

Universidad Nacional de la Patagonia San Juan Bosco

Doctorado en Ciencias de la Ingeniería - Facultad de Ingeniería

École des Ponts ParisTech

École Doctorale Sciences, Ingénierie et Environnement



TESIS DOCTORAL

**Lightweight cement slurries for
carbon dioxide geological storage wells**

Christian Marcelo Martín

Ingeniero Civil

Diciembre 2024

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Abstract

CO₂ capture and geological storage are essential for combating climate change. Studying the components of storage sites is crucial, including the integrity of the reservoir, the caprock, the casing, and the cement sheath of injection wells. This sheath is formed by injecting fresh cement into the annular space between the casing and the geological formation. The pressure exerted by the cement during installation, proportional to its specific weight, must be sufficiently high to ensure complete cementing, without exceeding the threshold that could damage the geological formation. The addition of lightweight materials, such as hollow glass microspheres (HGMS), makes it possible to control this pressure and ensures good cementing.

This work explores the use of HGMS in Portland cement for CO₂ injection wells, testing two classes of HGMS possessing a borosilicate glass outer shell and differing in mechanical strength and density. Laboratory experiments simulated the effects of supercritical CO₂ environments on these cement pastes, analysing carbonated and non-carbonated samples. Tests included uniaxial (UCS) and triaxial compression tests, elastic parameter measurements, mercury intrusion porosimetry analyses, scanning electron microscopy (SEM) images, and pH measurements using pH indicators.

First, the study focuses on the compatibility between HGMS and cement paste, assessing their pozzolanic activity and their ‘filler’ effect. HGMS showed meaningful pozzolanic activity, comparable to that of conventional additives. Mechanical tests showed significant variations in elastic parameters and UCS depending on the type of HGMS used. Microstructural analyses showed a correlation between the presence of HGMS and changes in porosity and a pore structure.

Second, the results show that carbonation significantly affected cement pastes containing HGMS, with a reduction in pore size. Rupture of HGMS during exposure increased interconnected porosity, accelerating carbonation. SEM images and pH tests confirmed the consumption of Ca(OH)₂ in samples containing HGMS. Pastes with HGMS showed marked reductions in Young’s modulus and UCS. The carbonated cement pastes showed a greater increase in shear strength with confining pressure.

The experimental results were used to model the behaviour of traditional and lightweight cement pastes under real conditions, using an open-source finite element software developed at École des Ponts. The model implemented solves the coupled chemo-poromechanical

equations and homogenises the elastic parameters according to the components of the cement matrix. The study extended this model to incorporate the homogenisation of elastic parameters due to the presence of HGMS, as well as the partial rupture of HGMS under high pressure, resulting in a variation in the porosity of the homogenised material, affecting both mechanical and transport properties. This improvement has enabled the model to be calibrated to predict the behaviour of light cement pastes in CO₂ injection wells.

In conclusion, this study highlights the complex role of HGMS in cement pastes used for CO₂ injection wells. Although they lighten cement formulations, their rupture under high pressure increases the carbonation rate and affects mechanical performance, highlighting the need to properly assess their long-term durability. The choice of HGMS must take into account their mechanical properties and pozzolanic activity. These results make it possible to improve the design of cement pastes for the geological storage of CO₂.

Keywords: Lightweight cement slurries, Hollow glass microspheres, CO₂ geological storage.

Resumen

La captura y el almacenamiento geológico de CO_2 son esenciales para luchar contra el cambio climático. El estudio de los componentes de los emplazamientos de almacenamiento es crucial, en particular la integridad del yacimiento, la roca sello, el casing y la camisa de cemento de los pozos de inyección. Este revestimiento se forma inyectando cemento fresco en el espacio anular entre el casing y la formación geológica. La presión ejercida, proporcional al peso en volumen, debe ser lo suficientemente alta para garantizar una cementación completa, sin sobrepasar el umbral que podría dañar la formación. La adición de materiales ligeros, como las microesferas huecas de vidrio (HGMS), permite controlar la presión y garantizar una cementación adecuada.

Este trabajo explora el uso de HGMS en el cemento Portland para pozos de inyección de CO_2 , probando dos tipos de HGMS con una cáscara exterior de vidrio de borosilicato y que difieren en resistencia mecánica y densidad. Los experimentos de laboratorio simularon los efectos de entornos de CO_2 supercrítico en estas pastas de cemento, analizando muestras carbonatadas y no carbonatadas. Las pruebas incluyeron ensayos de compresión uniaxial (UCS) y triaxial, mediciones de parámetros elásticos, análisis de porosimetría por intrusión de mercurio, imágenes de microscopía electrónica de barrido (SEM) y mediciones de pH mediante indicadores de pH.

En primer lugar, el estudio se centró en la compatibilidad entre las HGMS y la pasta de cemento, evaluando su actividad puzolánica y su efecto filler. Las HGMS mostraron una actividad puzolánica significativa, comparable a la de los aditivos convencionales. Los ensayos mecánicos mostraron variaciones significativas en los parámetros elásticos y el UCS en función del tipo de HGMS utilizado. Los análisis microestructurales mostraron una correlación entre la presencia de HGMS y los cambios en la porosidad y la estructura de los poros.

En segundo lugar, los resultados muestran que la carbonatación afectó significativamente a las pastas de cemento que contenían HGMS, con una variación del tamaño de los poros. La rotura de las HGMS durante la exposición aumentó la porosidad interconectada, acelerando la carbonatación. Las imágenes SEM y las pruebas de pH confirmaron el consumo de $\text{CA}(\text{OH})_2$ en las muestras que contenían HGMS. Las pastas con HGMS mostraron notables reducciones del módulo de Young y del UCS. Las pastas de cemento carbonatadas mostraron un mayor aumento de la resistencia al cizallamiento con el aumento de la presión

de confinamiento.

Los resultados experimentales se utilizaron para modelizar el comportamiento de pastas de cemento tradicionales y ligeras en condiciones reales, utilizando un software de elementos finitos de código abierto desarrollado en la École des Ponts. El modelo implementado resuelve las ecuaciones quimio-poromecánicas acopladas y homogeneiza los parámetros elásticos en función de los componentes de la matriz de cemento. El estudio amplió este modelo para incorporar la homogeneización de los parámetros elásticos debida a la presencia de HGMS, así como la ruptura parcial de las HGMS a alta presión, lo que da lugar a una variación de la porosidad del material homogeneizado, que afecta tanto a las propiedades mecánicas como a las de transporte. Esta mejora permitió calibrar el modelo para predecir el comportamiento de pastas ligeras de cemento en pozos de inyección de CO_2 .

En conclusión, este estudio destaca el complejo papel de las HGMS en las pastas de cemento utilizadas para pozos de inyección de CO_2 . Aunque aligeran las mezclas de cemento, su ruptura a alta presión aumenta la tasa de carbonatación y afecta al rendimiento mecánico, lo que pone de manifiesto la necesidad de evaluar su durabilidad a largo plazo. La elección de las HGMS debe tener en cuenta sus propiedades mecánicas y su actividad puzolánica. Estos resultados permiten mejorar el diseño de las pastas de cemento para el almacenamiento geológico de CO_2 .

Palabras clave: Pastas de cemento alivianadas, Microesferas huecas de vidrio, Almacenamiento geológico de CO_2 .

Chapter 1

General introduction

1.1 Motivation

In 1983, the United Nations established the World Commission on Environment and Development, which held its inaugural meeting in 1984. From this meeting emerged the report "Our Common Future" better known as the "Brundtland Report" published in 1987. For the first time, sustainable development was defined as "... development sustainable to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs..." [8].

Sustainable development can be divided into three fundamental aspects: economic, environmental, and social. True sustainable development integrates all three aspects, ensuring none are overlooked. The adoption of this concept in the study of modern topics highlights the finite nature of humanity's resources.

Directly related to this is the concept of environmental impact, defined as the changes experienced by elements of the environment due solely to the introduction of projects, programs, or human actions. In recent times, industrial advancements have led to significant environmental changes. In fact, the fourth assessment report by the Intergovernmental Panel on Climate Change (IPCC) from 2007 already identified the abrupt increase in greenhouse gases (GHG) concentrations in the atmosphere as the primary cause of climate change [9]. Moreover, the new sixth assessment report of the IPCC indicates that the GHG emissions not only keeps increasing, but also the rate at which it increases is growing [10].

Given the significant demand for energy and the consumption of resources related to human activities, it is projected that by 2050, even under the most optimistic scenarios, the global mean surface temperature compared to the years between 1850-1900 will increase by 1.5 °C [10]. Furthermore, the worst-case scenario predicts a rise in the global mean surface temperature by around 2.5 °C by 2050 and 5 °C by 2100 compared to the same period [10]. This ongoing trend requires various measures to minimize environmental impact. There are two main groups of mitigation measures:

- Reduction of sources: This involves using alternative energies to minimize GHG emissions, as well as improving energy efficiency. Examples of alternative energy include wind, solar, hydroelectric, among others.
- Enhancement of sinks: This aims to decrease existing GHG concentrations in the atmosphere. Natural processes such as plant consumption of carbon dioxide (CO₂) are hindered by widespread deforestation. Reforestation and carbon capture and storage (CCS) are potential solutions.

Both mitigation measures groups shall be applied to sufficiently reduce the impact of human activities on the environment within a safe period of time. Reducing the sources appears to be the most promising solution and is, maybe, the most popular. However, it is expected that energy supply will still be based on fossil fuels until – at least – 2050. In this context, a reliable and short/midterm solution should be applied to improve the current situation, for which CCS arises.

1.2 Carbon Capture and Storage

CCS is a climate change mitigation technology that can significantly reduce GHG emissions. Even though CCS projects are already underway worldwide, there is a need to accelerate the deployment of this technology to meet the goals set by the international climate change mitigation agreements [11]. Within this century, between 350 and 1200 gigatons of CO₂ will have to be captured and stored to achieve the sustainable development objectives without severely affecting human activities and behaviour [10].

The objective of CCS as an "enhancement of sinks" climate change mitigation activity is to decrease the CO₂ emissions and concentration in the atmosphere. The process mainly includes three key stages, as shown in Figure 1.2.1.

