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DRYING SHRINKAGE OF CEMENTITIOUS MATERIALS

AT EARLY AGE

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Summary

Throughout its service life, concrete undergoes volume changes occurring both in the fresh and in the hardened state. Drying shrinkage is considered one of the most significant deformation phenomena in hardened concrete, because of its magnitude and because it occurs throughout its whole service life. If the shrinkage is restrained by other structural elements (external restraint) or due to differential shrinkage in the cross-section (self-restraint), internal stresses develop that may result in visible cracking and/or micro-cracking. Cracking negatively affects the long-term performances of concrete elements, jeopardizing aesthetics and durability, eventually shortening their service life and increasing the maintenance costs.

At early-age, the premature exposure to drying (and hence occurrence of shrinkage) may further exacerbate the cracking susceptibility, as the material properties of cement-based materials are not yet completely developed. A fundamental understanding of the early-age properties and their development becomes of paramount importance to minimize drying shrinkage and in general the likelihood of cracking. At early-age, however, the continuous evolution of the microstructure due to hydration results in inconsistent and incomparable time-dependent and moisture-dependent measurements when approached at different early ages (or hydration stages). Hence, decoupling the hydration from the effect of drying by stopping the hydration reaction to achieve an unchanging system becomes essential.

In this work, the equivalent system approach “to arrest cement hydration” and enable the investigation of cement-based materials at early age on unchanging systems and at fixed degree of hydration is presented. The use of the equivalent approach allows investigations of moisture-dependent and time-dependent properties at early age that are otherwise difficult or impossible to perform because of the ongoing hydration and/or concurrence of drying, as for example in the case of drying shrinkage, creep/relaxation, and transport properties. These phenomena involve water transport and drying, which notoriously need long time to come to equilibrium. Specifically to this work, this approach is used to investigate the early-age drying shrinkage behavior and the (early-age) elastic properties as a function of the moisture content in cement-based materials.

The main idea behind the equivalent system approach for investigating cement based materials at fixed degree of hydration lies on the replacement of a specific amount of binder, which would be still unhydrated at a certain hydration age, by fine quartz filler. This can be accomplished at the mixing stage, knowing the degree of hydration at a given age measured on the real cementitious system and substituting it with quartz (replacement by volume).
In this study, mortar mixtures containing either Portland cement or cement blended with slag and silica fume are investigated at five hydration stages, corresponding to 1, 3, 7, 28, and 91 days.

Firstly, as to validate the equivalent system approach, a comprehensive comparison between real and equivalent systems, including a statistical analysis, in terms of the mechanical properties, porosity and pore size distribution as well as of the degree of hydration and calcium hydroxide content is performed. Results of mechanical properties support the validity of the approach. Microstructural characterization by means of mercury intrusion porosimetry shows comparable results in terms of total porosity and breakthrough radii. Thermogravimetric analysis shows comparable amounts of hydration products formed.

Further, the validation of the approach is extended to the material properties prior to cracking and the fracture properties. The elastic modulus, tensile strength and fracture energy in the real mixtures and in the equivalent ones, calculated by inverse analysis of the load-displacement curves obtained from the compact tension test (CTT), were compared and their difference statistically evaluated through the analysis of variance (ANOVA). The results obtained by the inverse analysis are afterwards verified by means of FEM simulations. Further, to validate the crack initiation and propagation in the real and equivalent systems, digital image correlation (DIC) is applied on a sequence of pictures acquired during testing. The elastic modulus, tensile strength, and fracture energy support the validity of the equivalent mortars approach. The load-displacement curves obtained by the CTT are also compared to those simulated by FEM, showing excellent correlations. DIC reveals the formation of similar crack patterns at comparable load levels between the two mortars.

These results suggest that the method can constitute a useful tool for studying the behavior of cementitious materials at early ages, in particular transport phenomena and shrinkage. As the moisture content strongly impacts the fundamental material properties of cement-based materials such as strength and elastic properties, which in turn are closely related to volume deformations and cracking susceptibility, the elastic modulus, tensile strength, and fracture energy at early-age are also determined on dried specimens from the load-displacement curves. In addition, a more systematic investigation on the influence of the decreasing moisture content on the elastic properties at early-ages is carried out through resonant ultrasound spectroscopy measurements on mortar samples and micro-indentation of paste samples. Results show that the elastic modulus remains constant at earlier ages at the different moisture contents, while at later ages a steady reduction is observed as the moisture content decreases.
On the contrary, results obtained through micro-indentation technique on paste samples show a large scatter at any moisture content, preventing from drawing any conclusion.

The ultimate drying shrinkage is experimentally investigated in three different cement-based mortars at the age of 91 days, with and without supplementary cementitious materials (SCM). Experimental results are compared to the predicted ones obtained by three different poroelastic approaches. The three different poroelastic models predict similar ultimate shrinkage as a function of the RH especially in the higher range (above about 50% RH). Further, the most important parameters that influence the predictions are discussed and their effect quantified. Finally, the uncertainty of the shrinkage predictions resulting from error propagation of the input parameters is estimated using a parametric bootstrap technique.

Afterwards, the investigation of ultimate drying shrinkage behavior is extended at the early-age period. The experimentally-measured ultimate drying shrinkage is compared with the predicted values obtained by poroelastic modeling (Biot-Bishop). The experimental ultimate drying shrinkage results both in the OPC and the slag-containing equivalent mortars at earlier ages is consistently lower than at later equivalent ages. The predicted ultimate drying shrinkage show very good agreement with the experimental results up to 54 % RH. At lower RH levels, the predicted shrinkage is overestimated.

Finally, the drying shrinkage including the moisture gradients is investigated. Firstly, the moisture gradients evolving during drying are experimentally measured by means of RH sensors placed at different depths from the drying front and compared to the predictions using the non-linear diffusion equation for moisture transport according to the diffusivity coefficients calculated from the desorption isotherms. Results show that the predicted RH profiles overestimate the RH experimentally measured. With the aim to predict the drying shrinkage, the experimental RH profiles are fitted. The calibrated diffusivity is afterwards validated comparing the experimental and predicted mass loss results.

The experimentally-determined drying shrinkage is higher at later ages in accordance with what observed for the case of the ultimate shrinkage measurements. Further, the shrinkage magnitude is comparable to the one obtained from the ultimate drying shrinkage measurements. The predicted drying shrinkage according to the calibrated diffusivity show good agreement with the experimental results except for the mortar 1 d. The latter, however, results to be more prone to carbonation, which might have induced additional carbonation shrinkage. Finally, results clearly show that the moisture content and the diffusivity are the most important parameters influencing the shrinkage behavior.
Riassunto

Nel corso della sua vita, il calcestruzzo è sottoposto a diverse deformazioni che possono avvenire sia nel suo stato liquido sia nel suo stato solido. La deformazione dovuta al ritiro a secco è considerata tra le più significative a causa del suo ordine di grandezza ma anche perché si estende per tutta la vita utile del calcestruzzo. Se le deformazioni nel calcestruzzo sono impedisite, per esempio dalla presenza di strutture adiacenti oppure a causa di contrazioni differenziali tra le superfici più esterne e le parti più interne del calcestruzzo, si sviluppano sforzi interni che possono generare fessure. Le fessure nel calcestruzzo non influenzano negativamente solo l’aspetto estetico, ma rappresentano soprattutto una minaccia per la sua durabilità, riducendone così la sua vita utile e aumentando i costi di manutenzione.

Nel calcestruzzo giovane, un prematuro essiccamiento può aumentare il rischio di fessure poiché le proprietà del materiale non sono ancora del tutto sviluppate. Uno studio delle proprietà del calcestruzzo nella giovane età e in generale il loro sviluppo diventa quindi essenziale per minimizzare il ritiro a secco e la probabilità di sviluppo di fessure ad esso associato. Una delle difficoltà più grandi nella giovane età dei materiali cementizi rappresenta l’impossibilità di scindere evoluzione della microstruttura (a causa dell’idratazione) dalle proprietà che, come il ritiro a secco, dipendono sia dal tempo che dal trasporto d’acqua all’interno della microstruttura.

In questa tesi, un nuovo approccio – **sistemi equivalenti** – è presentato come metodo per bloccare l’idratazione del cemento e allo stesso tempo permettere di indagare il ritiro a secco ad equilibrio e includendo i gradienti di umidità nella giovane età. L’idea alla base dei sistemi equivalenti consiste nel sostituire una quantità specifica di legante con del quarzo. La quantità di legante da sostituire corrisponde al volume di materiale non reagito determinato ad un certo livello di idratazione. In questo progetto, malte contenenti solo cemento Portland e malte contenenti cemento con slag e cemento con fumo di silice sono state analizzate a cinque livelli di idratazione corrispondenti a 1, 3, 7, 28 e 91 giorni.

Nella prima parte di questo lavoro, i sistemi equivalenti sono ampiamente indagati comparando differenti proprietà meccaniche, grado di porosità, grado di idratazione e quantità di idrossido di calcio con quelli misurati sui sistemi reali (ossia senza la sostituzione di legante con quarzo) alla stesso livello di idratazione. I risultati supportano la validità dell’approccio mostrando simili risultati. Inoltre, la comparazione delle proprietà del materiale tra i sistemi reali e quelli equivalenti è estesa anche alle proprietà della frattura e l’apertura della fessura. Le curve di sforzo-deformazione misurate sulle malte reali ed equivalenti usando il compact...
sion test mostrano risultati analoghi. Similmente, il modulo elastico, la resistenza a tensione e l’energia di frattura determinati dall’analisi inversa confermano la validità dell’approccio. L’apertura della fessura è stata analizzata usando la correlazione di immagini digitali. I risultati dimostrano che la formazione della fessura è simile tra i sistemi reali e quelli equivalenti.

In materiali cementizi l’umidità interna ha un forte impatto sulle proprietà, come per esempio la resistenza a compressione ed il modulo di elasticità, che a loro volta influenzano le deformazioni volumetriche e quindi il rischio di fessure. In tal senso, il modulo di elasticità dei sistemi equivalenti è stato analizzato in funzione del decrescente contenuto d’acqua attraverso spettroscopia di risonanza ad ultrasuoni e microindentazione. I risultati ottenuti dalla spettroscopia mostrano che il modulo elastico rimane costante in malte a giovane età, mentre è osservabile una riduzione del modulo elastico in funzione di un minore contenuto d’acqua. Dalle misure di microindentazione su pasta, invece, non è stato possibile osservare alcuna tendenza al comportamento del modulo elastico a causa della grossa dispersione di dati.

In questa tesi, sia il ritiro a secco ad equilibrio sia quello includendo i gradienti di umidità sono stati sperimentalmente misurati utilizzando i sistemi equivalenti. I risultati sperimentali sono stati comparati ai risultati calcolati attraverso modelli poroelastici. Nello specifico, sono stati comparati tra loro tre modelli basati sulla poroelasticità e la loro capacità di prevedere il ritiro a secco ad equilibrio è stato valutato contro i dati sperimentali di ritiro a secco ad equilibrio misurato su malte a 91 giorni. La comparazione di questi modelli dimostra che essi predicono un simile ritiro ad equilibrio fino a circa 50% di umidità relativa. Inoltre, sulla base di un’analisi statistica, in questa tesi sono discussi i parametri principali che influenzano i modelli. In seguito, l’analisi del ritiro a secco ad equilibrio è ampliata alla giovane età: i dati sperimentali dimostrano che il ritiro è minore alla giovane età. I risultati sperimentali sono successivamente comparati con quelli predetti dal modello (Biot-Bishop) ottenendo un buon accordo tra loro almeno fino a livelli di umidità pari a 54%.

Infine, il ritiro a secco includendo i gradienti interni di umidità è stato sperimentalmente investigato e i risultati comparati con quelli ottenuti dal modello tenendo conto dell’umidità interna. Inizialmente, quest’ultima è misurata attraverso una sonda di umidità posta a differenti profondità dalla superficie esposta all’essiccamiento. I dati sperimentali di umidità interna sono stati comparati con i valori calcolati usando l’equazione di diffusione non lineare. La diffusività è ottenuta sperimentalmente dalle isoterme di deassorbimento. I risultati mostrano che l’umidità predetta dal modello è sovrastimata. Al fine di migliorare le predizioni ottenute dal modello, la diffusività è calibrata in funzione dei dati sperimentali.
Misure sperimentali del ritiro a secco mostrano che nelle malte a giovane età il ritiro è minore (come per il caso di ritiro a secco ad equilibrio). Il ritiro misurato e quello ottenuto dal modello mostra un buon livello di accordo tranne che per i sistemi ad equilibrio ad un giorno in cui la malta è anche sottoposta a ritiro da carbonatazione. Infine, poiché i risultati mostrano chiaramente che la quantità d’acqua e la diffusività fortemente influenzano le predizioni del ritiro a secco, questi ultimi sono ampliamente discussi e statisticamente valutati.
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Chapter 1.
Introduction

1.1 Background
Several developed countries currently face the challenge of maintaining and rebuilding their civil infrastructures (roads, railways, bridges, dams - largely built of concrete). On the other hand, emerging market players are rapidly growing and the need for infrastructures is becoming more pressing (Infrastructure 2013). The increasing speed of design and construction has led to detrimental effects on the durability of the concrete (Pretorius and Kruger 2009).

While the construction community strives for improving the current practice techniques to minimize the occurrence of premature failure and increase the durability and service life of structures, in recent years, there has been an increasing interest in building in a more sustainable way. Portland cement, for example, has been partially substituted with supplementary cementitious materials (SCM) such as blast-furnace slag, fly ash and silica fume with the aim of improving the engineering properties of the concrete while at the same time decreasing the CO₂ emissions and the energy consumption of cement production.

Nevertheless, especially at early-age, cement-based materials may experience premature cracking even without mechanical loading, due to their low strength and strain capacity and the simultaneous volume reduction (in particular due to the loss of moisture), which may occur both in the fresh and the hardened state. Indeed, at early-age, the development of the material properties is determined by the time-dependent hydration process. At the same time, cement-based materials, when prematurely exposed to drying (which is often the case when the fast pace of construction encourages poor curing practices) will start to shrink while hydration is still in its earlier phases, further increasing the likelihood of cracking.
In this study, the early-age drying shrinkage behavior of cement-based materials containing either Portland cement or cement blended with SCM is investigated with a special approach designed to decouple the effects of the ongoing hydration.

According to ACI, early age refers to the period after final setting during which properties are rapidly changing (ACI-CT 2013). In ACI 231 it is suggested that for a typical type I Portland cement concrete cured at room temperature this period is approximately 7 days. In this work, early-age is considered the period after setting in which the material properties considerably evolve. Specifically, five different hydration ages are investigated, i.e. 1, 3, 7, 28 and 91 days. As it will be shown, already at 28 days and especially at 91 days, significant part of the hydration process has been reached and only small differences can be observed in terms of material properties changes.

Nevertheless, between 1 and 28 days the concrete’s properties are still considerably developing. If concrete at the same time is exposed to drying, due for example to inadequate curing in field practice, the occurrence of cracking may be exacerbated.

Cracks in concrete structures, besides being unsightly, may constitute preferred pathways that increase the ingress of aggressive species into the concrete such as sulfate ions, chloride ions or CO$_2$ which may all of them trigger deleterious mechanisms and possibly lead to cracking. Cracks might thereby accelerate the deterioration processes, resulting in structures with increased maintenance costs and reduced service life. In extreme cases, cracks induced by volume changes may even end up reducing the concrete load-carrying capacity and accelerating structural failure.

Within this context, a proper prediction of the volume changes in concrete structures at the designing stage remains one of the most efficient and economical strategies to account for the volumetric instability due to drying and enables further measures for minimizing stress development and possible cracking.

In order to go beyond the currently-existing empirical models and be able to predict the volume changes of different types of concrete (including a whole new range of SCM, fillers and admixtures), a fundamental understanding of the mechanisms and of the physical properties involved in the process are required. Once the mechanisms governing early-age shrinkage are well understood, it will be possible to robustly design concrete mixtures with reduced risk of cracking, increased durability and service life.

In this work, the early-age ultimate drying shrinkage at equilibrium and the shrinkage including the moisture gradients of mortars is both experimentally measured and modeled by means of poromechanics (Coussy 2005), considering mortar as an isotropic porous medium. Specifi-
cally, in the framework of poroelasticity, the constitutive shrinkage behavior of porous materials can be described knowing the mechanisms causing the volume change, their moisture state and their elastic properties.

1.2 Objectives and scope

The main objective of this work is to gain a fundamental insight into the drying shrinkage behavior of cement-based materials at early-age. The focus is on the early-age ultimate drying shrinkage behavior at equilibrium as well as the drying shrinkage development of macroscopic drying samples, the latter including the moisture gradients and also taking into account the impact of the developing intrinsic material properties (transport and mechanical properties).

The first goal is to properly decouple the early-age drying shrinkage behavior from the simultaneous ongoing hydration. This is accomplished through the use of model systems (equivalent systems), i.e., systems which reproduce the microstructure at given hydration stages and whose microstructures/properties do not evolve in time and during testing.

After an extensive validation of the equivalent system approach, the second goal of this work is to use such model systems to investigate the moisture-dependent and the time-dependent properties at early-age. Specifically, the influence of the moisture content on the early-age elastic modulus as well as on the ultimate drying shrinkage behavior and the shrinkage including moisture gradients at early-age are experimentally investigated.

Finally, the constitutive shrinkage behavior of porous materials is described by mechanistic modeling approaches, i.e., models based on the mechanisms causing the volume change, the moisture state of the mortar specimens and their mechanical properties. Specifically, poroelastic formulations are used to predict the volumetric deformations. The predicted ultimate drying shrinkage and the shrinkage including the moisture gradients results are validated against the experimental results obtained from the model systems at early ages.

1.3 Content and organization of the thesis

This thesis is divided into two main parts. The first part is dedicated to introducing and comprehensively validating the equivalent system technique. The latter is an approach based on the replacement of unhydrated binder with quartz filler which enables the measurements of early-age material properties on static and non-changing microstructures at a fixed degree of hydration over time and testing.
In the second part of this thesis, the equivalent system approach is used to investigate the moisture-dependent and time-dependent properties, such as the effect of the decreasing moisture content on the elastic modulus and the drying shrinkage behavior at early-age (both the ultimate drying shrinkage at equilibrium and the drying shrinkage of thick samples, including the effect of moisture gradients). Table 1.1 shows at glance the thesis contents. A detailed description of the chapter’s content is provided below.

Table 1.1. Content of the thesis: outline.

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Chapter 2 provides a literature review and background related to the volume changes and specifically the drying shrinkage occurring in cement-based materials. In addition, as the focus of this thesis is on the early-age behavior and the possibility to decouple the effects of the ongoing hydration from the simultaneous drying, a literature review on methods to stop hydration is given.

Chapter 3 introduces the equivalent system approach, which is designed to stop the hydration at predefined stages without altering the microstructure and to prevent further hydration during testing. The use of these model systems enables the measurement of time-dependent properties involving water transport and drying, which notoriously need long time to reach equilibrium, hence precluding the possibility to investigate the early-age behavior of hydrating cement-based systems. The chapter provides a comprehensive and systematic comparison of different microstructural properties as determined in the real systems and the equivalent systems. The majority of the main findings reported in this chapter have been published in Ce-
ment and Concrete Research in 2015 (Di Bella et al. 2015) and in a conference paper (Di Bella et al. 2015).

In chapter 4, the validation of the equivalent system approach is extended to the fracture properties as well as to the cracking initiation and propagation. The development of the elastic modulus, tensile strength, and fracture energy at different hydration stages was determined by inverse analysis of the load-displacement curves obtained by the compact tension test. In addition, the cracking initiation and propagation was followed by digital image correlation. This chapter was used to develop a 2016 paper submitted to Cement and Concrete Composites (Di Bella et al. 2016).

As the moisture content is of particular relevance in cement-based materials and it has a significant impact on their fundamental material properties, the influence of the decreasing moisture content on the elastic properties at early-ages has been investigated in chapter 5. The elastic modulus of thin samples of equivalent mortars was measured through resonant ultrasound spectroscopy after equilibrating at different RH levels. In addition, the elastic modulus of equivalent paste samples was determined by micro-indentation. Part of the results presented in this chapter was used to develop a journal paper in 2016 which has been published to Cement and Concrete Research (Di Bella et al. 2016). The results obtained with micro-indentation will be used to develop a conference paper in 2017.

In chapter 6, three different poroelastic approaches to predict the ultimate drying shrinkage are discussed and compared, including error propagation analysis. The prediction results are validated against the ultimate drying shrinkage measured on thin specimens of well-hydrated mortars equilibrated at different RH levels. The main findings reported in this chapter have been used to prepare a paper which has been published in Materials and Structures (Di Bella et al. 2017).

In chapter 7, the experimentally-determined ultimate drying shrinkage at early-age measured on the equivalent systems is presented. The predicted ultimate drying shrinkage by means of the Biot-Bishop approach is compared with experimental results at different equivalent ages. The content of this chapter will be used for a paper that is currently in preparation.

Chapter 8 is dedicated to investigate the early-age drying shrinkage development, including the effects of the moisture gradients. The drying shrinkage is modeled with the Biot-Bishop formulation and taking into account the moisture profile development. Experimental results are used to validate the modeled shrinkage obtained through finite element analysis. The results of chapter 8 are currently being developed into a journal paper.
A schematic thesis diagram to summarize the major blocks of this thesis is shown in Figure 1.1.

Figure 1.1. Schematic thesis diagram.
Chapter 2.
Literature review

This chapter is dedicated to a brief literature review covering the main topics treated in this work. As this work incorporates several subjects (i.e., early-age physical and chemical properties, elastic properties, drying shrinkage, and moisture transport), only the basic concepts are presented in this chapter. Nevertheless, the reader is provided with the main references that describe these subjects in greater details. Further, an in-depth discussion of specific topics is provided in the introduction of each chapter.

As in this thesis a new approach is introduced to investigate the time-dependent and moisture-dependent properties at early-age at a fixed hydration degree at early age, this chapter starts with a brief review of the main available techniques to stop the hydration. Afterwards, a general overview on the volume changes occurring in cement-based materials is given, with special emphasis on the drying shrinkage behavior, the factors affecting it and the moisture transport.
2.1 Introduction

Concrete undergoes several volume changes during its service life occurring both in the fresh and in the hardened state. Drying shrinkage refers to the volume reduction of the hardened concrete due to the loss of internal water towards the environment (Gilbert 2001). Apart from the environmental drying regime, drying shrinkage in cement based-materials is strictly related to the material properties development and, hence, to the microstructure development during cement hydration. For example, concrete’s drying shrinkage and its cracking susceptibility depends on several intrinsic parameters such as free shrinkage, tensile strength, stiffness, fracture toughness and creep/relaxation (Bissonnette et al. 1999). At early-age, the above-mentioned material properties, and in general the microstructural properties (such as porosity, pore size distribution and pore connectivity), are in continuous development due to the progress of cement hydration. As such, the characterization of time-dependent and moisture-dependent properties (i.e. drying shrinkage, moisture transport, or creep/relaxation) becomes difficult at early-age due to the impossibility to decouple the actual material property investigated from the ongoing hydration. A fundamental understanding of the drying shrinkage behavior at early-age is of paramount importance for predicting the development of concrete performance and, specifically, the likelihood of cracking. Indeed, at early-age, cement-based materials are particularly prone to drying shrinkage cracking, as the material properties are still developing, such as the tensile strength.

To properly access the early-age material properties of cement-based materials, it is often necessary to stop cement hydration. Several techniques are available in literature and main advantages and drawbacks are briefly discussed in the next paragraph. Afterwards, a general review on the main concepts related to volume changes in cement-based materials and specifically to drying shrinkage is provided.

2.2 Techniques to stop cement hydration

An ideal method to stop hydration should preserve the microstructure as well as the chemical and physical properties at a given degree of hydration, thereby enabling relevant measurements of unaltered material properties.
Different techniques are commonly used to stop the ongoing hydration. They are mainly divided into two categories: direct drying methods and solvent exchange methods. Both types of methods are based on the removal of free water from the hydrating microstructure: the former by evaporation or sublimation, the latter by replacing water with a solvent (such as isopropyl alcohol) that is then evaporated as well (Collier et al. 2008, Knapen et al. 2009, Zhang and Scherer 2011).

Oven-drying is one of the most widely-used techniques. However, many drawbacks have been associated with this method. From MIP measurements, Gallé showed that significant damage occurs, which mainly affects the capillary porosity domain (Gallé 2001). Microcracking induced by differential thermal expansion of aggregates and hardened cement paste as well as the buildup of high capillary pressure during oven-drying may alter the microstructure (Zhang and Scherer 2011). Further, temperatures above 100 °C may both lead to ettringite and AFm decomposition (Ye 2003) and induce further hydration, microstructure changes and favor carbonation (Knapen et al. 2009).

The D-drying method is believed to be an efficient method to completely remove the free water while preserving the microstructure (Taylor 1997, Knapen et al. 2009). However, the time for attaining a constant sample weight can take several days (depending on several variables such as vacuum level, sample size, etc.), resulting in an unsuitable method to stop the early hydration at a given time (Zhang and Scherer 2011).

Freeze-drying represents a good technique to preserve the microstructure by avoiding high capillary stresses. However, the freezing process associated with this method can cause stresses due to volume change, hydraulic pressure and crystallization pressure (Scherer 1993) and cause considerable microcracking (Collier et al. 2008). In addition, Zhang and Glasser showed that this technique may induce monosulfate degradation (Zhang and Glasser 2000). Nevertheless, this technique is considered to be effective in arresting hydration with a limited effect on the microstructure.

The solvent exchange method is a common technique used to stop hydration by the use of an organic solvent that replaces water. In the literature, contradictory arguments are reported concerning the chemical and physical interaction between the solvents and the cement hydrates (Korpa and Trettin 2006, Knapen et al. 2009, Zhang and Scherer 2011). For example Beaudoin (Beaudoin et al. 1998) concluded that solvents such as methanol and benzene could chemically react with calcium hydroxide. Knapen et al. reported that the remaining solvents may react with cement compounds or hydration products to form carbonate-like phases during further thermal analysis. Aligizaki reported no chemical interaction between isopropanol and
cement paste, concluding that isopropanol could be an acceptable fluid for solvent exchange (Aligizaki 2005). Another discussed topic is the long time necessary for the exchange liquid to diffuse through the sample (estimated as about 18 h for pieces of 1 mm size, see (Zhang and Scherer 2011)).

More recently, the supercritical drying method has been suggested as an alternative technique for stopping hydration while preserving the microstructure. However, this method is technically very challenging and the fluid used for exchange with pore water should be carefully chosen. For example carbon dioxide is usually used but it may be problematic when carbonation needs to be avoided (Zhang and Scherer 2011). Alternatively, Freon has been used however, it is immiscible with water and an exchange solvent must be used(Zhang and Scherer 2011).

All the different drying methods appear to affect the microstructures in different ways (Korpa and Trettin 2006). Desaturation, desorption, dehydration phenomena or possible reactions between hydration products and solvents may generate damage like microcracking, capillary porosity alteration, collapse of gel pores and mineralogical transformations (Gallé 2001).

In general, for the mere purpose of stopping hydration at early-age, freeze drying and solvent exchange with isopropanol have been identified as the most effective techniques to date (Zhang and Scherer 2011). Nevertheless, both techniques require the removal of water from the microstructure, precluding the possibility for further measurements involving water reintroduction into the sample, e.g., drying shrinkage, water transport, etc. If moisture is reintroduced into a sample with stopped hydration, unreacted cement grains may further react during the test, thereby altering the microstructure of the sample and affecting the results. Therefore, a method that creates a static microstructure after the hydration stops, even if the sample stays in contact with water, would be very useful.

In chapter 3, a recently-developed technique (Termkhajornkit et al. 2015) based on the replacement of unhydrated cement grains is employed to stop hydration at defined hydration stages and to obtain a representative early-age microstructure, while at the same time achieving a static system. After proper validation, this technique is used to investigate the time-dependent and moisture-dependent properties of mortars at early-age.

### 2.3 Volume changes

During their service life, cement-based materials undergo different types of volume changes that are a direct consequence of externally-applied loads or environmental loads (moisture
and/or temperature). In particular, the moisture migration in and out of cement-based materials induces volume changes. A reduction in volume, or shrinkage, is usually associated with the loss of moisture, while the ingress of moisture may lead to expansion (or swelling). Volume changes occur both in the fresh and the hardened state and even in sealed conditions, in which the water is internally consumed by the cement hydration and the capillary pores are emptied in a process called self-desiccation (Lura and Jensen 2007).

In the fresh state, before setting occurs, concrete behaves as a viscous suspension (Bentz 2008). Due to gravitational forces, the solid particles settle to the bottom and a correspondent volume of water rises up to the top (bleeding water). The settlement of the solid skeleton in saturated conditions is usually referred to as plastic settlement, which may lead to cracking due to the fact that concrete arches over the reinforcement (Kwak et al. 2010). Further, if on the concrete’s surface the evaporation rate is greater than the rate of bleeding, menisci are formed between the different cement particles resulting in capillary tension in the water, which leads to a volumetric reduction of the bulk called plastic shrinkage. As in the plastic state concrete has very limited strain capacity, restrained volume changes in this period may easily lead to plastic shrinkage cracking.

Plastic shrinkage and plastic shrinkage cracking are directly related to the loss of moisture from the surface and especially to its rate. Hence, every attempt to prevent or limit the evaporation rate may be beneficial, e.g., with external curing. Alternatives such as internal curing or the use of curing compounds have also shown to be a successful solution to mitigate plastic shrinkage cracking (Al-Gahtani 2010, Henkensiefken et al. 2010). Further, plastic shrinkage cracking susceptibility has also been related on the surface tension of the pore solution (Lura et al. 2007) which can be lowered by using shrinkage-reducing admixtures.

After setting, a volumetric contraction is observed even in sealed conditions (i.e. no moisture loss towards the environment) called autogenous shrinkage. Autogenous shrinkage finds its origin in the chemical shrinkage. The latter is a pure consequence of the fact that the volume of the hydration products is smaller than that of the reactants. Before setting, chemical shrinkage induces directly an actual reduction of the bulk volume. However, after setting, the solid skeleton resists such deformation and partially-empty pores are formed (Sant et al. 2006). The air-water menisci that are thus created induce capillary stresses in the pore water and a decrease of the internal relative humidity (self-desiccation). Autogenous shrinkage and the risk of autogenous shrinkage cracking is significantly exacerbated in concretes with low water-to-cement ratio, because of the reduced amount of available water for the reaction and their very fine pore structure that both promote self-desiccation.
Carbonation shrinkage is another form of shrinkage that concrete undergoes often in conjunction with drying shrinkage (the latter is the main topic of this thesis and is further discussed separately in the next paragraph). Carbonation shrinkage is usually associated to the reaction of the carbon dioxide (CO₂) present in the atmosphere with the cement products in presence of moisture to produce carbonates (Gervais et al. 2004). The extent of carbonation is greater when cement based materials are exposed to RH levels between 50% and 80% (Houst and Wittmann 1994).

Carbonation is accompanied by a decrease in pH and change in permeability. It further affects several physical properties (Pham 2013). For example, the pH of a carbonated concrete may drop from approximately 13 up to 9 (Brandt 2009) and it may lead to the depassivation of the steel reinforcement promoting carbonation-induced corrosion (Parrott 1994, Kulakowski et al. 2009). In turn, the carbonation products fill the matrix structure reducing the porosity. On one hand this may increases the compressive strength and the Young’s modulus (Khan and Lynsdale 2002). In addition, it has been shown that carbonation is accompanied by an increase in weight of the concrete (Gonen and Yazicioglu 2007).

Regarding to the carbonation shrinkage, it is greatest when carbonation occurs after drying, i.e. the shrinkage due to the simultaneous drying and carbonation is lower than that of the sum of drying shrinkage and subsequent carbonation shrinkage (Kamimura et al. 1965, Houst 1997, Mindess et al. 2003).

The so far discussed volume changes along with the drying shrinkage (the latter is separately discussed in the following section) are the response to the environmental loading (neglecting the temperature effects). Similarly to the deformation due to drying, concrete undergoes volume changes also when subjected to a sustained external load due to its viscoelastic nature (Nawy 2008). The increase in strain under a sustained stress is referred to creep. Relaxation, instead, refers to the gradual decrease in stress with time under a given level of sustained strain. While creep has been generally described as the consequence of water movements within the paste structure, several additional mechanisms have been proposed and studied such as plastic flow, load bearing hindered adsorbed water, bond breakage in slip and its reformation, solidification theory for short-term aging, and micro pre-stressed of creep sites in cement gel microstructure causing long term effect (Bažant 2001).

In this work, the investigated mortar specimens are treated as linear elastic, hence, the possible viscoelastic contributions are not taken into account during the deformation due to drying.
2.4 Drying shrinkage

Drying shrinkage is usually considered one of the dominant deformation phenomena in concrete because of its magnitude and because it occurs from setting throughout the whole service life. In conventional concretes, deformations in the range between 400 and 1000 x10^-6 microstrains can be expected and at the same time due to their magnitude they cannot be ignored in structural design (Mehta and Monteiro 1993). Further, as shrinkage is a property of the paste, mortars and paste specimens show higher drying shrinkage than concrete. For example shrinkage of mortars can be expected to range between 1000 and 2000×10^-6 (Bentz 2005), while up to and above 4000×10^-6 microstrains in case of pastes (Pease 2005). While cracking induced by drying shrinkage generally does not affect the structural integrity (Bissonnette et al. 2007), it may decrease the service life of concrete elements, eventually increasing the maintenance costs.

Drying shrinkage is the result of the loss of internal moisture to establish hygral equilibrium with the external environmental relative humidity (RH) (Neville 1995, Mindess et al. 2003). As water is lost from the pores in concrete, capillary tension builds up in the pore fluid and exerts a compression on the solid skeleton, leading to shrinkage of concrete. Further mechanisms that play a role at lower RH (especially below about 50%, when there is no capillary water in the pores) are changes in disjoining pressure and surface tension (Powers 1965, Ferraris and Wittmann 1987, Lura et al. 2003). The different mechanisms that fundamentally describe the shrinkage are discussed in details in the following section.

