PHAN, A. N., PHAN, T.M. 2008. Biodiesel production from waste cooking oils. *Fuel,* 87**,** 3490-6.

POSADA, J. A., RINCON, L. E. & CARDONA, C. A. 2012. Design and analysis of biorefineries based on raw glycerol: addressing the glycerol problem. *Bioresour Technol,* 111**,** 282-93.

PRIO, E. 2012. Glycerine Analysis Report.

PRUDÊNCIO JR, L. R. 1991. Strength evaluation of early-age shotcrete. *American Concrete Institute,* 1**,** 273-287.

PRYDE, E. H. 1984. Vegetable oils as fuel alternatives — Symposium overview. *Journal of the American Oil Chemists Society,* 61**,** 1609-1610.

RAHMAT, N., ABDULLAH, A. Z. & MOHAMED, A. R. 2010. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. *Renewable and Sustainable Energy Reviews,* 14**,** 987-1000.

RAMACHANDRAN, V. S. 1996. *Concrete Admixtures Handbook (Second Edition),* Park Ridge, NJ, William Andrew Publishing.

REFAAT, A. A. 2009. Different techniques for the production of biodiesel from waste vegetable oil. *International Journal of Environmenta and Science Technology***,** 183-213.

RIXOM, R. 1998. The economic aspects of admixture use. *Cement and Concrete Composites,* 20**,** 141-147.

RIXOM, R., MAILVAGANAM, N. 1999. Chemical Admixtures for Concrete. Third Edition ed.: E&FN Spon.

ROSSI, M., DELLA PINA, C., PAGLIARO, M., CIRIMINNA, R. & FORNI, P. 2008. Greening the construction industry: enhancing the performance of cements by adding bioglycerol. *ChemSusChem,* 1**,** 809-812.

SANTACESARIA, E., VICENTE, G. M., DI SERIO, M. & TESSER, R. 2012. Main technologies in biodiesel production: State of the art and future challenges. *Catalysis Today,* 195**,** 2-13.

SARMA, A. K., SARMAH, J.K., BARBORA, L., KALITA, P., CHATTERJEE, S., MAHANTA, P., ET AL. 2008. Recent inventions in biodiesel production and processing: a review. *Recent Patent Eng***,** 47-58.

SCHWAB, A. W., BAGBY, M. O. & FREEDMAN, B. 1987. Preparation and properties of diesel fuels from vegetable oils. *Fuel,* 66**,** 1372-1378.

SDA. 1990. *Glycerin: an overview,* New York, Glycerine & Oleochemical Division.

SECIL. 2004. *CEM I 42,5 R* [Online]. Available: http://www.secil.pt/pdf/CEMI425R.pdf [Accessed 20/2/2013 2013].

SHARMA, Y. C., SINGH, B., UPADHYAY, S.N. 2008. Advancements in development and characterization of biodiesel: a review. . *Fuel* 87**,** 2355-73.

SHEEDLO, M. 2008. A review of the processes of biodiesel production. *Basic Biotechnology eJournal*.

SHI, C., JIMÉNEZ, A. F. & PALOMO, A. 2011. New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cement and Concrete Research,* 41**,** 750-763.

SIDDIQUE, R. & BENNACER, R. 2012. Use of iron and steel industry by-product (GGBS) in cement paste and mortar. *Resources, Conservation and Recycling,* 69**,** 29-34.

SIKA 2011. Sika Antigel - Aditivo anticongelante para betão e argamassa.

SINGHABHANDHU A, T. T. 2010. A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock

. *Energy,* 35**,** 2493–504.

SNL, S. N. D. L. 2007. Standard Natural Sand.

SOUMANOU, M. M., BORNSCHEUER, U.T. 2003. Improvement in lipase catalyzed synthesis of fatty acid methyl esters from sunflower oil. *Enzyme Microb Technol 33(1)***,** 97-103.

SRIVASTAVA, A. & PRASAD, R. 2000. Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews,* 4**,** 111-133.

STARK, J. 2011. Recent advances in the field of cement hydration and microstructure analysis. *Cement and Concrete Research,* 41**,** 666-678.

SULAIMAN, A., WEI, F.L., LIM, S.J. 2007. Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase. *Proc Biochem,* 42**,** 951–960.

SUWANNAKARN, K. 2008. *Biodiesel production from high free fatty acid content feedstocks.* Doctor, Graduate School of Clemson University.

TAN, K. T., LEE, K. T. & MOHAMED, A. R. 2010. Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. *The Journal of Supercritical Fluids,* 53**,** 88-91.

TAYLOR, H. F. W. 1990a. 1 - Portland cement and its major constituent phases. *Cement Chemistry.* London: Academic Press.

TAYLOR, H. F. W. 1990b. *Cement Chemistry,* London, Academic Press.

TURHAN, Y. E. 2003. Concrete. *METU Press.*

TURKEL, S. 2003. Production of concrete in cold weather conditions. *Earthquake Symposium.* **,** 32-45.

VAN GERPEN, J. H. 2008. Commercial biodiesel production. *In: USA oilseed and biodiesel workshop billings*.

VASUDEVAN, P. T., BRIGGS, M. 2008. Biodiesel production - current state of the art and challenfes. *JIMB***,** 421-430.

VIVEK, G., A.K. 2004. Biodiesel production from Karanja oil. *Journal of Scientific and Industrial Research,* 63**,** 39-47.

WEISZ, P. B., HAAG, W.O., RODEWELD, P.G. 1979. Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape delective catalysis. *Science 206***,** 57-58.

WEN Z, J. M. 2009. Microalgae as a feedstock for biofuel production. *Communications and Marketing, College of Agriculture and Life Sciences, Virginia Polytechnic Institute and State University,* Publication 442-886,.

WINTER, N. B. 2009. *Understanding Cement*, WHD Microanalysis Consultants Ltd.

WISE, T., RAMACHANDRAN, V. S. & POLOMARK, G. M. 1995. The effect of thiocyanates on the hydration of portland cement at low temperatures. *Thermochimica Acta,* 264**,** 157-171.

XU, Y. Y., DU W, ZENG J, LIU DH 2004. Conversion of soybean oil to biodiesel fuel using lipozyme TL 1M in a solvent-free medium. *Biocatal Biotransformation 22(1)***,** 45-48.

YAZDANI, S. S., GONZALEZ, R. 2007. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. *Curr. Opin. Biotechnol.* , 18**,** 213-219.