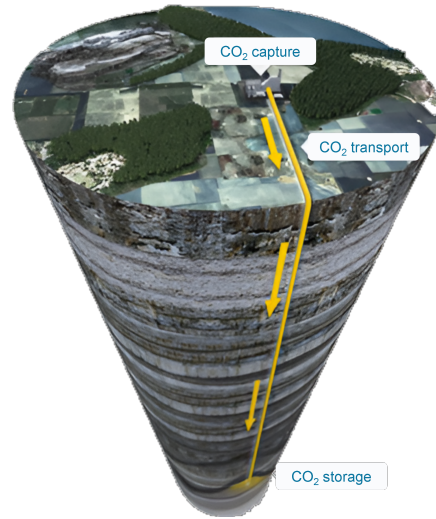


Figure 1.2.1: Stages involved in an underground CO₂ storage facility: Capture, Transport and Storage - Provided by Global CCS Institute

The capture of CO₂ can be performed from various punctual industrial sources – such as power plants – and directly from ambient air using innovative capture methods [12, 13].

Once captured, CO₂ is transported to the injection site. There are essentially two methods for transporting CO₂: discrete and continuous. The discrete method involves transportation via ships, trucks, or tanker railcars, which carry liquid CO₂ in insulated tanks of three types: high pressure type, low temperature type, and semi-refrigerated type [14]. The continuous method entails transportation through the use of pipelines, where CO₂ is compressed to a pressure exceeding 8 MPa to increase its density and prevent two-phase flow. Pipelines typically utilize materials susceptible to corrosion, which is only compatible with this use if the CO₂ is transported in a dry state (without moisture). Otherwise, the pipeline would require corrosion-resistant insulation.

Finally, the concluding – and more relevant for this research – step in the process is geological storage, which involves injecting CO₂ in a supercritical state (scCO₂) – at high pressures and temperatures – into rock formations. There are many types of geologic formations where this process can take place: depleted oil and gas reservoirs, deep saline aquifers, unmineable coal seams, basalts or reactive rocks, and shales are also being discussed [15, 16, 17, 18]. Furthermore, the rock formation should be porous, with formations that retain or have previously retained fluids being highly favourable in this regard, ensuring greater storage capacity and sealing properties at the scale of the storage site [19]. This characteristic is particularly beneficial for saline and depleted formations, while shales, with their initially low porosity, rely on fracturing to create space for storage.

CO₂ reaches the supercritical state at pressures higher than 7.1 MPa and at tempera-

tures higher than 30 °C. In this state, the fluid’s density increases, making it behave more like a liquid and allowing for efficient storage within geological formations. For this reason, scCO₂ is injected and stored at depths exceeding 800 m, where these needed conditions can be attained.

Once scCO₂ is injected to reach the reservoir for its final disposal, it is crucial to ensure the overall sealing of the injection system. This system comprises various components depicted in Figure 1.2.2, including reservoir rock, impermeable rock layer (caprock), metal tubing in the injection well (casing), and the cement annulus located between those two parts. Effective control is essential within and between these components.

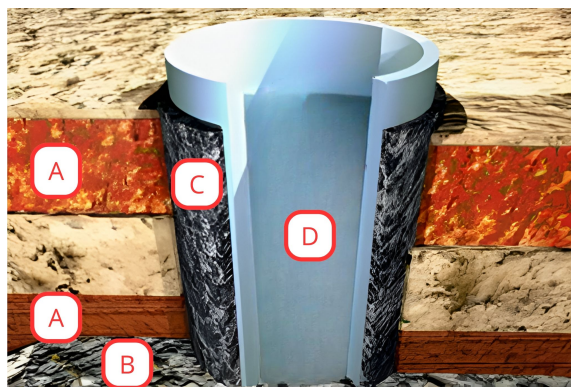


Figure 1.2.2: Schematic of supercritical scCO₂ injection well - A: Caprock; B: Reservoir; C: Cement sheath; D: Casing. Adapted from [1]

The integrity of the scCO₂ storage facility is of main importance. It is necessary to grant a proper zonal isolation to avoid any fluid migration. Figure 1.2.3 shows all the fluid migration paths that can be found within these facilities. They involve various and varied possibilities, such as contact of the reservoir formation with an aquifer, presence of a fault within the rock formation, and unsecured or not properly isolated injection/legacy wells.

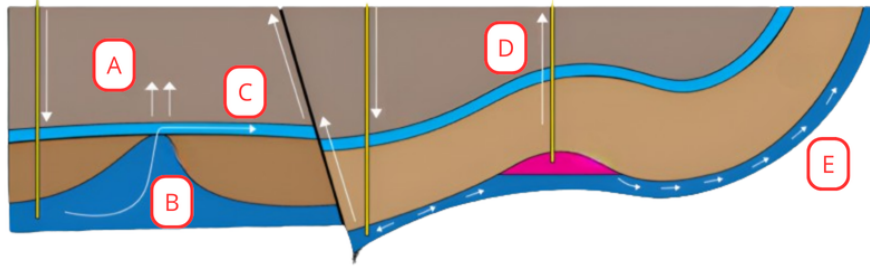


Figure 1.2.3: Possible fluid migration paths in a scCO_2 storage facility - A: CO_2 from B pushed into upper layers; B: leaks through a connection point between cap rock and upper aquifer; C: leaks along a fault line; D: leaks through a legacy well; E: dissolved CO_2 leaks through an escape point of the aquifer. Adapted from EnergyNow.ca

Among the possible fluid migration paths, this research focuses on injection/legacy wells, particularly on their cement annulus.

1.3 Deep well cementing

Let us now focus on the constructive method used to form the cement annulus. Recalling Figure 1.2.2, the system consists of three main parts, the casing, the cement annulus, and the rock formation. Each of these and also the interfaces between them are complex and require a deep study for being understood and for granting the integrity of the system.

Focusing on the cement annulus (also called cement sheath), this is achieved through an operation called deep well cementing. To begin with, clinker, water, and additives are mixed to obtain the cement slurry. Then, this fluid material is injected through the casing. Once the slurry reaches the end of this pipe, it will ascend through the annular space between the casing and the rock formation to its designated location. The resulting cement annulus is responsible for protecting the casing, containing the rock formation, and achieving zonal isolation – an imperative consideration in CCS projects.

During injection operations, the cement slurry should meet density requirements to ensure a proper pressure is exerted on the formation, high enough to overpass the pore pressure and grant the stability of the well at every depth, and low enough to avoid fracturing the rock formation, with the consequent material loss. For this purpose, the pressure exerted by the fluid cement slurry at every depth should be somewhere between the pore pressure and the fracture gradient – defined as the required pressure to generate fractures in a rock formation at a given depth.

Given the high density of conventional cement slurries, exceeding pore pressure at various depths typically poses minimal challenges. However, the fracture gradient, determined

by the properties of the rock formation, can complicate cementing operations, especially in situations where it is relatively low such as deep wells. In such cases, it becomes essential to carefully control the density of the cement slurry. This can be achieved through multistage cementing techniques [20] or by utilizing lightweight cements, allowing for a more precise density control and reduction of the pressure gradient applied to the formation [21].

On the one hand, multistage cementing is a technique used in deep well cementing operations to address challenges associated with varying formation pressures and depths. It involves the sequential placement of multiple cementing stages at different depths within the wellbore. Each stage typically consists of pumping a small volume of cement slurry, followed by setting a casing or liner packer to isolate the previous stage. This process allows for control of the pressure exerted on the rock formation and helps mitigate issues such as material loss and poor zonal isolation.

On the other hand, there are a variety of solutions to obtain lightweight and ultra-lightweight cement slurries, among which one can mention the use of water extenders, foam cement, or lightweight materials [22, 23]. Water extenders are those materials that, when added to the slurry formulation, allow the incorporation of a higher quantity of water without severely affecting the properties of the hardened cement paste. Foamed cement, obtained via nitrogen injection, contains nitrogen micro-bubbles which let the slurry reach a low specific weight [24]. Lightweight materials are used as cement replacement, and since their specific weight is smaller than that of cement, the specific weight of the slurry is reduced. Depending on the lightweight material used, the final properties of the hardened cement paste will vary.

Once the cementing method is defined and the cement slurry properly placed, the cement paste must reach the right properties to adequately achieve its main functions. The properties to be controlled include permeability, strength and elastic properties. Permeability must be reduced to avoid the generation of possible fluid migration paths through the cement sheath itself, thus ensuring zonal isolation. Strength is essential to withstand the stresses to which the cement annulus will be subjected over the life of the well, particularly due to the injection of scCO_2 . The elastic properties are also of great importance, as they directly govern stress development in response to interactions with the surrounding rock formation and casing.

1.4 The role of cement pastes

Considering the requirements that cement slurries/pastes must meet within the scope of this project, it becomes pertinent to delve into understanding the fundamentals of cement and its behaviour under specific conditions, such as those encountered in the context of scCO_2 injection wells. As previously discussed, cement sheath plays a pivotal role in ensuring the protection and stability of wells, particularly in CCS projects. Now, let's turn our attention to the characteristics and properties of cement that make it an essential

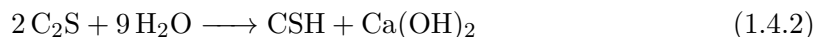
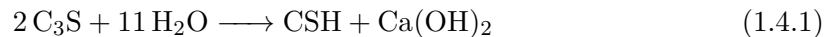
component in the construction of deep wells.

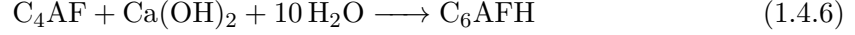
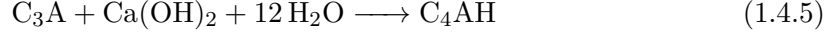
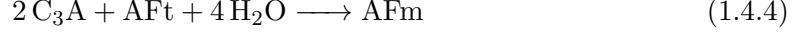
Cement is a widely used material in the construction industry. The main advantages of this material are its capability of taking the needed shape, while granting adequate durability and strength to the resulting structural element within a relatively low cost. These properties make cement one of the best solutions in the construction of deep wells.

Hardened cement is obtained through a series of chemical reactions between clinker and water, called cement hydration. The main compounds present in any type of clinker are (using the cement chemist notation) tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), and gypsum ($C\bar{S}H_2$). Each of these components play a key role in the chemical reactions involved in cement hydration, resulting in its hardening. A brief description is now provided [25]:

- C_3S : the most abundant compound in most cements. Responsible for the initial hardening in the hydration process, imparting early-age strength to the cement paste.
- C_2S : in contrast to C_3S , contributes to hydration at later ages, aiding in the increase of strength beyond the first week after mixing.
- C_3A : influences pumpability time by providing the cement with early-age strength (to a lesser extent than C_3S), releasing a significant amount of heat during the initial stages of hydration. Its content must be limited due to its role in increasing susceptibility to chemical sulfate attack.
- C_4AF : reacts quickly with water but does not produce much hydration heat or compressive strength. It affects the rheology and durability of the cement paste. Its content is also controlled in cements with high resistance to sulfate attack.
- $C\bar{S}H_2$: is added during final grinding and controls C_3A hydration, regulating cement setting time, strength development, drying shrinkage, and potential strength.