In the presence of restraint or in case of asymmetrical drying, shrinkage may lead to significant stresses build-up. A sketch is shown in Figure 2.1 (Fortin 2005). On the left side, shrinkage, the concrete slab is assumed to dry from two sides while it is fixed at the two ends. The hindered shrinkage causes the buildup of internal tensile stresses within the element. The right side of Figure 2.1 illustrates the warping in which the slab undergoes an asymmetrical differential shrinkage, i.e., the slab dries from one side, the concrete slab deforms. In both cases, when the stresses exceed the tensile strength of the material, visible cracking and micro-cracking occur.

Stresses due to differential shrinkage are usually parallel to the drying surface, leading to cracks having orientation perpendicular to the surface (Bisschop and Bentur 2003).
While cracks may also reduce the load-carrying capacity, they represent a preferential path for the transport of aggressive media into the concrete (Weiss 1999). Cracking is a complex phenomenon which is dependent on several factors, such as free shrinkage, mechanical properties of the concrete, age–dependent material properties and degree of restraint. The degree of restraint refers to a reduced ability of concrete to freely deform. Partial or full restraint in concrete may arises from internal and external causes as it will discussed later in this section.

At the same time, viscoelastic deformations have been reported to influence the magnitude of not only the deformation resulting from applied loading, but also of shrinkage of concrete (Acker 2004, Grasley and Leung 2011). Creep due to applied loads is usually a serious problem for concrete structures since it may lead to excessive deflections or in extreme cases even to structural failures (Bazant et al. 2012). On the other hand, stresses can be relaxed as schematically shown in Figure 2.2. The latter shows the time dependent strength development (blue line) compared to the stresses development due to shrinkage (black line) and due to shrinkage including creep component (red line). In the first case, the stresses exceed the strength and the specimen is expected to crack at early ages. Consequently creep in restrained concrete is in general beneficial, since it leads to stresses relaxation and thus decrease the probability of cracking (Benboudjema et al. 2005, Rodden et al. 2006). In case of restrained shrinkage, the stresses cannot be calculated using the Hook’s law, i.e. multiplying the free shrinkage by the elastic modulus as stress relaxation may reduce the stresses by 30-70%. Cal-
calculation of the stresses development of restrained conditions have been described for example in (Weiss 1999).

Figure 2.2. Sketch of the strength and stresses evolution over time in a restrained concrete element (Weiss 1999).

2.4.1 Factors affecting the drying shrinkage

The relative humidity of the medium surrounding the concrete greatly affects the magnitude of shrinkage. In fact, the driving force for the drying shrinkage is the withdrawal of water due to the difference in the internal relative humidity of the concrete and the environmental one to which the concrete element is exposed. Accordingly, during testing a proper RH should be defined. Different standard methods to measure the drying shrinkage have been developed in different countries. In Great Britain, for example, the samples are exposed to a temperature of 22±2 °C and a relative humidity of 55% as an average of the indoor RH (45%) and external one (65%) (BS-1920-8 2009). The ASTM C157 standard defines a relative humidity of 50% and temperature of 23°C. In Switzerland, according to the SIA code, the specimens are stored at 20 ± 2°C and 70 ± 5% RH (SIA 262/1). Due to the disagreement between the possible drying conditions, it becomes important to state at which relative humidity the shrinkage is measured.

Shrinkage is also greatly affected by the water to cement ratio and the curing age (Juenger and Jennings 2002). Both of them strictly influence the porosity. In addition, the curing age is related to the extent of hydration and amounts of hydration products (Helmuth and Turk 1967). It has been argued that not only the amount of CSH, but also its microstructure influences the drying shrinkage (Verbeck 1958, Helmuth and Turk 1967, Juenger and Jennings 2002). Spe-
cifically to the curing age, however, on the contrary to the mass loss measurements, drying shrinkage does not seem to be significantly affected (Bisschop and Bentur 2003).

Nevertheless, when dealing with concrete or mortar, the ratio between the amount of paste and aggregates becomes the most important factor. The grading, maximum size and shape of the aggregates are believed to slightly influence the drying shrinkage. However, their modulus of elasticity is one of the most important factors. Indeed, the aggregates exert a restraining effect, as it prevents the surrounding paste to shrink freely (Pickett 1956, Bisschop and Van Mier 2002). Several papers have been dedicated to estimate the concrete shrinkage starting from the shrinkage of the neat paste (Pickett 1956, Hansen and Nielsen 1965, Almudaiheem and McDonald 1993). For example, according to the Pickett model (Pickett 1956), the drying shrinkage of the concrete can be estimated by the shrinkage of the paste, the volume fraction of the aggregates and the correlation parameter which is a function of the aggregates restraining effects. Indeed, the elastic properties of the aggregate play an important role in determining the degree of restraint offered (Carlson 1938, Alexander 1996). More details about the shrinkage predictive models are provided in chapter 6.

Finally, concrete shrinkage is also influenced by the specimen’s size. In real concrete elements, shrinkage is a slow process due to the time it takes for the transport of water in the fine pore structure towards the drying surfaces. The drying process in cement-based materials is discussed in section 2.7.

2.5 Drying shrinkage mechanisms

Despite the great deal of research in the past decades, several uncertainties remain in describing the mechanisms behind the drying shrinkage of cement based materials (Roper 1966, Wittmann 1973, Hansen 1987). Nevertheless, it is generally agreed that more than one mechanism is involved during drying and their effectiveness depends on the water content and on its state within the porous body.

In the literature, drying shrinkage of cement-based materials is considered to be a consequence of changes in disjoining pressure, capillary pressure and surface free energy and combinations thereof, accompanying a decrease of saturation and internal RH, e.g. (Lura et al. 2003, Grasley and Leung 2011).

According to Derjaguin et al. (Derjaguin 1987) when the RH increases in a porous solid, the disjoining pressure, \( \Pi \) [Pa], can be seen as the force that pushes apart the solid particles overcoming the van der Waals attractions, due to increasing adsorption of water in the regions
where the full adsorption thickness cannot develop at a given RH, see also (Ferraris and Wittmann 1987, Duckheim and Setzer 2008). Conversely, when the RH decreases, desorption of water from the hindered adsorption regions leads to a decrease of the disjoining pressure, hence the solid particles are drawn together by the van der Waals attraction forces, resulting in net shrinkage.

Changes of capillary pressure \( (p_c) \) in the pore water represent another mechanism that is usually employed to describe the hygric strains in porous materials (Neville 1995). The capillary pressure is related to the formation of water-air menisci in partially-empty pores, which induce an isotropic compressive stress within the rigid solid skeleton that leads to bulk shrinkage. Changes in pressure exerted by the pore fluids on the skeleton that cause shrinkage, which can be considered to be due either to capillary or disjoining pressure, are related to the internal RH through the Kelvin-Laplace equation:

\[
p_c = \Pi = \frac{\rho RT \ln(RH)}{M} \quad \text{(eq. 2.1)}
\]

Where \( \rho \) [kg/m\(^3\)] is the density of the pore fluid, assumed as 1000 kg/m\(^3\), \( R \) is the universal gas constant equal to 8.314 [J/(mol K)], \( T \) [K] is the temperature (in this study, 293.15 K) and \( M \) [kg/mol] is the molar mass of the pore fluid, assumed equal to that of water 0.01802 kg/mol, (for a discussion of these parameters, see (Chen et al. 2013)).

At low RH (about below 40%), shrinkage and swelling are believed to be influenced by the surface free energy change due to de-/adsorption of water on the surface of the CSH (Duckheim and Setzer 2008). The surface energy change is greatest during adsorption of the first monolayer and becomes negligible with increasing amounts of adsorbed water (Mindess et al. 2003). Conversely, removal of adsorbed water causes shrinkage. It should be emphasized that most concrete structures are not continuously exposed to RH below 40% and consequently their internal RH rarely reaches such low levels (Andrade et al. 1999).

Even though drying shrinkage is often referred to a superposition of the three above mentioned mechanisms (or others) (Roper 1966, Wittmann 1973, Pihlajavaara 1974, Bažant 1986, Hansen 1987), the capillary tension is considered the main mechanism at relative humidity ranges above 40-50% RH. As it will be discussed in chapter 6, in this work the capillary pressure is considered the main mechanism behind the drying shrinkage for prediction purposes in the range in which the menisci are considered to be stable.
2.6 Mechanical and fracture properties development

Shrinkage and shrinkage cracking strictly depend (among others) on the mechanical properties development. Further, in order to properly model the volumetric deformation and eventually the likelihood of cracking, the mechanical properties and fracture properties need to be carefully assessed and used as input parameters.

During hydration, the development of the material microstructure is accompanied by changes in the mechanical properties such as compressive strength, tensile strength, modulus of elasticity, Poisson’s ratio, and fracture energy. The above mentioned properties represent those that are investigated in this work to validate the equivalent systems while afterwards used to model the drying shrinkage. For this reason a brief introduction is given in this section.

The development of the compressive strength is primarily related to the water-to-cement ratio (porosity), the type of cement, presence of chemical and mineral additives and finally, curing conditions.

Although the compressive strength is usually one of the most common studied parameter to address the concrete performance (Kumar and Bhattacharjee 2003), it is the tensile strength which determines the resistance to cracking and represents one of the outmost parameter to predict crack initiation.

Nevertheless, the determination of the tensile strength is not an easy task as the direct uniaxial tensile test (believed to provide the best estimate) is difficult to perform (Lamond 2006). Indeed, the direct tension test is more sensitive to eccentricities, rotational boundary conditions, and possibility of multiple cracking formations (Zhou 1988, Bazant 1992, Østergaard 2003). Hence, more often, the tensile strength is estimated by indirect test methods such as the three-point bending test, the wedge-splitting test or the compact tension test (CTT) (Wittmann et al. 1987, Shah et al. 1995, Østergaard et al. 2000). In this work the tensile strength is determined using the compact tension test. More details about the test procedure and the determination of the tensile strength are provided in chapter 4.

The elastic modulus of concrete is usually associated to the stresses generated in concrete, when assumed to behave elastically (i.e., excluding viscoelastic components). It has been observed that at early-age the development of the modulus of elasticity is higher than the strength gain, which reflects the cracking sensitivity at early age (De Schutter and Taerwe 1996, Bisschop and Bentur 2003).

The elastic modulus can be measured by static technique both in compression and in tension using extensometers to measure the strain. Alternatively, the elastic modulus can be obtained
from non-destructive methods. For example, non-destructive techniques to measure the dynamic elastic modulus based on the determination of the fundamental frequency or on the measurement of the pulse velocity (Swamy 1971, Almudaiheem and Al-Sugair 1992). In general, the elastic modulus determined dynamic methods are higher than those obtained through the static methods (Lamond 2006). Finally, the elastic modulus has also been calculated from indentation measurements. In this work, the elastic modulus of the mortars and pastes is investigated using static, dynamic and indentation techniques. More details are provided in chapter 5.

While both the strength and the elastic modulus increase with the ongoing of the hydration as the porosity decreases, contradictory results have been found for the Poisson’s ratio. The Poisson’s ratio in concrete has been shown to remain constant or tend to decrease with age (Bergström and Byfors 1980, Oluokun et al. 1991).

Boumiz at al. investigated the development of the dynamic Poisson’s ratio in paste and mortars at early age (Boumiz et al. 1996). They concluded that the Poisson’s ratio decrease with age. More recently, similar results were obtained by (Maruyama and Igarashi 2014) on cement pastes by means of ultrasonic pulse velocity measurements showing that the Poisson’s ratio increases with the age.

The above discussed material properties and their development is related to the behavior before cracking, however, also material properties such as the fracture energy becomes fundamental to investigate the post-cracking process. While the tensile cracking is related to the cracking initiation, the fracture energy influences the cracking propagation.

The fracture energy is defined as the amount of energy required to create a crack of one unity of area (Peterson 1980). The concrete fracture energy is strictly related to the increased number of bonds as a result of the cement hydration. Consequently, the fracture energy has been shown to increase with age mainly within the first 28 days (Wittmann et al. 1987, De Schutter and Taerwe 1997).

2.7 Drying process in cement porous materials

The drying process in cement based materials is usually assumed to occur as a two stages process (Scherer 1990, Lura et al. 2007). First, the direct evaporation of the surface and shallow sub-surface’s liquid water takes place, with a consequent constant rate decrease in mass of the specimen (constant rate period). The second stage still consists in an outward flux of water vapor through the surface. However, such vapor is the result of either evaporation of liquid
water brought from the sub-surface up to the surface or it is vapor that directly moved from the sub-surface to the surface and through it. This stage is typically described as being composed of two sub-stages (first and second falling rate period).

In the first falling rate period, both liquid flow and vapor diffusion occurs (Prat 2002, Lehmann et al. 2008). Sub-surface pores are gradually emptied of both liquid and vapor water. The liquid flow is driven by capillary forces (Yiotis et al. 2001). A system of liquid bridges allows liquid water to move up to the surface, where it can evaporate, guaranteeing still a high drying rate. This system of liquid bridges is continuous and it is said to be in the “funicular” state (Coussot 2000). The transition from the first to the second falling rate period is marked by a strong decrease in the drying rate. The system of liquid bridges becomes discontinuous and it is said to be in the “pendular state” (Yiotis et al. 2003). Such transition signals the evolution from a state where liquid flow is still possible along the network of liquid bridges and vapor diffusion contributes less to the drying rate to a state where liquid water flow is not anymore possible, isolated clusters of liquid water in the pendular state gradually dry out by evaporation and vapor diffusion from the sub-surface becomes the only process contributing to the drying rate (Bakhshi et al. 2012, Villani 2014).

In most general case, moisture state of a porous material like concrete can be described by mass conservation of water (continuity equation). At the macroscopic scale (usually considered to range from millimeters to meters), changes of moisture content in the volume of concrete, \( m_c \) [kg/m\(^3\)] in time \( t \) can be written with the following differential equation:

\[
\frac{\partial m_c}{\partial t} = div(j) + \frac{\partial m_s}{\partial t} \quad (eq. \ 2.2)
\]

Where \( j \) [kg/m\(^2\)/s] is a flux of moisture, expressing mass of water passing through a unit area in a unit of time, and \( m_s \) is a source or sink term. The latter is often used to describe a sink term due to hydration of cement and is not used in the case considered here. It should be mentioned that the water mass in eq. 2.2 accounts for different forms of water present in concrete, i.e. liquid water vapor and physically adsorbed water.

Different approaches have been used to describe transport of moisture in concrete at the macroscopic level and the challenge regards considering different physical mechanisms of moisture transport and their dependence upon the moisture state, i.e. non-linearity.

Since moisture transport can take place simultaneously involving different mechanisms, it is practically impossible to distinguish their individual contribution in the experimental tests. Therefore, one of the most commonly approach is to consider different physical mechanisms
of transport as resulting at the macroscopic level in an effective diffusion-like process, e.g. (Bażant and Najjar 1971, Bażant and Najjar 1972, Garbalińska 2006, Villani et al. 2014).

In this work, the moisture movement during drying of cement-based materials is described using the non-linear differential moisture diffusion equation and a diffusivity coefficient obtained from experimental data from DVS measurements. More details about the method to describe the drying process are provided in chapter 8 and in Appendix A.

2.8 Major Achievements

This work presents new insights into the drying shrinkage behavior of cement-based mortars with and without SCM, mainly focusing on the early age, by using the equivalent system approach. The latter is a new technique to investigate cement-based material properties at early age. The early-age represents the period in which the material is more prone to failure due to an incomplete development of its properties. The shrinkage predictions, obtained through poroelastic models, are validated by the experimental shrinkage measurements.

The early age behavior and specifically the experimental drying shrinkage (at equilibrium and including the moisture transport) were investigated using the equivalent system approach. The latter is shown to be a powerful technique enabling the investigation of time-dependent and moisture-dependent properties on samples with fixed degree of hydration.

In addition to the drying shrinkage, the moisture-dependent properties such as the elastic modulus as a function of the moisture content was investigated at early age making use of the equivalent systems. The elastic modulus is shown to decrease as the moisture content diminishes.

The experimental ultimate drying shrinkage is shown to be smaller at earlier ages than at later ages despite the higher stiffness owned by the mortars at later ages. It is shown that the interplay between the saturation degree and the bulk modulus governs the magnitude of shrinkage. To this end the main parameters influencing the ultimate drying shrinkage behavior such as the elastic properties and the saturation degree were widely investigated as well as the different shrinkage mechanisms evaluated (capillary pressure, disjoining pressure, and surface free energy). The saturation degree is shown to play a major role in the magnitude of the drying shrinkage and the capillary pressure is shown to appropriately describe the shrinkage behavior in relative humidity ranges between 50-100%.
Poroelastic models were used to predict the drying shrinkage of cement-based mortars. They showed a good agreement with the experimental results and proved their ability in predicting the shrinkage (paste diluted with aggregates). Note that the viscoelastic response is not taken into account.

Finally, it is shown that the poroelastic models can be successfully used in predicting the drying shrinkage including the moisture gradients. In this case, however, an appropriate evaluation of the transport properties (kinetics of drying) is required in order to improve the prediction of the drying shrinkage.
Chapter 3.
Microstructurally-designed mortars for studying early-age properties

In this chapter, the equivalent system approach is presented as a technique for stopping hydration without altering the microstructure by invasive methods. This technique is based on the replacement at the mixing stage of unhydrated cement/binder grains that would otherwise remain unhydrated in real systems at defined hydration stages with inert quartz particles. This technique allows studying hydration-dependent and/or moisture dependent properties in a static equivalent system, where these processes can be decoupled from hydration.

A comprehensive comparative investigation of the mechanical properties as well as the physical-chemical ones between real and equivalent systems are here presented and their difference statistically evaluated through the analysis of variance (ANOVA).
3.1 Introduction

The characterization of the early-age material properties in cement-based materials is of paramount importance as many deterioration processes are often associated or are believed to arise from the early-age i.e. when the hydration is still proceeding. While many cement-based properties (i.e. strength, elastic modulus, Poisson’s ratio, as well as fracture properties) can be more or less easily measured as a function of time, the determination of the early-age volumetric deformations such as drying shrinkage, creep, and/or relaxation at a given hydration degree is more complicated. Indeed, at early-age the microstructure of cement-based materials is continuously evolving due to hydration, which may interfere with an accurate determination of such long-term properties (Di Bella et al. 2015). Despite different methods in literature are available to stop the hydration process (see chapter 2), none of them seem adequate to decouple the effects of hydration from the ongoing drying and hence investigate moisture-dependent and time-dependent properties such as drying shrinkage.

Recently, a technique based on the replacement of unreacted binder by quartz to produce equivalent systems at given hydration stages has been presented (Termkhajornkit et al. 2015). Starting from the knowledge of the volume fractions of unreacted binder as a function of time, a new mixture is prepared in which the amount of unreacted binder is replaced with an equal volume of non-reactive quartz filler (Termkhajornkit et al. 2015).

Several types of measurements can be performed on the equivalent systems without being affected by the ongoing hydration, even though water does not need to be removed from the samples. Therefore, it represents a powerful technique for studying phenomena that are both dependent on cement hydration and at the same time influence cement hydration, such as moisture transport (e.g. water transport and drying), along with time-dependent properties such as early-age shrinkage and creep, for which it is difficult to decouple the effects of hydration and transport or loading.

The aim of this chapter is to validate this approach by a systematic comparison of mechanical properties and microstructural features between the real systems and the equivalent systems - both for OPC and cement blended with supplementary cementitious materials (SCM) - aided by the statistical analysis of variance (ANOVA). To this end, the similarity between the real and the equivalent microstructure was tested in terms of compressive strength, flexural strength and elastic moduli. Further, the microstructure is characterized by means of mercury intrusion porosimetry (MIP) and thermogravimetric analysis (TGA).
3.2 Equivalent systems

The concept of the equivalent microstructure relies on the substitution at the mixing stage (by volume) of the unreacted binder with quartz particles that simulate the unhydrated cement grains. This can be conceptually explained by means of Powers’ model (Powers et al. 1947) in which the volume fractions of each constituent in a portland cement paste at a given hydration stage can be derived from a set of empirical equations. These empirical equations are based on a comprehensive study of water sorption isotherms and chemically bound water measurements in hydrated cement pastes (Powers et al. 1947, Hansen 1986, Neville 1995, Brouwers 2004). It should be noted that the model by Powers is used here only to better explain the concept. The actual degree of hydration and the volumetric composition needed to determine the amount of inert filler replacement were determined based on the experimental investigations described at the end of this section.

According to Powers’ model, approximately 0.23 g of water per gram of cement is chemically bound at complete hydration and becomes part of the gel structure; this water is defined as non-evaporable water. It should be noted that the chemically bound water coefficient can be slightly different for modern cements (Neville 1995, Brouwers 2004). Approximately 0.19 g of water per gram of cement is further adsorbed on the surface of the gel. The remaining water occupies part of the capillary pores. Hydration stops according to the model when any of the three conditions takes place: 1) exhaustion of capillary water, 2) exhaustion of free space for hydrates to form (see also (Jensen and Hansen 2001)), 3) exhaustion of unreacted cement (Powers et al. 1947, Hansen 1986, Jensen and Hansen 2001). The studied method for creating the equivalent systems is based on reaching the third condition.

Finally, the cement paste undergoes a volume reduction called chemical shrinkage, due to the fact that the volume of the reaction products is smaller than the volume of the reactants (cement and water), corresponding approximately to 6.4 ml/100g cement reacted (Jensen and Hansen 2001). Based on these three characteristics it is possible to estimate the fractional volumes of gel solid, gel water, capillary pores, chemical shrinkage and unhydrated cement in the physical structure of portland cement pastes at different hydration stages (Hansen 1986).

In Figure 3.1a, the evolution of the phases by volume as a function of the degree of hydration is conceptually visualized in accordance with Powers’ model. The specific diagram refers to a cement paste with water to cement ratio equal to 0.51 in sealed conditions. A water-to-cement ratio (w/c) >0.42 theoretically allows for full hydration of the cement in sealed conditions.
(Hansen 1986). Let us assume now that the hydration reaction must be stopped at a given hydration stage “A”, as shown in Figure 3.1b. At this stage, a fraction of unhydrated cement is still present in the system. The replacement of this fraction with an inert material such as quartz particles with similar size distribution would allow for realizing an equivalent system at that given hydration stage (with equal porosity and equal volume fractions), but more importantly would also allow for “freezing” the microstructure also in the presence of water, since no additional cement is available for reaction.

Such approach allows obtaining static systems, i.e., whose microstructures do not change over time due to cement hydration because all the binder has reacted. Complete reaction is assumed to occur after at least 3 months of curing in moist conditions. An equivalent microstructure system relates to a predefined early-age hydration stage development of the system to be reproduced and it is built from the knowledge of the degree of hydration at a specified age of the real system. Specifically, knowing the volume fraction of unreacted binder in the system at a given hydration stage, a new mixture is formulated where the binder is replaced by an equal volume of inert quartz particles.

Figure 3.1. a) Portland cement paste with w/c 0.51 and b) equivalent microstructure approach at a given hydration stage A, where a fraction of the cement (corresponding to the unreacted cement at hydration stage A in the real systems) is replaced by inert quartz.

In this study, this approach is employed on three real mortar and cement paste mixtures with and without SCM: OPC, OPC + 45% Slag and OPC + 45% Fly ash (by volume). The three real systems were formulated in order to maintain the same water-to-binder ratios and paste-
to-aggregate ratios by volume. For each real mixture, five different hydration stages were investigated, corresponding to five different ages: 1, 3, 7, 28 and 91 days.

The volume fraction of reacted/unreacted material was experimentally determined by (Termkhajornkit et al. 2015). Table 3.1 shows the degree of hydration determined on the real mixtures. The degree of hydration of the OPC systems was determined through quantitative powder X-ray diffraction (QXRD) using Rietveld analysis, while the degree of hydration of the systems containing SCM was obtained coupling SEM image analysis and chemical shrinkage measurements. More details about the degree of hydration calculations of the three real systems can be found elsewhere (Meulenyzer et al. 2013, Termkhajornkit et al. 2015).

Table 3.1. OPC and the SCM determined at five different hydration ages in the real paste mixtures

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>OPC 100% (%)</th>
<th>OPC+45% Quartz (%)</th>
<th>Slag (%)</th>
<th>Fly ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42</td>
<td>47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>62</td>
<td>67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>73</td>
<td>79</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>85</td>
<td>90</td>
<td>42</td>
<td>8</td>
</tr>
<tr>
<td>91</td>
<td>91</td>
<td>94</td>
<td>62</td>
<td>34</td>
</tr>
</tbody>
</table>

In this study, quartz is used as inert material to represent the unreacted binder in the equivalent systems. However, due to the fine particle size distribution of the quartz used in place of unhydrated binder, some extent of chemical reaction may be expected. For example, De Weerdt et al. concluded that the quartz filler was not completely inert when tested in an alkaline solution with a pH of 13.5 mixed with Ca(OH)₂ (De Weerdt et al. 2011). On the other hand, Deschner et al. reported that no pozzolanic reactivity was observed by TGA within the first 90 days (Deschner et al. 2012). Benezet and Benhassaine concluded that crystallized quartz shows some degree of pozzolanic reactivity, which is a function of the particles’ fineness (Benezet and Benhassaine 1999). As shown by our TGA study presented in the results section, the quartz filler used had only low pozzolanic reactivity.

The model assumes that in the equivalent systems all cement is completely reacted and the remaining inert filler is unreacted. It should be noted that the spatial distribution of hydrated/unhydrated phases will not be identical in the real and in the equivalent systems. In par-
ticular, in the real systems the inner parts of large cement grains remain unreacted, while the outer parts react. It will be however shown that the difference in spatial distribution of the hydrated and unhydrated phases are only of minor importance compared to the volumetric ratios of the phases (the latter being equivalent between the two types of systems) when considering non-evaporable water content, mechanical properties, total porosity and even pore structure. Finally, it is important to emphasize that the reference age of the equivalent systems is just an approximation of their intended age. In fact, due to errors in the quantification of the degree of hydration in the real systems as well as the fact that not all the residual cement may completely hydrate in the equivalent systems, some deviation of the equivalent microstructure from the real systems at a given age may occur. This is, however, not compromising the method itself as the main goal of this technique is not necessarily to reproduce a precise age of the system, but rather to “freeze” the microstructure of the real systems at a precise hydration stage.

### 3.3 Materials and mixtures design

The cement used is an ordinary portland cement (OPC) CEM I 52.5 N with a density of 3.13 g/cm³. QXRD carried out on the OPC revealed the following mineralogical composition (by mass): 61.2% C₃S, 16.2% C₂S, 6.6% C₃A, 10.5% C₄AF and 1.8% CaSO₄. The oxide composition of the OPC, slag, fly ash and silica fume are shown in Table 3.2.

In the real mixtures, 45% (by volume) of cement was replaced by slag and fly ash, respectively. Slag with density of 2.92 g/cm³ and fly ash type F with density 2.09 g/cm³ were employed as cement replacement.

In the equivalent systems, different amounts of binder are replaced by inert quartz according to the volume of unreacted binder at a given age in the corresponding real systems. The quartz used in place of the unhydrated cement (and of unreacted slag or fly ash in case of systems containing SCM) has a density of 2.65 g/cm³ and a particle size distribution comparable to that of the cement (Figure 3.2a).
Table 3.2. Chemical composition of the cement, slag, fly ash and silica fume.

* value below the detection limit

<table>
<thead>
<tr>
<th></th>
<th>CEM I 52.5 N</th>
<th>Slag</th>
<th>Fly ash</th>
<th>Silica fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ %</td>
<td>20.10</td>
<td>35.82</td>
<td>54.70</td>
<td>91.4</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>5.02</td>
<td>11.16</td>
<td>23.28</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>3.14</td>
<td>0.27</td>
<td>3.82</td>
<td>0.28</td>
</tr>
<tr>
<td>CaO %</td>
<td>64.48</td>
<td>42.29</td>
<td>10.92</td>
<td>0.06</td>
</tr>
<tr>
<td>MgO %</td>
<td>0.99</td>
<td>8.31</td>
<td>1.08</td>
<td>0.05</td>
</tr>
<tr>
<td>K₂O %</td>
<td>0.87</td>
<td>0.34</td>
<td>0.84</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O %</td>
<td>0.17</td>
<td>0.18</td>
<td>3.15</td>
<td>0.04</td>
</tr>
<tr>
<td>SO₃ %</td>
<td>3.33</td>
<td>1.99</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO₂ %</td>
<td>0.23</td>
<td>0.47</td>
<td>0.67</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn₂O₃ %</td>
<td>*</td>
<td>0.22</td>
<td>0.06</td>
<td>*</td>
</tr>
<tr>
<td>P₂O₅ %</td>
<td>0.33</td>
<td>*</td>
<td>0.08</td>
<td>0.36</td>
</tr>
<tr>
<td>ZrO₂ %</td>
<td>*</td>
<td>0.02</td>
<td>0.05</td>
<td>0.68</td>
</tr>
<tr>
<td>SrO %</td>
<td>*</td>
<td>0.03</td>
<td>0.10</td>
<td>0.02</td>
</tr>
</tbody>
</table>

With the intent to speed up the slag reaction and obtaining almost complete hydration within the first 3 months of curing, the slag used in the equivalent systems was ground (Figure 3.2b). In addition, the fly ash portion (used in the real system) was replaced by silica fume with density 2.34 g/cm³ in the equivalent system (Figure 3.2c). Again, this was mainly done to speed up the pozzolanic reaction, since fly ash reacts only slowly. According to previous studies, even the silica fume will not completely react (Poulsen 2010). To take this fact into account, the equivalent systems are designed assuming (based on (Poulsen 2010)) that only 70% of the silica fume will react after 3 months, see also (Termkhajornkit et al. 2015).

While the particle size distribution of the cement, slag and fly ash was obtained by laser diffractometry, the one of the silica fume was obtained through dynamic light scattering due to the smaller sizes involved.
The sand used to produce the mortar samples had density 2.65 g/cm³, medium grain size D50 312 μm, maximum size of 650 μm and water absorption of 0.2%.

Table 3.3 shows the mixture proportions used for the three real mortar systems: the aggregate, the binder and the water content are kept constant by volume. Note that the mass of cementitious materials changes due to the different densities of the cement, slag and fly ash (hence the w/b by mass). For each of the three real systems, 5 equivalent mortar mixtures are obtained, representing different hydration stages. Real and equivalent OPC and blended pastes were also prepared on the basis of the mortar mixtures design, without sand.

Table 3.3. Mixture proportions of the tested mortars by mass [kg/m3].

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>Slag</th>
<th>Silica fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>528</td>
<td>313</td>
<td>312</td>
</tr>
<tr>
<td>Slag</td>
<td>-</td>
<td>156</td>
<td>-</td>
</tr>
<tr>
<td>Silica fume</td>
<td>-</td>
<td>-</td>
<td>97</td>
</tr>
<tr>
<td>Water</td>
<td>306</td>
<td>306</td>
<td>306</td>
</tr>
<tr>
<td>Sand</td>
<td>1331</td>
<td>1331</td>
<td>1331</td>
</tr>
<tr>
<td>Quartz</td>
<td>60</td>
<td>101</td>
<td>132</td>
</tr>
</tbody>
</table>

The mortar was mixed in a Hobart mixer in accordance with the standard NF EN 196-1. The cement, SMC and quartz filler (the latter only in the equivalent systems) were weighed and carefully mixed by hand to homogenize the dry mixture. The dry cementitious mixture and the water were then placed in the mixing bowl and mixed at low speed for 30 s. While mix-
ing, the sand was added within a time window of 30 s followed by additional 30 s mixing at higher speed. After 90 s rest, the mortar was again mixed for final 60 s at high speed.

Prismatic samples of size 40×40×160 mm³ were cast in two layers on a vibrating table. After casting, the specimens were covered with a plastic sheet and kept in an environmental chamber for 48 h at 20 °C and 100% RH.

The cement pastes were prepared from the same mix designs as for the mortars but excluding the sand. The cement pastes were mixed in a Waring laboratory blender mixer at 3000 rpm. Cement, quartz and SCM were first mixed dry by hand. The dry binder was then added to the water in the mixer bowl and mixed for 60 s followed by 60 s rest and final 60 s of mixing.

Several samples were cast in cylindrical plastic containers with diameter 35 mm and 70 mm long. After casting, they were continuously rotated at 5 rpm for 48 h at 20 °C to prevent segregation.

After demolding, both mortar and paste samples were wrapped in wet towels and sealed in plastic bags to avoid drying and carbonation. They were then cured in an environmental chamber at 20 °C and 100% RH until testing.

3.4 Experimental methods

The compressive and flexural strength of the three real mixtures (OPC, OPC + 45% Slag and OPC + 45% Fly ash) and the equivalent mixtures were measured in accordance with EN 196-1 on prismatic samples of dimensions 40×40×160 mm³. For each mixture, both the flexural and the compressive strength of the real mortars were measured at 1, 3, 7, 28 and 91 days and compared with the strength of the equivalent systems at completely hydrated binder. Two to three samples were tested for each mixture/age.

The static elastic modulus of the real and equivalent systems was determined on two 40×40×160 mm³ mortar prisms for each testing age according to EN 196-1. Two extensometers were used to measure the displacement while the sample underwent loading cycles up to 30% of its average compressive strength.

Thermogravimetric analysis (TGA) provides reliable information about the cement paste matrices, such as the amount of non-evaporable water (H) and the content of calcium hydroxide (CH) in plain and blended cement pastes.

At a given testing age, the sample was crushed using a mortar and pestle and the solvent exchange technique was applied to stop hydration, first with isopropanol for 15 min and afterwards the sample was flushed with ether. The powder was subsequently dried in an oven at 40
°C for 15 min and then directly tested. This procedure was applied in both real and equivalent systems to remove free water and therefore arrest the hydration in the real systems and eliminate the influence of the free water on the water loss measurement. Replicate samples were obtained from independent grinding and solvent exchange procedure performed on a single specimen.