Each of these compounds undergoes chemical reactions to form the final products of the cement hydration process. It shall be outlined that advances in the understanding of the hydration mechanisms of cement are constantly being developed, and the theories have drastically evolved in the past century [26]. In general terms, the chemical reactions could be written as shown in Equations 1.4.1 to 1.4.6 [25, 27]. There exists four main hydration products of cement hydration, i.e. calcium hydroxide ($Ca(OH)_2$), calcium silicate hydrate (CSH), hydrated calcium trisulphoaluminate (AFt), and hydrated calcium monosulphoaluminate (AFm). Other phases shown in these equations, such as C_4AH and C_6AFH , are minor products of cement hydration.





Cement pastes must exhibit adequate strength and durability to meet project requirements. Strength refers to the ability of cement pastes to withstand loads, while durability refers to its ability to resist deterioration over time due to environmental factors. Inter-connected porosity, the amount of connected empty spaces in the cement paste structure, significantly impacts its behaviour, directly affecting permeability and diffusivity – the ease of fluid flow and the speed of ion movement through the material, respectively.

Hydration degree refers to the percentage of cement compounds that had undergone their respective hydration reaction. Achieving 100% hydration ensures complete reaction. As shown in Equations 1.4.1 to 1.4.6, adequate water content is essential for cement hydration. However, excess water increases cement paste porosity, leading to higher permeability and diffusivity, which makes cement paste more vulnerable to external corrosive agents.

Another issue to take into consideration when studying the strength and durability of cement pastes is the presence of admixtures. An admixture could be any material added before or during mixing, excluding water. These materials can disperse cement within the aqueous phase, alter cement hydration rates, react with cement by-products, or remain inert [28]. Among all the possible interactions between cement paste and admixtures, in this work the focus is set on the filler effect and the pozzolanic activity.

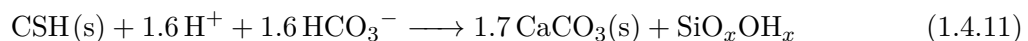
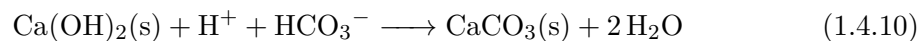
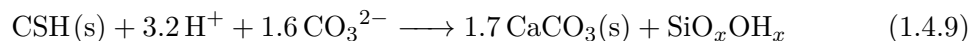
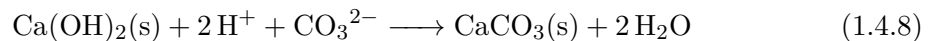
On the one hand, the filler effect refers to the impact that the addition of fine particulate materials to the cement have on its early hydration. This effect is due to their physical presence, which influences the development of the microstructure and strength of the cement [29]. This enhancement is observed through an increase in the hydration of all major cement phases, along with an increase in the quantity of chemically combined water and the liberation of $\text{Ca}(\text{OH})_2$ per unit weight of cement. The presence of micron-scaled particles in the filler material serves as nucleation sites, facilitating the formation of hydrates during early stages of curing [30]. Admixtures presenting the filler effect will consequently increase the degree of hydration of the cement, improving its strength and durability.

On the other hand, a pozzolan is a material containing silica and alumina, that lacks significant cementitious value on its own. Nevertheless, when finely divided and exposed to moisture, pozzolanic materials chemically react with the $\text{Ca}(\text{OH})_2$ present in the hydrated cement to form secondary CSH. Therefore, pozzolanic materials are known for increasing

the cement paste strength and durability. The reactivity of these materials relies on their chemical/mineralogical composition, fineness, the water to cement (w/c) ratio, and the proportion used [2, 31].

Both, the strength and the durability of the cement paste play a key role when studying cement use in deep wells. The importance of the cement annulus in these projects is paramount and constitutes one of the main factors to be studied when analysing the integrity of the system. Particularly, in the context of scCO₂ geological reservoirs, high pressure, high temperature, and scCO₂ saturation are attained. Even when subjected to these extreme conditions, the cement annulus should grant the well stability, contain the casing, and act as a seal to avoid fluid migration [32].

Under these conditions, hydrated cement will undergo changes in its chemical composition related to variations in its microstructure, porosity and mechanical behaviour. To begin with, carbonic acid (H₂CO₃) is formed by the reaction of the scCO₂ with water, as shown in Equation 1.4.7. Subsequently, bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻) are produced upon dissociation of the carbonic acid. These two dissociation products of carbonic acid chemically react with cement main hydration products, i.e. Ca(OH)₂ and CSH, leading to cement paste carbonation. This process results in the formation of calcium carbonate (CaCO₃) and water for Ca(OH)₂, and CaCO₃ and SiO_xOH_x (amorphous silica) for CSH, as depicted in Equations 1.4.8 to 1.4.11 [33, 34, 35, 36, 37, 38].



From the thermodynamic point of view, the first cement hydration product to be consumed by this reaction shall be Ca(OH)₂ [33]. Carbonation of Ca(OH)₂ happens through a dissolution-precipitation reaction, and its kinetics are initially faster than the carbonation of CSH. It is expected that the induced decrease in the pH up to 12.5 will be followed by the beginning of the CSH carbonation. Nevertheless, it has been proven that in actual carbonation exposure conditions, some changes in this expected behaviour might occur, which may lead to a simultaneous carbonation of Ca(OH)₂ and CSH [39, 40].

The formation of CaCO_3 during this process leads to its precipitation in the cement matrix pores. In their research, Dalton et al. studied the CaCO_3 formation for portland cement pastes under different CO_2 exposures and its precipitation in the cement matrix's pore structure [41].

Some studies highlighted the decrease in porosity and permeability during an initial stage of supercritical carbonation due to the CaCO_3 crystal precipitation [33, 42, 43]. However, for longer periods of exposure, the cement paste appears to present a significant degradation, corresponding to an increase in porosity [42, 43, 44]. This appears to be related to the dissolution of CaCO_3 , as depicted in reaction 1.4.12.

Moreover, the advancement of cement paste carbonation is controlled by the diffusion of the supercritical fluid. This is directly linked to the interconnected porosity, which in turn is also influenced by the w/c ratio. In this regard, the research of Costa et al. studied the impact of cement paste density on carbonation resistance when exposed to scCO_2 conditions [45]. Different cement paste densities were achieved by changes in the w/c ratio, and the advancement of the carbonation was measured in terms of the decrease in the pH, related to the consumption of the $\text{Ca}(\text{OH})_2$. As expected, it was found that higher cement paste density correlates with diminished carbonation, evidenced by a reduction in the carbonated area. Moreover, a clear relationship emerges between cement paste density and carbonation advancement.

The role of admixtures in the behaviour of hydrated cement shall also be taken into consideration. Particularly, a RILEM report deeply discusses this subject, focusing on supplementary cementitious materials (SCM) [40].

One fundamental difference lies in the reduced presence of $\text{Ca}(\text{OH})_2$ in cements with SCM, attributed to its consumption during the pozzolanic reaction. Consequently, carbonation proceeds more rapidly in the primary CO_2 -binding phases, such as CSH in systems using silica fume or calcium aluminosilicate hydrate in systems incorporating blast furnace slag, fly ash, metakaolin, and other alumina-rich SCM.

The carbonation of these hydrates significantly contributes to the coarsening of the pore structure [40] and changes in the mechanical behaviour. This poses challenges for cement paste durability, as carbonation induces structural changes that affect the material ability to withstand chemical or physical degradation.

Hence, it is essential to recognize the complex nature of carbonation kinetics, which are influenced by various factors including cement composition, water content, cement paste porosity, SCM properties and content percentage, carbonation conditions (e.g., CO_2 concentration, relative humidity, temperature), and material preconditioning. Therefore, a thorough examination of the cement annulus employed in deep scCO_2 injection wells, focusing on the degradation caused by the carbonation of cement hydration products, is essential. This assessment must be conducted through a comprehensive and meticulous experimental campaign to ensure the integrity of the cement sheath throughout its entire lifecycle.

1.5 Use of Hollow Glass Microspheres

Among various supplementary materials, hollow glass microspheres (HGMS) are very popular and widely used [24]. HGMS are lightweight, high strength materials manufactured from soda-lime borosilicate glass. These consist of hollow glass spherical bubbles with a wall thickness that provides them with high strength while also granting low density, as shown in Figure 1.5.1. Their glass wall is mainly composed of SiO_2 (60% - 87%) [46]. They are produced with a particle size varying between 20 and 70 μm , apparent densities from 100 to 800 kg/m^3 , and crush strengths up to 186 MPa. Such properties make them very suitable for their application in deep wells.

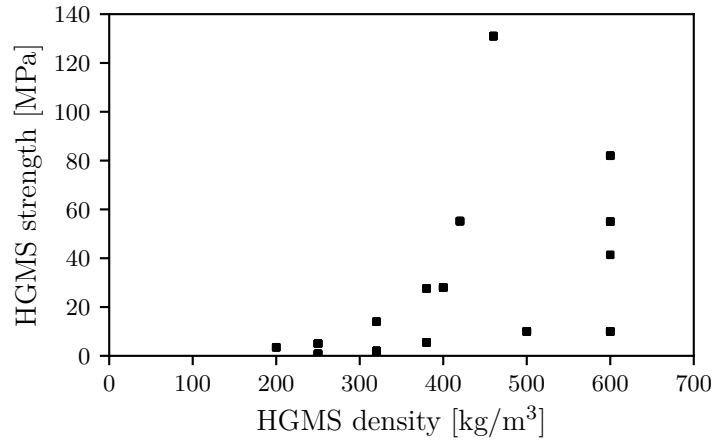


Figure 1.5.1: HGMS density vs. HGMS crushing strength. After [2]

Al-Yami et al. [20] compared the solution of multistage cementing with plain cement slurries and HGMS lightweight cement slurries. The equivalent circulating density – and thus the lower circulation loss – achieved with HGMS cement slurries is sufficiently low to avoid the technical difficulties related to the multistage method. Moreover, in the research of Anya [23], it is stated that the applicability of HGMS in the deep well cementing industry is not as difficult as other possible solutions.

The first reported field application of HGMS in the hydrocarbon industry dates back to 1980 [47] when it was intended to overcome the low-pressure gradient of an offshore wellbore in the Gulf of Mexico. Two cementing jobs were accomplished using a cement slurry with HGMS. A low-density cement slurry (1115 kg/m^3) with better mechanical properties than the lightweight cement slurries previously used was achieved. Following this first and successful field application, HGMS have been widely studied to comprehend their behaviour under the conditions present in oil-wells. These studies are mainly centred on the properties obtained on cement slurries with different classes and percentages of

HGMS.

Abdullah et al. [48] attempted to design slurries for cementing wells that go through formations with low fracture gradients. They fulfilled the requirements involved in this application with the addition of HGMS in proportions ranging from 12% to 20% by weight of cement. They designed slurries with densities between 1500 kg/m^3 and 1730 kg/m^3 and compressive strength ranging from 17 MPa to 33 MPa. These authors also demonstrated that the most widespread lightweight deep well slurries, which are obtained by increasing the w/c ratio, were inappropriate because of their low compressive strength and still too high density.

Mata and Calubayan [49] analysed the relationship between density, cement replacement percentage, HGMS crush strength (or class), and compressive strength of cement slurries. They kept constant the w/c ratio, and four target densities were considered: 1260 kg/m^3 , 1320 kg/m^3 , 1380 kg/m^3 , and 1440 kg/m^3 . These densities were achieved by replacing cement with HGMS in different percentages. It is interesting to notice from this research that the class of HGMS with the highest crush strength is not the one that yields the highest compressive strength for a targeted density of a cement slurry. Nevertheless, there is a relationship between HGMS' density and slurry's compressive strength. The lower the HGMS' density, the lesser the amount needed in the slurry to decrease the density, therefore, the higher the compressive strength of the resulting paste.

These results are confirmed by those depicted in Figures 1.5.2 and 1.5.3. These illustrate concisely the results discussed previously, along with those obtained by other authors [24, 46, 47, 48, 49, 50, 51]. Figure 1.5.2 shows a relationship between HGMS proportion and cement paste compressive strength, while Figure 1.5.3 evidences that no correlation is noticed between HGMS strength and cement paste compressive strength. In fact, the highest cement paste compressive strength corresponds to the lowest HGMS strength.

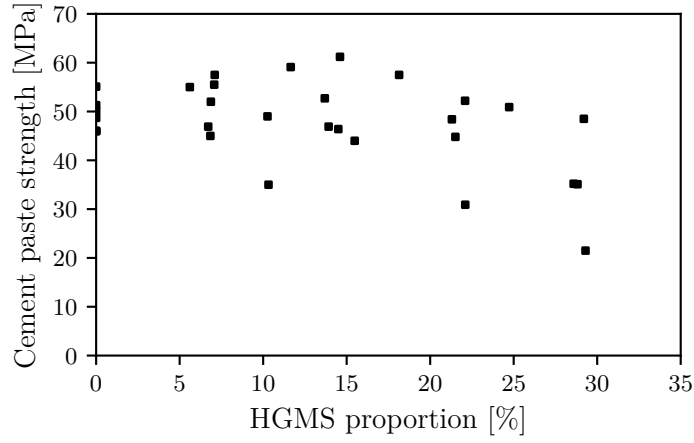


Figure 1.5.2: Cement paste with HGMS properties: Cement replacement by HGMS vs. cement paste compressive strength. After [2]

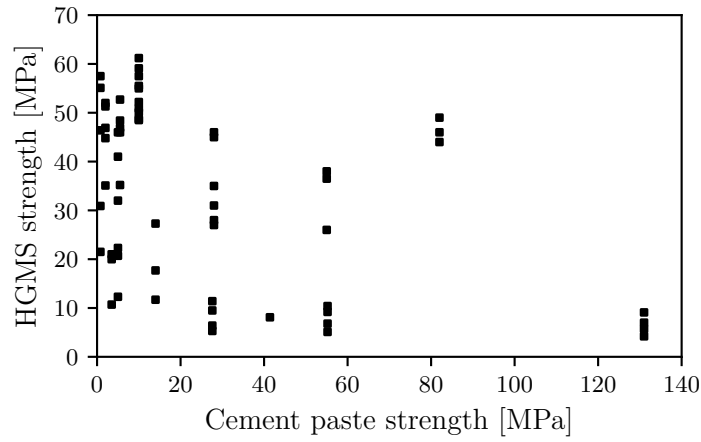


Figure 1.5.3: Cement paste with HGMS properties: HGMS crushing strength vs. cement paste compressive strength. After [2]

In a more general way, Figure 1.5.4 shows a correlation between the density of cement pastes and their compressive strength, with variations attributed to both the density of the HGMS and the extent of cement replacement by HGMS.

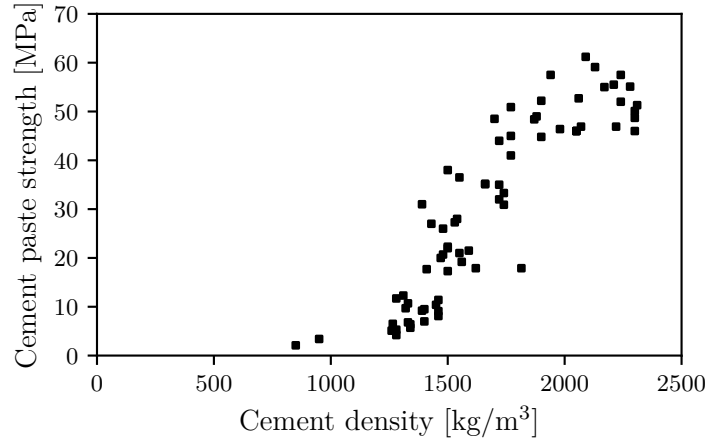


Figure 1.5.4: Cement paste with HGMS properties: Cement paste density vs. cement paste compressive strength. After [2]

HGMS were also studied as addition for engineered cementitious composites [51, 52, 52]. Composites were designed with fly ash, silica fume, polyvinyl alcohol fibres and HGMS. Fly ash was replaced by different classes of HGMS, from which a decrease in density ranging from 300 to 700 kg/m³ was obtained. It was concluded that increasing the dosage of HGMS implies decreasing the compressive strength of the resulting lightweight composite. An interesting conclusion from this research is that, for identical volume fractions of fly ash replacements, the lightweight composite with the HGMS of higher crush strength, yielded the higher compressive strength. Hence, the strength of the HGMS is also relevant for the strength of the cement paste.

1.6 Problem statement and objectives

As already discussed, the stability and durability of the cement paste used in scCO₂ injection wells is a critical concern in the context of geological storage of CO₂. Plain cement pastes may not be adequate for cementing deep wells, particularly CO₂ injection wells. In this context, cement pastes with HGMS stand out. The use of HGMS in class G cement pastes offers a potential solution by reducing the density of the cement slurries/pastes. However, the effect of HGMS on the properties of cement pastes, particularly considering their carbonation in presence of scCO₂, remains poorly understood.

Hence, the overall objective of this work is to study the stability of wells cemented with cement slurries lightened with HGMS of different classes when subjected to the conditions existing in a scCO₂ injection well. For this purpose, the evolution of the physical, chemical and mechanical properties of class G cement pastes with HGMS when subjected to the presence of scCO₂ are evaluated through both laboratory tests and numerical modelling.

To accomplish the main objective of this research, the following specific objectives and corresponding hypotheses are set:

- Specific objectives
 1. Study of the behaviour of class G cement pastes lightened with HGMS.
 2. Verify the suitability of HGMS lightweight class G cement pastes to be used in scCO₂ injection wells.
 3. Conceptualise the mechanical and chemical behaviour of HGMS lightweight class G cement pastes through analytical and numerical modelling, allowing the numerical simulation of CO₂ geological storage applications at the scale of an injection well.
- Hypothesis
 1. Replacing cement with HGMS is useful for reducing the density of class G cement slurries without severely affecting its mechanical properties.
 2. The designed lightweight class G cement pastes are suitable for deep wells.
 3. Through the use of analytical and numerical models, the behaviour of cement pastes containing HGMS in CCS applications can be simulated and predicted to optimise the design and execution of these projects.

These objectives are fulfilled through an extensive and diverse experimental program, with a deep analysis of the corresponding results, and by developing a theoretical and numerical framework based on the obtained results.

The behaviour of class G cement pastes lightened with HGMS is analysed in terms of the chemical interactions between these materials. The filler effect and the pozzolanic activity are assessed through a set of laboratory tests, including modified Chapelle test, isothermal calorimetry, thermogravimetric analyses, X-ray diffraction, uniaxial compressive strength, and scanning electron microscopy. These comprehensive analyses provide insights into the material properties and interactions, forming the foundation for subsequent evaluations under scCO₂ conditions.

Changes in microstructure, understood as those related to the pore structure, phases dissolution, and mineral precipitation, are assessed from mercury intrusion porosimetry on cement paste and HGMS powder specimens, pH measurements before and after exposure to scCO₂ environments, and scanning electron microscopy. Such microstructural evaluation provides a detailed understanding of the alterations occurring within the cement matrix when in contact with scCO₂, setting the stage for further investigation into how these changes impact the mechanical properties of the cement pastes under CCS conditions.

The last experimental subject to be discussed within this work involves the evaluation of the mechanical properties, particularly, the influence that different aspects such

as water content, and use of HGMS of different classes have on supercritical carbonation mechanisms, and how these mechanisms then translate into the mechanical behaviour of lightened cement pastes. To accomplish this, different mechanical properties of the cement pastes are measured before and after exposure to scCO_2 . Elastic properties are obtained through ultrasonic wave velocity measurements, and through drained and undrained triaxial tests at various confining pressures. Also, the strength of the cement pastes is obtained through uniaxial compression and drained triaxial compression tests at different confining pressures.

To extend the understanding gained from the experimental work, the elastic properties of materials containing hollow spherical inclusions (representing the HGMS) are homogenised, considering imperfect interfaces between the spheres and the cement matrix. Furthermore, a chemo-poromechanical model accounting for the carbonation of the cement hydrates is adapted to accurately represent the chemical phenomena occurring in the scCO_2 injection well, and their impacts on the mechanical behaviour of the cement sheath. These numerical models are then calibrated and validated to simulate the mechanical and chemical changes in the cement pastes, providing a comprehensive framework for predicting the performance of HGMS class G cement pastes subjected to scCO_2 conditions.

In summary, this research seeks to provide a comprehensive understanding of the influence of HGMS on cement paste behaviour, particularly in the context of scCO_2 injection wells. It investigates, both experimentally and numerically, various aspects of HGMS - cement paste hydration products interactions, from chemical interactions to mechanical properties.

1.7 Outline of the research

The research is structured into seven main chapters, as follows:

- Chapter 1 - **General introduction**: This chapter provides an overview of the research context and significance. It introduces the problem statement, outlines the structure of the research, and presents the research objectives and hypothesis.
- **Part I - Experimental characterization**
 - Chapter 2 - **Materials and methods**: This chapter details the materials, experimental setups, and methodologies used throughout the research. It provides a comprehensive description of the experimental procedures, testing protocols, and analytical techniques employed in the study.
 - Chapter 3 - **Interaction between HGMS and the cement paste**: Given the physico-chemical properties of HGMS, this chapter focuses on understanding the possible filler effect and pozzolanic activity of this admixture. It also delves

into the change in the main properties of cement pastes due to the use of HGMS, i.e. strength and microstructure.