Further, the TGA was also employed to monitor the pozzolanic reactivity of the quartz used in this study. The direct pozzolanic reactivity was quantified by mixing 50 g of quartz with 50 g of calcium hydroxide, 7.5 g of calcium carbonate and 135 g of a 0.3M solution of potassium hydroxide. The samples were stored in a chamber at 20 °C, under sealed conditions, and continuously rotated at about 5 rpm to avoid sedimentation. After 1 day and 91 days, the reaction was stopped as described above for the paste samples.

Approximately 50 mg of sample powder was employed for each test. The weight of the sample was continuously monitored while heating up in the temperature range 30-980 °C at 20 °C/min in a N2-atmosphere.

The pore structure of the three real paste mixtures (total porosity and pore size distribution) was characterized by means of MIP and compared with their respective equivalent systems.

At the end of each curing period (in both the real and the equivalent systems), the samples were crushed in small pieces of about 5 to 10 mm and immersed in isopropanol for 3 days to stop hydration. Afterwards, the solvent was decanted and the samples were dried in an oven at 40 °C for the following 3 days. After drying, the samples were stored in nitrogen-filled desiccators containing silica gel, to prevent carbonation and hydration. Right before testing, the samples were further crushed to smaller sizes (approximately 2-3 mm in diameter) and about 1 g of each sample was tested with Pascal 140/440 (Thermo Fischer Scientific Inc.) porosimeters. The mercury was firstly intruded up to 200 kPa into the sample using a Pascal 140. Then, it was moved to a Pascal 440, where the pressure was increased up to a maximum of 200 MPa.

The mercury intrusion data were then converted into an equivalent pore size distribution with the Washburn equation, assuming a contact angle of 130° and a surface tension of mercury of 0.48 N/m² (Kaufmann et al. 2009).

Differences in properties between real and equivalent systems were assessed statistically by means of analysis of variance (ANOVA). Two-way ANOVA was applied with crossed factors: age (5 levels) and system type (2 levels: real or equivalent). The null hypothesis of no significant difference between the system types was tested by comparing the p-value against the assumed significance level α=0.05 (a p-value below 0.05 allows rejecting the null-
hypothesis of no difference). This procedure was performed for mechanical properties, non-evaporable water content determined with TGA, total porosity and breakthrough radius determined with MIP.

3.5 Results and discussion

3.5.1 Compressive and flexural strength

Figures 3.3a, 3.3b, and 3.3c show the compressive strength results of the three mortars (OPC, slag and fly ash/silica fume) comparing real and equivalent systems as a function of time. The term equivalent age has been here adopted to distinguish between the curing time of the real systems and the age represented by the equivalent systems. For the real systems, the equivalent age obviously corresponds to their actual age.

A two-way analysis of variance (ANOVA) was performed independently for each dataset (OPC, slag and fly ash/silica fume) presented in Figure 3.3, with equivalent age and system type (real/equivalent) as factors. The ANOVA shows that there is a statistically significant difference (at significance level of 5%) between real and equivalent systems for OPC and slag, while no significant difference exists for the fly ash/silica fume system. Note that the comparison with ANOVA assesses the whole evolution of the properties in time. Both for the OPC and slag systems, the differences increase systematically with time and do not exceed 5 MPa (10% of the average strength) at 91 days. The higher strength of the real system compared to the equivalent system is most likely due to the fact that the equivalent systems are slightly underestimating the degree of hydration occurred in the real systems.

Despite the significant difference obtained by the two-way analysis of variance in terms of compressive strength, the trends obtained between the real and equivalent systems for all types of mortars show that the difference in strength is minimal at early age while they do not exceed 5 MPa at later ages.

Comparing Figure 3.3a with Figures 3.3b and 3.3c, it can be noted that while the replacement of cement with slag and fly ash does not affect the final compressive strength at 91 days, a delayed strength gain is observed at earlier ages in the systems containing SCM. In general, results show that the compressive strength results show an overall reasonable agreement between the real systems and the equivalent systems.

Further, it should be noted that the equivalent systems in this work are used to investigate the drying shrinkage behavior as such the small difference observed in terms of compressive
strength will not necessarily influence the shrinkage behavior for which, for example, the elastic properties play a much more important role.

The flexural strength results of the mortar specimens are shown in Figure 3.4. Similarly as for the compressive strength, also here the ANOVA shows a statistically significant difference for OPC and slag, while no significant difference exists for the fly ash/silica fume system. As for the compressive strength, the flexural strength is higher for real than for equivalent systems, with the difference increasing in time, most probably due to the more advanced hydration of the former. The difference reached 1.7 MPa for the OPC systems.

Figure 3.3. Compressive strength comparison between real and equivalent systems: a) OPC, b) slag c) fly ash/silica fume. Error bars represent standard deviation.

Figure 3.4. Flexural strength comparison between real and equivalent systems: a) OPC, b) slag and c) fly ash/silica fume. Error bars represent standard deviation.
3.5.2 Static elastic modulus

The evolution of the elastic moduli of mortars as a function of equivalent time is shown in Figure 3.5. The differences between real and equivalent systems are not statistically significant (at 5% significance level) for all three materials (OPC, slag, fly ash/silica fume). Furthermore, it can be seen that the use of SCM independently in either real or equivalent systems does not significantly affect the final elastic modulus at 91 days, which is consistent with what previously observed for the compressive and flexural strength.

![Figure 3.5. Static elastic modulus comparison between real and equivalent systems: a) OPC, b) slag and c) fly ash/silica fume. Error bars represent standard deviation](image)

3.5.3 Thermogravimetric analysis

First, TGA was employed to monitor the pozzolanic reactivity of the quartz over time (up to three months), as shown in Figure 3.6. After 91 days, an increase of mass loss compared to 1 day is observed especially between 105 and 250 °C, corresponding to the loss of bound water from the CSH produced by the pozzolanic reaction. The total mass of water lost from CSH, assumed as the loss between 33 and 250 °C (Dilnesa 2011) was 0.008 g/g at 1 day and 0.018 g/g at 91 days (respect to the initial mass of the sample). The calcium hydroxide content was determined based on the water mass loss at temperatures between 330 and 550 °C (Dilnesa 2011) and corrected for the carbonation based on the CO₂ measured at temperatures between 550 and 850 °C, the latter assumed to be significant only at 91 days (at 1 day the CO₂ release was assumed to be due to residual calcium carbonate content). It was equal to 0.434 g/g at 1 day and 0.411 g/g at 91 days (respect to the initial mass of the sample). This 5% change indicates that the quartz sand used in this study has only very limited reactivity. In any case, the absolute differences of 0.010 g/g for CSH and 0.023 g/g for calcium hydroxide
should be compared to the reproducibility of the TGA method, which can be assessed from ranges of duplicate measurements obtained from independently prepared samples and represented by error bars in Figs 3.7 and 3.8. The differences between the duplicated samples reached 0.013 g/g for non-evaporable water content and 0.030 g/g for calcium hydroxide (on average 0.006 g/g and 0.013 g/g, respectively). Therefore, the observed changes can be assumed to be within the reproducibility range of the method. This suggests that the quartz filler used in this study exhibits only limited pozzolanic reactivity and is suitable to replace and represent unhydrated cement in the equivalent microstructures.

Figure 3.6. Cumulative and differential TGA curves of the inert quartz to test the pozzolanic reactivity.

For all the systems the amount of non-evaporable water increases as hydration proceeds (Figure 3.7). The real systems show statistically significantly higher non-evaporable water content (hence a slightly higher degree of hydration), which is consistent with strength results for the OPC and slag systems (Figures 3.3a, b and 3.4a, b). The absolute differences between non-evaporable water did not exceed 0.030 g/g (respect to the initial sample mass) for the OPC and slag systems, which corresponds to 12% of the non-evaporable water content at 91 days, Figure 3.7. Higher differences were observed for the fly ash/silica fume system and reached 0.057 g/g, corresponding to 24% of the non-evaporable water content at 91 days, Figure 3.8.

It should be noted that the differences in the amount of non-evaporable water may be caused by a different ratio of the inner and outer products between the real and equivalent systems. In
the equivalent systems, the inner product is supposed to be less due to substitution of part of
the cement grains and SCM with quartz particles.

Figure 3.7 shows a reduced amount of non-evaporable water at early ages in blended systems
compared to the OPC system. Only after 91 days, the non-evaporable water content measured
in the fly ash blended pastes becomes similar to the one measured in the OPC systems.
Furthermore, as expected, the blended pastes containing slag and fly ash show an overall re-
duced content of CH due to the pozzolanic reaction, see Figure 3.8.
The CH results (Figure 3.8) show no statistically significant differences between real and
equivalent systems.

Figure 3.7. Non-evaporable water content of the real and equivalent microstructures obtained
by TGA analysis: a) OPC, b) slag and c) fly ash/silica fume. Error bars represent ranges of
duplicate samples.

Figure 3.8. Calcium hydroxide content of the real and equivalent microstructures obtained by
TGA analysis: a) OPC, b) slag and c) fly ash/silica fume. Error bars represent ranges of dupli-
cate samples.
3.5.4 Mercury intrusion porosimetry

Despite several drawbacks (Diamond 2000), MIP represents a useful procedure to investigate the complex pore space of cement-based materials, covering nearly the whole range of pore sizes, i.e., capillary pores and micro-pores, and the related material properties, e.g., transport, self-desiccation, etc. (Hua et al. 1995, Diamond 2000, Cui and Cahyadi 2001, Wild 2001, Chen et al. 2013). In any case, MIP is here solely used as a qualitative method to compare the pore structure of the real and equivalent systems.

The total porosity of real and equivalent systems of the three mixtures is shown in Figure 3.9 as a function of equivalent time. As expected, the porosity decreases with equivalent age, due to the hydration products filling up part of the available capillary space. The equivalent systems follow very closely the trend of the real systems (no statistically significant difference was found with ANOVA). According to the water-to-binder ratio (1.6 by volume), the systems have an initial porosity of about 62%. After 1 day of hydration, the porosity of the OPC system drops to 42%, while systems containing slag and fly ash show slightly higher porosity (45% and 50%, respectively).

To verify the reproducibility of the MIP measurements, duplicate samples for the real OPC and slag systems were measured. In Figure 3.9a and 3.9b, the error bars represent the range of duplicate measurements. Although the reproducibility of this test method has been shown to be very good in some previous studies (Ye 2003), with variation of total porosity ranging between 2% and 6% (Hearn and Hooton 1992, Cook and Hover 1999, Wyrzykowski et al. 2014), higher variation is shown in Figure 9, especially in the slag real system at 7 days. A number of factors may be responsible for such scatter. One of the major reasons may be due to the high w/b used, which in the case of paste samples may have led to segregation, while no significant segregation was observed in the mortar mixtures. It should also be noted that in the real systems the hydration reaction is stopped by solvent exchange, which may further contribute to the scatter of the results.
While the real and equivalent systems show no significant difference in total porosity as measured by MIP, a similar pore size distribution would also be required when the equivalent microstructure concept is used to study, e.g., transport properties or shrinkage. However, as long as comparing total porosities as measured with MIP is straightforward, assessing the differences of the overall size distributions of pores is a more challenging task. Figure 3.10 shows some examples of duplicate measurements of the MIP pore size distribution curves to give an indication of the reproducibility of the method.

Figure 3.9. Total porosity comparison between real and equivalent systems: a) OPC, b) slag and c) fly ash/silica fume. Error bars represent ranges of duplicate samples.
Figure 3.10. Cumulative pore size distributions obtained from duplicate samples: a) and b) of OPC – equivalent systems; c) and d) comparison of the duplicate samples between OPC real and equivalent systems.

Figure 3.11 shows the pore size distributions of the three real and equivalent systems at different equivalent ages as a function of the pore radius. In Figure 3.11a and b, very similar trends are observed between the OPC real and the OPC equivalent systems, in particular if the typical scatter of the pore size distributions (see Figure 3.10) is taken into account. The comparison between real and equivalent systems containing SCM (Figure 3.11 from c to f) is less favorable at early ages, while better agreement was observed starting from 28 days.
Figure 3.11. Cumulative pore size distribution from MIP measurements: a) and b) OPC; c) and d) slag; e) and f) fly ash/ silica fume systems.
While the total porosity results showed only very small differences between real and equivalent systems, the pore size distributions showed slightly larger differences, especially at earlier ages. Indeed, structural differences between the real and the equivalent systems in terms of spatial distribution of the hydration products may be expected and may contribute to a refinement of the pore size distribution.

Nevertheless, in this chapter (and in the following one) those material properties are investigated that are believed to be the key factors in controlling the drying shrinkage, which eventually is the main goal of this work. For example, in first approximation the total porosity directly affects the strength and the elastic properties of the material, both of them directly related to the shrinkage behavior and likelihood of cracking. On the other hand, the pore size distribution has an impact on the sorption isotherms and the transport properties, which in turn regulate the kinetics of the drying shrinkage. Throughout this work, the differences in those properties have been assessed as will be shown in the following chapters.

In order to quantify such differences in the pore size distribution between real and equivalent systems, the breakthrough radius is analyzed. The breakthrough pore radius represents the minimum radius of pores that are percolated (Winslow and Diamond 1970) and it has been related to transport properties (Hearn and Hooton 1992). It is found as the radius at which a sudden increase in intruded mercury volume is observed and it can be conveniently identified as the first peak on the differential pore size distribution.

It should be noted, that the transport properties becomes of paramount importance in terms of drying shrinkage kinetics.

The logarithms of breakthrough radii are compared for the tested systems in Figure 3.12. Statistically significant differences were found for all systems. These differences may originate from the different spatial distribution of the hydration products in the equivalent systems containing quartz filler. Kokaba et al. reported that filler addition may lead to refining the microstructure by decreasing the capillary porosity (Kocaba et al. 2012). At the same time, it can be expected that the apparent pore size distribution as accessed with MIP would be very much affected by changing the connectivity of the pores, namely due to the ink-bottle effect (Diamond 2000). Further, an additional source of error may come from stopping the hydration in the real systems, especially at early age.

The difference in breakthrough radius is highest for the systems with fly ash/silica fume at ages up to 7 d. It should be noted that, given the assumptions used to design the equivalent systems containing silica fume starting from systems containing fly ash (Termkhajornkit et al. 2015), this was expected to be the system type with the largest differences. Moreover, unlike,
e.g., for the strength results, no systematic trend can be identified in the pore size distribution differences between the equivalent and real systems. Therefore, the differences are most probably also due to the high scatter of the MIP results, as made clear by the duplicate measurements presented in Figure 3.10.

In order to estimate the influence of change in breakthrough radius to, e.g., transport properties, the approach presented by Cui and Cahyadi (Cui and Cahyadi 2001) for calculating the permeability of cement paste is used. They showed that the permeability of cement paste at different ages can be predicted with good approximation based on porosity measurements with MIP. In this approach, the permeability is estimated based on the General Effective Media approach as a mixture of the permeabilities of two pore populations: gel and capillary pores. The permeability of the capillary pore-phase is calculated with the Katz-Thomson model (Katz and Thompson 1986) as a function of the total volume of capillary pores and the breakthrough radius. According to the model by Cui and Cahyadi (Cui and Cahyadi 2001) for cement paste at early ages, the prediction with the Katz-Thompson model gives reliable results, while at later ages the contribution of the low-permeability gel porosity starts to dominate. In Table 3.4, the permeability as well as the respective breakthrough radii, used as input to calculate the permeability itself according to the Cui and Cahyadi model, are reported. At 1 day the finer pore structure of the equivalent system results in a lower permeability, $2.1 \times 10^{-17} \text{ m}^2$ compared to $8.0 \times 10^{-17} \text{ m}^2$ for the real system. The slightly higher difference in radii at 3 days between the real and the equivalent systems would cause a lower permeability of $5.9 \times 10^{-19} \text{ m}^2$ for the equivalent system compared to the $9.2 \times 10^{-18} \text{ m}^2$ for the real system. However, the differences in radii at 7, 28 and 91 days are significantly lower, hence resulting
in permeability values with similar magnitude. Such differences would have only negligible effect on the transport phenomena, see e.g. (Baroghel-Bouny et al. 2014). Moreover, it should be noted that these estimated differences are similar to typical scatter in measured permeabilities of cementitious materials, e.g. (Kollek 1989, Ye et al. 2006). Based on these estimations, it can be concluded that the observed differences in breakthrough radii between the real and equivalent systems are reasonably low.

Table 3.4. Breakthrough radii and corresponding calculated permeability according to Cui and Cahyadi

<table>
<thead>
<tr>
<th>OPC sample</th>
<th>Breakthrough radius (m)</th>
<th>Permeability (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Real</td>
<td>Equivalent</td>
</tr>
<tr>
<td>Eq. age (days)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.0·10⁻⁷</td>
<td>1.1·10⁻⁷</td>
</tr>
<tr>
<td>3</td>
<td>1.1·10⁻⁷</td>
<td>2.7·10⁻⁸</td>
</tr>
<tr>
<td>7</td>
<td>4.9·10⁻⁸</td>
<td>2.8·10⁻⁸</td>
</tr>
<tr>
<td>28</td>
<td>2.5·10⁻⁸</td>
<td>2.5·10⁻⁸</td>
</tr>
<tr>
<td>91</td>
<td>1.8·10⁻⁸</td>
<td>2.9·10⁻⁸</td>
</tr>
</tbody>
</table>

3.6 Conclusions

This chapter is dedicated to a critical evaluation of a recently-developed approach to characterize the early-age properties of cement based materials, based on creating equivalent microstructures in which the residual unhydrated binder is replaced with inert quartz filler. Special emphasis is given to those properties that are believed to be the key factors for the drying shrinkage behavior of cement-based materials. Further materials properties are investigated in the following chapter.

The mechanical properties and the microstructural features of three real mixtures with and without SCM (45% by volume of cement replaced by slag or fly ash) were investigated and compared with those of the equivalent systems at specified hydration stages. Difference in properties between the real and the equivalent systems were assessed statistically by means of ANOVA.

Compressive and flexural strength results showed similar trends between the real and the equivalent systems. Even though, ANOVA revealed significance difference between the real and the equivalent systems, which systematically increased with time, the difference in com-
pressive strength did not exceed 10% of the average strength at 91 days, with the real systems systematically showing higher strengths.

It should be also emphasized that the equivalent system technique is used in this work as to investigate the drying shrinkage behavior at early age. Hence, material properties such as the elastic properties are known to play a much important role for the shrinkage. Indeed, although this approach is based on replacing different amounts by volume of binder with quartz filler, the introduction of the latter in place of binder particles did not significantly affect the static elastic modulus.

Amounts of non-evaporable water in the real and equivalent systems showed statistically significantly differences. The differences however only reached 0.03 g/g for the OPC and slag systems (corresponding to about 12% of non-evaporable water content at 91 days), while for the real fly ash system and the equivalent silica fume system the comparison was less favorable, with the differences reaching 0.06 g/g (corresponding to about 24% of the non-evaporable water content at 91 days). Indeed, the silica fume equivalent systems were formulated on the basis of the fly-ash systems with several rough approximations, which resulted in larger differences between the real and the equivalent systems. No significant differences were observed for calcium hydroxide content.

The total porosity obtained by the first intrusion results showed no significant differences between all real and equivalent systems. On the other hand, the comparison of the pore size distribution results was less favorable, especially at earlier equivalent ages. However, as shown by the estimations of permeability based on the observed pore radii, these differences should have only limited influence on the transport properties.

Due to the larger differences observed with regard the system containing silica, the equivalent system OPC+Silica fume will not be used to investigate the time-dependent and the moisture-dependent properties, drying shrinkage and elastic modulus in the following chapters. On the other hand, in light of the satisfactory agreement between the results of the real and equivalent systems obtained with regard to the OPC systems and the OPC+ Slag systems, the equivalent system approach represents a promising alternative to the commonly-used methods to stop hydration. Specifically, the approach based on equivalent systems enables to test samples without drying of the microstructure, which is the main drawback of the commonly-used methods to stop hydration. In particular, it opens the possibility to carry out measurements of sorption isotherms, transport properties, creep, free and restrained shrinkage at early ages, for which it is usually not possible to decouple the effects of ongoing hydration during the measurements.
Chapter 4.

Early-age fracture properties of microstructurally-designed mortars

This chapter compares the fracture properties as well as the crack initiation and propagation of real and equivalent mortars. The development of the elastic modulus, tensile strength, and fracture energy at different hydration stages were determined by inverse analysis of load-displacement curves obtained by the compact tension test. Further, the impact of the moisture content on the aforementioned material properties was also tested on oven-dried equivalent mortars. Finally, digital image correlation was used to follow the crack initiation and propagation.

The elastic modulus, tensile strength, and fracture energy support the validity of the equivalent mortars approach. The load-displacement curves obtained by the compact tension test were also compared to those simulated by finite element method showing excellent correlations. Digital image correlation revealed the formation of similar crack patterns at comparable load levels between the two mortars. At early-age, the moisture content has a considerable influence on the tensile strength and the fracture energy.
4.1 Introduction

Cracks and micro-cracks in structural concrete, besides being unsightly, more importantly may accelerate deterioration resulting in increased maintenance costs and reduced service life (Mehta 2001, Di Bella et al. 2012). Cement-based materials are particularly susceptible to cracking at early-ages, when the material properties are still developing and the rate of shrinkage and thermal deformations is high (Springenschmid 1998, Holt and Leivo 2004). A precise knowledge of the mechanical properties, and in particular of the fracture properties, is at the basis of virtually every approach for modeling crack initiation and propagation. Indeed, advanced modelling approaches taking into account the formation of cracks as well as their propagation necessarily require several time-dependent material properties to be known, such as e.g., tensile strength, elastic modulus, Poisson’s ratio, and volumetric deformations as well as fracture properties (De Schutter 2002, Østergaard 2003).

While most of the aforementioned properties can be more or less easily measured as a function of time, the determination of the early-age volumetric deformations such as drying shrinkage, creep, and/or relaxation at a given hydration degree is more complicated. Indeed, at early-age the microstructure of cement-based materials is continuously evolving due to hydration, which may interfere with an accurate determination of such long-term properties. Further, even in the case in which the testing time required to measure material properties, such as e.g. the elastic modulus or the tensile strength, is short enough to neglect microstructural changes due to hydration, additional limitations may be encountered at early-age. For example, the assessment of the dependency of material properties on the moisture content or changes in temperature at early-age is challenging. In fact, the introduction or the withdrawal of water as well as a change in temperature at early-age may result in a change in the microstructure evolution.

In the previous chapter, the equivalent system approach has been presented as a method to investigate the early age properties decoupling the effects of the hydration. Further, chapter 3 provides a comprehensive and systematic comparison between the real systems and the equivalent systems investigating mechanical properties (compressive strength, flexural strength and elastic modulus) as well as degree of hydration and calcium hydroxide content by thermogravimetric analysis (TGA) and pore structure by mercury intrusion porosimetry (MIP). Results supported the validity of the equivalent systems approach.

In the present chapter, the validation of the approach is extended to the fracture properties.
While the most straightforward method to determine the fracture properties of cement-based materials is represented by the direct tension test, it bears several disadvantages. For example, the direct tension test is more sensitive to eccentricities, rotational boundary conditions, and possibility of multiple cracking formations (Zhou 1988, Østergaard 2003). Hence, more often, the materials properties are estimated by indirect test methods such as the three-point bending test, the wedge-splitting test or the compact tension test (CTT) (Wittmann et al. 1987, Shah et al. 1995, Østergaard et al. 2000).

In this chapter, the material properties prior to cracking and the fracture properties of one real (at five stages of hydration) and five respective equivalent mortar mixtures were obtained by inverse analysis of load-displacement curves obtained from the CTT. Specifically, the material properties were obtained by inverse analysis based on the hinge model (Østergaard et al. 2000, Skoček and Stang 2008). The results obtained by the inverse analysis were afterwards verified by means of FEM simulations using the commercial finite element package TNO DIANA. For further validation of crack initiation and propagation, digital image correlation techniques were applied on a sequence of pictures acquired during testing. This non-destructive approach based on the comparison of consecutive digitized images taken during deformation allows for the derivation of the full-field surface displacement and strains of objects under load (Chu et al. 1985, Pereira et al. 2012). Finally, the material properties deduced by means of inverse analysis i.e., elastic modulus, tensile strength, and fracture energy of the real and equivalent mortar mixtures, were compared and their difference statistically evaluated through the analysis of variance (ANOVA) (Oehlert 2010) to validate the equivalent-systems technique. Additionally, differences between the equivalent and real systems regarding the peak points on the load-displacement points (peak force and crack mouth opening) were statistically evaluated using multivariate ANOVA (MANOVA).

Afterwards, the equivalent approach is employed for the first time to investigate the effect of the moisture content on the elastic modulus, tensile strength, and fracture energy at early-age.

4.2 Experimental methods

The mortar mixture was prepared as described in chapter 3. In this case only the OPC mortars at different ages (real and equivalent) are investigated without any addition of SCM. Table 3.3 reported the mixture proportions.
After mixing, the mortar was cast into a customized formwork (125 × 150 × 10 mm³) equipped with two insertions to accommodate the two rods for the tensile load transmission during testing (Figure 4.1).

After 24 hours, the samples were demolded and the equivalent mortar samples were wrapped in wet towels and sealed in plastic bags for at least three months of curing in an environmental chamber at 20 °C and 100% RH. Similar to the equivalent mortar samples, real mortar samples were wrapped in wet towels and sealed in plastic bags, except for the 1 d sample that was directly tested after demolding. The remaining samples were cured in an environmental chamber at 20 °C and 100% RH until testing at 3, 7, 28, or 91 days of age.

During the compact tension test, an eccentric tensile load (at constant displacement rate of 0.12 mm/min) was applied by means of two rods with a diameter of 20 mm to promote initiation and propagation of a single crack at the tip of the notch. The notch was introduced into the sample by water-cooled saw cutting to induce local stress concentrations and create the conditions for the initiation and propagation of a single crack. The notch thickness and length was 0.5 mm and 60 mm, respectively. The geometry of the sample is shown in 4.1. The sample’s thickness was 10 mm which promotes plane stress conditions (Pereira et al. 2012), while also reducing the time to reach mass equilibrium to investigate the effect of the moisture content (see section 4.5). The crack mouth opening displacement (CMOD) was measured using a clip gage that was placed on the notched surface of the sample.

Figure 4.1. a) Specimen’s geometry used for the CTT, the dimensions indicated are in (mm); b) setup for the CTT testing including the camera for DIC
The experimentally-determined load-displacement curves from the CTT were employed to obtain the fracture material properties through inverse analysis based on the hinge model (CHM). Ulfkjaer et al. (Ulfkjaer et al. 1995) (with further improvements by Olesen (Olesen 2001)) presented a semi-analytical method for describing the fracture propagation for Mode-I, i.e., the hinge model.

The main advantage of the CHM consists in the fact that it yields analytical solutions for the entire load-crack opening curve. Later, Østergaard (Østergaard et al. 2000) proposed an inverse analysis algorithm based on the CHM to retrieve information from the wedge splitting test. However, in the CHM the derivation of an analytical solution including multi-linear softening material behavior remained troublesome. Skoček and Stang (Skoček and Stang 2008) extended the inverse analysis for wedge splitting tests based on the CHM including multi-linear softening behavior with the intent to increase the accuracy of test simulations. In the present study, inverse analyses including multi-linear softening behavior developed in (Skoček and Stang 2008) is employed to simulate the CTT results and to calculate the elastic modulus, tensile strength, and fracture energy. Figure 2 shows the implementation of the CHM, developed in (Ulfkjaer et al. 1995) and (Olesen 2001), to the wedge splitting test geometry. The CHM simulates the area directly surrounding the propagating crack using the loading and deformation shown in Figure 2(b) and the stress distribution in Figure 2(c). The rigid boundaries of the cracked hinge provide a joint to the bulk (uncracked) specimen, which is controlled by Hooke’s law. The comparison and minimization of differences between experimental results and outputs of the CHM via inverse analysis allows for the estimation of the concrete tensile strength, \( f_t \), elastic modulus, \( E \), and cohesive crack relationship, \( g(w) \).

Throughout the inverse analysis, the bulk specimen is assumed to behave linear elastically, whereas the cracked state is determined by a stress-crack opening relationship:

\[
A = \begin{cases} 
    \sigma_{e}(\varepsilon) = E \varepsilon & \text{pre-cracked state} \\
    \sigma_{w}(w) = g(w)f_t & \text{cracked states}
\end{cases}
\]  

(eq. 4.1)

where \( E \) is the elastic modulus, \( \varepsilon \) elastic strain, and \( \sigma_{w}(w) \) stands for the stress-crack opening relationship (softening curve) with crack opening \( w \). The multi-linear softening curve, \( g(w) \), is defined as (for \( N > 2 \)):

\[
g(w) = b_i - a_i w \quad \text{with} \quad w_{(i-1)} < w < w_i
\]

(eq. 4.2)

where \( w_i \) corresponds to the intersection of \( i \)-th and \( i + 1 \)-th line and has the form

\[
w_i = \frac{b_i - b_{i+1}}{a_i - a_{i+1}}
\]

(eq. 4.3)

for \( i < N \) and
with \( N \) equal to the number of lines in the softening curve.

The inverse analysis to determine the tensile strength, Young’s modulus, and cohesive relation consists then of three steps that are repeated until convergence is reached. In the first step the Young’s modulus is determined from the experimental data corresponding to the elastic loading. Once the Young's modulus is found, the tensile strength and the first descending branch of the softening curve \( a_1 \) are computed. Finally, \( N - 1 \) computations are performed to find \( a_i \) and \( b_i \), with \( i = 2 \ldots N \) defining the multi-linear softening behavior. A sketch of the multi-linear softening curve is shown in Figure 4.2(d). Additional details on the CHM and the inverse analysis approach are available in the literature, see e.g. (Østergaard et al. 2000), (Skoček and Stang 2008), (Ulfkjær et al. 1995), and (Olesen 2001),

\[
\begin{align*}
  w_N &= w_e = \frac{b_N}{a_N} \\
  &\text{(eq. 4.4)}
\end{align*}
\]

Figure 4.2 (a) The wedge split test specimen with the cracked hinge model applied (after (Østergaard et al. 2000)), (b) loading and deformation of the hinge (after (Olesen 2001)), (c) the assumed stress distribution (after (Olesen 2001)), and (d) sketch of the multi-linear softening curve (after (Pease 2011)).

In addition to the clip gage measurements, digital images were repeatedly captured at 10 s intervals using a Nikon D800 36.3 megapixel (7360 \( \times \) 4912 pixels) camera body with a 60 mm focal length macro lens (AF-S Micro Nikkor 60 mm f/2.8G ED). Prior to loading of the test specimens, three images were captured of the specimen surface and a fourth image including a scale. The lens was placed approximately 1000 mm from the specimen surface, resulting in images covering a region of application of approximately 65 \( \times \) 65 mm\(^2\), with each pixel repre-
senting $11.7 \times 11.7 \, \mu m^2$ of physical space. A LED ring flash was affixed directly to the lens to evenly light the specimen surface. Captured images were subsequently processed with a commercially-available software package (GOM 2009), which utilized a stochastic speckle pattern to identify unique regions, called facets, on the specimen surface at each measurement time. The stochastic speckle pattern on the specimen surface was created prior to testing using black and white spray paint. The facet size within the commercially available software package was set to $15 \times 15$ pixels ($175 \times 175 \, \mu m^2$). The software tracked movements of the facets and utilized standard DIC techniques to compute deformations of the specimen surface. Additional information on the hardware used and the DIC technique is available in (Chu et al. 1985, Berfield et al. 2007, GOM 2009, Savic et al. 2010).

Finally, a statistical evaluation of the differences between the real and equivalent material properties investigated in this study, i.e., elastic modulus, tensile strength, and fracture energy was performed by means of ANOVA. Specifically, a two-way analysis of variance was applied taking into account two fixed factors; the five hydration ages and the two systems (real and equivalent). The null hypothesis of no significant difference was tested by comparing the p-value to the significance level $\alpha$ (assuming $\alpha = 0.05$). Similarly, MANOVA using the Pillai test (Team 2014) was performed for the peak points on the load-displacement curves experimentally obtained by CTT.

4.3 Compact tension test results

4.3.1 Load-displacement curve

In Figure 4.3, the load-displacement curves obtained for the equivalent and real mortars are compared. For ease of illustration, the various testing ages are presented in two graphs. In Figure 4.3a, the equivalent ages of 1, 7 and 91 days are shown; while in Figure 4.2b the remaining results for the equivalent ages of 3 and 28 days are presented. The curves shown represent the average behavior of three repetitions of each test. It should be noted that the term equivalent refers to the equivalent mortars which were cured for a minimum of 91 days before being tested and reproducing a given hydration age. On the other hand, the real mortars were tested at the actual age indicated.

In general, the load-displacement curves as a function of the hydration age for all specimens tested show a similar shape, which is typical for quasi-brittle materials, i.e. they exhibit moderate strain hardening prior the attainment of the peak load, followed by rapid strain softening.
(Karihaloo and Huang 1991). Nevertheless, the area below the curve increases as the hydration age increases. Similarly, the peak load is a function of the age: the highest peak load is obtained for 91 d old mortars (ranging between 310 and 340 N) while the lowest peak load was measured on the 1 d old specimens (approximately 140 N).

In general, it can be observed from the presented results that the equivalent mortar specimens follow the load-displacement behavior exhibited by the real mortars as a function of time. Excellent agreement between the measured load-displacement curves are observed for mortars at 1 and 7 days. For the remaining test specimens, it should be noted that the equivalent mortars systematically show a reduced peak load. Such difference may be due to an underestimation of the degree of hydration in the real mortars, which will result in a higher replacement of cement binder with quartz in the equivalent mortars as discussed in chapter 3.

While on one hand the evaluation of the degree of hydration could be improved by increasing the number of samples measured or combining different techniques, it should be noticed that some inherent limitations may arise by the test methods itself or the sample preparation (for example when stopping the hydration by isopropanol). Nevertheless, it should be emphasized that predicting a precise hydration age was not the goal of the equivalent systems, but having a microstructure that enables the investigation of time dependent and moisture dependent properties without changing in time or during testing.

It should be also emphasized that the slight deviation seen in the real specimen at 91 days at the beginning of the post-peak phase can be due to the testing method such as a shift of the clip gage.
Figure 4.3. Load-displacement curves comparison measured on the real and equivalent mortars at different hydration ages: a) 1 d, 7 d, and 91 d; b) 3 d and 28 d. The error bars represent the standard deviation calculated at the load peaks and the displacement measured on the different repetitions for each age.

Moreover, it should be noted that discrepancies between the real and equivalent mortars as seen in Figure 4.3 also arise from the reproducibility related to the CTT method itself. To illustrate this point, Figure 4.4 shows the load-displacement curves of all tested specimens for one real and one equivalent age, i.e. 3 days. To analyze this issue, the peak points of the curves (i.e., simultaneously the peak forces and the crack mouth opening corresponding to the peak forces) were compared between the real and equivalent systems using two-way MANOVA (with age and type of system as crossed factors). No statistically significant differences (at significance level of 0.05) were found in this case between real and equivalent systems (the P-value according to the Pillai test was 0.66), whereas the specimen age was found to be a significant factor (P-value below 0.01).

The actual differences between the real and the equivalent mortars will be discussed more in detail with regard to the materials properties investigated (elastic modulus, tensile strength, and fracture energy) by means of ANOVA in the following section.
4.3.2 Inverse analysis

Results of the inverse analysis are shown in 4.5, in which experimental and modelled load-displacement curves are compared to each other. For the sake of brevity, only results of equivalent mortars at the equivalent age of 3 and 91 days are shown, including three repetitions for each equivalent age. As can be seen from the presented results, excellent agreement between load-displacement curves determined by inverse analysis and experimentally determined load-displacement curves is obtained. For example the three experimental load-displacement curves at 91 days directly overlap with the simulated ones.

Figure 4.5. Comparison of the measured and the computed load-displacement curves for the a) 3 d equivalent mortars and b) 91 d equivalent mortar samples.
Figure 4.6 (a through c) shows the comparison of the material properties between the equivalent and the real mortars in terms of the elastic modulus, tensile strength, and fracture energy obtained by inverse analysis. Error bars represent the standard deviation.

As evident from Figure 4.6, the elastic modulus and the tensile strength increase with age and reduction of porosity, as expected. Similarly, the fracture energy increases with time due to the increase in number of bonds forming in the mortar as cement hydration proceeds (Petersson 1980, Wittmann et al. 1987).

Comparable results in terms of elastic modulus and fracture energy were found for the real and the equivalent mortars (Figures 4.5a and 4.5c). Most of the determined values fall within one standard deviation of the mean except for the results of the mortar specimens with an equivalent age of 7 d, for which the results clearly diverged. It should be noted that only two repetitions were available with regard to the 7 d real mortar, as one sample broke during demolding. While at 7 d the tensile strength results obtained by inverse analysis for the real and the equivalent mortars are similar, erroneous values were returned by the inverse analysis in terms of elastic modulus and more obviously in terms of fracture energy. This is also shown by the experimental load-displacement curve (in Figure 4.2a), where the OPC real 7 d curve rapidly approaches zero already at a crack mouth opening of approximately 0.14 mm, hence resulting in a reduced fracture energy. Further, the initial slope is much steeper compared to the other results. No data are available for the real mortar at 28 days as all samples inadvertently broke during handling. The tensile strengths of the real and the equivalent mortars are also comparable, ranging approximately from 1 to 2.5 MPa for the equivalent ages investigated in this study.

The two-way analysis of variance on the test results obtained by inverse analysis taking into account the whole evolution of the elastic modulus, tensile strength and fracture energy showed that no statistically significant differences (at significance level of 0.05) exist between the real and the equivalent mortars, hence supporting the validity of the equivalent method approach. The P-values for the considered factor (real or equivalent system) were: 0.15, 0.26, 0.12, for the fracture energy, tensile strength and E-modulus, respectively.
Figure 4.6. Comparison of the real and equivalent mortars: a) elastic modulus, b) tensile strength, and c) fracture energy as a function of the equivalent age.

As to further validate the elastic modulus results obtained by the inverse analysis, in Figure 4.7 the elastic moduli evolution as a function of the equivalent age obtained by inverse analysis are compared to the statically and dynamically determined elastic modulus measurements on companion specimens, as presented in chapter 3 and chapter 5. The static elastic modulus was determined on $40 \times 40 \times 160 \text{mm}^3$ mortar prisms as described in chapter 3. The dynamic elastic moduli were measured on prisms with similar geometry using SIMORUS. The latter is presented in chapter 5.

The elastic moduli of the real and equivalent mortars obtained by inverse analysis of the CTT results are closer to the corresponding statically-determined elastic moduli, this is expected
considering the similar time spans of both tests. An exception is the real mortar with an
equivalent age of 7 days, for which the elastic modulus falls in between the experimentally-
measured dynamic and static elastic modulus. For the equivalent mortars (Figure 4.6b), excel-
lent agreement between the statically-determined elastic moduli and elastic moduli deter-
mined by means of the inverse analysis is found for the equivalent ages of 1, 7, and 91 d. For
equivalent ages of 3 and 28 d, the results are still within one standard deviation of the mean
elastic modulus.

Figure 4.7. Comparison of the elastic modulus results obtained by inverse analysis and meas-
ured on companion specimens by means of static and dynamic techniques.

4.3.3 FEM simulation of the CTT load-displacement

To further validate the data obtained by inverse analysis, the tensile response of the CTT was
modeled using the commercial finite element package TNO DIANA. The CTT was simulated
by means of a 2D model assuming plane stress conditions and consisted of 9550 triangular el-
ements with 4932 nodes representing the concrete, steel, and crack domains (see Figure 4.8).
Fillets were used at the tip of the notch to reduce artificial stress intensities in this region (see
Figure 4.8b). The crack path was predefined and modelled by means of zero-thickness inter-
face elements assuming Mode-I fracture. Tension softening of the material was described
based on a cohesive discrete cracking model in which multi-linear softening relations are
adopted from (Østergaard et al. 2000). A nonlinear solution of the system of equations was
obtained using a standard Newton–Raphson method with a displacement-controlled convergence criterion.

To investigate the impact of varying mesh sizes on the solution of the problem, a range of interface discretization were studied for an exemplary loading scenario. The number of zero-thickness interface elements along the predefined crack path (see Figure 4.8) was varied between 10 and 100 elements. The input parameters determined by inverse analysis of CTT results are presented in Table 4.1. For the investigation of the effect of varying mesh sizes on the solution, the results of the surface crack width predicted by the FEM model for the various mesh sizes were normalized to the results obtained with 100 elements discretizing the predefined crack path.

Results of the mesh analysis, given in Figure 4.9, indicate that the influence of the crack interface discretization was negligible (<0.1% difference between the different mesh sizes) for more than 20 crack interface elements. Accordingly, the crack interface was discretized with 100 elements for all solutions.

The input data, i.e., elastic modulus, tensile strength, and cohesive relations, were obtained from the inverse analysis of experimentally determined load-displacement curves at the different hydration ages; see Section - Load-displacement curve. While the Poisson’s ratio \( \nu \) was assumed to be 0.2, it has no influence on the results, due to the geometry that is close to plane stress conditions. An overview of the input parameters for all simulations is provided in Table 4.1.

<table>
<thead>
<tr>
<th>Equivalent system</th>
<th>( E )</th>
<th>( f_t )</th>
<th>( a_1 )</th>
<th>( b_1 )</th>
<th>( a_2 )</th>
<th>( b_2 )</th>
<th>( a_3 )</th>
<th>( b_3 )</th>
<th>( N_st )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>17.89</td>
<td>1.26</td>
<td>57.85</td>
<td>1</td>
<td>13.23</td>
<td>0.50</td>
<td>1.64</td>
<td>0.13</td>
<td>40 steps</td>
</tr>
<tr>
<td>3d</td>
<td>19.87</td>
<td>1.50</td>
<td>51.58</td>
<td>1</td>
<td>22.06</td>
<td>0.75</td>
<td>1.96</td>
<td>0.14</td>
<td>2.5E-4 mm</td>
</tr>
<tr>
<td>7d</td>
<td>24.73</td>
<td>1.89</td>
<td>47.82</td>
<td>1</td>
<td>15.13</td>
<td>0.46</td>
<td>0.54</td>
<td>0.06</td>
<td>70 steps + 4 mm</td>
</tr>
<tr>
<td>28d</td>
<td>29.59</td>
<td>1.70</td>
<td>35.48</td>
<td>1</td>
<td>7.25</td>
<td>0.37</td>
<td>2.32</td>
<td>0.17</td>
<td>1.0E-2 mm</td>
</tr>
<tr>
<td>91d</td>
<td>27.22</td>
<td>2.48</td>
<td>46.15</td>
<td>1</td>
<td>23.66</td>
<td>0.70</td>
<td>1.38</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: \( E \) – Young’s modulus (GPa), \( f_t \) – tensile strength (MPa), \( a_i \) and \( b_i \) – parameters defining multi-linear softening curve (see also Section 4.2), and \( N_st \) – applied displacement scenario in FEM model.
In Figure 4.10, the experimentally-determined load-displacement curves of the equivalent mortars at different equivalent ages are compared to the results from the finite-element calculations. As can be seen from the presented results, numerically determined load-displacements curves are in excellent agreement with the experimental data for all equivalent ages except 28 d, which confirms the validity of the inverse analysis results. The difference observed at 28 days could be due to the fact that the crack was not really straight rising from a mixed-mode behavior, or that the crack did not initiate at the notch, or branched. Results of the digital image correlation for the equivalent mortar at 28 days, see Figure 4.11, clearly indicates a ‘bending’ of the crack, i.e. the crack does not follow the predefined crack path in the FEM model, which may explain the differences observed between the experimental data and FEM predictions.

Figure 4.8. a) CTT specimen simulated by means of a 2D model assuming plane stress conditions using the commercial finite element package TNO Diana; b) Fillets used at the tip of the notch to reduce artificial stress intensities.
Figure 4.9. Normalized surface crack width as a function of the number of interface elements.

Figure 4.10. Comparison of the measured and the simulated load-displacement curves for the a) 1 d, 7 d, and 91 d equivalent mortars and b) 3 d and 28 d equivalent mortar samples.
4.4 Digital image correlation

A sequence of pictures was taken during the CTT at intervals of 10 s. Digital image correlation techniques were applied to identify crack initiation and propagation and more importantly whether cracking behavior was comparable at different load levels for the equivalent and real mortar samples.

In Figure 10, the evolution of the crack initiation and propagation during CTT for two different hydration ages is shown. The comparison of the real and equivalent mortars behavior at ages of 1 d and 3 d is shown in Figure 4.12a and Figure 4.10b, respectively.

In Figure 4.10, the displacement interpolated at the facets overlay on top of the documented area is also shown. However, it should be noted that the facets overlay is here solely used to better observe the crack initiation and propagation.

To directly compare the crack initiation and propagation in the real and equivalent mortars during testing, four different stages of the load-displacement curve are reported. For each hydration age, the first three stages are marked in the corresponding load-displacement curves. Stages 1 and 2 represent available strain fields right before and after cracking has occurred. During propagation (stage 3), one picture for the real and one for the equivalent mortars were selected at approximately similar loads. Finally, stage 4 was selected as the last strain field before the sample completely split. Stage 4 is not marked in the respective load-displacement curve, but it is shown in the respective pictures sequence.

The cracks are generally straight, starting at the tip of the notch and propagating to the opposite edge without signs of branching. This observation further reinforces the applicability of the applied inverse analysis and FEM approach to determine the fracture and the mechanical
properties of the real and equivalent mortar systems. Besides the shape of the crack, it should be noted that in stage 3 a direct comparison of the real and equivalent mortar suggest a similar crack opening for the applied load.

Further, this analysis extends the validity of the equivalent approach. Indeed, besides the similarity of the materials properties investigated in this chapter and the previous one, the equivalent systems also show a similar cracking behavior.

In light of the excellent agreement of the material properties investigated in this chapter between the real and equivalent mortars and the similarity of the crack patterns at comparable load levels, the equivalent system approach further confirms the results shown with regards to the material properties investigated in the previous sections as well as the evaluation and conclusions reported in chapter 3. This powerful technique can therefore be used to investigate several hydration-dependent properties such as drying shrinkage, creep/relaxation, early-age cracking, and transport properties at early age. The early-age drying shrinkage behavior and modeling of cement-based mortars through the use of the equivalent systems is discussed in chapters 6, 7, and 8.
Figure 4.12. Sequence of frames showing the crack patterns on the surface of the specimens at different loading levels. Comparison between real and the equivalent mortars at a) 1 d and b) 3 d of hydration. The Real point 4 and the Equiv. point 4 (not marked in the top images: Splitting force versus Crack mouth opening) represent the last strain field before the sample completely split.

4.5 Early-age fracture properties as a function of moisture content

In general, in real field conditions concrete is subjected to drying as soon as exposed to the environment (once the curing period is over). The investigation of the materials properties at early age such as the elastic modulus becomes of paramount importance. Thus, besides allow-
ing for the simulation of different stages of the evolution of the microstructure with unchanging systems, the equivalent approach allows also to study the same system at different stages of drying in regard for example to elastic modulus, tensile strength, and fracture energy. In real cement based materials, it is possible to investigate the effect of moisture content only on mature samples, since the drying process takes several days to months to complete and rapid drying may lead to (micro)cracking and deterioration of the mechanical properties.

Equivalent mortar samples reproducing the equivalent ages of 1, 7, and 91 d with the geometry shown in Figure 4.1 were prepared. Three specimens repetition at each equivalent age were tested. Those ages were chosen as the microstructure and hence the material properties are quite different.

After 3 months curing, the samples were placed in an oven at 50 °C for about 1 month. It should be noted that due to the reduced thickness employed to measure the load-displacement curve, the drying of the samples was obtained in a reduced time (equilibrium was reached within approximately 3 weeks), while minimizing possible cracking due to occurrence of moisture gradients (self-restraint). The mass loss of the sample was monitored over time (every 48 h) and equilibrium was assumed to be reached once the mass difference between two consecutive measurements was below 0.1%. Further, the temperature of 50 °C was chosen to minimize possible microstructural damage such as crack formation due to differential shrinkage, and possible temperature-induced microstructural changes (Gallé 2001). For example, ettringite starts to decompose above 60 °C (Murat 1982, Gallé 2001).

Figure 4.13 (from a through c) shows the comparison between the elastic modulus, tensile strength, and fracture energy results for the equivalent systems in saturated and dried conditions. The error bars represent the standard deviation.

While the elastic modulus does not seem to be affected by the moisture content, the tensile strength appears to be dependent on the moisture content, which confirms the results of previous studies (Rossi 1991). For each of the equivalent ages investigated, the tensile strength of the dried specimens is approximately two times higher. This is in accordance with the general strength reduction observed in cementitious material at higher moisture contents (Li 2004, Yurtdas et al. 2006). Similar trends are observed for the fracture energy, which also increases for lower moisture contents; however, it should also be noted that the standard deviation associated with the results from the dried specimens is much higher.

It should be noted that in real field exposures, especially at early age when the concrete is more susceptible to cracking, drying will induce on one hand the shrinkage and hence an in-
creased cracking potential in restrained conditions, but on the other hand drying will also increase the tensile strength of the skin concrete.

As the moisture state in cement-based materials strongly affects their material properties, the effects of the moisture content on the elastic modulus are systematically investigated in the next chapter. Indeed, the elastic modulus in turn may influence the drying shrinkage behavior. For this reason, the following chapter investigates the influence of the moisture content on the elastic modulus.

Figure 4.13. Comparison equivalent mortars in saturated and dry conditions a) elastic modulus b) tensile strength and c) fracture energy as a function of the equivalent age.
4.6 Conclusions

In this chapter, the validation of the equivalent system technique applied to OPC mortars has been extended to the determination of fracture properties. The elastic modulus, tensile strength, and fracture energy, obtained by inverse analysis of the load-displacement curves for the real and equivalent mortar mixtures, were compared. The differences between the real and the equivalent mortars were statistically quantified by means of ANOVA. Further, the crack initiation and propagation in the real and equivalent mortars was monitored by means of DIC. The experimentally-determined load-displacement curves obtained by means of the CTT for real and equivalent mortars showed excellent agreement.

The elastic modulus, tensile strength, and fracture energy results determined by inverse analysis based on the hinge model also supported the hypothesis of similarity between the real and equivalent mortars. The statistical analysis through ANOVA and MANOVA showed that no statistically significant difference (at significance level of 0.05) was observed for the material properties investigated.

To validate the accuracy of the results obtained by the inverse analysis, a FEM model simulating the sample tested in CTT was built. Excellent agreements between experimentally determined and computed load-displacement curves were found for all mortar systems.

Further, the elastic modulus results obtained by inverse analysis were compared to static and dynamic elastic moduli measured on companion specimens. Good agreements between results obtained by inverse analysis for both the real and equivalent mortars with the statically determined ones were obtained for most of the test specimens.

Finally, the DIC technique revealed that crack initiation and propagation evolved similarly in the two systems at similar load levels.

Experimental results suggest that the equivalent approach is a powerful method to investigate hydration-dependent and/or moisture-dependent properties. The use of the equivalent approach indeed allows investigations at early age that are otherwise difficult or impossible to perform because of the ongoing hydration while on the other hand moisture-dependent testing requires drying.

To this end, the effect of the moisture content on the elastic modulus, tensile strength, and fracture energy at early-age was investigated. The tensile strength at all ages appears to be the most sensitive to the presence of moisture, increasing systematically upon drying. Despite a less pronounced difference, also the fracture energy seems to increase as the moisture level decreases. On the other hand, the elastic modulus does not seem to be affected.
Chapter 5.

Early-age elastic properties as a function of the moisture content

The moisture content is of particular relevance in cement-based materials, as it has a strong impact on their fundamental material properties. For example, it directly affects their strength and elastic properties, which in turn are closely related to volumetric deformations and cracking susceptibility.

In this chapter, the effects of the internal moisture content decrease, due to drying, on the elastic modulus of cement-based paste and mortar samples were investigated at early age making use of the equivalent system method.

The elastic modulus of the OPC and slag containing equivalent mortar samples at the five equivalent ages (1, 3, 7, 28 and 91 days) was measured by resonant ultrasound spectroscopy (RUS). In addition, the elastic modulus as a function of the moisture content was also measured by micro-indentation on the equivalent paste samples.
5.1 Introduction

After placement, curing practices are considered essential for the strength development and the durability of concrete (Neville 1995, ACI 2001, Aıtcin 2003). However, once the curing period is over (normally when a substantial amount of cement has not yet reacted), concrete structures are usually exposed to the environment, mostly resulting in water loss due to evaporation towards the environment at lower RH. The water loss due to drying results in significant changes of the materials properties such as transport and mechanical properties, while at the same time inducing a volume reduction (Bażant and Najjar 1972, Yurtdas et al. 2006, Di Bella et al. 2016).

Generally, the mechanical properties, both in terms of strength and elastic modulus, have been shown to depend on the moisture content. An in-depth understanding of the strength and elastic modulus dependences on the internal RH of cement-based materials may be important at the designing stage of a concrete structure, when calculating both the free volumetric deformations and the stress induced by restrained deformations.

A reduction in strength and elastic properties has been observed in correspondence of an increase in the water saturation degree due, for example, to an increase in the environmental RH, thus of the internal one. This type of dependence from the RH, which we term “weakening with increasing RH”, has been shown, for cement-based materials, both within a broad, e.g., from 10% to 90% (Duckheim 2008), and a narrow, e.g., 10% to 40% (Pihlajavaara 1965, Wittmann 1973, Zech and Setzer 1989), range of RH values. In those ranges, this type of weakening has been also observed via different types of elastic properties measurements and at different probing length scales, e.g., by dynamic and macroscopic measurements, based upon ultrasound waves (Pihlajavaara 1965, Wittmann 1973, Wittmann et al. 1987, Zech and Setzer 1989), but also at the microscopic scale, using micro-indentation (Sorelli et al. 2015). In addition to cement-based materials, such weakening has been shown to occur in many other porous materials, such as rocks (Winkler and Murphy 1995, Baud et al. 2000, Pimienta et al. 2014).

A reduction in strength and elastic properties has been observed in correspondence of an increase in the water saturation degree. In addition to cement-based materials such weakening effect has been shown to occur in many porous materials, such as rocks and Vycor glass (Pihlajavaara 1965, Wittmann 1973, Sellevold and Radjy 1976, Zech and Setzer 1989, Winkler and Murphy 1995, Baud et al. 2000, Pimienta et al. 2014).
While the effect of the moisture content on the strength has been widely investigated with experimental results clearly confirming a general weakening at higher moisture contents (Wittmann 1973, Li 2004, Burlion et al. 2005, Yurtdas et al. 2006, Di Bella et al. 2016), only few studies have investigated in a systematic way the dependence of the elastic modulus on the moisture content in cement-based materials. Furthermore, these few studies report contradictory results. For example, Sereda et al. (Sereda et al. 1966) measured the elastic modulus at different equilibrium RH conditions on thin cement paste samples from the load-deflection curve using a miniature testing machine, concluding that the elastic modulus remains constant in the region between 0 to 50% RH, while an increase was observed above 50% RH. Zech and Setzer (Zech and Setzer 1989) measured the elastic modulus of thin cement paste samples using dynamic techniques. The elastic modulus decreased until about 40% RH (local minimum), then it increased up to 12% RH (local maximum), followed by a decrease while approaching 0% RH. This means that they observed a weakening with increasing RH only within the interval 12% - 40%, as mentioned before. A local minimum in elastic modulus at about 40% was also observed for cement pastes by Wittmann [9]. Also in this case, weakening with increasing RH was limited to a range of low RH values. However, in these measurements, the elastic modulus monotonically increased with decreasing RH below 40%.

Duckheim (Duckheim 2008) measured the elastic modulus of thin cement paste samples in desorption and adsorption using a three-point flexural test. With desorption, he observed a small reduction of the elastic modulus right below 100% RH followed by a continuous increase of the elastic modulus up to about 5% RH. Below 5% RH, a stronger reduction was observed. His measurements showed weakening with increasing RH within the broadest RH range among all the previously cited works. All of these studies thus differed in terms of RH intervals within which the weakening with increasing RH was observed. However, such weakening was always observed as a common pattern. From the drying point of view, we notice that it corresponds to an increase in elastic modulus with decreasing RH, i.e., decreasing moisture content.

Other studies reported a different general pattern. Beaudoin et al. (Beaudoin et al. 2010) measured the static elastic modulus in compression on thin paste samples as a function of the moisture content, reporting loss of stiffness during drying, with a substantial decrease below 20% RH. Further, they showed that the response of the elastic modulus is non-linear with respect to the moisture content and depends on the drying-wetting history.

Yurtdas et al. (Yurtdas et al. 2006) measured the elastic modulus of mortars with uniaxial and triaxial tests. In that study, performed on relatively thick mortar samples left drying at labora-
tory conditions, decreases in elastic modulus with decreases in moisture content were observed as well, contrary to the trend of the strength, which increased with decreasing moisture content. Burlion et al. measured the elastic modulus of concrete samples exposed to drying at laboratory conditions (60% RH) (Burlion et al. 2005), reporting a reduction of the elastic modulus during the drying process. Other authors investigated the effect of the moisture content on concrete and mortar specimens which were oven-dried (at different temperatures and for different duration) (Almudaiheem and Al-Sugair 1992, Rossi et al. 1992, Yaman et al. 2002, Malaikah 2004). However, It should be noted that the use of relatively thick specimens or rapid drying (especially oven-drying) may result in a non-equilibrated internal moisture content and, more importantly, may introduce changes in the microstructure due to further hydration of residual unreacted binder, degradation of some products of hydration (Pihlajavaara 1968, Gallé 2001, Ye 2003) or micro-cracking (Idiart et al. 2012), all of them eventually altering the resulting mechanical properties. Finally, lack of control of the atmosphere in the oven (as well as in uncontrolled testing environments) may lead to carbonation, another source of microstructural changes that may affect the mechanical properties (Jerga 2004, Fabbri et al. 2009, Knapen et al. 2009).

Figure 5.1 shows the elastic modulus measurement results obtained for paste samples at different RH values by different authors using different measurement techniques, clearly showing different dependencies between the two variables. Each elastic modulus value, of each measurement, is normalized by its value at the lowest RH.
Figure 5.1. Elastic modulus as a function of RH for cement paste according to (Sereda et al. 1966, Ramachandran et al. 1981, Zech and Setzer 1989, Duckheim 2008, Beaudoin et al. 2010, Alizadeh et al. 2011). For each dataset, the elastic modulus value is normalized by the value at 0% RH.

As a non-unique dependence of the elastic modulus from the moisture content has been observed, several mechanisms have been suggested to explain it. Wittman (Wittmann 1973) ascribed the effect of the water content on the elastic modulus of hardened cement pastes to the roles of the surface energy and the disjoining pressure. Namely, the adsorption of water at RH up to 50% decreases the surface energy of the solid skeleton, while at higher RH the disjoining pressure overcomes the Van der Waals attraction and begins to separate the solid surfaces. Similarly, Zech and Setzer (Zech and Setzer 1989) proposed that for RH decreasing below 40% the increasing surface free energy leads to a compression of the gel particles and is responsible for the increased elastic modulus. However, below about 12% RH, hydrates lose their bound water, causing irreversible changes to the micro-structure that in turn induce a decrease of the elastic modulus.

Although there is no accepted description of the physical process involved in the changes of mechanical properties during drying, two competitive effects are usually referred to affect the elastic properties. On the one hand, the capillary pressure inside the pores increases as the moisture content decreases, imposing a volumetric pressure that compresses the material and leads to an overall, macroscopic stiffening effect (Yurtdas et al. 2006). On the other hand, micro-cracking, due to differential drying or the presence of aggregates in the matrix acting as
restraints, contributes to a degradation of the elastic properties (Burlion et al. 2005, Yurtdas et al. 2006). The interplay between capillary pressure and micro-cracking has been suggested to be at the basis of the mechanical properties dependence on the moisture content (Yurtdas et al. 2006). However, other processes may contribute as well in determining how the elastic moduli vary in correspondence of a decrease in moisture content due to drying. Alizadeh et al. (Alizadeh et al. 2011) investigated the changes in the viscoelastic properties of synthetic C-S-H samples dried at low RH (less than 11%). They observed a significant decrease in the elastic modulus with moisture loss and hypothesized that such reduction could be attributed not only to micro-cracking but also to other microscale phenomena such as collapse of the C-S-H layers when interlayer water is removed and possible cross-linking of silicates (Beaudoin et al. 2010, Alizadeh et al. 2011).

5.2 Experimental methods

5.2.1 Resonant ultrasound spectroscopy

The dynamic elastic modulus, $E$, and shear modulus, $G$, of the mortar samples were measured using resonant ultrasound spectroscopy (RUS). This method is a non-destructive technique that measures the sample resonance frequencies to determine the elastic moduli (Migliori and Darling 1996, Wu et al. 2010). It consists in exciting one or more vibration eigenmodes and in measuring the corresponding resonance frequencies. The excitation typically consists in applying a sinusoidal vibration to the sample surface via a piezoelectric transducer in contact with the sample. The frequency of the excitation signal is varied within a given range. In correspondence of each frequency, the vibration of the sample surface at another location is measured via another contact piezoelectric transducer or a non-contact sensor, e.g., a laser vibrometer. Since the resonance frequencies are functions of the elastic moduli, the mass and the sample geometry, the dynamic elastic moduli can be estimated by inverse analysis, once geometry and mass of the sample are precisely known.

General RUS consists in exciting several vibration eigenmodes during a single measurement, obtaining a response spectrum (amplitude of surface vibration at a given point as a function of the sinusoidal excitation frequency, where the amplitude peaks in correspondence of the resonance frequencies). The inverse analysis consists then in a nonlinear best fitting of the response spectrum starting from initial guesses for the elastic moduli (Visscher et al. 1991, Zadler et al. 2004). A significant number of resonance frequencies should be contained within the spectrum, in order to increase the likelihood of convergence to reliable estimates by the
best fitting algorithm. A minimum threshold number of such resonance peaks highly depends upon the type of material and on the sample geometry. Resonance spectra of highly attenuating materials, e.g., concrete, typically do not contain several clearly identifiable peaks. Several RUS measurements with different sample/source/receiver positioning and respective spectra fusion are then needed to achieve a synthesized spectrum with a sufficient number of peaks, and more sophisticated processing can aid in the extraction of the peak parameters (Remillieux et al. 2015).

An alternative to general RUS, called single mode RUS (SIMORUS), consists in adopting a source/receiver configuration that preferentially, even though not exclusively, excites a specific type of vibration eigenmodes. Under certain constraining assumptions about the sample geometry and aspect ratios, an analytical formula can be derived for the relationship between one specific eigenmode’s resonance frequency and one elastic modulus.

SIMORUS was implemented following the ASTM C 215-08 standard for the measurement of E and G of concrete samples (ASTM-C215 2008). Such standard is based upon the theory of elastic rods, thus it can be applied only to either cylinders or prisms that are very elongated along one direction compared with the other ones.

Two measurements were performed according to ASTM C 215-08, one to excite mainly longitudinal vibration eigenmodes, the other one to excite torsional ones. From the resonance spectra of each measurement, the 1st longitudinal and the 1st torsional eigenfrequencies can be estimated, respectively. Based upon approximations inherent to the theory of elastic rods, E and G are related to those resonance frequencies according to analytical equations (Eq. 2 and 3 in ASTM C215-08).

SIMORUS was based upon the following components: a periodic signal generation card (National Instruments, NI, PXI-5406 16-bit) to create the source sinusoidal signal; a fixed gain (50×) high voltage amplifier (Tegam 2350) to amplify such signal before feeding it to a source piezoelectric transducer; a receiver piezoelectric transducer directly connected to an acquisition and digital-to-analog conversion card (NI PXI-5122); a NI PXIe-1073 chassis integrating the generation and acquisition cards, connected to a laptop via a NI PXI card.

The sample was supported in correspondence to its middle line along the longitudinal axis. At such position, the sample is expected to have a nodal point (zero vibration amplitude). The excitation frequencies ranged from 1 to 40 kHz.

The overall measurements were automatized using the resonance inspection techniques and analyses (RITA©) software developed by the Wave Physics Team, Solid Earth Geophysics Group, at the Los Alamos National Laboratory (Payan et al. 2014).
While general RUS measurements do not require knowing which resonance frequency (peak position in the spectrum of Fig. 2) is associated to which eigenmode, SIMORUS necessitates eigenmode identification to be sure that a chosen and estimated resonance frequency corresponds to the eigenmode of interest. Eigenmode identification is particularly relevant for the actual implementation of the ASTM C215-08 standard, because of the approximations based upon the elastic rod theory. Such theory is strictly valid only for infinitely long and thin rods. The formulation used in the ASTM standard takes into account the finite length and cross-section of the cylindrical or prismatic sample, considering correction factors (Pickett 1900). However, the departure of the sample geometry from an ideal elastic rod leads to longitudinal and torsional resonance spectra which contain mainly but not only peaks associated with the respective eigenmodes. This fact implies that, for example, the first peak in the spectrum from the longitudinal measurement may not be the one associated with the first longitudinal eigenmode but it may be associated with the first torsional eigenmode. The latter eigenmode has typically frequency much lower than the first longitudinal one.

Identification of the vibration eigenmodes was performed with the aid of the finite element method based modal analysis as implemented in Comsol Multiphysics 5.2©. Such analysis took into account the geometry and the density of the sample. Initial guesses for E and G were chosen based upon longitudinal wave ultrasound pulse velocity (UPV) measurements performed on the same samples used for the SIMORUS ones and on typical values for the Poisson ratio of similar mortars (ranging between 0.2 and 0.25).

Finally, the measured and the modelled spectra were compared to discriminate between the first longitudinal and first torsional resonance frequencies.

An additional confirmation that a certain peak frequency corresponded to the 1st longitudinal eigenmode was obtained by exciting sinusoidally the investigated sample at that frequency and measuring by a Polytec OFV 505 head/OFV 5000 controller laser vibrometer the surface vibration at several points along a line parallel to the sample longitudinal direction, in order to calculate a linear profile of the maximum vibration amplitude field in that direction and recognize the typical pattern due to the 1st longitudinal eigenmode.
5.2.2 Micro-indentation

Indentation techniques have been widely used during the past years to characterize the mechanical properties of materials at micro- and nano-scale. For example, mechanical properties of thin films, coatings or other small features such as different phases in bone are usually determined by means of such methodology (Barbier et al. 2005, Zhang et al. 2008). Thanks to the accessible small range scale along with the simplicity and the reduced operational time, micro- and nano-indentation have gained more and more interest. Initially, micro-indentation was typically employed to determine the hardness and the elastic modulus of the investigated materials. More recently, it has also been used to study several mechanical properties including micro-strength, fracture toughness as well as viscoelastic properties, especially thanks to improvements made in the theoretical analysis of the test data resulting from the load/displacement curves (Desaeger and Verpoest 1993, Harding et al. 1994, Vandamme and Ulm 2013, Zhang et al. 2013).

In a micro-indentation measurement, an indenter of known geometry is forced into the surface of the material to be tested by applying an increasing load (a force) up to a maximum value $P_{\text{max}}$ (loading phase). The maximum load is kept constant for a given time (holding phase) and finally the load is reduced until complete withdrawal of the indenter (unloading phase). The resulting load-displacement curve is used to calculate the mechanical properties of interest for the tested material.
The measured indentation depth consists of both plastic and elastic deformation. During unloading, the recovery of the elastic deformation is analyzed according to a model for the elastic contact problem, leading to the solution for the calculation of the elastic modulus. More details on the theoretical background regarding the calculation of the elastic modulus from an indentation test can be found elsewhere (Oliver and Pharr 1992, Oliver and Pharr 2004).