- Chapter 4 - [Microstructural insights into cement paste supercritical carbonation](#): This chapter examines the influence of HGMS on supercritical carbonation mechanisms in deep well cement pastes. It discusses the changes in the pore structure that HGMS induce. Additionally, this study examines the impact of mechanical stresses on the chemical changes in cement pastes with HGMS in CO₂ injection wells.
- Chapter 5 - [Mechanical properties](#): Here, the focus is set on how HGMS affect the mechanical performance of cement pastes after being carbonated in conditions representative of those expected in scCO₂ injection wells. The discussion delves into the effects of the presence of HGMS on the alterations in mechanical behaviour induced by scCO₂ environments, highlighting their interaction with the cement matrix and impact on material durability.

- **Part II - [Modelling](#)**

- Chapter 6 - [Homogenisation of the elastic parameters](#): An analytical model is developed to predict the elastic parameters of lightweight cement pastes with HGMS. The proposed micromechanical model requires only the elastic properties of the cement matrix and the HGMS, as well as their dimensions and volume fraction.
- Chapter 7 - [Chemo-poromechanical model](#): This chapter involves adapting and improving an existing model to better represent the influence of HGMS on the behaviour of cement pastes under scCO₂ injection well conditions. This includes the determination of elastic properties to account for HGMS, considering HGMS rupture under high pressures and its effect on elastic and fluid transport properties.
- Chapter 8 - [Final considerations](#): This chapter synthesizes the findings and contributions of the research. It summarizes the key insights gained from the laboratory testing and numerical modelling efforts. Additionally, it discusses the implications of these findings for the understanding and application of HGMS in cement paste behaviour within scCO₂ injection well environments, and highlights potential opportunities for future research and application in this field.

Part I

Experimental characterization

Introduction to Part I

This part details the experimental methodologies developed to investigate the behaviour of cement pastes with HGMS under CCS injection well conditions. The research focuses on understanding the interactions at both micro and macro scales, employing a combination of advanced techniques to analyse the material's structural and mechanical properties. These methods were chosen to accurately capture the complex processes involved, from the chemical reactions during cement hydration to the changes in the pore structure and in the mechanical performance of the cement pastes. The experimental methods here set the stage for the analysis that follows and give insights into the behaviour and durability of cement pastes under the environmental conditions found in a CCS injection well.

Chapter 2

Materials and methods

2.1 Materials

The cement used in this research is a class G moderate sulphate-resistant portland cement [53] provided by Petroquímica Comodoro Rivadavia (Argentina), mixed with HGMS27 and HGMS41 from 3M (Figure 2.1.1), polycarbonate-based superplasticizer (SP) (ADVA 570, GCP Applied Technologies) with a solid residue by oven drying of 33.9% mass percent according to ASTM C 494 [54] and deionized water. HGMS27 and HGMS41 have respectively crush strengths of 27 and 41 MPa, apparent densities of 280 kg/m^3 and 460 kg/m^3 , and mean particle sizes (D50) of $30 \text{ }\mu\text{m}$ and $40 \text{ }\mu\text{m}$.

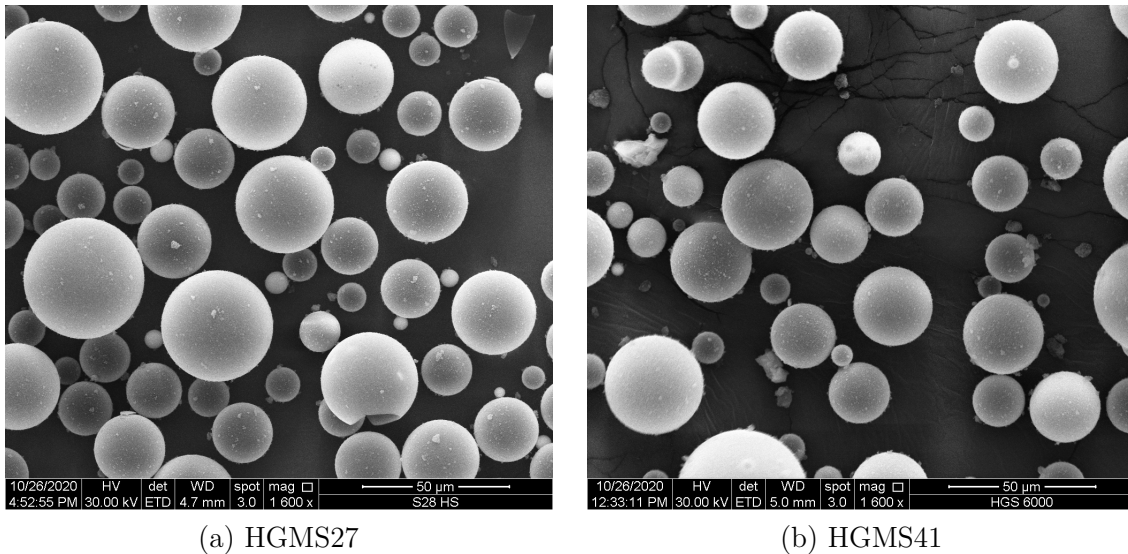


Figure 2.1.1: SEM images at 1600x of both classes of HGMS used in this research

Class G cement possesses special physico-chemical characteristics that make it suitable for use in deep well cementing. Tables 2.1.1 and 2.1.2 present its chemical composition [55] and main properties [53], respectively.

Cement	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Free CaO	MgO
Class G	50%	30%	5%	12%	1.1%	1.9%

Table 2.1.1: Chemical composition of class G cement

Thickening time	Compressive strength	
	Curing temperature: 38 °C	Curing temperature: 60 °C
90 to 120 minutes	> 2.1 MPa	> 10.3 MPa

Table 2.1.2: Physical-mechanical requirements of class G cement paste

The cement slurry required for proper well cementing must be pumped from the surface to great depths, larger than 800 meters in the context of CO₂ geological storage. Hence, the fundamental reason for using special cements, differing from those commonly used in the construction industry, lies in the high pressures and temperatures to which the cement paste is subjected in addition to the corrosive environment.

There exists a considerable challenge in maintaining conventional cement slurry in a fresh state during the pumping stage under these conditions. If it were to harden prior to the required time, it would obstruct the continuous flow of cement slurry injection, preventing proper cementing. Conversely, if the setting time is longer than necessary, it could result in greater material losses and a potential fluid flow to the surface.

Analysing the chemical composition, it can be seen that the percentages of C₃S and C₂S in class G cement indicate a controlled hydration process, avoiding significant early-age hydration (associated with high C₃S content) and significant late-age hydration (associated with high C₂S content). Additionally, the low percentage of C₃A supports this controlled hydration rate, as higher C₃A content would accelerate the process. This low C₃A content also contributes to the moderate sulfate resistance characteristic of this cement. This ensures that adequate strength and durability are attained at convenient curing times for the well cementing process.

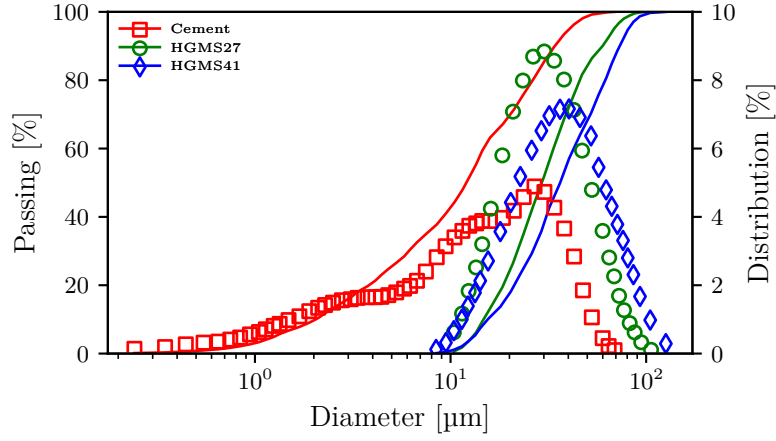


Figure 2.1.2: Particle size distribution for class G cement, HGMS27 and HGMS41

Figure 2.1.2 shows the particle size distribution of class G cement and both HGMS classes as analysed by Compagnie Industrielle des Lasers (CILAS) with the accompanying report. Furthermore, Table 2.1.3 shows the oxide composition as obtained from X-ray fluorescence spectroscopy carried out at the Universidad Nacional de San Martín in Buenos Aires, Argentina.

Table 2.1.3: Oxide composition of class G cement, HGMS41, and HGMS27

Oxide	Cement	HGMS27	HGMS41
SiO ₂	19.30	60.30	60.90
CaO	52.20	11.40	11.00
Na ₂ O	0.53	6.37	5.98
Br ₂ O	1.74	0.84	0.90
P ₂ O ₅	0.14	0.57	0.56
SO ₃	2.09	0.27	0.29
Al ₂ O ₃	3.30	0.08	0.14
MgO	3.27	0.08	0.10
Fe ₂ O ₃	18.20	0.04	0.05

2.2 Specimens preparation

Cement pastes were designed with two water to solids weight (w/s) ratios. The first one, of 0.44, corresponds to the w/s ratio specified by the American Petroleum Institute for class G cement pastes [53]. Also, a w/s ratio of 0.60 was used to get some insights into the mechanisms of cement paste carbonation changes due to changes in the water content. HGMS were added as 10% of cement weight replacement.

The decision to replace cement with HGMS, rather than adding HGMS, follows the methodology outlined in ASTM C 311 [56], which specifies the replacement of a portion of the cement by mass with the test material, rather than its addition. Although ASTM C 311 [56] specifies a replacement of 20% by mass, this was reduced to 10% due to the significant density difference between cement and HGMS. Higher replacement percentages resulted in segregation in the fresh state as the HGMS floated to the surface. This resulted in the formation of two distinct phases on curing, making the material unsuitable for consistent testing.

In addition, ASTM C 311 [56] considers SCM such as HGMS as cementitious constituents. Adopting the w/c ratio in this context could lead to bias, as it would not be fully consistent with this interpretation. Therefore, the w/s ratio has been adopted to ensure consistency with the intent of the standard and to maintain comparability between cement pastes.

The resulting classifications and dosages of cement pastes are presented in Table 2.2.1. CS refers to cement paste, the two following numbers correspond to HGMS (00: no HGMS, 27: HGMS27, 41: HGMS41) and the two last numbers correspond to the w/s ratio (0.44 and 0.60).

Table 2.2.1: Pastes classification, dosages, and densities

Paste	Cement [kg/m ³]	HGMS27 [kg/m ³]	HGMS41 [kg/m ³]	Water [kg/m ³]	SP [kg/m ³]	ρ [kg/m ³]
CS0044C00	1320.2	—	—	580.9	—	1988
CS2744C00	829.0	92.1	—	405.3	2.8	1388
CS4144C00	952.5	—	105.8	465.6	2.1	1601
CS0060C00	1313.8	—	—	788.3	—	1803
CS2760C00	828.3	92.0	—	552.2	—	1287
CS4160C00	950.6	—	105.6	633.7	—	1472

In Table 2.2.1, the ending C00 refers to the non-carbonated sample, i.e. carbonated for 0 days. Although this will be explained in more detail later in Subsection 2.3.4, it is important to note that pastes that have been carbonated for XX days will have the ending

CXX.

The superplasticizer was added to the slurries with w/s ratio of 0.44 with partial cement replacement by HGMS to obtain a fluidity equal to that of CS0044C00. Its proportion was established at 0.3% and 0.2% liquid weight for cement slurries CS2744C00 and CS4144C00 – with HGMS27 and HGMS41, respectively.

Cement specimens were prepared following the guidelines of the American Petroleum Institute Recommended Practice [57]. For this purpose, a specially designed mixer capable of reaching the required high revolutions per minute (RPM) was used.

According to these guidelines, water shall be added to the mixing machine followed by the cement, which is added within 15 seconds while the mixing machine is working at 4000 RPM. Then the RPM are increased to 12000 and kept constant for 35 seconds.

For cement pastes with HGMS27 and HGMS41, given the important difference in density between HGMS and cement, these dry materials needed to be mixed before. Therefore, the necessary amount of each of them was poured into a dry vessel and mixed by hand until reaching a homogeneous dry material.

Another limitation in the mixing due to the presence of the HGMS is related to their possible rupture. As aforementioned, HGMS have a given strength which could be over-passed throughout the mixing procedure. A solution to this issue can be found in reducing the RPM [58]. This should be achieved while maintaining the applied mixing energy [59], for which the mixing times have to be increased, as shown in Equation 2.2.1.

$$\frac{E}{M} = \frac{k\omega^2 t}{V} \quad (2.2.1)$$

where E is the mixing energy in kJ, M is the mass of the cement slurry in kg, k is an experimentally determined constant equal to $6.1 \times 10^{-8} \text{ m}^5/\text{s}$, ω is the rotational speed in radians/s, t is the mixing time in s, and V is the volume of the slurry in m^3 .

Following this principle, Table 2.2.2 shows the two mixing times adopted (t_1 and t_2) corresponding to each mixing stage (ω_1 and ω_2) for each cement slurry, ensuring that each slurry achieved the same mixing energies (E_1 and E_2).

Table 2.2.2: Mixing parameters for each mixing stage and different cement slurries

Slurry	V [L]	M [kg]	ω_1 [RPM]	ω_2 [RPM]	t_1 [s]	t_2 [s]	E_1 [kJ]	E_2 [kJ]
CS0044C00	0.5	0.95	3000	6000	26	166	300	6400
CS2744C00	0.5	0.76	3000	6000	34	208	310	6390
CS4144C00	0.5	0.66	3000	6000	38	238	300	6400

Once the proposed slurries were obtained, the moulds corresponding to each test were filled. 24 hours after mixing, the hardened specimens were removed from the moulds and

subjected to wet curing with water saturated with quicklime until the curing time of the corresponding test was reached. Those specimens which had reached the desired curing time were stored, before being tested, under saturated dry surface conditions using plastic films to ensure air-tightness.

The curing protocol was designed to ensure consistency across all specimens and was carried out at ambient pressure and temperature at ITPN (Argentina), where the cement pastes were produced. These specimens were then transported to the Navier laboratory (France) for carbonation testing under the desired conditions of 90°C and 20 MPa with CO₂. Due to the multi-stage nature of the experimental campaign, curing under high pressure and high temperature conditions was not feasible.

2.3 Methods

2.3.1 Modified Chapelle test

The pozzolanic activity of the HGMS was characterized using the modified Chapelle test outlined in NF P18-513 [60]. This test involved determining the amount of consumed Ca(OH)₂ per gram of HGMS in a solution of 2 g of calcium oxide (CaO) in 250 ml of water, maintained at a temperature of 90 °C for 16 hours. The modified Chapelle test serves as a direct measurement of the Ca(OH)₂ consumption of SCM, providing information on their pozzolanic activity, as described in Equation 2.3.1.

$$m_{\text{Ca(OH)}_2} = \frac{V_1 - V_2}{V_1} \frac{18500}{7} \quad (2.3.1)$$

where $m_{\text{Ca(OH)}_2}$ is the mass (in milligrams) of Ca(OH)₂ consumed by a gram of HGMS, V_1 is the hydrogen chloride (HCl) (0.1 N) volume required to titrate 25±2 ml of filtrate solution of the blanc experiment and V_2 is the HCl (0.1 N) volume required to titrate 25±2 ml of filtrate solution of the experiment with HGMS.

Two modified Chapelle tests were performed on HGMS41 samples and three on HGMS27 samples.

2.3.2 Isothermal calorimetry

The hydration process of cement slurries, with and without the addition of HGMS, was investigated using heat flow calorimetry conducted on a TAM AIR isothermal heat conduction calorimeter manufactured by TA Instruments.

The calorimetric analysis was performed in 10 ml tubular glass ampoules, where cement slurries were mixed according to the proportions specified in Table 2.2.1, without any superplasticizer. The glass ampoules were filled with cement and HGMS and then sealed. The lid used had both a mixing device and a water inlet. Once the ampoule filled with cement and HGMS was placed in the device, the required amount of water was injected,

and a mixing process lasting 180 seconds started. Both water injection and mechanical mixing were conducted within the confines of the calorimeter.

The tests were carried out following the guidelines of the standard ASTM C 1679 [3]. The entire process was conducted at a constant temperature of 20 °C with a precision of 0.2 mW/g of dry material.

The heat flow calorimetry technique allows monitoring the heat generated during the cement hydration process. The heat released during cement hydration (exothermic) was recorded by the calorimeter as a function of time, providing information about the reaction kinetics and the overall heat release evolution during the early stages of cement hydration.

By comparing the heat flow data from cement slurries with and without cement replacement by HGMS, it is possible to assess the impact of HGMS on the hydration process. The presence of HGMS may alter the heat evolution profile, indicating potential changes in the reaction rate and degree of cement hydration.

2.3.3 Thermogravimetric Analysis (TGA)

A Shimadzu TGA-50 was used for thermogravimetric analyses (TGA), in which a mass of $(9 \pm 1 \text{ mg})$ of powdered hydrated cement slurry (sieve No. 200) was heated from room temperature to 800 °C with a heating rate of 10 °C/min in a nitrogen atmosphere (30 ml/min). While the temperature increased, the sample mass was measured with a precision of 0.01 mg.

TGA is a widely used technique to measure the amount of Ca(OH)_2 present in cement pastes, since significant mass loss due to Ca(OH)_2 dehydration is appreciated. It happens between 440 °C and 520 °C, and, by obtaining the mass loss within these temperatures, the amount of Ca(OH)_2 in the sample can be calculated as expressed in Equation 2.3.2.

$$\text{Ca(OH)}_2 = \frac{M_{\text{Ca(OH)}_2}}{M_w} \frac{m_{440} - m_{520}}{m_i} \quad (2.3.2)$$

where $M_{\text{Ca(OH)}_2}$ is the Ca(OH)_2 molar mass, M_w the water molar mass, m_{440} the mass of the sample at 440 °C, m_{520} the mass of the sample at 520 °C, and m_i the initial mass of the sample.

The amount of Ca(OH)_2 in cement pastes reaches a maximum after a particular curing time and, if there is no carbonation, it remains constant with time. This value varies between 12% and 15% in mass, depending on the type of cement analysed and the cement content [61, 62, 63]. In this research, cement samples with and without HGMS were tested at 7, 28 and 56 days of curing time, as depicted in Table 2.3.1.

Table 2.3.1: TGA tests on cement samples

Specimen	HGMS class-content	w/s ratio	Curing time [days]	Quantity
CS0044C00	0%	0.44	7	5
			28	7
			56	2
CS2744C00	HGMS27-10%	0.44	7	5
			28	2
			56	2
CS4144C00	HGMS41-10%	0.44	7	5
			28	4
			56	2

Samples were subjected to freeze-drying when necessary to maintain the curing time at which the test was to be performed. This method is described in Subsection 2.3.10.

2.3.4 Supercritical carbonation

The cement specimens used in this research were subjected to high pressure and high temperature conditions of 20 MPa and 90 °C, respectively, in a CO₂ saturated atmosphere in presence of water for 60 and 120 days. The specimens were first saturated in water for 24 hours in a CaO saturated solution. Any remaining entrapped air was removed by applying a vacuum to the container for 1 hour. A volume of 1 litre of distilled water was added to a specially designed carbonation cell, shown in Figure 2.3.1. The saturated specimens were then placed into the carbonation cell. The cell was sealed, and the pressure was gradually increased to reach an approximate value of 8 MPa of CO₂ pressure using a pump.

The temperature was then raised in increments of 10 °C every 2 hours, ensuring that the pressure did not exceed 20 MPa. This continued until the final conditions of 90 °C and 20 MPa were reached. These conditions were maintained for 60 and 120 days to investigate the effects of prolonged exposure to supercritical CO₂ on the cement specimens. The mounting method and the carbonation conditions were chosen to follow up previous work conducted by the research group [64].

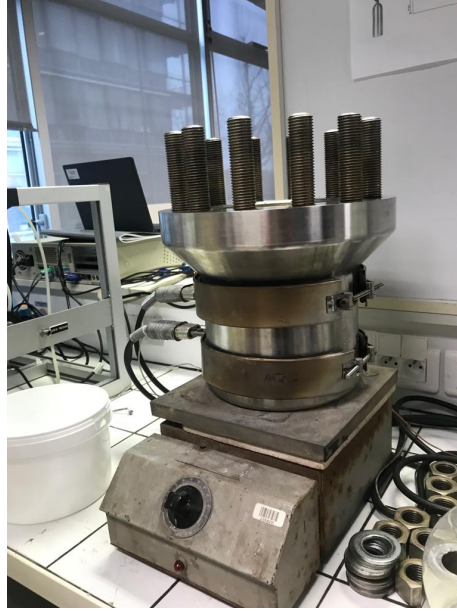


Figure 2.3.1: Supercritical carbonation cell

To distinguish the specimens before and after various scCO_2 exposure times, a specific convention is introduced in Table 2.3.2. "C00", "C60", and "C120" was added at the end of the specimens' name respectively, for 0, 60, and 120 days of carbonation. Furthermore, given that some tests were performed to assess the properties of the external and internal parts of the cylindrical carbonated specimens, the names of the specimens were modified by adding "EXT" or "INT" for the external or internal parts of the specimen as depicted in Figure 2.3.2, respectively.