5.3 Experimental procedure

5.3.1 Resonant ultrasound spectroscopy

The OPC and the slag containing mortar mixtures were prepared as described in chapter 3. The materials and mixture proportions are reported in Table 3.3.

Two different mortar sample geometries were prepared: prismatic samples (40 × 40 mm² in cross-section and 160 mm long) and thin plate samples (6 mm thick, 40 mm wide and 160 mm long). Each mortar sample was cast in two layers on a vibrating table. After casting, the specimens were covered with a plastic sheet and kept in an environmental chamber for 48 h at 20 °C and 100% RH. After demolding, the samples were wrapped in wet towels, sealed in plastic bags and stored in an environmental chamber at 20 ± 0.5 °C and 100% RH for no less than 3 months.

To simplify, in the rest of the text, the two sample geometries will be addressed as thick prismatic and thin plate samples, respectively.

Thick prismatic mortar samples (equivalent and real) as well as thin plate mortar samples (equivalent) were tested using RUS. While the thick prismatic real and equivalent mortar samples were tested to confirm the equivalence between the two (for samples conditioned at 97% RH only), the thin plate equivalent samples were sequentially stored in distinct desiccators, each with a different RH, to investigate the elastic properties dependence on decreasing moisture content. It should be noted that thin samples were used to investigate the effects of the decreasing moisture content as they would allow a shorter time to reach equilibrium while minimizing possible micro-cracking due to differential shrinkage thanks to the reduced thickness. The drying protocol started after a minimum of 3 months of curing. Right after curing, the thin plate mortar samples were stored in desiccators at 97% RH for approximately 6 months in order to homogenize the initial internal RH in the specimens. The RH was decreased step-wise in small RH steps to minimize micro-cracking arising from differential shrinkage. Constant RH environments in the different desiccators were obtained using supersaturated salt solutions in the following protocol order: 97% K₂SO₄, 94% KNO₃, 75% NaCl,
54% Mg(NO\(_3\))\(_2\), 33% MgCl\(_2\), 11% LiCl. The same samples were moved to the lowered RH environment once equilibrium was reached. Equilibrium was assumed when the difference in mass between two consecutive measurements was 0.1% or smaller over a period of two weeks. The time needed to reach equilibrium at each RH step depended on both the RH level and the specimen. In general, the samples were kept at any given RH level for about 4 months.

The desiccators containing the samples were flushed with nitrogen to keep a CO\(_2\)-free atmosphere to prevent carbonation. Once the measurements at all the different RH levels were carried out, the samples were subjected to a final drying in desiccators containing silica gel (~1% RH) to measure the elastic modulus in the dry state.

5.3.2 Micro-indentation

The OPC and the slag containing pastes were prepared as described in chapter 3, in section 3.3.

After approximately 8 months of curing, the equivalent paste samples were conditioned at different RH levels. It should be noted that only the equivalent OPC paste mixtures were tested with this technique and not the slag systems. As for the mortar specimens (see previous section), the RH in the desiccators was controlled by saturated salt solutions: 97% K\(_2\)SO\(_4\), 94% KNO\(_3\), 85% KCl, 75% NaCl, 54% Mg(NO\(_3\))\(_2\), 33% MgCl\(_2\). Also in this campaign, the desiccators were regularly flushed with nitrogen. In this case, however, the samples were not conditioned at 11% and afterwards dried in silica gel as for the mortar samples.

Starting with an equilibrium condition at 97% RH, all the samples planned to be tested were placed in the desiccator. In correspondence of each equilibrated RH step, the elastic modulus was measured in one sample, while the other samples were moved to the lower RH level. Approximately one month before testing, the target surface of the specimen subjected to micro-indentation was polished with 4 discs of silicon carbide abrasive paper with increasing grit. The samples were polished for about 3 minutes without water or solvents in accordance with Zhang et al. (Zhang et al. 2014). At the end of the dry polishing step, the samples were put back in the desiccator at the intended RH until testing. In general, the samples underwent a minimum of three months conditioning before being tested, except for the samples conditioned at 33% RH which were kept in that environment for at least 5 months.
The micro-indentation measurements were performed with the apparatus available at the Lafarge Research Center. The instrument was calibrated according to the standard (ASTM-E2546 2007). The micro-indenter is equipped with a sealed environmental chamber in which the RH was adjusted through the use of saturated salt solutions, avoiding localized RH changes in the sample during indentation. Further, to avoid carbonation, the environmental chamber was continuously flushed with CO₂-free air during the test. The test was carried out at controlled temperature of 20 ± 0.5 °C.

At the testing age, the paste samples were placed on a remotely controlled indentation platform.

The samples were fixed by applying a tiny drop of superglue at the interface between the bottom of the sample and a steel plate, to avoid possible movements of the sample during loading. On each sample tested, 8 micro-indentation tests were performed with a Vickers indenter probe and a holding phase of 20 seconds. Table 5.1 summarizes the setting parameters used during the experiments.

Table 5.1. Experimental setting parameters adopted for the micro-indentation measurements.

<table>
<thead>
<tr>
<th>Indenter</th>
<th>Vickers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum indentation load P&lt;sub&gt;max&lt;/sub&gt;</strong></td>
<td>20 N</td>
</tr>
<tr>
<td><strong>Holding phase</strong></td>
<td>20 s</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>20 ± 0.2 °C</td>
</tr>
<tr>
<td><strong>Relative humidity</strong></td>
<td>97%, 94%, 85%, 75%, 54%, 33%, 11%</td>
</tr>
</tbody>
</table>

### 5.4 Results

#### 5.4.1 Real vs equivalent mortars and sample size effect as determined through RUS

As to validate the equivalent systems method, the elastic modulus results of the thick equivalent mortar mixtures are compared to those measured in the real mortar mixtures both for the OPC and the slag-containing mixtures (Figure 5.3). Thick prismatic mortars specimens conditioned in desiccators at 97% RH were tested. The elastic modulus is plotted as a function of the equivalent age. The term “equivalent age” is synonymous of curing age for the real samples. However, for the equivalent systems, it is used to emphasize the idea that they have achieved a microstructure simulating that of the real samples cured for the corresponding
time. In reality all the equivalent samples were cured for a minimum of 3 months to be sure about their steady-state conditions (Di Bella et al. 2015, Termkhajornkit et al. 2015).

The results in Figure 5.3 are obtained as the average of two distinct samples at each equivalent age. Further, for each sample, the SIMORUS measurement was repeated up to three times, each time slightly changing the position of the sensors, in order to avoid possible erroneous measurements due to the local presence of either an aggregate or a pore. The error bars represent the standard deviation. However, it should be noted that due to the high repeatability of the measurement, very often the error bars are smaller than the size of the markers indicated in the figures.

In general, the elastic modulus of the mortar samples increases as the specimen equivalent age increases due to the progress of the hydration reaction and hence the larger volume of hydration products in the microstructure and the reduced porosity. With regard to the real and equivalent mortars comparison, the elastic modulus results show smaller values for the equivalent system specimens compared with the corresponding real ones, at any equivalent age, the difference lying in the range of 0.5 - 3 GPa for both the OPC and slag mortars, thus indicating a good agreement between real and equivalent systems in both cases. Less agreement can be noted in the OPC mortar at the equivalent age of 7 days. In this case, the real mortar shows a much higher elastic modulus than the respective equivalent. On the other hand, the OPC mortar real value at 7 days is even higher than the one observed at 28 and 91 days.

Finally, comparing the general elastic modulus development of the OPC and slag mortars at the different equivalent ages, the OPC mortars show higher elastic modulus values than the slag-containing systems, as the porosity of the latter is higher at early ages due to the slowly-reacting slag. Eventually, at 91 days, the elastic modulus results of the two systems are very similar.
Figure 5.3. Dynamic elastic modulus, $E$, measurements by single mode resonant ultrasound spectroscopy. Comparison between real and equivalent thick prismatic mortar samples conditioned at 97% RH: a) OPC mortar; b) slag mortar.

A further confirmation of the agreement between the elastic modulus values of real and equivalent systems comes from the comparison, for either class of specimens, of dynamic values, measured in this work by the SIMORUS method, and quasi-static ones, measured within the context of the same project, but published elsewhere, with two different techniques (direct measurement of quasi-static compressive load force-displacement curves (Di Bella et al. 2015) and indirect measurement by inverse analysis of compact tension tests, CTT (Di Bella et al. 2016)). Figure 5.4 shows this type of comparison for the OPC mortars only conditioned at 97% RH. It can be observed that, independently of the equivalent age and both for the real and the equivalent systems, the elastic modulus obtained by SIMORUS, i.e., a dynamic value, is approximately 20-30% higher than the one obtained by the quasi-static techniques. Precisely, the real specimens exhibit an average relative difference in dynamic vs static elastic modulus of 31% while the equivalent ones 28%, the average being calculated over the different equivalent ages. This relative difference values are in line with what obtained by other authors (Mehta and Monteiro 1993, Neville 1995, Lamond 2006) and it is usually explained by the fact that the dynamic tests are carried out at lower stress levels compared to the static ones. Further, the elastic modulus is dependent on the rate at which the load is applied (Ross et al. 1996, Rossi and Toutlemonde 1996). The differences in the elastic modulus observed between dynamic and static tests may be also due to local water redistribution from load-bearing water layers toward larger pores (Wyrzykowski and Lura 2014).
Figure 5.4. Comparison between dynamic and quasi-static elastic modulus measurements for the thick prismatic OPC real and equivalent mortars kept at constant relative humidity of 97% RH and at any equivalent age. Each marker represents an average value. The error bars are based upon standard deviations and, when not visible, are smaller than the size of the marker itself. The filled markers refer to the dynamic values measured in this work, as reported in Figure 5.3(a). The quasi-static values were obtained with two different measurement techniques (quasi-static compressive loading, direct measurement of load-displacement curves, label “quasi-static”, and indirect measurements by inverse analysis of load-displacement curves obtained during compaction tension tests, label “CTT”) and are reported in other articles, Ref. (Di Bella et al. 2015) and (Di Bella et al. 2016), respectively.

In the equivalent system method, it is assumed that, after 3 months of curing, the binder has completely reacted and that a static system, not changing anymore in time, is created. To validate this assumption, the elastic modulus was measured again by SIMORUS on the same thick prismatic equivalent mortar samples kept in desiccators at RH 97% after 1 year. Figure 5.5 reports the comparison between the results for the equivalent samples cured for about 3 months and cured for 1 year. The results show a perfect overlap between the two datasets, confirming that the equivalent systems were indeed in equilibrium and static, i.e., there was no further modification of the elastic properties due to possible ongoing hydration.
Figure 5.5. Dynamic elastic modulus, E, measurements by single mode resonant ultrasound spectroscopy. Comparison of the elastic modulus after 3 months and one year of curing in the equivalent thick prismatic mortar samples kept at constant relative humidity of 97%.

In Figure 5.3 and in Figure 5.5 the elastic modulus results were directly obtained by SI-MORUS measurements on prismatic mortar samples 40 × 40 mm² in cross-section. To investigate the impact of the moisture content on the elastic modulus, thin plate samples (thickness 6 mm) were actually used to allow reaching internal moisture equilibrium in a reasonable time while reducing possible micro-cracking due to self-restraint.

Such thin plate samples depart even more than the thick prismatic samples from the elastic rod assumption used for the calculation of the elastic modulus as described in the ASTM standard (ASTM-C215 2008). In Figure 5.6, the elastic modulus results measured on the prismatic samples are compared with those obtained from the thin plate samples. The results show a very good agreement, guaranteeing that the plate geometry did not introduce additional biases or errors in the elastic modulus estimation. The OPC equivalent thin plate mortar at 7 days shows a relatively higher elastic modulus than the respective thick prismatic sample. However, a much larger standard deviation is associated to that point.
5.4.2 Effect of the decreasing moisture content as determined through RUS

The effect of the decreasing moisture content on the equivalent OPC and slag mortar mixtures as a function of the equivalent age is shown in Figure 5.7a and b, respectively. In general, it can be observed that at earlier ages the elastic modulus is not influenced by the moisture content. Specifically, in spite of the greater standard deviation, the elastic modulus of the OPC mortars at the equivalent ages of 1 and 3 days remain almost constant as the moisture content changes. Starting at 7 days and continuing at 28 and 91 days, results show that there is a steady decrease of the elastic modulus as the moisture content decreases. At these equivalent ages, the elastic modulus reduces approximately of 15% from the starting equilibrium condition of 97% RH to 11% RH. Further, it can be noticed that no variation is observed between 33% and 11% RH as well as for the samples that were dried in silica gel.

Similar to the OPC mortars, at earlier ages slag mortars do not seem to be effected by the decrease in moisture content. However, in this case no variations are observed even at the equivalent age of 7 days. The reduction of the elastic modulus at later ages (i.e. 28 and 91 days), instead, is more pronounced than for the OPC mortars. The elastic modulus reduces of up to 25% from the equilibrium state at 97% RH to 11% RH. Finally, the elastic modulus measured at 33% RH, 11% RH, and after drying in silica gel remained constant.

The reduction of the elastic modulus with the decreasing moisture content observed in the OPC mortars and the slag containing mortars is in accordance with findings by Sereda et al.

Figure 5.6. Dynamic elastic modulus, E, measurements by single mode resonant ultrasound spectroscopy. Comparison between prismatic and plate samples conditioned at 97% RH.
(Sereda et al. 1966), in terms of trend: a monotonic decrease in elastic modulus with decreasing RH, from high RH values up to a certain value (approximately 50% in the case of (Sereda et al. 1966), see Figure 5.1, while 33% in our case), below which the elastic modulus achieves more or less a plateau value. Such a plateau in the range of low RH values has not been observed in the other published works, e.g., in those reported in Figure 5.1. On the contrary, some of those studies show the largest decrease and decrease rate in elastic modulus at RH below 15%-20% (Ramachandran et al. 1981, Beaudoin et al. 2010, Alizadeh et al. 2011).

It should be noted that during the SIMORUS measurements, the samples were kept at room conditions (20° C and RH ranging between 40% and 50%), which could have led to some limited adsorption/desorption depending on the equilibrium RH of the sample. However, the testing time for each sample did not exceed 4 minutes (including the sample positioning and repetitions). Right after testing the samples were rapidly sealed in plastic bags and afterwards placed back in the desiccators. As the period of time required for testing each sample is extremely shorter than the one needed for reaching equilibrium (from 2 to 3 months according to the RH step), the authors believe that the measurement itself had no significant impact on biasing the elastic modulus values.
Figure 5.7. Dynamic elastic modulus, E, measurements by single mode resonant ultrasound spectroscopy. Effect of the moisture content on the elastic modulus in a) equivalent OPC mortar mixtures and b) equivalent slag mortar mixtures.

To judge whether the reduction of elastic modulus at lower RH observed by SIMORUS would also be observed in quasi-static measurements, the results obtained with SIMORUS are compared with those measured through CTT (chapter 4). Figure 5.8 shows the elastic modulus results obtained by inverse analysis of the CTT measurements on samples conditioned at 97% RH compared to the results obtained on similar OPC mortar samples dried in an oven at 50° C until equilibrium was reached. More details about the CTT measurements and respective results can be found in (Di Bella et al. 2016). No significant difference is ob-
served, at any equivalent age, between the specimens at 97% RH and the dried ones. These CTT measurements would hint at an absence of (or a lower) dependence of the quasi-static elastic modulus from the moisture content, compared with the corresponding stronger dependence of the dynamic elastic modulus.

Figure 5.8 Indirect measurements of the quasi-static elastic modulus by inverse analysis of load-displacement curves obtained during compaction tension tests (CTT) [6]. The estimates refer to OPC equivalent mortar specimens either conditioned at 97% RH (triangles) or oven dried at 50°C (diamonds).

The equivalent systems, used in this investigation as a technique to assess the effects of the decreasing moisture content on the elastic modulus, show a good agreement with the corresponding real mortar samples in terms of elastic modulus measured at a given age. This agreement suggests that the equivalent system approach can be used to investigate the moisture-dependent properties at early age, which would not be otherwise feasible by other current techniques (Di Bella et al. 2015). This has been also discussed in (Di Bella et al. 2016) with respect to their applicability to investigate the fracture properties as well. In general, it can be noted that the elastic modulus results for the real systems are systematically slightly higher (a few GPa) than those obtained in their respective equivalent systems. This is likely due to the fact that the equivalent systems have been designed based upon slight underestimations of the degree of hydration occurred in the real systems (Di Bella et al. 2015). Indeed, some uncertainty on the degree of hydration may originate from the methods used to determine the volume fraction of the reacted/unreacted binder, which is used to build the equivalent systems. In addition, it should be emphasized that the quartz possesses a lower elastic modulus than the cement grains. In general, the elastic modulus of composite materials like concrete depends
on the mechanical properties of the constituent materials and their respective volume fractions. Several authors have measured the elastic modulus of some of the clinker phases by nano-indentation, concluding that the elastic modulus ranges between 125 and 145 GPa (Velez et al. 2001, Chamrova 2010). On the other hand, the elastic modulus of quartz has been determined in the range of 65 and 100 GPa (Ohno 1995, Heyliger et al. 2003, Ogi et al. 2004). Calculations of effective elastic moduli or of their possible ranges of values, based upon composite theories and models, e.g., the Hashin-Shtrikman theory (Hashin and Shtrikman 1963, Nielsen 1982), introducing simplifications in the description of the mortars as composites, confirm lower values of the elastic moduli for the equivalent systems compared with the real ones, just based upon the different elastic moduli of unhydrated clinker and the quartz filler. The reduction in the elastic modulus by substituting cement with quartz filler is much smaller in our specimens (2-3 GPa) compared with the reduction in the theoretical composite models we used for the calculations (order of 10 GPa for the upper Hashin-Shtrikman bound and order of 1 GPa for the corresponding lower bound), likely due to more complicated microstructural effects, e.g., packing of the quartz grains within the hydrating mortar microstructure, not taken into account by simplistic composite theories as the Hashin-Shtrikman one. Despite such difference and the simplistic Hashin-Shtrikman assumptions, such calculations suggest not only that a reduction in the dynamic elastic modulus of the equivalent specimens compared with that of the real one should be expected but also the range for such reduction, within which our observations fall.

The elastic modulus at early age, i.e., 1 and 3 days for the OPC mortars and 1, 3 and 7 days in the slag-containing mortars, does not seem to be affected by the moisture content as it remains almost constant (despite the larger standard deviation observed). At later ages, the elastic modulus becomes smaller as the moisture content is decreased. This effect seems to occur up to 50-30% RH, while a further reduction of the RH and moisture content does not affect the elastic modulus.

Such elastic modulus reduction has been explained, for example, by the occurrence of micro-cracking due to differential shrinkage or restraining effects exerted by the presence of the aggregates (Burlion et al. 2005, Yurtdas et al. 2006). Specifically, the samples tested in this study contained sand and quartz grains that could have contributed to the occurrence of micro-cracking. However, it should be also noticed that such reduction is not observed at earlier ages, i.e., when the tensile strength is even lower and the likelihood of micro-cracking should be even higher.
One possible explanation for the difference between the equivalent specimens up to 3 or 7 days of equivalent age (OPC and slag mortars, respectively) and equivalent specimens of larger equivalent age could consist in taking into account the balance between the drying shrinkage-induced micro-cracking and the role of capillary forces, already mentioned in the Introduction. We remind that the physical models adopted by Wittman [9] and Zech and Setzer [10] to explain why below 40-50% a decrease in RH led, in their measurements, to an increase in elastic modulus is based upon two main mechanisms: (1) an increase in surface tension and a decrease in the water meniscus’ curvature radius with decreasing RH, both leading to an increase in the capillary forces; (2) a corresponding increase of “packing” of the hydration products’ solid skeleton, leading to higher effective elastic moduli of the skeleton itself.

The compaction effect of increasing capillary forces with decreasing RH should be expected to be larger at earlier equivalent ages, when the solid network percolates and fills up less efficiently the overall volume available. At later equivalent ages, a more developed and space percolating solid skeleton should be able to withstand more the overall compressive effect of the increasing capillary forces, even though becoming a more “brittle” structure than the one at earlier ages. Thus, while at earlier equivalent ages the compaction effect of capillary forces may partly compensate the elastic modulus reduction by shrinkage-related micro-cracking, eventually leading to a quasi-constant elastic modulus as we observe, such compensation should be smaller at later equivalent ages. Considering also the higher brittleness the microstructure acquires at later ages, due to the formation, e.g., of larger crystalline structures as Portlandite needles, we hypothesize that micro-cracking could take over capillarity-driven compaction, leading to an overall macroscopic reduction in elastic modulus.

A question related with our results for the later equivalent age specimens remains unanswered: why we did not observe a significant, additional decrease in elastic modulus at RH smaller than 33%.

According to what suggested in several previous works ((Zech and Setzer 1989, Beaudoin et al. 2010, Alizadeh et al. 2011, Wyrzykowski and Lura 2014), an additional process occurs at such low RH, especially below 11% (corresponding to the thickness of a single monolayer of adsorbed water). The process is the change in status and/or the displacement toward larger pores of structural water in the inter-layer space of hydration products, mainly C-S-H, leading eventually to the structural collapse of the products’ structures.

One possible answer to that question may reside in the very long time scale associated with such displacement of inter-layer structural water at the lower RH values. As previously mentioned, we allowed each specimen achieving an internal RH equilibrium condition, at each
RH level of the drying protocol, by storing it for maximum 4 months inside the respective environments. We assessed the achievement of such equilibrium based upon reaching a relative mass change below 0.1%. Despite the specimens, conditioned at the different RH levels, showed to be in such equilibrium, the actual additional displacement of structural water may have occurred in smaller degree in between the steps at lower RH, within the time of 4 months. Future work should investigate whether longer conditioning times at lower RH levels may lead or not to further additional decrease in the elastic modulus. This would be in agreement with several hypotheses suggesting that long term, slowly occurring macroscopic deformations, as creep ones, may be related also with such displacements of structural water and consequent collapsing of layered silicates as C-S-H (Beaudoin et al. 2010, Wyrzykowski and Lura 2014).

From an engineering point of view, on the one hand, the reduction of the elastic modulus as the moisture content decreases, observed already after one week (which represents the typical duration of curing practices), may impact the concrete’s performances. While a reduction in the elastic modulus may exacerbate the volumetric deformations (Di Bella et al. 2017), it will also lower the self-induced stresses (Leemann et al. 2011), so that the impact on the likelihood of cracking might be minor. On the other hand, the tensile strength measured on companion samples and reported elsewhere (Di Bella et al. 2016), becomes higher in dried conditions, in agreement with what also observed in other studies (Li 2004, Yurtdas et al. 2006).

In this work, the dynamic elastic modulus was obtained by single mode resonant ultrasound spectroscopy (SIMORUS), since this technique allows measurements on extremely thin samples that can be conditioned at low RH without inducing cracking due to differential shrinkage.

The comparison of the elastic modulus results obtained through dynamic measurements and those obtained from quasi-static ones reveals that with the latter the elastic modulus is smaller, a very well established result for, among others, cement-based materials (Mehta and Monteiro 1993, Lamond 2006) and validated also for our real and equivalent mortar specimens (Fig. 5.4). Among the possible causes of such difference between dynamic and quasi-static values, one mechanism related with the moisture content has been suggested: the higher degree of local redistribution of water from load-bearing water layers to larger pores, occurring with the higher stresses involved in the quasi-static measurements compared with the dynamic ones (Wyrzykowski and Lura 2014). This explanation is relevant also for a decrease in elastic modulus due to a decrease in moisture content and is in agreement with the results of the present work: a reduction of RH can also reduce the thickness of the load-bearing water
layers or can remove the layers themselves, at very low RH, with the consequence that the
dynamic elastic modulus may be similar to the static one at low RH.
The same moisture content decrease-related mechanism should be in principle at play in the
case of quasi-static elastic modulus values. As we discuss in the Introduction Section, results
reported in the literature do not always agree with each other, even though they may be biased
by the drying methods used on still hydrating specimens, contrary to our equivalent speci-
mens with temporally invariant microstructure. Quasi-static elastic modulus measurements in
specimens conditioned at 97% RH and oven dried have been performed within the context of
the same project this work belongs to. Figure 8 reports preliminary results of such measure-
ments, obtained by inverse analysis of the compaction tension test (CTT) measurements [6].
Such values, at most of the equivalent ages, are close to the quasi-static values obtained by
standard compressive loading measurements, being the two types of measurements performed
within similar strain rates ranges.
In this case, the quasi-static elastic modulus does not seem to be as strongly dependent on the
moisture content as the dynamic one, at any equivalent age investigated. The high experi-
mental scatter of the CTT measurements compared to the resonant ultrasound spectroscopy
ones employed in this thesis may hide a smaller effect of drying. In any case, these results call
for a more complete study of whether and how strongly the elastic modulus dependence on
the moisture content, observed by measuring dynamic values, translates also to the case of
quasi-static values.

5.4.3 Effect of the decreasing moisture content as determined through micro-indentation

The elastic modulus results of the equivalent OPC paste mixtures as a function of the equiva-
lent age and conditioned at different RH levels (97%, 94%, 85% and 75%, 54% and 33%) are
shown in Figure 5.9. It should be emphasized that the inner parts of the samples very likely
did not reach moisture equilibrium within the conditioning time. Nevertheless, the technique
is based on surface measurements. Surface regions were very likely in equilibrium with the
external RH as the samples were kept at a given RH level for a minimum period of 3 months.
The results reported in Figure 5.9 were obtained as the average of 8 measurements per each
sample. The error bars in that plot represent the standard deviation. Although not as clear as
previously observed for the mortar mixtures, the elastic modulus of the cement pastes increas-
es as the specimen equivalent age increases. However, it is readily observable that most of the
measurements were characterized by large scatter, probably due to spatial inhomogeneity arising from the sample as well as from the test itself.

Figure 5.9. Elastic modulus, $E$, by micro-indentation. Effect of the decreasing moisture content on the equivalent OPC paste mixture.

As for the influence of the moisture content, Figure 5.9 clearly shows that, for each equivalent age, most of the results either overlap or fall within the boundaries set by ± one standard deviation at the different RH levels. This situation prevents us from drawing any conclusion with regard to the influence of the moisture content on the elastic modulus. Only at the equivalent age of 91 days a trend may be recognized up to RH 75%, according to which samples with higher moisture content show a slightly higher elastic modulus. However, this conclusion is doubtful due to the increased elastic modulus at RH values below 75% and the inherent high standard deviation at any RH levels.

It should be noted that even though the samples were conditioned in a step wise fashion to minimize the occurrence of microcracking this does not rule out the possibility that still due to the conditioning some self-restrained induced microcracking occurred which could have also influenced the scatter observed.

To validate the results obtained by the micro-indentation technique, the elastic modulus results as a function of the equivalent age obtained from the paste conditioned at 97% RH were used as input for two homogenization schemes. The calculated elastic modulus after homoge-
ization was afterwards compared to the experimental values obtained on prismatic mortar samples (40 × 40 mm² cross-section and 160 mm long) by RUS and conditioned at 97% RH. The rationale for using homogenization schemes is the following. The elastic modulus determined by microindentation was measured on the cement paste. To validate the values obtained, the elastic modulus obtained through microindentation technique is used as input to calculate the respective one in the two-phase composite material (the mortar) and compared it with the one obtained by RUS.

Considering a composite microstructure made of spherical inclusions (the sand aggregates) embedded in an infinite medium (the cement paste), the effective properties of the composite material can be obtained making use of the Mori-Tanaka scheme, as described in (Azoti et al. 2011).

\[
K = K_m + \frac{f(K_m - K_a)(K_a + G_m)}{3K_m + 4G_m + 3(1-f)(K_m - K_a)} \tag{1}
\]

\[
G = G_m + \frac{5fG_m(G_m - G_a)(3K_m + 4K_m)}{5G_m(3K_m + 4G_m) + 6(1-f)(G_m - G_a)(K_m + 2K_m)} \tag{2}
\]

where the K and G are the bulk modulus and the shear modulus of the composite materials, respectively. The K and G containing the subscripts a and m indicate the bulk modulus and shear modulus of the aggregate and matrix, respectively. \(f\) is the volume fraction of the aggregates.

In addition, the range of possible values for the elastic moduli of the composite material was estimated using the Hashin-Shtrikman bounds (Hashin and Shtrikman 1963, Arns et al. 2002). Accordingly, two relationships, one for the lower bound and one for the upper bound, are given for the calculation of the bulk and shear moduli of a composite material. The Hashin-Shtrikman bounds are given by:

\[
K = K_m + \frac{f_a}{K_a + K_m} \frac{1}{3K_m + 4G_m} \tag{3}
\]

\[
G = G_m + \frac{f_a}{G_a + G_m} \frac{1}{6(K_m + 2G_m)G_m} \tag{4}
\]
To compute the upper and lower bounds, the bulk and shear moduli of the aggregates and matrix as well as their volume fractions need to be interchanged in the equations 3 and 4. The bulk and shear moduli of the composite determined through the Mori-Tanaka scheme and Hashin-Shtrikman bounds are finally used to calculate the elastic modulus of the mortar. Table 5.2 summarizes the properties of the phases taken into account for the homogenization, i.e. the cementitious matrix (paste including quartz replacing the unhydrated cement) and the aggregates as macroscopic inclusions. The elastic modulus of the matrix at the different equivalent ages was obtained by micro-indentation. For the time being and in the absence of direct measurements, the Poisson’s ratio values of the paste were extrapolated from (Maruyama and Igarashi 2014), which reports the development of Poisson’s ratios from ultrasonic pulse velocity measurements made on cement paste with similar water-to-cement ratios as used in this study. The elastic modulus and the Poisson’s ratio of the sand were assumed to be equal to 70 GPa and 0.17 respectively in accordance with previous investigations (Dvorkin 2008).

Table 5.2. Paste (matrix) and sand (inclusions) properties used to carry out the homogenization.

<table>
<thead>
<tr>
<th>Equiv. age [days]</th>
<th>Elastic modulus [GPa]</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Matrix</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.5</td>
<td>0.35</td>
</tr>
<tr>
<td>3</td>
<td>9.5</td>
<td>0.3</td>
</tr>
<tr>
<td>7</td>
<td>15.5</td>
<td>0.27</td>
</tr>
<tr>
<td>28</td>
<td>18.3</td>
<td>0.25</td>
</tr>
<tr>
<td>91</td>
<td>19.6</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>Inclusions</strong></td>
<td>/</td>
<td>70.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.17</td>
</tr>
</tbody>
</table>

In Table 5.2, the dynamic elastic modulus results, obtained by SIMORUS on the thick prismatic mortar samples at 97% RH, are plotted against the upscaled results obtained by micro-indentation after homogenization. The experimental results fall right in between the lower and the upper bounds as determined by the Hashin-Shtrikman model with the experimental values being much closer to the lower bound at the equivalent ages of 7, 28 and 91 days. It should be noted that the Mori-Tanaka scheme directly overlap with the Hashin-Shtrikman lower bound.
Despite the fact that the experimental results fall within the lower and upper bounds in the Hashin-Shtrikman model, at the equivalent age of 1 and 3 days the experimentally-determined elastic modulus is higher than what modelled by the Mori-Tanaka scheme. It should be emphasized that at earlier ages the differences between the lower and upper bounds are quite large, approximately 12 GPa at 1 day and 8 GPa at 3 days. Nevertheless, the elastic modulus obtained from the paste after homogenization is comparable to the one obtained by RUS measurements on the mortar samples. Although the homogenization returned values qualitatively and quantitatively (especially at later ages) comparable with those obtained by RUS, it should be emphasized that micro-indentation does not seem to be a suitable technique to investigate the influence of the moisture content due its inadequate reproducibility.

Figure 5.10. Elastic modulus of mortars obtained through homogenization (dotted lines) compared with the elastic modulus directly measured by single mode resonant ultrasound spectroscopy for thick prismatic mortar samples made only with ordinary Portland cement and conditioned at 97% RH (diamonds).

5.5 Conclusions

In this study, the effect of the decreasing moisture content on the elastic modulus of cement-based mortar mixtures was investigated at early-age through single mode resonant ultrasound spectroscopy. In addition, the the effect of the decreasing moisture content on the elastic modulus was also measured by micro-indentation on pastes.
To enable the investigation of the elastic properties at early-age, the mortars were properly designed (equivalent systems) to decouple the effects of hydration and drying. The use of equivalent mixtures enabled to stop the hydration, resulting in static systems which did not evolve over time and during the drying process. Hence, thanks to this approach the elastic properties can be fundamentally investigated at early-age removing the influence of hydration.

The comparison of the elastic modulus measured, before starting drying, on the equivalent mortar systems and the real ones at different equivalent ages showed a good agreement, with small differences falling within ranges to be theoretically expected due to the substitution of unhydrated clinker with quartz filler, considering even simplistic composite theory calculations. This agreement within those difference ranges confirmed the validity of the equivalent mortars approach. Further, to validate that no microstructural changes occurred with time, as it is assumed that complete hydration of the residual binder occurs within 3 months, the elastic modulus was measured on the same samples again after one year. Results showed a perfect overlap between the initial measurements and the ones carried out one year later.

On the influence of the decreasing moisture content, the elastic modulus results (by single mode resonant ultrasound spectroscopy) showed that at earlier ages the elastic modulus remains constant both in the OPC and the slag mortars. At later ages, the elastic modulus slowly but steadily decreases up to 33% RH. At lower RH levels the elastic modulus remains constant. Similar results were obtained for the slag mortar mixtures. However, in this case, the reduction was more marked than for the OPC equivalent mortars.

The reduction of the elastic modulus as a consequence of drying can play an important role both on the magnitude of the free shrinkage and on the self-induced stresses, hence on the likelihood of cracking.