Table 2.3.2: Pastes classification after carbonation

Paste	Carbonated 60 days		Carbonated 120 days	
	External	Internal	External	Internal
CS0044C00	CS0044C60EXT	CS0044C60INT	CS0044C120EXT	CS0044C120INT
CS2744C00	CS2744C60EXT	CS2744C60INT	CS2744C120EXT	CS2744C120INT
CS4144C00	CS4144C60EXT	CS4144C60INT	CS4144C120EXT	CS4144C120INT
CS0060C00	CS0060C60EXT	CS0060C60INT	CS0060C120EXT	CS0060C120INT
CS2760C00	CS2760C60EXT	CS2760C60INT	CS2760C120EXT	CS2760C120INT
CS4160C00	CS4160C60EXT	CS4160C60INT	CS4160C120EXT	CS4160C120INT

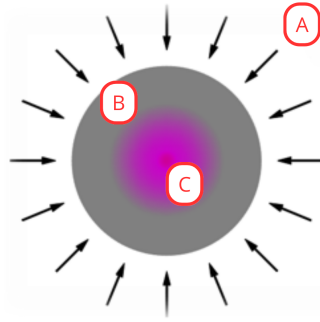


Figure 2.3.2: Cross-section of a cylindrical cement specimen subjected to supercritical carbonation - A: CO_2 flow from the cell to the specimens; B: external part of carbonated cement specimens; C: internal part of carbonated cement specimens

2.3.5 Mercury Intrusion Porosimetry (MIP)

Since the aim of the cement sheath is to isolate the stored CO_2 and avoid fluid migrations, its interconnected porosity is a fundamental factor for its performance [65]. Thus, it is necessary to measure the porosity of each of the proposed pastes. MIP tests were performed to understand the effect of the presence of HGMS and to evaluate the effect of exposure to CCS conditions on the pore structure of the studied cement pastes.

The equipment utilized is a Micromeritics AutoPore IV 9500 with a maximum pressure of 230 MPa. This test implies placing a small sample of about 1 cm^3 in a penetrometer (small recipient capable of supporting internal pressures higher than 200 MPa) which will be filled with mercury. Then, the mercury pressure is gradually increased in steps, and the apparatus quantifies the volume of mercury that is injected to reach each pressure step. The assembly process of a penetrometer containing a cement sample is shown in Figure 2.3.3.



Figure 2.3.3: Assembly of a penetrometer with a cement sample

The physics behind this test are related to the surface tension and contact angle between mercury and the material being studied (Scrivener, Snellings, and Lothenbach 2016). Surface tension is defined as a force per unit length, associated with the mercury's cohesion, which generates the lowest potential energy. This variable depends on three factors: the nature of the liquid (cohesion), the surrounding medium, and the temperature at which it is found. The contact angle of a given liquid is the angle between the liquid-air and liquid-solid interfaces, and determines the ability of the liquid to wet the solid with which it is in contact. It is closely related to the cohesion of the liquid and to the adhesion between the liquid and the solid. Usual values of surface tension (γ) and contact angle (θ) for mercury in contact with hydrated cement paste are 0.480 to 0.485 N/m and 130 ° to 140 °, respectively. By knowing the values of these parameters and considering perfectly cylindrical pores, it is possible to obtain a relationship between the applied mercury pressure (P) and the pore entry size diameter (D) that is going to be penetrated at that pressure by Equation 2.3.3.

$$D = -\frac{4\gamma \cos(\theta)}{P} \quad (2.3.3)$$

Two key measurements result from MIP tests: the accumulated porosity and the pore entry size distribution. These parameters are discussed in more detail in Chapter 4. The

pore entry size distribution refers to the size distribution of pores accessible to mercury at different pressures, indicating the entry points of mercury into the pore structure. From the total volume of mercury injected throughout the test, the actual interconnected porosity of the sample as probed by mercury can be estimated as shown in Equation 2.3.4.

$$\theta_{Hg} = \frac{V_{intrusion}}{V_{sample}} \quad (2.3.4)$$

where θ_{Hg} stands for the porosity as measured by the MIP test, $V_{intrusion}$ is the volume of intruded mercury at a given pressure step, as given by the testing machine, and V_{sample} is the volume of the sample tested. Since, V_{sample} is not a known value, but its mass was measured right before the test, Equation 2.3.4 could be easily rewritten as:

$$\theta_{Hg} = \frac{V_{intrusion}\gamma_{dry}}{M_{sample}} \quad (2.3.5)$$

where γ_{dry} is the specific weight of the dried specimen, calculated as its dry mass divided by its volume. This specimen is later used to extract the smaller sample for testing in the MIP, where M_{sample} is the mass of that sample.

Each of the pressure steps in this test was applied with an equilibration time of 120 seconds to ensure that all pores of the corresponding entry pore size are filled.

The test needs the samples to be completely dry. For this purpose, the cement samples of 1 cm³ were freeze-dried, using the protocol described in Subsection 2.3.10.

The MIP test was conducted a minimum of two times for each cement specimen, for non-carbonated and carbonated states. In the case of carbonated specimens, measurements were taken from both the external (EXT) and internal (INT) parts of the cement specimens. Table 2.3.3 summarizes all the tests performed.

Table 2.3.3: MIP tests on cement samples

Specimen	HGMS class-content	w/s ratio	Condition	Quantity
CS0044C00	0%	0.44	Non-carbonated	2
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2
			Carbonated 120 days - EXT	2
			Carbonated 120 days - INT	2
CS2744C00	HGMS27-10%	0.44	Non carbonated	2
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2
			Carbonated 120 days - EXT	2
			Carbonated 120 days - INT	2
CS4144C00	HGMS41-10%	0.44	Non carbonated	2
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2
			Carbonated 120 days - EXT	2
			Carbonated 120 days - INT	2
CS0060C00	0%	0.60	Non carbonated	2
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2
CS2760C00	HGMS27-10%	0.60	Non carbonated	3
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2
CS4160C00	HGMS41-10%	0.60	Non carbonated	2
			Carbonated 60 days - EXT	2
			Carbonated 60 days - INT	2

Additionally, the test was utilized to analyse the behaviour of HGMS27 and HGMS41. To carry out this analysis, a penetrometer specifically designed for powder samples was employed. This penetrometer allows establishing the initial vacuum without letting loose particles to exit the penetrometer. This test was performed two times on each class of HGMS. In the tests on HGMS, the focus was on determining the pressure at which the HGMS break under isotropic stress conditions.

In this type of test, the mercury pressure is increased until it reaches the point where all powder particles are surrounded by mercury. Subsequently, the pressure is further increased and, in traditional powder samples, the porosity of the individual particles is measured. However, in the case of HGMS powder samples, the HGMS will break once the pressure exceeds a certain threshold, due to the limited strength of the HGMS. Once the rupture occurs, mercury intrudes into the void space within the HGMS. This allows for

the determination of the rupture point and estimation of the volume of broken HGMS.

2.3.6 Scanning Electron Microscopy (SEM)

SEM images were obtained to conduct a qualitative analysis of the microstructure of cement pastes. This imaging technique allowed to explore the influence of various factors, including the w/s ratio, replacement of cement with HGMS, and carbonation, on the cement paste microstructural characteristics.

The SEM images were taken using a FEI QUANTA 250 FEG apparatus, which provided high resolution images of the cementitious samples. The samples were prepared by carefully fracturing the cement pastes specimens. When necessary, the samples were freeze-dried as explained in Subsection 2.3.10

2.3.7 Ultrasonic wave velocity

The ultrasonic wave velocity was measured on the cylindrical specimens of each paste to determine their elastic properties. These should be consistent with those obtained from quasi-static mechanical tests. However, factors such as poromechanical effects or creep make them differ [66, 67, 68].

From the wave velocities measurements, the elastic properties of each paste can be deduced according to Equation 2.3.6. The densities can be obtained by measuring the mass and volume of each saturated cement specimen. To determine the mass densities, the mass of each specimen was measured using a calibrated analytical balance with a resolution of 0.001 g. The volume of each specimen was measured using a calibrated Vernier caliper with a resolution of 0.01 mm, measuring the diameter at three different heights and taking the average. The height was also measured three times, after rotating the specimen, to ensure that the measurements were representative.

All measurements were performed under controlled laboratory conditions to minimize environmental influences. Using these precise instruments and procedures, the mass density results varied by no more than 20 kg/m³.

$$G = \rho V_s^2 \quad ; \quad K = \rho \left(V_p^2 - \frac{4}{3} V_s^2 \right) \quad (2.3.6)$$

Equations 2.3.6 for calculating K and G are valid for homogeneous, isotropic and linear elastic materials, but they could be applied to heterogeneous materials as long as the size of the representative elementary volume (l) is much smaller than the wavelength of the ultrasonic pulse used (λ) [69]. This is known as the separation of scale requirement, and it should be verified since lightweight cement pastes used in this research are heterogeneous materials. For the measurements in this study, the frequency of the ultrasonic pulse was 500 kHz. With the measured velocities, the wavelength (at least 4 mm, depending on the specimen) was verified to be significantly larger than the microspheres (approximately 30

and 40 μm) and the representative elementary volume of the material to consider that the separation of scale requirement is satisfied ($l \ll \lambda$).

By evaluation of the bulk and shear moduli, the other elastic parameters (E and ν) can then be calculated using classical relationships shown in Equation 2.3.7:

$$E = \frac{9KG}{3K + G} \quad ; \quad \nu = \frac{3K - 2G}{3K + G} \quad (2.3.7)$$

2.3.8 Uniaxial Compressive Strength (UCS)

The UCS test is a standard method used to evaluate the unconfined mechanical strength of cementitious materials. In this study, UCS was initially employed to assess the pozzolanic activity of HGMS in terms of the Strength Activity Index (I_{SA}), following the American Standard ASTM C 311 [56].

The UCS for obtaining the I_{SA} was measured according to ASTM C 109 [70], which specifies the use of cubic specimens with 5 cm sides. Also, the standard was adapted for well cement pastes with the proportions given in Table 2.2.1. The test involved comparing the strength of plain cement pates and cement pastes with 10% in weight replaced by HGMS. UCS measurements were conducted after 7 and 28 days of curing time. Six specimens of each paste were tested at both curing times using an INSTRON 5900 series Universal Testing System equipped with a spherical head. The compression rate was set at 0.7 mm/min [70].