Elastic modulus results obtained by the micro-indentation technique on the OPC paste samples showed high scatter, preventing any possible conclusion on the effect of the moisture content. Nevertheless, to verify the results obtained by such technique, two homogenization schemes were used to model the elastic properties of the OPC mortar mixtures, namely the Mori-Tanaka scheme and the Hashin-Shtrikman bounds. The experimentally-determined elastic modulus results obtained by resonant ultrasound spectroscopy on the thick prismatic samples conditioned at 97% RH fit very well with the predicted values, especially at later ages, i.e. 7, 28 and 91 days.
For future research, it is suggested that an in-depth and systematic investigation on the effect of decreasing moisture content on the static elastic modulus could also employ the equivalent system approach, similarly to the present study. However, the experimental challenges of performing static measurements of elastic modulus on samples with very small cross-section cannot be understated. In addition, new measurements, either dynamic or static, should investigate the role played by the RH equilibration time at very low RH levels, eventually increasing the equilibration time when stepping down to very low values, e.g., below 11%, to assess whether loss of structural water from inter-layer regions in C-S-H may still occur and contribute to a further reduction in elastic modulus.
Chapter 6.
Evaluation of the ultimate drying shrinkage of cement-based mortars with poroelastic models

In this chapter, three different poroelastic approaches to predict the ultimate drying shrinkage are compared and validated against the experimentally-determined ultimate drying shrinkage of three different cement-based mortars, with and without supplementary cementitious materials (SCM), was investigated.

The different poroelastic models predict similar ultimate shrinkage as a function of the relative humidity especially in the higher range (above about 50% RH). The experimentally-measured ultimate drying shrinkage is predicted reasonably well by the different models, with the highest deviations observed for the slag-containing mortars. The most important parameters that influence the predictions are discussed and their effect is quantified. The uncertainty of the shrinkage predictions resulting from error propagation of the input parameters is estimated using a parametric bootstrap technique.
6.1 Introduction

During their service life, concrete structures undergo several types of volume changes as a result of the material’s response to internal chemical processes and external and/or environmental load. Drying of moisture to the environment leads to drying shrinkage (a volume reduction) resulting from the drop in the internal RH in the pores of the concrete. If the volume reduction due to shrinkage is hindered by internal or external restraint (Weiss et al. 1998, Bisschop and Van Mier 2002), residual tensile stresses build up that may lead to warping and/or micro- and macro-cracking (Ytterberg 1987, Bissonnette et al. 2007). Eventually, damaged concrete structures experience reduced durability and service life, which has a tremendous economic impact. Prediction of the volume changes of concrete structures at the design stage remains one of the most efficient and economical strategies to account for the volumetric instability due to drying and enables further measures for minimizing stresses development and possible cracking.

During the past years, several shrinkage models have been suggested to estimate the magnitude and the rate of the time-dependent deformations. They can be divided into two main categories: phenomenological models and mechanistic models.

Belonging to the first group, the ACI 209R model (ACI-209 2008), the Eurocode 2 (EN-1992-1-1 2008), the B3 model (Bažant and Baweja 1995), the CEB-FIP model (CEB-FIP 1990) or the GL 2000 (Gardner and Lockman 2001) are all empirical models obtained through best-fit analysis of experimental data. Several drawbacks are usually associated with these models, mostly due to the large uncertainty in predicting the shrinkage and the considerable amount of input parameters that are required (Bazant and Chern 1984, Almudaiheem 1992, Bažant 2001). Al Manasser and Lam (Al-Manaseer and Lam 2005) performed a statistical evaluation of four shrinkage models (ACI 209R-92, CEB 90, B3 and GL 2000), concluding that the B3 model and the GL2000 models lead to the best predictions, whereas the ACI 209R-92 model overestimates the short-term shrinkage strains and underestimates the long-term ones (Theiner et al. 2014). It is possible to improve the shrinkage prediction when short-term measurements (about 1 to 3 months) are available (Bažant 2001). Despite some attempts of taking into account shrinkage deformations of structures made with denser concrete (Jonasson 2009), autogenous shrinkage or presence of chemical admixtures, (Wendner et al. 2013, Bazant et al. 2014), the shortcoming of the aforementioned models is based on the excessive amount of data necessary for validation of these models, and their limited applicability to non-standard materials.
Based on the fact that the drying shrinkage of mortar and concrete is driven by the shrinkage of the cement paste and depends on its volume fraction in the composite, other researchers have tried to derive models from the theory of elasticity and composite theory (Pickett 1956, Hansen and Nielsen 1965, Almudaiheem 1992). Nevertheless, while using paste or mortar to finally estimate shrinkage of concrete has the advantage of dealing with less material and smaller samples, such approach would still need long-term measurements, because the shrinkage of the paste is needed as input.

Proper prediction of concrete volume changes requires a fundamental understanding of the mechanisms and of the physical properties involved in the process, to be able to embrace different types of concrete mixtures and applications. To this end, the volume changes of an isotropic porous medium such as concrete can be described by means of poromechanics (Coussy 2005).

Accordingly, in the framework of poroelasticity, in which the solid skeleton of the porous material is considered to behave elastically, the constitutive shrinkage behavior of porous materials can be described knowing the mechanisms causing the volume change, their moisture state and their elastic properties.

Coussy et al. (Coussy et al. 1998) modelled the macroscopic shrinkage of cement paste and concrete on the basis of the thermodynamics of open continua. Baroghel-Bouny et al. concluded that the model based on capillary stresses was “quite suitable at least for engineering purposes” (Baroghel-Bouny et al. 1999). On the contrary, Vlahinić et al. stated that “the experimental results of elastic shrinkage during drying of hardened cement paste are consistently greater than predictions” and provided a new constitutive formulation in the effective stress framework, considering the weakening of the solid skeleton upon drying (Vlahinić et al. 2009). Similarly, Rougelot et al. included the effects of saturation in the bulk modulus of the matrix (Rougelot et al. 2009). Both studies, (Vlahinić et al. 2009) and (Rougelot et al. 2009), considered a partially saturated porous medium as a saturated material in which desaturated pores are included in the matrix as closed porosity. Such approach leads to the dependence of the compressibility of the porous body upon saturation, assuming that a decrease in the saturation corresponds to a decrease of the bulk modulus of the skeleton.

Bentz et al. (Bentz et al. 1998) investigated the shrinkage behavior of porous Vycor glass using an analytical method based on work by Mackenzie (Mackenzie 1950) (equivalent to the Biot-Bishop formulation discussed in section 6.2) and obtained good agreement between simulation and experiments only in the upper RH range (between 94% and 80%).
Lura et al. modeled the autogenous shrinkage of cement based pastes using the Biot-Bishop formulation, obtaining good predictions only in the higher RH range (Lura et al. 2003). At lower RH the underestimation of the measured shrinkage was attributed to the influence of creep and to the pozzolanic reaction of the silica fume. Indeed, in the above-mentioned poroelastic models, the material is treated as porous, isotropic and linear elastic, excluding possible microcracking or creep effects. Grasley and Leung (Grasley and Leung 2011) described shrinkage of hardened cement paste including a viscoelastic component making use of solidifying and poroviscoelastic models with intrinsic aging of the calcium-silicate hydrate (CSH).

In this chapter, the experimentally-determined drying shrinkage at moisture equilibrium of three mortars is compared with predictions obtained by three different mechanistic models that consider different mechanisms and solid response causing the shrinkage. The three mortars are an Ordinary Portland Cement (OPC) mortar and two additional mortars where 45% (by volume) of the cement in the paste was replaced by slag and silica fume, respectively. Three different formulations for description of drying shrinkage were examined. The first one is the classical Biot-Bishop (Biot 1941, Bishop 1959) poroelastic approach for unsaturated media using the concept of averaged pressure exerted by pore fluids. The second poroelastic approach by Coussy et al. (Coussy et al. 1998), instead of an averaged pressure, takes into account an equivalent pore pressure that includes a term for the surface free energy. Finally, the third approach is a modification of the Biot-Bishop approach that accounts for the weakening of the solid skeleton during drying, as proposed by Vlahinić et al. (Vlahinić et al. 2009). These approaches are presented in detail in section 6.2.

One of the key aspects in modeling based on experimentally-determined input data is the assessment of the uncertainty of the model predictions that originates from the combined errors of the input (random) data. This aspect should be addressed with propagation of uncertainty (also referred to as error propagation) (Kass et al. 2014). Analytical solutions for propagation of uncertainty can become a very tedious task if the function of the input data is complex, i.e. it involves many parameters that are not independent, like in the case of shrinkage predictions described in section 2. In order to overcome this difficulty, a parametric bootstrapping technique (Kass et al. 2014) is used here for estimation of uncertainty of drying shrinkage predictions.
6.1.1 Estimation of uncertainty of model predictions – parametric bootstrapping

Bootstrapping is a statistical method that belongs to a broader class of resampling methods (Chernick 2011). It consists in simulating a large number of samples (pseudo-data) by resampling from the original data with replacements and drawing conclusions based on the simulated data. Bootstrapping is a powerful and robust technique in particular for assessment of errors of the estimates (Chernick 2011, Kass et al. 2014).

In the particular case presented here, the function for which the uncertainty propagation is estimated is the shrinkage prediction (according to the three different models), while the input experimental parameters are obtained in the simulations.

For the simulations, a parametric bootstrap technique was used. The generated bootstrap samples (pseudo-data) were obtained by sampling from the assumed underlying distributions. It was assumed that the material properties and the imposed RH all have normal distributions. Therefore, the unknown parameters of the distributions were the mean and the standard deviation. These parameters were assumed to be equal to the corresponding estimates (mean and standard deviation) of the original experimentally-determined data. The random properties considered were those measured in the experiments for which the variability could be estimated: saturation, static elastic modulus, Poisson ratio and porosity. Additionally, the imposed RH was attributed the standard deviation (never exceeding 0.7% RH) based on the experimental measurements published in (Greenspan 1977). The bulk modulus of the solid skeleton was assumed as a constant value based on literature (Grasley et al. 2007). For the latter parameter, the effect of the assumed variability was separately estimated.

The procedure of calculating the uncertainty at each considered RH for each considered system can be summarized as follows:

a. for each random property, estimate the parameters of the underlying normal distributions (mean and standard deviation) from the experimental data;

b. for each random property, draw a sample of the same size as the original data from the corresponding normal distributions;

c. calculate the average of the simulated data for each of the parameters;

d. calculate the shrinkage according to the models described in section 2.2;

e. Repeat steps b-d 9999 times

f. from the vector of the calculated shrinkage values (calculated from 9999 generated data sets plus 1 original dataset) determine the 2.5% and 97.5% quantiles;

g. use the determined quantiles as bootstrap 95% confidence intervals.
6.2 Drying shrinkage modeling: poroelastic formulations comparison

The deformation of a porous saturated body can be described using the approach developed by Biot (Biot 1941, Biot 1955) and Biot and Willis (Biot and Willis 1957), see also (Bishop and Blight 1963, Skempton 1984, Scherer 2004):

\[ \varepsilon_v = p \left( \frac{1}{K_b} - \frac{1}{K_s} \right) \]  
(eq. 6.1)

where \( K_b \) [Pa] is the drained bulk modulus of the porous body and \( K_s \) [Pa] is the bulk modulus of its solid skeleton. According to this approach, in absence of any external loads the volumetric deformations are solely due to changes in pore water pressure \( p \) [Pa].

The extension of this approach to partially-saturated porous materials was developed by Bishop (Bishop 1959), who introduced the concept of two fluids at different pressures (\( p_w \) for water and \( p_g \) for gas pressure) occupying the pores. After assuming the volumetric saturation degree with liquid pore water \( S_w \) [-] as averaging factor, the average pore pressure in the pores can be expressed as \( p = S_w p_w + (1 - S_w) p_g \) (Lewis and Schrefler 1987, Hutter et al. 1999). Neglecting the contribution of the gas pressure and further considering that \( p_c = p_g - p_w \), the average pore pressure reduces to \( p = -S_w p_c \). This leads to the following equation:

\[ \varepsilon_v = -S_w p_c \left( \frac{1}{K_b} - \frac{1}{K_s} \right) \]  
(eq. 6.2)

where \( p_c \) increases due to decrease of RH (drying), which can be conveniently calculated with the Kelvin-Laplace equation (eq. 2.1), as discussed in chapter 2. In this thesis, this approach will be called Biot-Bishop approach.

Coussy et al. provided a formulation to describe the drying shrinkage of cement based materials introducing the concept of equivalent pore pressure \( \pi \) [Pa] in place of the averaged pressure into equation (2) (Coussy et al. 2004). The equivalent pore pressure takes into account also the contribution of the interface energy \( U \) [Pa], and was expressed as \( \pi = p - U \), where the latter term is (Coussy et al. 2004):

\[ U(S_w) = \int_{S_w}^{1} p_c(S_w) \, dS_w \]  
(eq. 6.3)

and can be calculated knowing the desorption isotherm \( p_c(S) \). Finally, the following equation describing volumetric deformations is obtained:

\[ \varepsilon_v = -(S_w p_c + U) \left( \frac{1}{K_b} - \frac{1}{K_s} \right) \]  
(eq. 6.4)

A third approach to model the volumetric deformation of unsaturated porous materials was developed by Vlahinić et al. (Vlahinić et al. 2009). According to Vlahinić et al., a correct as-
ssessment of the extent of weakening of the solid due to desaturation of pores would allow accurate predictions of the volumetric strains. In their approach, the partially-saturated system is thought as fully saturated where the pores are filled with water, while drying affects only the bulk modulus of the effective solid. In other words, the bulk modulus of the solids changes with drying and the relationship is expressed in terms of the degree of water saturation.

In the model by Vlahinić et al. (Vlahinić et al. 2009), the constitutive formulation for a partially saturated porous medium can be written as:

\[ \varepsilon_v = -S_w p_c \left( \frac{1}{K_b} - \frac{1}{\bar{K}(S_w)} \right) \]  
(eq. 6.5)

where \( \bar{K} \) [Pa] is the effective bulk modulus and can be calculated knowing the total porosity \( \phi_0 \) [-] as:

\[ \bar{K} = K_s - \frac{(K_s-K_b)(1-S_w)}{(1-S_w\phi_0)} \]  
(eq. 6.6)

According to the three approaches described above, drying shrinkage can be calculated knowing the driving mechanisms, the degree of saturation, the bulk moduli and the total porosity (notice that the total porosity is necessary only in the last approach by Vlahinić et al. (Vlahinić et al. 2009)).

For simplicity, in the rest of the thesis the three models will be addressed as Biot-Bishop model (equation 3), Coussy et al. model (equation 5) and Vlahinić et al. model (equation 6), respectively.

It should be noted that all the three models are based on the pore pressure. As it was discussed in chapter 2, changes in pressure exerted by the pore fluids on the skeleton that cause shrinkage, can be considered to be due either to capillary or disjoining pressure and are related to the internal RH through the Kelvin-Laplace equation (eq. 2.1). Further details can be found in (Di Bella et al. 2017).

Further, except for the porosity, which is used solely in the Vlahinić et al. model, it can be seen that all three formulations are based on the same set of experimental data. As long as experimental determination is rather straightforward for the capillary pressure (environmental condition) and mechanical properties of the porous body (\( K_b \)), for the saturation (and porosity) and for bulk modulus of the solid skeleton (\( K_s \)), the used input data must be based on assumptions. In order to study this problem, we analyzed the influence of different assumptions regarding input parameters on the final results in detail in section 6.4.2.
6.3 Experimental Methods

Three equivalent mortar mixtures were prepared: one containing OPC as binder (with partial replacement by quartz powder, see later) and two in which 45% by volume of the cement was replaced by slag and silica fume, respectively. In all the three a very small portion of binder was replaced by quartz. The binder replacement corresponds to the system reproducing the 91d hydration. The samples were prepared and cured as described in chapter 3. Table 3.3 reported the mixture proportions.

After mixing, the mortar was poured into steel molds to form the 150×40×6 mm³ samples. The samples were cast in two layers of about 3 mm each on a vibrating table. The ends were provided with cast-in gauges able to accommodate the tip of a length comparator to enable shrinkage measurements (Figure 6.1).

After casting, the specimens were covered with a plastic sheet and kept in an environmental chamber for approximately 48 h at 20 °C and 100% RH. After demolding, the mortar samples were wrapped in wet towels and sealed in plastic bags to avoid drying and limit carbonation. They were then cured for at least 3 months in an environmental chamber at 20 °C and 100% RH.

At the end of the curing period, the samples were placed in desiccators filled with nitrogen gas (to avoid carbonation) and they were subjected to step-wise RH decrease, with RH controlled by saturated salt solutions. Once the samples reached moisture equilibrium at each RH step, they were moved to the next (lower) RH level. Equilibrium at each RH step was assumed to be reached once the change in mass between two consecutive measurements was smaller than 0.1% over a period of two weeks. It should be noted that no further shrinkage was noticed on the samples once mass equilibrium was reached at the different RH levels. Small RH steps were used in this study to minimize moisture gradients within the sample, reducing the risk of cracking due to differential shrinkage and self-restraint (Bisschop 2002). In addition, the reduced thickness used in this study allowed reaching equilibrium faster. Three samples were measured for every mortar type.
6.3.1 Saturation degree and porosity

The equilibrium moisture properties of porous materials such as cement-based materials can be understood, quantified and predicted by sorption isotherms (desorption and adsorption), which reflect microstructural features such as total porosity, pore size distribution and degree of connectivity as well as the liquid properties (Baroghel-Bouny et al. 1999, Espinosa and Franke 2006, Villani et al. 2014). In this study, desorption isotherms were obtained from the mass-loss measurements carried out on the same thin mortar samples used to measure the shrinkage at equilibrium. The mass change was monitored at different RH steps (97.6%, 94.6%, 85.1%, 75.5%, 54.4%, and 33.1%) obtained with saturated salt solutions at 20±0.3 °C. Once equilibrium was reached, the samples were moved to the following RH step.

Since the saturation degree was calculated as the ratio of the mass of water in the sample to the mass of water in the sample at full saturation (virgin state at the beginning of the tests), an important point was the determination of the reference dry state. For this purpose, companion samples were dried in the oven, using two different temperatures: 50 °C or 105 °C. In Figure 6.2, the saturation degree results of the three mortar mixtures as a function of the RH are shown as obtained with two different drying regimes (50°C and 105°C) used to determine the reference dry mass of the samples. For both drying temperatures, a very small scatter between triplicate samples within each system was obtained, with standard deviation not exceeding 0.01.

Porosity is understood here as a water-accessible porosity, i.e., it was determined based on the initial mass of water in the sample, obtained by referencing a sample mass to its dry mass, the
latter obtained as for the saturation degree using two different temperatures: 50 °C and 105 °C. Sample volume was determined based on Archimedes’ principle by weighing the saturated samples in air and after immersion in water. The results are presented in Table 6.1. In Figure 6.2, the saturation degree is obtained from the mass loss results measured on the thin equivalent mortars specimens at 91d. It is interesting to note that the saturation results after drying at 105°C are comparable to those obtained through DVS (at similar drying regime). This will be discussed in the next chapter.

Figure 6.2. Saturation degree as a function of the RH for the three equivalent mortars at 91d determined by using dry reference mass after drying at 50 °C and at 105 °C. Error bars (not exceeding 0.01) represent standard deviation from the three samples for each dataset.

6.3.2 Bulk moduli

The bulk modulus of the porous solid $K_b$ was calculated from the combination of the static elastic modulus and the Poisson’s ratio $\nu$ determined by a dynamic technique. The static elastic modulus of the mortar was measured on three (or two for the silica fume system) mortar prisms (40×40×160 mm$^3$) for each mixture in accordance with EN 196-1. The samples were equipped with two extensometers that monitored the displacement while loaded up to 30% of the compressive strength. The Poisson’s ratio was determined by resonant ultrasound spectroscopy (RUS) on two samples or on one sample (for the silica fume system). In this method, the vibration eigenmodes are excited over a certain frequency range and the correspondent eigenfrequencies are measured. Finally, the eigenfrequencies are used to calculate the elastic
properties knowing density and geometry (Migliori and Darling 1996, ASTM-C215 2008, Wu et al. 2010). Table 6.1 shows the bulk moduli used as input for modeling.

Estimating the error of the static elastic modulus or Poisson ratio can be done in a straightforward way by using the standard deviation obtained from the measurements performed on replicate samples. For the bulk modulus, being a function of the parameters determined experimentally using for each a different method, the propagation of uncertainty was obtained by means of parametric bootstrapping, similarly as described in section 6.1.1.

While the bulk modulus of the porous solid $K_b$ can be calculated from the elastic modulus $E$ and the Poisson’s ratio, the determination of the bulk moduli of the skeleton $K_s$ is not trivial. The latter depends on the bulk moduli of all the solid phases forming the mortar. The main problem derives from the determination of $K_s$ for the intrinsically-porous CSH. Grasley et al. experimentally quantified the $K_s$ of cement paste and concrete at early-age (Grasley et al. 2007). Results ranged between 40 and 55 GPa. Further, they also suggested that the $K_s$ of mature concretes is expected to be in the same range as the one of the aggregates, since cement particles (with high $K_s$) are converted to less stiff hydration products. In this study, the bulk modulus of the solids was assumed to be 38 GPa. This value was chosen using the effective medium approach by Hashin and Shtrikman (Hashin and Shtrikman 1963) and considering that 50% of the mortar is occupied by sand and 50% by cement paste.

Table 6.1. Bulk modulus calculated from static elastic modulus and dynamically-determined Poisson’s ratio. The water-accessible porosity was measured by referencing the initial saturated sample mass to the dry mass after oven storage at 50 °C and at 105 °C. Errors estimates refer to standard deviation obtained from the replicate measurements or with a parametric bootstrapping technique (for bulk modulus).

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>Slag</th>
<th>Silica fume</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Static elastic modulus $E$ (GPa)</strong></td>
<td>$26.7\pm1.2$</td>
<td>$25.9\pm0.7$</td>
<td>$25.4\pm0.6$</td>
</tr>
<tr>
<td><strong>Dynamic Poisson’s ratio, $\nu$</strong></td>
<td>$0.199\pm0.024$</td>
<td>$0.231\pm0.006$</td>
<td>$0.181\pm0.007$</td>
</tr>
<tr>
<td><strong>Bulk modulus $K_b$ (GPa)</strong>*</td>
<td>$14.8\pm0.9$</td>
<td>$16.0\pm0.4$</td>
<td>$13.3\pm0.3$</td>
</tr>
<tr>
<td><strong>Water-accessible porosity, 50 °C (%)</strong></td>
<td>$14.0\pm0.7$</td>
<td>$14.0\pm0.8$</td>
<td>$18.0\pm0.7$</td>
</tr>
<tr>
<td><strong>Water-accessible porosity, 105 °C (%)</strong></td>
<td>$21.0\pm0.1$</td>
<td>$22.0\pm0.8$</td>
<td>$26.0\pm0.1$</td>
</tr>
</tbody>
</table>

* Estimated based on parametric bootstrapping
6.4 Drying shrinkage: comparison of experiment and simulations

6.4.1 Experimental results

Figure 6.3 shows the measured shrinkage strains at moisture equilibrium of the three mortar mixtures as a function of the RH. The shrinkage results were calculated as average of three specimens. The error bars represent the standard deviation of the three measured samples. The mortars containing SCM show systematically higher shrinkage than the OPC mortars especially at RH levels below 85%. Until 75 %RH, no substantial differences are observed between mortars with slag or silica fume. At lower RH levels, however, the ultimate shrinkage of the silica fume mortar is higher than for the slag mortar.

It should be noted that the experimental results shown in Figure 6.3 (and later in Figures 6.4-6.6) refer to the first drying branch, with the saturated state as a reference point, similarly as in (Setzer et al. 2008, Maruyama 2010). This is at odds with some previous studies, e.g. (Vlahinić et al. 2009), where the sample had been initially dried before the shrinkage measurements took place. The reason for neglecting the first shrinkage branch and analyzing only the second and subsequent drying cycles in the discussion of shrinkage mechanisms was to avoid the irreversibility (and hence – the postulated non-elasticity) of shrinkage observed in the first adsorption that followed the initial first desorption (Vlahinić et al. 2009). We do not support this approach and note that, when the possible influence of irreversible phenomena is eliminated, shrinkage occurring in the first drying cycle can be in fact explained based on poroelastic theory. As possible non-elastic phenomena that may lead to irreversible shrinkage, one can name microcracking and carbonation shrinkage. The former was avoided by an extremely slow drying process (step-wise drying) of the miniature samples in order to minimize the moisture gradients and therefore the buildup of stresses due to self-restraint. The latter was avoided by drying the samples in nitrogen atmosphere. The same approach was also applied in the works by Setzer (Setzer et al. 2008) and Maruyama et al. (Maruyama 2010). Their results clearly show that the irreversibility of shrinkage observed upon resaturation (manifested in the fact that the absolute shrinkage, referred to the virgin saturated state, is higher on adsorption than on the preceding desorption) is in fact due to the well-known hysteresis of the sorption isotherm (Setzer et al. 2008). In other words, the hysteresis (irreversibility) in shrinkage stems directly from the different water content equilibrium states on desorption/adsorption, and it becomes negligible when shrinkage is plotted as a function of water content, as evidenced in (Setzer et al. 2008, Maruyama 2010). Following this observation, it can be concluded that drying shrinkage of cementitious materials in the first drying cycle can
be explained with the poroelastic approaches investigated in this chapter. Moreover, it would be also possible to apply this approach to explain hysteresis of drying shrinkage, as its effect is accounted for by means of the saturation degree used as input parameter.

Figure 6.3. Ultimate drying shrinkage as a function of RH. Error bars represent standard deviation of three samples.

6.4.2 Drying shrinkage predictions vs experimental shrinkage

The modelling results according to 1) the Biot-Bishop model, 2) the Coussy et al. model and 3) the Vlahinić et al. model are presented and compared with the experimental data in Figures 6.4 and 6.5, for the two sets of saturation degree data, determined by referencing to dry mass at 105 °C and 50 °C, respectively. The bootstrapped 95% confidence intervals are also presented in Figures 6.4 and 6.5. Regarding propagation of uncertainty, it can be noted that the confidence intervals increase at decreasing RH, which for an approximately constant variability of the input parameters is due to the scaling effect of the pressure (because the pore pressure increases exponentially with a RH decrease, see eq.1). It was found that more than half of the width of the confidence interval is due to the variability of the experimentally-determined Poisson ratio. The width of the confidence band resulting from propagation of uncertainty of the experimental data is relatively narrow (below ±100 μm/m) for RH above about 75%RH. It should be reminded that this regards only the error of the determined parameters according to a certain assumed method, and does not include the effect of different possible assumptions, like the effect of saturation degree or bulk modulus of solid skeleton discussed further.
It can be seen that, except for the slag mortar, all three models are capable of predicting the shrinkage with good accuracy for RH above 54%, and especially above 75%. It should be noted, that equilibrium RH below about 50% will not be reached in most of engineering structures around the world. In this RH range the difference between the saturation degrees determined using two different temperatures as reference is of minor importance, compare Figures 6.4 and 6.5. For the Slag mortar, all three models underestimated the high shrinkage observed experimentally.

The differences between the three models and their sensitivity to the determined saturation degree start to be significant at RH below about 54%RH. With both sets of saturation degree data, the additional term considered in the Coussy et al. model due to interfacial phenomena (see equation (4)) leads to an approximately constant slope of the strain-RH curve along the whole range of analyzed RH. This is not in agreement with the experimental data presented in Figure 3 and other published experimental data (Setzer et al. 2008, Weiss et al. 2008), where a bi-linear character of the strain-RH curve was observed, with a decrease of slope around 40-50%RH. On the other hand, using the Biot-Bishop model or Vlahinić et al. model one can account for the change in slope in the curves. Of these two models, for RH below about 54%, the Biot-Bishop model provided better agreement with experimental data when the saturation degree was obtained by referencing to dry mass at 105 °C, see Figure 4, while the Vlahinić et al. model agreed better for the saturation degree obtained by referencing to dry mass at 50 °C. This leads to observe that the assumptions in the determination of the saturation degree have a key influence on the model predictions. Indeed, in all three models, this parameter directly governs the driving force of shrinkage (equations 6.2, 6.4, 6.6) and in the Vlahinić et al. model it additionally controls the poroelastic response (equation 7). The porosity used as an input parameter in the latter model is also prone to the effect of different reference state; it is however of negligible importance compared to saturation degree.

As underlined by Hansen (Hansen 1986), evaporable water in cement-based system (and therefore the determined saturation degree or porosity) is a relative term dependent upon the method of drying used. Using oven drying at around 100 °C is a commonly-applied method for determination of the reference dry mass in cementitious materials. It was reported in (Hansen 1986) that oven drying at around 105 °C allows to remove approximately the same water amount as drying at vapor pressure of 0.007 bar at 25 °C. At the same time, as reported by Zhang and Scherer (Zhang and Scherer 2011), determination of dry mass at 105°C may be prone to an error due to decomposition of part of hydration products (in particular ettringite...
and CSH) at this temperature. This would lead to an overestimation of the determined saturation degree.

On the other hand, lower drying temperatures may not allow to remove all free water from the samples. The hypothesis of insufficient drying at 50 °C for the tested sample is confirmed by the very low porosity determined when using dry mass at 50°C, see Table 6.1. The predicted drop of shrinkage observed for the Biot-Bishop and also Vlahinić et al. models for slag and silica fume mortars at 33%RH (Figure 6.5), is due to very low degrees of saturation determined for these mortars when referenced to dry mass at 50 °C, and may be another indication that using this temperature lead to an underestimation of the actual saturation degree.

Figure 6.4. Comparison of the predicted values by the three different formulations with the experimental results obtained for the three mortars: a) OPC, b) slag and c) silica fume. Error bars represent 95% confidence intervals (obtained from bootstrapping in the case of predictions and from normal distributions in the case of experimental data). The saturation degree used in the model was obtained by referencing to dry mass at 105 °C.

Figure 6.5. Comparison of the predicted values by the three different formulations with the experimental results (see caption of Figure 6.4). The saturation degree used in the model was obtained by referencing to a dry mass at 50 °C.
Another parameter of which determination is not straightforward is $K_s$; in the simulations this parameter was assumed as constant (as defined in the previous sections). In order to estimate the influence of this parameter on the predicted shrinkage strains, in lack of direct experimental data regarding its variability, a simple estimation was performed. The originally assumed $K_s$ value (38 GPa) was varied in the range of ± 3 GPa; the results are presented in Figure 6.6 for the OPC mortar and the dataset with saturation degree obtained at 105 °C. From such estimation it is deduced that the parameter $K_s$ is of secondary importance at the RH levels considered. In addition, it should be noted that higher $K_s$ values would consistently have a smaller influence on the shrinkage predictions.

In previous studies, the Biot-Bishop model has been shown to substantially underestimate the shrinkage predictions of cement pastes (Bentz et al. 1998, Lura et al. 2003, Rougelot et al. 2009, Vlahinić et al. 2009, Grasley and Leung 2011). On the contrary, our results show, that, considering the discussed uncertainty of the saturation degree, the Biot-Bishop model can describe reasonably well the experimental data on mortars, especially when the saturation degree is determined by drying at 105 °C, both regarding the trend and the magnitude of shrinkage. This satisfactory performance of the Biot-Bishop model may be due to the fact that the experimental conditions in the present study allowed to reduce to a minimum the irreversible, non-elastic shrinkage component. This concerns e.g. avoiding carbonation shrinkage, that may have been occurred in other published results, e.g. (Vlahinić et al. 2009). Furthermore, viscoelastic effect may lead to underestimate the shrinkage when using a poroelastic approach, as shown in (Grasley and Leung 2011). Unlike for the cement pastes tested in e.g. (Vlahinić et al. 2009, Grasley and Leung 2011), for the mortars presented here, the macroscopic manifestation of viscoelastic behavior, i.e. creep deformation contributing to the measured shrinkage, may have been limited due to the restraining action of the aggregates.
Figure 6.6. The effect of the assumed bulk modulus of the solid skeleton (studied only for the OPC mortar) \( K_s = 38 \text{ GPa} \) (as in Figure 6.4), \( K_s = 35 \text{ GPa} \) and \( K_s = 41 \text{ GPa} \) in the three different models: a) Biot-Bishop, b) Coussy et al., c) Vlahinić et al.

6.5 Conclusions

In this chapter, the ultimate drying shrinkage as a function of the equilibrium RH of three cement-based mortars was investigated, namely the OPC mortar and two mortars where a portion of the cement was replaced by slag or silica fume.

The measured ultimate drying shrinkage was compared to the predicted shrinkage obtained through mechanistic models. Specifically, three different modeling approaches based on poroelasticity were employed to describe the ultimate shrinkage of unsaturated mortars and their predictive ability evaluated. Further, the propagation of the uncertainty was also addressed by means of parametric bootstrapping.

Mortar mixtures including SCM showed a systematic increase of the ultimate shrinkage as a function of the RH in comparison to the OPC mortar. At RH levels below 75%, the silica fume mortar showed the highest shrinkage.

Comparison of the experimental ultimate shrinkage results with the predictions obtained by the three model formulations for unsaturated media showed that all three models were able to predict the ultimate shrinkage-RH trends with good accuracy for RH above about 54%RH. For lower RH, the Biot-Bishop model and Vlahinić et al. model allowed to predict the bilinear character of the shrinkage-RH curves, with change of slope around 50%RH. This is in agreement also with the previously published literature data. On the contrary, the Coussy et al. model results in approximately constant shrinkage-RH slope.

It was found that one of the most crucial parameters in predicting of shrinkage is the saturation degree that is used in the poroelastic model as a parameter directly governing the driving force, i.e. changes in pore pressure. This parameter depends on the assumed reference method.
for determination of free water content. The effects of two different oven drying temperatures, 105 °C and 50°C on the predicted shrinkage were used to highlight the importance of this parameter.

The agreement between the predicted and observed shrinkage, especially for the Biot-Bishop model and Vlahinić et al. model, was good for the OPC and silica fume mortar. For the slag mortar mixtures, all applied models underestimated the very high shrinkage observed experimentally at RH already above 54%RH. The results in general suggest that the shrinkage of mortars can be described using poroelastic approaches as long as possible non-elastic phenomena are avoided, in particular when the material is protected from carbonation and microcracking.
Chapter 7.
Ultimate drying shrinkage of cement-based mortars at early-age

In this chapter, the ultimate drying shrinkage of mortar mixtures containing either Portland cement or cement blended with slag is investigated at early-ages through the use of the equivalent systems.

The ultimate drying shrinkage is measured on thin samples in controlled conditions: different relative humidity levels (decreased in a step-wise fashion) and avoiding carbonation. Experimental results showed that the ultimate drying shrinkage is systematically lower at earlier ages and increases as the hydration proceeds. Further, the slag-containing mortars show consistently higher shrinkage than the mortars containing cement only.

The experimentally-measured ultimate drying shrinkage is compared with the predicted values obtained by poroelastic modeling. Specifically, predictions are made using the Biot-Bishop approach, as discussed in the previous chapter.
7.1 Introduction

At early ages, cement-based materials undergo continuous changes within the microstructure due to the ongoing hydration; hence, the respective material properties keep changing. This becomes critical when long-term, time-dependent properties are investigated at early age. Indeed, at early age the microstructure of cement-based materials is continuously evolving, thus time-dependent and moisture-dependent measurements are inconsistent and incomparable when approached at different early ages (or hydration stages). This is of particular interest at the modeling level. Indeed, at early-age an inconsistent data base may render predictions impossible. Hence, the necessity to decouple the hydration from the effect of drying by stopping the hydration reaction to achieve an unchanging system that can be studied only in terms of time-dependent shrinkage.

A fundamental understanding of the shrinkage behavior at early-age becomes of paramount importance as, during the first days, the likelihood of cracking due to drying shrinkage may be exacerbated as the tensile strength and the fracture toughness may not be enough to resist the environmental loading (De Schutter and Taerwe 1997, Kim et al. 2004).

Further, a proper assessment of the relationship between the drying shrinkage behavior at early-age and its dependence on the changing material properties is of significance to properly model the volume deformations and hence prevent or mitigate early-age cracking.

In this chapter, the early-age ultimate drying shrinkage is measured on thin equivalent mortar samples conditioned at different RH levels. A reduced thickness (see chapter 6) was chosen to speed up the time at which equilibrium is reached but more importantly to minimize self-restraint effects (Almudaiheem and Hansen 1987, Bisschop 2002).

The early-age ultimate drying shrinkage at different equivalent ages is measured making use of the equivalent system approach. Afterwards, the experimental results are compared to the predicted ones according to the Biot-Bishop formulation as introduced chapter 6. It should be noted that in chapter 6 it was concluded that, up to approximately 50% RH, all the three poroelastic models there presented are able to accurately predict the ultimate drying shrinkage and that the drying regime used to calculate the saturation degree directly affects the predictions. Nevertheless, in this chapter only the Biot-Bishop approach is used to predict the ultimate drying shrinkage, since it represents the simplest approach with the least amount of input required but still capable to accurately predict the shrinkage. Further, as in many standard procedures cement-based materials are dried to a reference temperature of 105 °C, such as
ASTM C-642, the saturation degree used as input in the Biot-Bishop model is determined with respect to such temperature.

7.2 Experimental methods

The ultimate drying shrinkage as a function of the RH was measured on thin plate samples equipped with customized cast-in studs properly made to accommodate the tip of the comparator as described in section 6.3 (Figure 6.1). The samples were prepared and cured as described in chapter 3. Table 3.3 reported the mixture proportions.

After curing, the specimens were placed in a desiccator and subjected to different RH levels obtained through the use of saturated salt solutions. Initially, the samples were conditioned at 97% RH to homogenize the starting internal RH conditions within the different specimens ages. Afterwards, the samples were conditioned at different RH levels corresponding to 93%, 86%, 75%, 54% and 33% RH. At thermodynamic equilibrium, the internal RH of the sample corresponds to the RH of the environment (Baroghel-Bouny 2007). Each RH step was kept constant until mass equilibrium was reached. Equilibrium was assumed when the change in mass between two consecutive measurements was lower than 0.1% over a two-week period. It should be noted that the same samples went through all the RH levels in a step-wise fashion.

A step-wise drop in RH was adopted to minimize the formation of internal moisture gradients that may have led to surface cracking due to self-restraint (Hwang and Young 1984, Bisschop and Van Mier 2002). Further, the samples in the desiccators were flushed with nitrogen to minimize carbonation.

The material properties of the mortars, i.e., bulk moduli and saturation degree, representing the key parameters to be used as input in the Biot-Bishop model for unsaturated porous media were experimentally determined as follows. The bulk modulus of the porous solid was calculated by the combination of the elastic modulus obtained by static technique (shown in chapter 3) and the Poisson’s ratio obtained by resonant ultrasound technique (RUS) (shown in chapter 5).

The saturation degree was calculated through the analysis of the desorption isotherm curves obtained by the dynamic vapor sorption analyzer (DVS). This method allows the use of smaller samples and hence reduces the test duration. A thin mortar sample, approximately 1 mm thick and about 12 mm$^2$ in cross-section, was cut using a precision diamond saw from a larger sample previously kept wrapped in wet towel and sealed in a plastic bag. After cutting, the sample was immersed in water until testing (approximately 12 hours). Before being placed
on the crucible of the DVS, the sample was gently wiped off with a paper tissue to eliminate the excess of water from the surface. The sample was then subjected to a stepwise desorption process. At the beginning, the sample was allowed to equilibrate at RH of 98%; afterwards the sample underwent a reduction in RH with 10% steps up to 30% RH. At the end of the RH cycle, the sample was dried at 105 °C until equilibrium was reached. Each RH step was maintained until moisture equilibrium was reached. In this case, the sample was allowed to equilibrate for 12 h or 0.001% change in mass (of initial mass of the sample) over 15 min at each humidity step.

### 7.3 Material properties of the mortars

#### 7.3.1 Saturation degree

As mentioned in chapter 6, the saturation degree is a crucial parameter in poroelastic modeling and its impact is different if calculated from drying at 105 °C or 50 °C. Nevertheless, even though drying at 105 °C may lead to decomposition of part of the hydration products, drying at 50 °C does not necessarily remove all the free water and the real internal relative humidity remains unknown. In this investigation, the saturation degree is calculated from drying at 105°C as this temperature regime is typical of standard procedures such as ASTM C-642.

While in Figure 6.2 the saturation degree for the three equivalent mortars at 91d calculated from the mass loss results measured on the thin specimens was shown, 7.1 shows the saturation degree as function of the RH with regard to the equivalent OPC and slag-containing mortars at the different ages determined through DVS. Both in the OPC and the slag-containing mortar systems, the degree of saturation at a given relative humidity level is lower at earlier ages. For example, at RH values below about 98%, the sorption isotherm curves are shifted towards lower degree of saturation which corresponds to lower contents of water. This is due to the fact that only a small portion of the binder has reacted at early age and most water is present in the mortars as free water, which can be lost already at very high RH.

It is interesting to note that the saturation degree obtained on the OPC and slag-containing mortars at 91 d (Figure 7.1) are similar to those obtained in Figure 6.2 (calculated from the mass loss of the thin samples).

While in the OPC mortars the degree of saturation uniformly decreases from later to earlier ages, a much more pronounced difference is shown in the slag mortars between the saturation degree obtained from the mortars at 28 and 91 days and the ones measured at earlier ages. It should be noted that the degree of saturation of the slag mortars at 1, 3 and 7 days is much
smaller (even lower than the OPC). This can be explained by the fact that at early-age only a very small portion of binder has reacted due to the presence of slag (hence higher quartz content in the equivalent systems) in comparison to the OPC mortar.

From Figure 7.1 it is clear that the saturation of the slag-containing mortars at early age (1d, 3d and 7d) is much lower at a given RH level than in the OPC mortar (at similar ages). It should be noted that the slag mortars at early age contain higher amounts of quartz as the contribution of the slag starts at later ages. Specifically, as discussed in chapter 3, the slag-containing mortars at 1d and 3d do not contain slag as its contribution to the reaction products was not measured at such early age. At later ages (after 7d), the contribution of the slag is well marked by a much higher saturation degree observed at the ages of 28d and 91d.

Finally, it should be also mentioned that the degree of saturation of the slag mortar at 91 days was measured only up to 40% RH.

Figure 7.1. Saturation degree as a function of the relative humidity obtained by DVS measurements on the OPC equivalent mortars (a) and slag equivalent mortars (b).
7.3.2 Bulk moduli

The experimentally-determined static elastic modulus as well as the calculated Poisson’s ratio and bulk modulus concerning the OPC and slag-containing mortars as a function of the equivalent age are shown in Table 7.1. The error estimates with regard to the static elastic modulus represent the standard deviation from the replicate measurements. The error estimates associated with the Poisson’s ratio and the bulk modulus, instead, were calculated by parametric bootstrapping (as described in section 6.1.1).

As expected, the elastic moduli increase as more and more hydrates are formed (or conversely as the porosity decreases). At early age, the elastic modulus of the OPC mortars is consistently higher than the one measured on the slag mortars. However, at later ages (after 28 and 91 days of hydration) the elastic moduli of the OPC and slag-containing mortars attain similar values.

The Poisson’s ratio is calculated from the dynamic elastic modulus and the shear modulus determined by RUS on two replicate samples. The measurement was repeated twice for each sample. It should be noted that the dynamic elastic modulus is between 15% and 25% higher than the static elastic modulus, in agreement with other studies, see for example (Lamond 2006).

The OPC mortar systems show higher Poisson’s ratio at 1 day and it decreases at later ages (as previously observed (Swamy 1971)), stabilizing around the value 0.2, except at 3 days where it approaches 0.17. However, it should be emphasized that results show higher standard deviation estimates at the equivalent ages of 1, 3, and 7 days.

In the slag mortar systems, instead, the Poisson’s ratio keeps increasing with age, starting at approximately 0.15 and approaching 0.23 after 91 days.

Finally, combining the results obtained by the static elastic modulus and the Poisson’s ratio as obtained by RUS measurements, the bulk modulus of the mortar was calculated. The latter describes the compressibility of the material under hydrostatic loads and it is used as input in the model to describe the volumetric change.

The bulk modulus of the solid skeleton ($K_s$) of the equivalent mortars at different ages was calculated using the dilution model for composites (Hashin and Shtrikman 1963) taking into account that the replacement of the unreacted binder with quartz increases the volumetric fraction of material having a bulk modulus in the range of that of the aggregates. The bulk modulus of the skeleton obtained range between 38 and 40 GPa for the OPC mortars. Such
values are in agreement with what concluded by Grasley et al. with regard to the $K_s$ of cement based materials (Grasley et al. 2007).

Table 7.1. Bulk moduli of the mortars at different equivalent ages calculated from the statically-determined elastic modulus and dynamically-determined Poisson’s ratio. The error estimates represent the standard deviation obtained from sample replicates* or through bootstrapping technique**.

<table>
<thead>
<tr>
<th>Equivalent age [days]</th>
<th>OPC equivalent mortars</th>
<th>Slag equivalent mortars</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E-modulus [GPa]*</td>
<td>Poisson’s ratio**</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>16.9 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23.7 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>24.0 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>24.9 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>26.7 ± 1.2</td>
</tr>
</tbody>
</table>

7.4 Drying shrinkage as a function of the hydration age

7.4.1 Experimental results

Figures 7.2a and 7.2b show the ultimate drying shrinkage and the mass loss of the OPC mortars as a function of RH at the five different equivalent ages, respectively. Both the ultimate shrinkage and the mass loss are calculated as the average of three specimens for each equivalent age.

Despite the fact that the ultimate drying shrinkage at the five equivalent ages is similar at higher RH levels, results show that consistently the samples with higher content of hydrates (hence lower quartz replacement) show higher shrinkage. This becomes gradually clearer as the RH reduces: for example, the ultimate shrinkage of the OPC 1d mortar sample at 57% RH is approximately -527 microstrains while it reaches -689 microstrains in the case of the OPC equivalent mortar sample at the age of 91 days.

Although at later ages the mortars contain higher amounts of hydration products, it should be noted that the bulk moduli at later ages is higher. As observed in the previous chapter, the internal amount of water plays an important role (along with the bulk properties) on the shrinkage magnitude. Thus, even if the mortar at 91d is the stiffest one, it also represents the one
that shrinks the most. Indeed, at later ages, while the stiffness remains relatively constant, the driving force at low RH can be much higher as the saturation is higher.

The mass loss results of the thin samples in the desiccator confirm the results about the sorption isotherms measured with the DVS.

Figure 7.2. OPC mortar mixtures: a) ultimate drying shrinkage and b) mass loss as function of the relative humidity. Error bars represent standard deviation.

The ultimate drying shrinkage and mass loss of the slag-containing mortar samples as function of the RH at different equivalent ages are shown in Figure 7.3 (a and b). Similarly to the OPC mortars, for a given RH, the slag samples show higher ultimate shrinkage at later ages. It should be noted that the ultimate drying shrinkage measured at the equivalent ages of 28 and 91 days is very similar. It should be also noted that the slag 1d mortar does not follow the shrinkage trend followed by the mortars reproducing the other equivalent ages with the results falling in between the slag 7d and the slag 28d samples. The higher shrinkage observed, in the case of the slag 1d mortar, is very difficult to be explained if it is considered that the slag mortar mixture at 1d is very similar to the one of the OPC at 1d, containing even higher quartz substitution, hence, even a smaller shrinkage than the one observed for the OPC 1d should be expected. A possible explanation is that the slag 1d mortar, whereas similar to OPC 1d, is somewhat more porous and definitely more compliant, as confirmed by its bulk modulus (Table 7.1), which is about half that of the OPC 1d. This is also confirmed by the fact that the mass loss measurements follows the expected trend with the slag 1d showing the highest mass loss, while the least amount of water is lost at 91d.
Figure 7.3. Slag mortar mixtures: a) ultimate drying shrinkage and b) mass loss as function of the relative humidity. Error bars represent standard deviation.

Figure 7.4 shows the drying shrinkage, the saturation degree and the bulk modulus results of the OPC mortar systems at 1d and 91d. The differences in drying shrinkage at early and later ages can be explained according to the Biot-Bishop equation from the differences in the saturation degree and bulk modulus. Assuming the capillary pressure being constant at a given RH level, the saturation degree governs the drying shrinkage behavior. At a given RH level, at early age, the saturation degree is much smaller than the one measured at later ages, and in turn influencing the driving force for shrinkage. Further, it is observed, that even though the bulk modulus of the mortar at 1d is approximately 2/3 of the one at 91 days, it shrinks less, highlighting that the saturation degree overcomes the effects of the bulk modulus.

Similarly to Figure 7.4, Figure 7.5 shows the drying shrinkage, the saturation degree and bulk modulus results of the slag-containing mortars at 1d and 91d. Even though the saturation degree at a given RH level is higher at later ages, in this case the mortar at 1d shows a much higher shrinkage than the one at 91d. Such difference can be explained by the much large difference in bulk moduli obtained at early and later ages. Indeed, the bulk modulus of the slag-containing mortar at 1d is approximately 1/3 of the one measured on the mortar at 91d, hence exhibiting a much less stiff behavior.

Finally, it should be emphasized that the “reversal behavior” observed in this investigation, i.e. the fact that the slag-containing mortar shows higher shrinkage at early age, may suggest
that a special attention should be paid in real field application at early age when concretes including slag are used.

Figure 7.4 Drying shrinkage (left), saturation degree (center) and bulk modulus (right) results as a function of the relative humidity for the OPC equivalent mortars at 1d and 91d.

Figure 7.5. Drying shrinkage (left), saturation degree (center) and bulk modulus (right) results as a function of the relative humidity for the slag-containing equivalent mortars at 1d and 91d.

In addition, results show that the mortars including significant amounts of slag (such as at 28d and 91d) have higher ultimate drying shrinkage than the OPC mortars at similar ages (Figure 7.2a and 7.3a).

It should be noted that the mixture proportions were prepared in volume basis as to take into account the different densities between the OPC, slag and quartz.

In literature, inconsistent drying shrinkage results have been reported with regard to the effect of the slag presence as partial replacement of the cement on the drying shrinkage behavior.
(Brooks et al., Hogan and Meusel 1981, Tazawa et al. 1989). Comparative studies have reported higher or similar free drying shrinkage. Hooton et al. performed a critical review on the effect of slag on drying shrinkage results collected from literature (Hooton et al. 2009). They concluded that the shrinkage of concrete containing slag is slightly higher; however, when corrected to a constant paste content, the difference is reduced.

Deshpande investigated the influence of slag addition on the drying shrinkage accounting for the different slag density and formulating the mixes in volume basis (Deshpande 2007). He concluded that the ultimate shrinkage was little affected by the presence of the slag. Similar conclusions were drawn by (Yuan et al. 2015).

Finally, it is also interesting to note that the ultimate drying shrinkage as a function of the decreasing RH shows a non-linear dependence which has been argued to be typical of mortar and concrete (on the contrary of cement paste) likely due to presence of aggregates (Cebeci et al. 1989, Hubler et al. 2014). Indeed, as the paste matrix shrinks, the aggregates act as restraint, reducing the deformation. This, in first approximation, could also explain the differences in shrinkage magnitude observed at the different equivalent ages.

7.4.2 Drying shrinkage predictions vs experimental shrinkage

In Figure 7.6 the experimental ultimate drying shrinkage results of the OPC mortars at different equivalent ages as a function of relative humidity are compared to the predicted shrinkage results according to the Biot-Bishop formulation.

The predicted values are in reasonable agreement with the experimental results at any equivalent age and especially at RH levels higher than 54%. At lower RH, the models consistently overestimate the experimental results.

In Figure 7.7 the measured ultimate drying shrinkage of the slag-containing equivalent mortars is compared with the predicted values.

Up to the equivalent age of 28 days, the predicted values show an excellent agreement with the experimentally-determined values at the different RH levels investigated. Most of the result fall within the confidence interval obtained from the bootstrapping technique. Only the predicted values at 91d underestimate the experimental results. It should be also mentioned that the experimental results with regard to the slag systems at 1, 3 and 7 days show wider error bars than at later ages.
Carefully looking at the overall results in Figure 7.7, it is apparent that systematically the predictions first overestimate the ultimate drying shrinkage at earlier ages, while the shrinkage is underestimated at later ages, namely, at 91d.

The observed underestimation of the drying shrinkage with increasing ages (reduced amount of quartz) can be associated with the viscoelastic contributions that are not taken into account in this model.

In previous studies, the underestimation of the predicted ultimate shrinkage (already at RH levels below approximately 85% RH) has been addressed as one of the major limitations of the Biot-Bishop model for unsaturated porous materials, which assumes elastic behavior. When applied to cement-based pastes, as discussed in section 6.1 such underestimation has been explained taking into consideration the viscoelastic nature of the cementitious paste (Li et al. 2015).

In the presence of aggregate, the Biot-Bishop approach seems to be effective in predicting the ultimate drying shrinkage. This might be explained by the fact that the dilution of aggregates in mortars reduces the viscoelastic behavior as observed for the case of cement paste. More details can be also found in (Di Bella et al. 2017)

Nevertheless, except for the slag mortar at 91 days and RH levels below 54%, the Biot-Bishop model predicts very well the ultimate drying shrinkage. It should be noted that such RH level represents the usual range of relative humidity in several countries in Europe and North America (FIB 2012). In addition, at lower RH levels the shrinkage is overestimated in the case of the OPC equivalent mortar, while it is overestimated at later ages only in in the equivalent mortar containing slag.

It should be noted that the experimental drying shrinkage results at 91d in Figures 7.6 and 7.7 are the same that were shown in chapter 6. Here they are modeled through the Biot-Bishop approach. The results are here reported only for having a complete overview of the ultimate drying shrinkage behavior from 1d to 91d.
Figure 7.6. Comparison of the experimental results obtained for the OPC equivalent mortars at different equivalent ages with the predicted values according to the Biot-Bishop formulation. Error bars represent 95% confidence intervals (obtained from bootstrapping in the case of predictions and from normal distributions in the case of experimental data).
Figure 7.7. Comparison of the experimental results obtained for the slag containing equivalent mortars at different equivalent ages with the predicted values according to the Biot-Bishop formulation. Error bars represent 95% confidence intervals (obtained from bootstrapping in the case of predictions and from normal distributions in the case of experimental data).
7.5 Conclusions

In this chapter, the early-age ultimate drying shrinkage as a function of the RH was measured making use of the equivalent system approach. Thus the time-dependent and moisture-dependent shrinkage behavior was measured on static microstructures with fixed degree of hydration.

Two mortar mixtures were investigated, either containing only OPC along with different amount of quartz to replace the unhydrated grains, or OPC blended with slag (along with different amounts of quartz). The early ages investigated correspond to 1, 3, 7, 28 and 91 days.

Ultimate drying shrinkage results both in the OPC and the slag-containing equivalent mortars showed that at earlier ages the shrinkage is consistently lower than at later equivalent ages. This has been shown to result from the interplay between the amount of water content (saturation degree) at a given hydration stage and RH level and the bulk moduli, in agreement with the Biot-Bishop description. Further, the different amount of quartz in place of the unreacted binder grains may contribute to the ultimate shrinkage differences observed as they may act as restraints. An exception is the mortar system at 1d which shows higher shrinkage than in the mortars at 3d and 7d which is still well explained by the interplay of the degree of saturation and bulk modulus. While the slag mass loss measurements show consistent values with what expected, i.e. higher loss of water at earlier ages, the increased shrinkage may be the consequence of the particularly reduced bulk modulus resulting in a more complaining behavior of the slag-containing system at 1d. This is also shown by the reduced bulk modulus of the slag-containing mortar at 1 d, which is approximately 1/3 the one measured on the OPC mortar at 1d.

Nevertheless such behavior is still well predicted by the Biot-Bishop approach, confirming that the interplay of the saturation degree and bulk modulus govern the ultimate drying shrinkage. Further, The predicted ultimate drying shrinkage by means of the Biot-Bishop formulation show very good agreement with the experimental results up to shrinkage measured at 54 % RH, both for the OPC and the slag-containing mortars.

At lower RH levels, the predicted shrinkage is overestimated. Exception is made for the slag 91d mortar, in which systematically the Biot-Bishop model underestimates the ultimate shrinkage. Such underestimation in the slag-containing mortars at later ages (28d and 91 d) can be due to viscoelastic effects which are not taken into account in the Biot-Bishop approach.
Nevertheless, the Biot-Bishop model predicted very well the ultimate drying shrinkage up to 54% RH, which represents the typical range of RH for several countries in Europe and North America.
Chapter 8.

Drying shrinkage of cement-based mortars including moisture gradients

In real field applications, the majority of concrete elements are large enough so that drying takes place slowly and moisture gradients are formed throughout their cross-section. Eventually, the water transport will result in an uneven distribution of water throughout the cross-section, resulting in differential shrinkage that may lead to micro-cracking due to self-restraint.

In this chapter, moisture gradients evolving during drying and the resulting shrinkage are investigated as a function of time. The moisture profiles are both experimentally determined by means of RH sensors placed at different depths from the drying front and also calculated using a non-linear diffusion model for moisture transport and the finite element method for space discretization.

Finally, the experimentally-determined drying shrinkage results measured on thick prismatic samples as a function of time are compared to the predicted shrinkage results obtained as a combination of the moisture transport model and the poroelastic model, i.e., the non-linear diffusion formulation and the Biot-Bishop formulation, respectively.
8.1 Introduction

Drying shrinkage is the result of internal moisture loss as the moisture leaves the concrete’s pores. When the environment is at lower RH than the internal RH in the concrete pores, moisture gradually moves from the inner parts of a concrete element towards the exterior environment. Understanding the drying process in cement-based materials is of paramount importance to understand, predict and limit drying shrinkage and the associated likelihood of cracking.

The moisture loss from the concrete is a time-lapsed process that takes place at a drying surface and leads to migration of moisture from inner parts of an element toward the surface. As concrete dries out, a non-uniform moisture distribution throughout its cross-section induces differential shrinkage that may lead to micro-cracking due to self-restraint (Bisschop and Van Mier 2002). Self-restraints arise from the differential shrinkage and depends on the specimen size and the drying rate (Bažant and Rafshol 1982, Almudaiheem and Hansen 1987). The magnitude of the measured shrinkage has been shown to vary considerably depending on the size and shape of the concrete element (Carlson 1937, Ross 1944, Bažant and Najjar 1972).

Hence, true free (unrestrained) drying shrinkage measurements cannot be made and the specimen size should be always reported with the shrinkage results (Brooks 2014). In order to minimize the self-restraint effects in laboratory measurements, very small samples need to be used with limited gradients (see chapters 6 and 7 of this thesis).

The ability of concrete to transfer moisture and the rate of this process depend on several parameters such as the matrix’s porosity and its connectivity, as well as on how severe the drying conditions are (Hall and Hoff 2011). Further, the transport must necessarily depend on the transported medium. As long as pore fluid (with properties assumed as those of pure water) is considered here, the transport mechanisms and effectiveness will still depend on the state of the moisture: vapor, liquid water and adsorbed water. Specifically to cement-based materials, the drying behavior is complicated due to the wide range of pore sizes, difference in material composition and ongoing hydration (Weiss 1999). In this work, the difficulty arising from the ongoing hydration is overcome by the use of the equivalent system approach.

As mentioned in chapter 2.7, one of the most commonly used approaches to describe the movement of water within cement based materials is through an apparent diffusivity. This approach includes different physical mechanisms of the transport, specific for different states of
water in pores, and conveniently writes them in terms of one, effective transport mechanism, e.g. (Bažant and Najjar 1971, Bažant and Najjar 1972, Garbalińska 2006, Villani et al. 2014). Assuming 1-dimensional (along the x axis) diffusion process at the macroscopic level, and neglecting the source/sink term, one can write the mass conservation of water species in concrete as:

\[ \frac{\partial mc}{\partial t} = \frac{\partial}{\partial x} \left[ D_{mc}(mc) \frac{\partial mc}{\partial x} \right] \]  

(eq. 8.1)

where \( D_{mc}(mc) \) is the non-linear effective diffusivity coefficient with the mass moisture content per unit volume of concrete, \( mc \) (kg/m\(^3\)), as potential. The term effective used in the latter parameter accounts for the fact that the formal diffusivity is used to describe together vapor diffusion, liquid flow mechanisms and surface diffusion of adsorbed water. The non-linearity of equation (8.1) stems from the dependency of the diffusivity coefficient on the moisture content.

In this work, equation 8.1, with the diffusivity coefficient obtained from experimental data from DVS measurements is used to determine the moisture content and, consequently, RH profiles. Afterwards the profiles are used as an input for the Biot-Bishop model to predict the drying shrinkage. As discussed in previous chapters, the Biot-Bishop approach represents a simple but at the same time powerful approach for predicting the shrinkage. Indeed, the shrinkage can be easily predicted if the mechanisms behind the shrinkage, the saturation degree and the elastic properties are known. In this work, the saturation degree and the elastic properties are experimentally determined. The mechanisms behind the drying shrinkage are based on the on the changes in pore pressure which can be considered due to either the capillary pressure or disjoining pressure and both are related to the internal RH through the Kelvin-Laplace equation (eq. 2.1).

Equation (8.1) is discretized in space using the Finite Element Method (FEM) and in time using Backward Differentiation Formula (BDF) implicit time stepping method and solved with the COMSOL Multiphysics software (Comsol 2016).

The non-linear diffusivity coefficients were calculated from the desorption data using the kinetics of the mass change in the dynamic desorption measurements (performed with DVS) according to the method proposed by (Garbalińska 2006, Anderberg and Wadsö 2008) and presented in chapter 7. The non-linear diffusivity coefficients are calculated as a function of moisture content (i.e., state variable of the water mass conservation, equation 8.1). The mois-
ture content is calculated from the desorption isotherm knowing the bulk density. The latter was calculated according to ASTM C642.

The diffusivity (with the moisture content as potential) is evaluated from the kinetics of the mass loss as determined in the DVS. Specifically, the diffusivity is calculated at each RH step from the initial part (10-30% of the total measurement step), in which the mass change is linear with respect to the root square of time (corresponding approximately to 10 to 40% of the total change in mass). The diffusivity, \( D_{mc} \), is calculated as:

\[
D_{mc} = \frac{L^2 \pi}{16} \left[ \frac{\partial}{\partial t} \left( \frac{\Delta m(t)}{\Delta m_\infty} \right) \right]^2 \quad \text{(eq. 8.2)}
\]

Here \( L \) is the samples thickness (m), \( \Delta m(t) \) (g) is the mass change at time \( t \) (s) and \( \Delta m_\infty \) (g) is the mass change at equilibrium. More details regarding the calculation and the assumptions of the model to calculate the diffusivity are provided in the Appendix A.

The FEM calculations of equation 8.1 provide the distribution of moisture content \( mc \) in the analyzed samples. Next, the state variable - moisture content - is transformed to internal RH based on the sorption isotherms as determined with the DVS measurements. For this purpose, the latter characteristic is linearized with polynomial fitting (see Figure 8.2). Finally, shrinkage is calculated by introducing into the model the mechanical equilibrium equation, with the constitutive relationship relating strains to moisture state according to Biot-Bishop approach. The latter was introduced in chapter 6.

The strains of concrete are coupled with the moisture state equation (8.1) by means of the constitutive relationship referred to as the Biot-Bishop model. In the latter, a product of two parameters resulting from moisture state appears: capillary pressure and saturation degree. The saturation degree is calculated from the moisture content obtained from equation 8.1 by means of sorption isotherms determined with the DVS (and linearized, Fig. 8.2) and bulk density. The capillary pressure is calculated from the RH obtained as described previously using the Kelvin-Laplace equation (eq. 2.1).

It should be also mentioned that, for simplicity, the model does not include viscoelastic effects and does not include cracking.

The scheme of the calculations is as follows:

1. Calculating the RH distribution with the defined model and using moisture transport properties (diffusivity coefficient determined with the DVS) in prismatic samples drying from one surface. The results can be then compared to the experimentally-
measured RH profiles (see below section 8.4). Next, by fitting the calculated RH profiles to the experimental data, the adjusted diffusion coefficients are obtained.

2. The two sets of diffusivity coefficients, i.e. the ones experimentally calculated and these calibrated in step 1), are next used to calculate drying and drying shrinkage of companion samples. For calculating deformations, the Biot-Bishop model is used. As a validation, deformations obtained with the model are compared to those determined experimentally. Additionally, the experimentally measured mass loss is compared with the predicted results, the latter obtained by integrating the moisture content over the whole domain used in the calculations.

8.2 Experimental methods

Drying shrinkage as a function of time was measured on the thick prismatic equivalent mortar samples (40 × 40 mm² cross-section and 160 mm long) at the five equivalent ages. The samples were prepared and cured for at least 3 months as described in chapter 3. Table 3.3 reports the mixture proportions. After curing, the samples were initially conditioned at 97% RH to homogenize the initial internal RH between the different samples for approximately 2-3 months. Afterwards, the samples were placed in a climatic chamber at 20° ± 0.3° C and 57% ± 3% RH. The length change was measured through a comparator with accuracy ±0.001 mm as a function of time up to 400 days.

The moisture profiles of the equivalent mortars were measured on companion prismatic samples (40 × 40 mm² in cross section and 125 mm long) prepared in the same way as for the shrinking prismatic samples. The samples were cured for 1 year wrapped in wet towels and sealed in plastic bags. As schematically presented in Figure 8.1, at the age of 1 year, each sample was drilled at different depths (from the drying surface) and all the faces except one were sealed using aluminum tape. The holes had diameter of 6 mm and depth of 25 mm.

The RH was measured placing a capacitive, needle-type RH probe (HC2-C05 by Rotronic) with nominal accuracy ± 1.5% in each hole until equilibrium was reached (this took approximately 20 minutes). After each measurement, the hole was closed again using aluminum tape and the same type of measurement was carried out in the following hole.

In order to improve the accuracy of the RH results, the sensors were pre-calibrated by means of salt solutions before the measurements.
Figure 8.1. Schematic representation of the $40 \times 40 \times 125$ mm$^3$ prism with holes at different positions to measure the relative humidity profiles. Drying is allowed only from one surface, the rest of the prism is sealed by aluminum tape.

These results were used as the basis for modelling according to the step 1) described in the previous section. The material properties such as the bulk moduli and the saturation degree used to predict the drying shrinkage according to the Biot-Bishop approach were presented and discussed in the previous chapter (Table 7.1 and Figure 7.1).

8.3 Numerical simulations

The measured RH profiles and the free drying shrinkage results are compared with the FEM simulations.

For the moisture state, equation 8.1 was discretized in space by using tetrahedral finite elements. For the case of moisture profile samples, the samples were discretized using 10439 finite elements. The geometry of drying shrinkage samples was discretized in space using 11425 tetrahedral finite elements. In both cases the time discretization used steps of 1 d, from the start of drying until 400 days. The initial conditions regarding the state variable, moisture content ($mc$), were assumed after the experimental data from sorption isotherms measured with DVS, corresponding to the initial RH, 97% RH.

For the boundary conditions (BC), third-type BC (convective BC) were used. This type of BC requires two parameters: the value of state variable in the distance from the boundary, and the exchange coefficient. The former one was assumed as equal to the moisture content corresponding to 57 %RH (RH in the climate room) according to the sorption isotherm. The latter parameter was assumed as $2.78 \times 10^{-9}$ m/s after literature (Nellis and Klein 2009).

The calculated moisture contents in space and time are transformed to internal RH based on the sorption isotherms as determined with the DVS (see Figure 8.2a). Those results are com-
pared to the experimentally determined RH profiles (see section 8.4). Afterwards, the moisture content together with the saturation degree (Figure 8.2b), both determined from the desorption isotherms, are used to predict the shrinkage (see section 8.5).

Figure 8.2. a) Relative humidity vs moisture content and b) saturation degree vs relative humidity. Both were obtained from the desorption isotherms through DVS for the OPC 28d mortar. The fitted curves are the constitutive relationships used in the model.

Figure 8.3 shows the actual experimental samples used to measure the RH profiles and the shrinkage, (a) and (c), respectively. In addition, Figure 8.3 shows the respective 3D modeled specimens, (b) and (d), respectively.

The material is modeled as homogenous, isotropic and linear elastic (i.e., creep/relaxation contributions to strains/stresses are neglected). All input parameters were experimentally-determined as described in the previous chapter (bulk moduli and saturation) and in the present one (diffusivity coefficients).
Figure 8.3. a) Example of a mortar sample drying from one side used to measure the relative humidity profile b) geometry used in modelling of sample shown in (a); c) Example of a sample used for drying shrinkage measurements allowed to dry from two opposite surfaces d) geometry used in modelling of sample shown in (c). Drying surfaces in (b) and (d) are indicated in blue.

### 8.4 Drying shrinkage moisture profiles

#### 8.4.1 Relative humidity profile measurements

Figure 8.4 shows the internal RH profiles directly measured on the OPC mortars at the five equivalent ages. To avoid confusion, in Figure 8.4a only the OPC equivalent mortars at the equivalent ages of 1, 7 and 91 days are plotted, while the OPC equivalent ages corresponding to 3 and 28 days are shown in Figure 8.4b. Note that the number in parenthesis indicates the time after which the measurements were carried out from the beginning of the drying process. After 3 days of drying, the equivalent OPC 1d sample had the highest RH, while it becomes the one with the lowest internal RH after 364 days of exposure to drying. Similar behavior is shown for the case of the OPC 3d, except that after 364 days the RH measured is similar to the one of the OPC 91d.

It should be emphasized that the OPC 1d mortar contains the highest content of water that did not react, which explains the higher initial RH. Further, the lower RH measured on the same
sample after 364 days compared to the other equivalent ages is due to the higher interconnected porosity of the system, enabling for a faster reduction in moisture content.

It should be also noted that due to the sample size and accuracy of the method to determine the RH profiles, some deviation from the real RH distribution behavior may occur. Further, the two RH sensors used were systematically placed in the same holes. Results in Figure 8.4a seem to suggest, at least during the first 112 days of measurements, that the two sensors slightly deviate one from the other. Although the sensors were calibrated against salt solutions at the beginning of the test, no calibration was performed afterwards. Consequently, it is not possible to define which sensors between the two is over- or under-estimating the measurements.

Figure 8.4. Relative humidity profiles evolution as a function of the depth from the drying surface: OPC equivalent mortars

It should be noted that this chapter treats the results related to the OPC equivalent mortars only. This is due to the fact that the experimental RH profiles of the slag-containing mortars were not measured due to lack of material. As it will be shown in the following sections, the experimentally-determined RH profiles are needed to retrieve the fitted diffusivity and afterwards, predict the drying shrinkage. Nevertheless, the experimental results concerning the diffusivity, the drying shrinkage and the mass loss of the slag mortars at different equivalent ages are presented in Appendix B.
8.4.2 Relative humidity moisture profile predictions

In this section, the experimentally-determined RH profiles are compared to the predicted profiles according to the model described in section 8.3.

Figure 8.5 shows the diffusivity coefficients as a function of the RH for the OPC measured at different equivalent ages.

Due to the fact that vapor diffusion is a less efficient transport process than liquid flow transport, the diffusivity coefficients become smaller as the RH decreases, except at very high RH (around 95%), where the diffusivity coefficients are sometime even lower than at the following (lower) RH step. The first measurements, however, could be influenced by the initial stabilization of the sample in the DVS chamber. Anderberg and Wadsö pointed out that errors in the calculated diffusion coefficients may be associated to comparatively large steps in RH and the resulting lack of equilibrium (Anderberg and Wadsö 2008).

Nevertheless, the diffusivity coefficients of the OPC mortars become smaller as the equivalent age increases. This is due to the development of the microstructure resulting in a more refined pore structure and increased tortuosity of the pore channels.

In the OPC systems, the equivalent systems reproducing 7, 28 and 91 days hydration show similar diffusivity, while they are much larger at earlier ages (1 and 3 days).

Figure 8.5. Moisture diffusivity calculated from the sorption isotherms at different equivalent ages for the OPC equivalent mortars

In order to input the non-linear diffusivity coefficients in equation 8.1, the experimental results in Figure 8.5 were fitted using exponential curves. In Figure 8.6, the diffusivity of the OPC mortar and the fitted curves are shown.
Figure 8.6. Experimentally-determined diffusivity coefficients in the OPC equivalent mortars and fitting curves used as input into eq. 8.1.

In Figure 8.7, the experimental RH profiles measured in the OPC mortars at different equivalent ages (section 8.4.1) are compared to the predicted RH profiles according to eq. 8.1 and using the diffusivity coefficients as input (Figure 8.6).

Systematically, the predicted moisture profiles overestimate the RH compared to the experimental RH profiles, i.e. higher RH is obtained in the model than the one experimentally measured.

There can be different reasons of such disagreement, e.g.:

- boundary conditions imposed on the surface of the specimen. No direct measurements of the conditions around the sample were performed, and the only known parameter was the RH controlled in the room;
- systematic error of the experimentally determined diffusivity coefficients or their approximations (fitted curves);
- experimental errors in measured RH profiles;
- errors of other experimental parameters used for modelling;
- other mechanisms that may contribute to the moisture state, e.g. carbonation process.
The analysis of the sensitivity of predictions to the most significant model parameters is presented in section 8.6. This concerns the effect of the defined diffusivity coefficient and the effect of sorption isotherms (affecting both the relation between the moisture content and calculated RH, as well as the initial conditions used in the modelling).

One important aspect regarding the error in the experimentally-determined RH profiles regards the sample geometry. The drying specimens used for measuring the RH profiles had holes drilled in them (the holes were necessary to accommodate the RH sensors). In the range of RH where the liquid water transport is most effective, these holes may have acted as possible obstacles on the flow paths. On the other hand, as the RH decreased and diffusion-driven transport became more important, the holes may have led to increased transport speed, since diffusion in air filling the drilled hole is faster than would be otherwise in concrete. Finally, the time needed to place the sensor before each RH measurement may have led to exposing the interior of the sample to accelerated drying around the hole. This may have also led to a systematically lower RH readings – in fact, the sensor placed in the sample is not measuring the actual exact RH in the mortar, but the RH in the confined space surrounded by the sample. The RH in this space should be dominated and stay in equilibrium with internal RH of the mortar, may have been however to a certain extent have been disturbed by opening of the holes.
Figure 8.7. Comparison of experimental vs predicted RH profiles for the OPC equivalent mortars. The predicted RH profiles are calculated from eq. 8.1 using the diffusivity coefficients as calculated according to (Anderberg and Wadsö 2008).
The results presented in Figure 8.7 were obtained with one set of diffusion coefficients and sorption isotherms as an input.

Figure 8.8 show the moisture content (a) and diffusivity results (b) as calculated from the desorption isotherms on two equivalent OPC mortar samples at the age of 28 days. The two repetitions show that some scatter can be expected. This is further investigated and discussed in section 8.6.

Figure 8.8. Comparison of the moisture content (a) and the diffusivity (b) calculated on two separate OPC mortar specimens at the equivalent age of 28 days.

Figure 8.9 a and b shows the RH profiles results (experimental vs calculated) using the diffusivity and sorption isotherms as obtained from two repeated measurements at the equivalent age of 28 days presented in Figure 8.8.

The diffusivity measured in the OPC 28d rep sample is approximately 2 times (on average) larger than the one measured in the OPC 28d sample. Indeed, the OPC 28d rep results (Figure 8.9b) show that the profile predictions get closer to the experimental measurements when the higher value of the experimentally determined diffusivity is used.

From those results, it seems clear that uncertainty in the diffusivity values directly affects the calculated RH profiles.
Unfortunately, due to the large amount of equivalent ages and mortars systems investigated, the desorption isotherm and diffusion coefficient were measured twice only for the OPC 28d specimen, while the other OPC and slag-containing samples were measured only once.

Figure 8.9. Comparison of the experimental vs the modeled RH profiles. The calculated RH profiles were obtained from two diffusivity coefficients calculated on two replicate OPC 28d samples.

As the RH profiles are essential in further modeling of shrinkage, calibration of diffusivity was performed by fitting the RH profile data. In fitting, the trends of the diffusion vs. RH were maintained the same as determined experimentally, while the overall magnitude was increased. Figure 8.10 shows the fitted experimental RH profiles. This is accomplished by using diffusivity coefficients that are 5 times larger than those calculated from the desorption isotherms.
Figure 8.10. Comparison of experimental vs predicted RH profiles for the OPC equivalent mortars after fitting the diffusivity coefficients (increased 5 times with respect to the experimentally-determined values).
8.5 Drying shrinkage including moisture gradients as a function of the hydration age

8.5.1 Free drying shrinkage measurements: experimental results

Figure 8.11a and Figure 8.11b show the experimentally-measured drying shrinkage of the OPC mortar specimens at the different equivalent ages. Similarly, Figure 8.11c and Figure 8.11d show the respective mass loss results as a function of time of the five equivalent OPC mortars.

Both the drying shrinkage and the mass loss are calculated as the average of three specimens for each equivalent age.

The drying shrinkage steeply increases with time and the rate reduces after approximately 60 days, when a sudden change in slope is visible in Figure 8.11a. On the other hand, the mass loss results show an abrupt change in slope already after about 25 days (especially for the OPC 1d samples).

As expected from the results discussed in chapter 7, the mass loss is higher in the mortars containing higher amounts of water, while the respective shrinkage is the smallest.

It should be noted that the initial shrinkage rate is similar for all five equivalent ages. On the other hand, the magnitude of the drying shrinkage is influenced by the hydration age. Similarly to the results obtained on the thin samples at equilibrium regarding the ultimate shrinkage, the final shrinkage shown in Figure 8.11 is consistently higher in the mortars containing lower amount of quartz (higher amounts of hydrates). It is also interesting to note that the final shrinkage results measured on the thick samples are comparable with those measured on the thin samples (measured at RH 54%), suggesting limited effects of self-restraint on the long-term shrinkage of the larger samples.
Figure 8.11. Experimentally-determined drying shrinkage at the different equivalent ages (a) and (b), and their respective mass loss (c) and (d) as a function of time for the OPC equivalent mortars. Error bars represent the standard deviation from the repetition of three samples at each equivalent age.

8.5.2 Drying shrinkage measurements: experimental results vs predicted values

A validation of the used model parameters may be obtained by studying the intermediate step in calculation of the drying shrinkage, i.e. the moisture state. This was performed by comparing the total mass of the samples measured while undergoing drying shrinkage measurements and the ones obtained from the model. The latter was obtained by integrating the moisture content results obtained with moisture state equation 8.1 over all finite elements.

In Figure 8.12 the experimental mass loss results are compared to those predicted using two sets of diffusivity data: either calculated directly from experimental data on desorption isotherms, or using the calibrated diffusivity data obtained by fitting the RH profiles (see section
8.4.2), i.e., diffusion coefficients that are five times larger than those determined experimentally.

Results show that the increased diffusivity used to fit the RH profiles predicts much better the mass loss results. For example the predicted mass results at the equivalent age of 3 days show an excellent agreement with the experimental ones. The mass loss rate at any equivalent age is well predicted. Less precise is the prediction of the total mass loss. The least agreement is shown in the mortar OPC at 1d. However, it should be emphasized that at 1 d the desorption isotherm at high RH intervals is very steep. Consequently, the initial value of moisture content used as input in the model is prone to high uncertainty, and hence also the final moisture content. This will be discussed further in section 8.6.
Figure 8.12. Comparison of the experimental mass loss results measured on the OPC mortars using two diffusivity values.
In Figure 8.13, the experimental drying shrinkage results of the OPC equivalent mortars are compared to the predicted values using the model as described in section 8.3. For each equivalent age, the drying of the samples used for drying shrinkage measurements is modeled using the diffusivity as obtained from the sorption isotherms, with which a good fit of the RH profiles could not be obtained (Figure 8.7), and additionally the diffusivity calibrated by fitting the RH profile experimental results, i.e. increased 5 times (Figure 8.10). Results show that at the equivalent ages of 1, 28 and 91 days, the experimental shrinkage rates fall in between the two diffusivity datasets used at each age as input for the modeling. Nevertheless, the final shrinkage is very well predicted.

At the equivalent ages of 3 and 7 days, the modelled drying shrinkage results overestimate the experimental ones. It should be noted, however, that the rate is still comparable and fall within the two diffusivity calculations. The difference in the final shrinkage between the experiments and the models may due to uncertainties in the initial and final moisture content and the uncertainties regarding the trend of the sorption isotherm (see parametric sensitivity analysis in section 8.6). Considering that the moisture state could be predicted with a good agreement using the calibrated diffusivity values (i.e. increased 5 times compared to the experimentally determined data), for two different experimental datasets (i.e. moisture profiles in section 8.4.2, and mass loss in this section), the disagreement of the experimental data on shrinkage and the modelling results may be likely due to the constitutive relationship coupling moisture state and shrinkage, i.e. the Biot-Bishop equation. The detailed analysis of the factors responsible for such disagreement was presented for the shrinkage at equilibrium results in chapter 6.

Finally, it should be emphasized that if the drying kinetics is correctly retrieved, the drying shrinkage is well predicted by the Biot-Bishop approach. In this work only the diffusivity was fitted to the experimentally determined RH profile with the intent to improve the moisture transport behavior, all the other material properties were experimentally determined. While the main goal of this thesis was to investigate the drying shrinkage of cement-based materials at early age, the use of an improved moisture transport models which for example correctly assess the boundary conditions, should lead to better predictions without the need of using fitting parameters.
Figure 8.13. Experimental drying shrinkage of thick samples vs predicted shrinkage for OPC mortars
By carefully examining the results presented in Figure 8.12, it can be noted that the mass of the specimens at 1d and 3d slightly increases at later ages, which could be a result of the ongoing carbonation (Lamond 2006). Indeed, as drying shrinkage occurs, the mortar samples also undergo carbonation shrinkage. Opposite to the thin plate samples to determine the ultimate drying shrinkage, the thick prismatic samples were not protected against carbonation (the thin samples were conditioned in desiccators whose environment was flushed with nitrogen to reduce the CO$_2$). Further, it is known that carbonation shrinkage is higher at intermediate humidity levels, between 60% and 80% (Verbeck 1958).

Figure 8.14 shows the carbonation front of the OPC equivalent samples after approximately 250 days. The extent of carbonation was determined by spraying a phenolphthalein solution on the surface of the broken samples. The pink-colored areas indicate that the pH is above 9 or 10; the uncolored areas correspond to lower alkalinity and indicate carbonation.

In Figure 8.9, the carbonation front is visibly deeper at the ages of 1 and 3 days, i.e., in those systems which have higher porosity. This evidence is consistent with the fact that the experimental shrinkage measured on the OPC mortars at the equivalent ages of 1 day and 3 days is higher than the one obtained from the predictions.

Figure 8.14. Carbonation front measured on the OPC equivalent mortars at the ages: a) 1d; b) 3d; c) 7d; d) 28d; and e) 91days.

8.6 Parametric sensitivity

As shown so far, the prediction of the drying shrinkage includes several parameters, each of them strongly contributing to the sensitivity of the model. In this section, the main emphasis
is put on the uncertainty related to the diffusivity and the moisture content, which depends on
the measured desorption isotherms.

In Figure 8.15 the effect of the diffusivity (while all the other parameters are not changed and
are as obtained experimentally on the OPC 28d sample) is shown on the RH profile predic-
tions and afterwards on the drying shrinkage predictions. The two boundary curves corre-
spond to the values of diffusivity as determined in the repetitive measurements, and the mid-
dle curve corresponds to the average values of the experimental datasets (averaged before
fitting the curves).

In Figure 8.16, the diffusivity is kept constant (in this case same as the one calculated from
the desorption isotherm at 28d) while the sorption isotherms (affecting both the moisture con-
tent vs. RH and the initial conditions of the simulations) are varied according to the two repe-
titions obtained from the OPC 28d mortar samples.

Figure 8.15. Effect of the diffusivity on the RH profiles prediction and drying shrinkage.
Figure 8.16. Effect of the moisture content on the RH profiles prediction and drying shrinkage.

It can be seen that the experimental scatter in the diffusivity affects strongly the moisture profiles and consequently also the shrinkage rate, while not leading to a considerable difference in terms of the ultimate shrinkage. On the contrary, the difference in terms of sorption isotherms leads to a considerable effect on the ultimate shrinkage, mainly due to uncertainty in the initial (and therefore also ultimate) moisture content.

8.7 Conclusions

This chapter presented the experimental data on drying and drying shrinkage in the OPC mortars at early-age taking into account the moisture gradient evolution; the results for the slag mortars are presented in Appendix B. The experimental RH profiles were directly measured on the mortar samples using a RH sensor which was placed in drilled holes at different depths from the drying surface. The drying shrinkage was measured on large prismatic mortar samples. FEM modelling was applied for predictions of moisture state and shrinkage of the samples. A poroelastic approach was used, with the moisture state equation written in terms of moisture content and using non-linear diffusion for moisture transport, and strains written in terms of the poroelastic approach (Biot-Bishop).

The experimental investigation corresponding to early age was enabled by the use of the equivalent systems. Comparison of the experimental RH profiles and the predicted ones according to the diffusivity coefficient as determined from the desorption isotherms measured through DVS showed that the predicted RH profiles overestimate the RH experimentally.
measured. While several factors may be responsible for such disagreement, the most im-
portant reason is very likely related to the underestimation of the diffusivity coefficient de-
termined in desorption measurements with DVS. In addition, the experimental procedure fol-
lowed to determine the RH profiles may have led to an accelerated drying.
As the internal moisture state is fundamental when modeling the drying shrinkage, the exper-
imentally-determined RH profiles were fitted. A good fitting was obtained using a five times 
larger diffusivity than measured with DVS. As to validate the fitted diffusivity, the experi-
mental mass loss results were compared to those obtained integrating the moisture content 
over the whole domain used in the calculations. Results showed that the calculations using the 
calibrated diffusivity are able to predict the mass loss measurements with good accuracy. 
Some deviations were observed in terms of total mass loss, which appear to be related to the 
uncertainties in the initial conditions, i.e., the initial moisture content.
The experimentally-determined drying shrinkage was higher at later ages. This is similar to 
what observed on the thin mortar specimen regarding the equilibrium drying shrinkage. Fur-
ther, the shrinkage magnitude was similar to that measured on the thin samples conditioned at 
similar RH conditions.
Finally, the drying shrinkage was modeled combining the moisture state calculations and the 
Biot-Bishop approach. Drying shrinkage predictions agreed reasonably well with the experi-
mental results when the calibrated diffusivity was used for the calculations. In particular, the 
use of the latter improved the predicted shrinkage rate. On the other hand, the final shrinkage 
was very well predicted at any age, except for the mortar at 1d. However, the increased 
shrinkage can be explained by the fact that the samples undergone carbonation. The increased 
carbonation observed especially on mortars with equivalent age 1d is directly related to its 
higher porosity compared to more mature samples.
The moisture content and the diffusivity were shown through parametric sensitivity analysis 
to greatly influence the RH profile and shrinkage predictions. It should be noted that both the 
moisture content and the diffusivity are fundamental parameters to predict the shrinkage in-
cluding the moisture gradients. Calculations made according to two repetitions obtained from 
the OPC 28d, showed that the scatter in the diffusivity strongly affects the moisture profiles. 
Similarly, changes in the initial moisture content greatly affect the final shrinkage predictions.
Chapter 9.
Conclusions and future work

9.1 Conclusions

This work presented an alternative approach, based on the replacement of unreacted binder by quartz, to investigate the early age time-dependent and moisture-dependent material properties of cement-based materials at early age: the equivalent system approach. Specifically, equivalent mortars with and without SCM such as slag, fly ash and silica fume were used to investigate the ultimate drying shrinkage and the drying shrinkage including the moisture gradients at early age.

After thorough validation, the equivalent system approach is used to investigate the early age ultimate drying shrinkage and the drying shrinkage including the moisture gradients. The ultimate drying shrinkage and the one including moisture gradients were experimentally measured on the equivalent mortars at different ages (1, 3, 7, 28 and 91 days) and their results compared to the predictions obtained from poroelastic approaches while taking into account the moisture transport using the non-linear diffusion equation.

Further, as the elastic modulus plays an important role both on the magnitude of the drying shrinkage, on the self-induced stresses and both eventually on the likelihood of cracking, the equivalent system approach was also used to investigate the effect of the decreasing moisture content on the elastic modulus at early age.

The main findings are summarized here. Firstly, the validity of the equivalent system approach was comprehensively investigated by comparing several material properties as measured in the real systems and the respective equivalent systems. Their difference was also assessed statistically by means of ANOVA. Comparison of the mechanical properties such as the elastic modulus, fracture energy as well as compressive, flexural and tensile strength, support the validity of the equivalent system approach. A systematic, slight underestimation of the mechanical properties was shown by the
equivalent systems, which is very likely due to an underestimation of the resulting degree of hydration and hence an overdosing of the quartz in the equivalent systems in place of the un-reacted binder.

Microstructural characterization by means of mercury intrusion porosimetry showed comparable results in terms of total porosity. However, a comparison of the pore size distribution showed slightly larger deviations, especially at earlier ages. Further, amounts of non-evaporable water measured through thermogravimetric analysis in the real and equivalent systems showed statistically significant differences, especially in the case of real fly ash system and the equivalent silica fume system. Such disagreement appears to be the result of the assumptions and rough approximations that were made to substitute the fly ash in the real system with silica fume, with the aim to speed up the reaction. For this project, the silica fume equivalent mortar systems were discarded as not optimal for effectively reproducing the fly ash system at early age.

The elastic modulus, tensile strength and fracture energy obtained by inverse analysis of the load-displacement curves obtained by means of the CTT in the real and equivalent mortars also showed excellent agreement supporting the validity of the equivalent system approach. Finally, the equivalent systems showed to be able to reproduce the crack initiation and propagation in compact tension tests of the real systems when subjected to similar load levels, as determined through DIC.

Investigation of the effect of the decreasing moisture content on the elastic modulus of cement-based mortar mixtures at early-age was performed through resonant ultrasound spectroscopy and micro-indentation technique.

The elastic modulus results measured in the equivalent mortars (by RUS) showed that at earlier ages the elastic modulus remains constant both in the OPC and the slag mortars. At later ages, the elastic modulus slowly but steadily decreased up to 50-33% RH. At lower RH levels the elastic modulus remained constant. An even more pronounced reduction of the elastic modulus with the decreasing moisture content was observed for the slag mortar mixtures.

Regarding the elastic modulus results obtained by the micro-indentation technique on the OPC paste samples, they were affected by high scatter, preventing any possible conclusion on the effect of the moisture content. These results showed that micro-indentation is too inaccurate for the purpose of this investigation. Nevertheless, and considering the large scatter, the results obtained after homogenization from the micro-indentation test broadly agreed with those measured on the prismatic samples conditioned at 97% RH, especially at later ages, i.e. 7, 28 and 91.
In this work, the experimental ultimate drying shrinkage results obtained from three different equivalent cement-based mortars (including SCM) at the age of 91 days were compared to the predicted values using poroelasticity-based approaches based on the pore pressure. Changes in pore pressure due either to capillary or disjoining pressure are assumed related to the internal RH through the Kelvin-Laplace equation. The three different poroelastic formulations were compared, evaluating their predictive ability and addressing the propagation of the uncertainty by means of parametric bootstrapping.

From an experimental point of view, the mortar mixtures including SCM showed systematically higher ultimate shrinkage as a function of the RH in comparison to the OPC mortars. The different poroelastic models predicted similar ultimate drying shrinkage as a function of the relative humidity, especially in the higher range (above about 50% RH). The experimentally-measured ultimate drying shrinkage was predicted reasonably well by the different models, with the highest deviations observed for the slag-containing mortars.

The results, in general, suggested that the shrinkage of mortars can be described using poroelastic approaches as long as possible non-elastic phenomena are avoided, in particular when the material is protected from carbonation and microcracking. In addition, the presence of aggregate seems to minimize possible viscoelastic contributions that have been observed in previous studies for the case of pastes.

Further, it was found that one of the most crucial parameters in predicting shrinkage is the saturation degree that is used in the poroelastic model as a parameter directly governing the driving force, i.e. changes in overall pressure exerted by the pore fluid on the solid skeleton. This parameter depends on the assumed reference method for determination of free water content (drying temperatures investigated 105 °C and 50 °C). Nevertheless, several standard procedures when drying cement-based materials usually use 105 °C as reference temperature. The latter was also used as reference for determination of the saturation in order to investigate the ultimate drying shrinkage at early age.

Investigation of the ultimate drying shrinkage at earlier ages (i.e. 1, 3, 7 and 28) was performed on the OPC and slag-containing equivalent mortars. Experimental results showed that at earlier ages the shrinkage is consistently lower than at later equivalent ages. This was observed to depend on the interplay between the saturation degree and the bulk modulus at a given equivalent age. An exception was given by the slag containing mortar at 1d, whose shrinkage was higher than the respective mortars at 3d and 7d, which was explained by the
much lower bulk modulus. Further, it is emphasized how such finding in terms of increased shrinkage at early age may be of significance for real field practice.

Nevertheless, such “reversal behavior” was still well described by the Biot-Bishop model, confirming its good ability in predicting the ultimate drying shrinkage of mortars. Indeed, comparison of the experimental results with the predicted ones at the different equivalent ages showed very good agreement up to shrinkage measured at 54 % RH. At lower RH levels, the predicted shrinkage was overestimated. Only in the slag-containing mortars at later ages an underestimation of the predicted ultimate drying shrinkage against the experimental ones was observed probably due to the viscoelastic effects which are not taken into account in the model.

Finally, the early-age drying shrinkage including the moisture gradients was experimentally investigated and the results compared to the predicted ones using a poroelastic approach (Biot-Bishop) with moisture state equation written in terms of moisture content and using the non-linear diffusion for moisture transport.

As the internal moisture state is fundamental when modeling the drying shrinkage, firstly the RH profiles evolution within the mortar specimens were investigated. Comparison of the experimental RH profiles and the predicted ones according to the diffusivity coefficient as determined from the desorption isotherms measured through DVS showed that the predicted RH profiles overestimate the experimentally-measured ones. While several factors were found to be responsible for such disagreement, with the most important being the underestimation of the diffusivity coefficient and a possible inaccurate experimental procedure for the determination of the RH profiles, the experimentally-determined RH profiles were also fitted using a five times larger diffusivity. Experimental mass loss results validated the 5 times larger calibrated diffusivity showing a very good agreement with the experimental mass loss measurements. Some deviations were observed in terms of total mass loss which is more related to the initial conditions, i.e., the initial moisture content as also confirmed by the parametric sensitivity analysis.

The experimentally-determined drying shrinkage results showed that the shrinkage is higher at later ages, in accordance with what observed for the ultimate drying shrinkage. Further, the shrinkage magnitude was similar to that measured on the thin samples conditioned at similar RH conditions.

Finally, the drying shrinkage was modeled combining the moisture state calculations and the Biot-Bishop approach. Drying shrinkage predictions agreed reasonably well with the experimental results when the calibrated diffusivity was used for the calculations. In particular, the
latter improve the predicted shrinkage rate showing that if the transport properties are properly evaluated, the Biot-Bishop approach is able to predict not only the ultimate drying shrinkage but also the shrinkage including the moisture gradients. Further, in agreement with what observed for the ultimate drying shrinkage, the final shrinkage of the specimens including the moisture gradients was very well predicted at any age, except for the mortar at 1d. However, in this case, the observed increased shrinkage was shown to be directly related to the ongoing of carbonation.

According to the parametric sensitivity, it was found that accurate determination of the moisture content and the diffusivity is of paramount importance as they represent fundamental parameters to predict the shrinkage including the moisture gradients. Hence, a special attention should be given to their determination.

9.2 Future work

In light of the satisfactory agreement between the results of the real and equivalent systems obtained, the equivalent approach represents a promising alternative to the commonly-used methods to stop hydration and a powerful method to investigate hydration-dependent and/or moisture-dependent properties.

In particular, it opens the possibility to carry out measurements of sorption isotherms, transport properties, creep, drying shrinkage, cracking and carbonation at early age. While the ultimate drying shrinkage and the drying shrinkage including the moisture gradients have been the major topic of this thesis, this approach could be used to investigate for example the creep properties, which could be combined with approaches developed in this work in order to predict drying shrinkage behavior encompassing the viscoelastic contributions. A further step would consist, for example, in taking into account quantitatively the effects of carbonation on the magnitude of the drying shrinkage at early age.

Further, it is suggested that an in-depth and systematic investigation on the effect of decreasing moisture content on the static elastic modulus could also employ the equivalent system approach, similarly to what has been done in the present study (using dynamic techniques). However, the experimental challenges of performing static measurements of elastic modulus on samples with very small cross-section cannot be understated.

Finally, with the aim to improve the matching of the materials properties between real and equivalent systems (such as compressive strength or elastic modulus, to mention two examples) a more in depth investigation of the degree of hydration is essential before than prepar-
ing the equivalent systems. Alternatively, the volume of binder to be replaced by quartz should be properly adjusted taking into account the observed slightly underestimation of material properties. Further, it should be mentioned that in this work fine quartz was used, however, any non-reactive material, with properties similar to the unreacted binder to be replaced, could be used.
References


ACI-CT (2013). "ACI Concrete Terminology." American Concrete Institute.


Brooks, J. J., P. J. Wainwright and M. Boukendakji "Influence of Slag Type and Replacement Level on Strength Elasticity, Shrinkage and Creep of Concrete." Special Publication 132.


BS-1920-8 (2009). "Testing of Concrete Part 8: Determination of drying shrinkage of concrete for samples prepared in the field or in the laboratory." British Standards.


Derjaguin, B. V. (1987). Some results from 50 years' research on surface forces, Springer.


Dilnesa, B. Z. (2011). Fe-containing hydrates and their fate during cement hydration: thermodynamic data and experimental study, ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE.


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Pease, B. J. (2005). The role of shrinkage reducing admixtures on shrinkage, stress development, and cracking, Purdue University.


Pickett, G. (1900). Equations for computing elastic constants from flexural and torsional resonant frequencies of vibration of prisms and cylinders.


Appendix A

The diffusivity coefficients are determined from the evaluation of the desorption isotherm (Anderberg and Wadsö 2008). Specifically, they are calculated from the kinetics of the mass change at each equilibrium relative humidity step. Seven desorption steps for each sample were performed starting from 97% down to 30% RH.

In Figure A.1 is shown the step measurement between 80% and 70% RH as obtained from the desorption isotherm of the mortar OPC 1d through DVS. In Figure A1a it is shown that initially the mass changes quite rapidly, followed by a relatively long time to attain equilibrium. The sample was allowed to equilibrate for 12 h or 0.001% change in mass (of initial mass of the sample) over 15 min at each humidity step.

![Figure A.1. a) Step measurement of the mass plotted as a function of the time as obtained from the desorption isotherm in equivalent mortar sample OPC 1d; b) Measurement step of the mass plotted as a function of the square root of time. The slope of the initial linear part, approximately 10-30% of the mass step is used to calculate the diffusivity.](image)

When the mass change is plotted as a function of the square root of time an initially linear mass change is obtained (Crank 1979, Garbalińska 2006). The diffusivity can be calculated from the slope at each RH step of the sorption isotherm corresponding to 10% to 30% of the total change in mass according to Step measurement of the mass plotted as a function of the time as obtained from the desorption isotherm in equivalent mortar sample OPC 1d.

\[
D_{mc} = \frac{L^2 \pi}{16} \frac{\partial}{\partial \sqrt{t}} \left( \frac{\Delta m(t)}{\Delta m_\infty} \right)^2 \quad \text{(eq. A.1)}
\]

Here \( L \) is the samples thickness (m), \( \Delta m(t) \) (g) is the mass change at time \( t \) (s) and \( \Delta m_\infty \) (g) is the mass change at equilibrium for that given RH step.
Appendix B

In this appendix are reported the results regarding the diffusivity as well as the drying shrinkage and mass loss of the slag containing mortars.

The diffusivity results, Figure B.1, show that at 1 day the diffusivity coefficient is up to one order of magnitude larger than at later ages, while at the other equivalent ages the diffusivity coefficients are more similar. The extreme difference in diffusivity coefficient at 1 d can be explained by the high binder/quartz replacement.

![Figure B.1. Moisture diffusivity calculated from the sorption isotherms at different equivalent ages for the equivalent slag-containing mortars.](image)

In Figure B.2 (a and b) are shown the drying shrinkage results of the slag-containing mortars at different equivalent ages, the respective mass loss results are shown in Figure B.2 (c and d). The initial drying shrinkage rate of the mortars at the different ages is similar except for the slag mortar at 91 days. Further, the differences in the drying shrinkage results at the different ages are more marked in comparison to the OPC mortar systems.

As observed for the ultimate drying shrinkage measurements (chapter 7), the slag 1d system shows higher shrinkage than the samples at 3d and 7d. This trend is similar to what was presented and discussed in the previous chapter and there discussed. The mass loss measurements follow the trend expected with moisture loss decreasing systematically with age from 1d to 91d. The long-term drying shrinkage at 1d is similar to the one measured on the slag 28d system. The major difference between the slag samples at 1d and 28d consists in the
shrinkage rate, which is markedly higher at 1d due to the higher interconnected porosity and hence higher diffusivity coefficient (Figure B.1).

In general, the magnitude of the drying shrinkage measurements is slightly higher than the ultimate drying shrinkage measurements at 54% RH (chapter 7).

However, it should be noted that conversely to the thin plate samples used to measure the ultimate drying shrinkage, the thick prismatic samples were dried in a regular climatic chamber and hence exposed to the environmental CO₂. Consequently, the increased shrinkage could also be associated to the simultaneous carbonation process. This is discussed in more detail in the following section.

Figure B.2. Experimentally-determined drying shrinkage at the different equivalent ages (a) and (b), and their respective mass loss (c) and (d) as a function of time for the Slag equivalent mortars. Error bars represent the standard deviation from the three samples at each equivalent age.