Cylindrical specimens were used to measure the strength and obtain results comparable with those from triaxial compression tests. UCS tests were performed on a 100 kN testing machine at a constant rate of 0.7 mm/min. The reaction force was measured with a precision of 0.1 N, from which the UCS values were obtained for all specimens. The average UCS values were calculated from at least three specimens to ensure reliable results. A list of the tests performed is shown in Table 2.3.4.

Table 2.3.4: UCS tests on cylindrical cement specimens

Specimen	HGMS class-content	w/s ratio	Condition	Quantity
CS0044C00	0%	0.44	Non carbonated	3
			Carbonated 60 days	2
CS2744C00	HGMS27-10%	0.44	Non carbonated	3
			Carbonated 60 days	2
CS4144C00	HGMS41-10%	0.44	Non carbonated	3
			Carbonated 60 days	2
CS0060C00	0%	0.60	Non carbonated	3
			Carbonated 60 days	2
CS2760C00	HGMS27-10%	0.60	Non carbonated	3
			Carbonated 60 days	2
CS4160C00	HGMS41-10%	0.60	Non carbonated	3
			Carbonated 60 days	2

2.3.9 Triaxial compression tests

The triaxial compression test is a widely used technique in the characterization of materials, where cylindrical specimens of 38.1 mm in diameter and 76.2 mm in height are subjected to specific loading conditions to evaluate their mechanical behaviour under different states of stress.

The triaxial compression tests were conducted using a specially designed testing system for high pressure and high temperature triaxial compression tests of up to 150 MPa and 200 °C, respectively. Figure 2.3.4 shows a global view of the testing system and the confinement cell, where the specimens are placed.

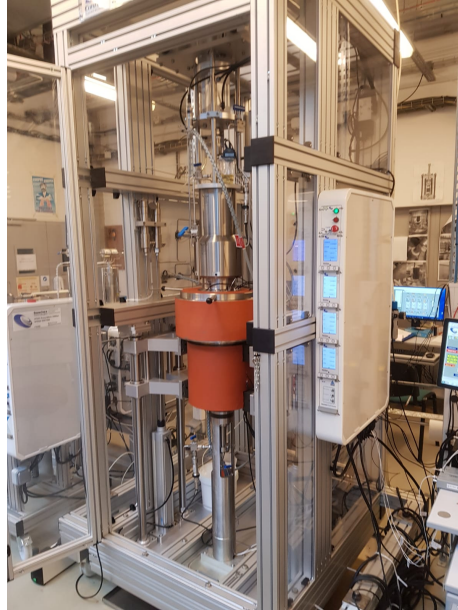


Figure 2.3.4: View of the testing system and the confinement cell of the triaxial testing system

To measure the strains undergone by the specimens, two types of devices were used: Linear Variable Displacement Transducers (LVDT) and Strain Gage cells (SG). The LVDTs were placed on two opposite generatrices of the cylindrical specimen to measure axial strains. These can be seen in Figure 2.3.5, which shows that the LVDTs are mounted on metal discs placed around the specimen. This arrangement allows the LVDTs to measure the relative displacement between the upper and lower discs. As the discs are in fixed contact with the specimen at different heights (corresponding to different sections), the measured displacement accurately reflects the change in length of the specimen between the sections where the discs are positioned. The SGs were used to measure local radial strains, with two SGs positioned on opposite generatrices of the specimen. To attach the SGs to the surface of the specimens, the area where they were to be placed was first cleaned by lightly sanding the surface. The SGs were then carefully positioned using adhesive tape. They were then fixed using a cold-curing ethyl-based cyanoacrylate glue that cures in 1 minute, and requires 24 hours to set. This specially designed glue is used to avoid interfering with the measurements of the strains of the specimens.

Before placing the specimens in the triaxial machine, they underwent an initial saturation process. For this purpose, the specimens were fully immersed in CaO saturated water for 24 hours. Then, the container with the specimens and CaO saturated water was then connected for 1 hour to a vacuum pump to remove any trapped air in the specimens.

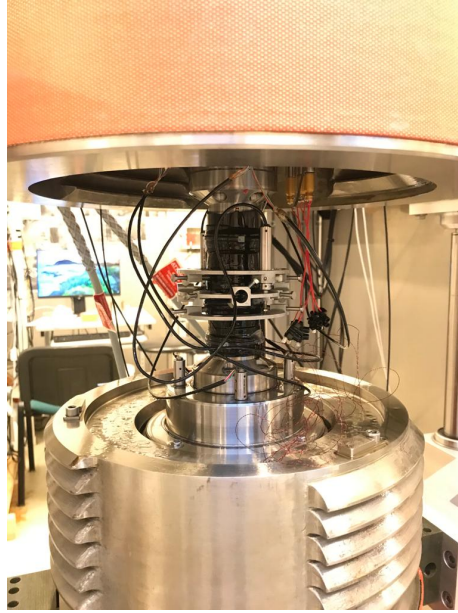


Figure 2.3.5: Specimen prepared for triaxial compression test, showing the local strain measurement system

After this initial saturation stage, the specimen is mounted in the apparatus as shown in Figure 2.3.5. The SGs are attached first, followed by the black flexible membrane (impermeable sleeve) and finally the discs to which the LVDTs are fixed. The membrane hermetically seals the entire surface of the specimen and extends above and below the height of the specimen. The excess membrane at both ends is securely attached to the machine heads using high-vacuum grease.

The membrane serves a vital purpose: it isolates the specimen from the fluid (oil) used to generate the confining pressure (p) in the triaxial apparatus. This isolation allows for different pore and confining pressures within the specimen, while preventing oil contamination.

Once the specimen is mounted, the seal of the membrane is tested by creating a vacuum within the specimen and ensuring that it is maintained for a period of time (1 to 2 hours). Once the seal is confirmed, the cell is sealed and filled with oil to create the confining pressure. The confining pressure is gradually increased to 6 MPa, followed by an increase in the pore pressure to 5 MPa. The difference between the confining pressure and the pore pressure ensures that the pressure inside the membrane (where the specimen is located) is always lower than the pressure outside the membrane. This, together with the previous vacuum control, ensures that no oil leaks from the cell into the membrane.

The specimen is held under these conditions for 48 hours to complete a second saturation stage, ensuring a uniform pore pressure of 5 MPa throughout the specimen. After this, the

triaxial tests begin. Within this work, 2 types of drainage conditions were considered for tests on saturated cement specimens, namely drained and undrained tests.

In undrained tests, the mass of fluid inside the specimen remains constant (closed boundaries), resulting in changes in pore pressure when stress conditions are altered and induce poromechanical couplings. Drained tests are those in which the pore pressure is kept constant throughout the test by ensuring that mechanically induced fluid overpressure dissipate by allowing the pore fluid to flow in or out of the specimen.

For undrained tests, the confining and deviatoric (q) pressures were increased at a rate of 0.1 MPa/min, while for drained tests, these pressures were increased at a rate of 0.025 MPa/min [71].

The static elastic moduli (K and E) are determined from the stress-strain curves obtained during the triaxial tests, specifically in the initial elastic region before plastic strains occur. These values are calculated from the slopes of the curves in the elastic range. K is derived from the relationship between changes in p and volume strain, while E is calculated from the relationship between q and axial strains, assuming linear elastic behaviour of the material. To ensure the accuracy of the values obtained, multiple measurements were made for each type of test (drained and undrained), and the results were averaged. For each parameter, the same pressure range was used for all specimens in order to obtain comparable results.

For both drained (index d) and undrained (index u) conditions, the elastic parameters, specifically the bulk (K_d , K_u) and Young moduli (E_d , E_u), were determined. Furthermore, the behaviour until reaching the compressive strength at different confining pressures was assessed under drained conditions. In the context of this research, triaxial compression tests were performed on cement pastes with varying w/s ratios and partial cement replacement with HGMS, both before and after being subjected to supercritical carbonation. Tables 2.3.5 and 2.3.6 list the triaxial compression tests performed on the different cement specimens at 15 MPa and 30 MPa of confining pressure, respectively.

Table 2.3.5: Triaxial compression tests with confining pressure of 15 MPa

Specimen	Test	Quantity
CS2744C00	K_d	2
	K_u	2
	E_d	2
	Strength	1
CS2744C60	K_d	2
	K_u	2
	E_d	2
	Strength	1
CS4144C60	K_d	2
	K_u	2
	E_d	2
	Strength	1

Table 2.3.6: Triaxial tests with confining pressure of 30 MPa

Specimen	Test	Quantity
CS0044C00	K_d	3
	K_u	3
	E_d	3
	Strength	2
CS0044C60	K_d	2
	K_u	2
	E_d	2
	Strength	1
CS2744C00	K_d	2
	K_u	2
	E_d	2
	Strength	1
CS4144C00	K_d	3
	K_u	3
	E_d	3
	Strength	2
CS4144C60	K_d	2
	K_u	2
	E_d	2
	Strength	1

2.3.10 Freeze-drying

Freeze-drying emerges as the preferred method for drying cement specimens, offering a dual benefit: halting hydration for consistent comparisons and meeting the requirements of some specific tests previously outlined. This approach stands justified by its ability to preserve composition, minimize chemical interactions, and mitigate atmospheric carbonation effects, all while maintaining the specimen's porosity and permeability [72]. Rapid freezing in liquid nitrogen prevents the formation of damaging ice crystals, safeguarding the integrity of the microstructure. Moreover, by eliminating the use of solvents, freeze-drying minimizes potential alterations to specimen properties and reduces moisture exposure, thus curtailing carbonation compared to oven drying. Ultimately, freeze-drying facilitates accurate assessments of porosity and permeability, crucial for comprehending the behaviour of cement pastes.

When needed, the freeze-drying method was used to dry the cement specimens. This technique involves subjecting the specimens to the freezing temperature of liquid nitrogen, followed by a drying process under reduced pressure. During freeze-drying, the frozen

water in the specimens undergoes sublimation, directly transitioning from the solid state to vapour without passing through the liquid phase. This method allows for the removal of moisture from the specimens while preserving their structural integrity.

In the present work, millimetre-sized fragments of cylindrical specimens, typically less than 1 cm in size, were frozen by direct immersion in liquid nitrogen at -196 °C. These fragments were obtained by breaking the cylindrical cement specimens. If necessary for the specific test, they were sanded slightly to ensure consistent shapes from sample to sample. Subsequently, specimens were dried at low temperature (-50 °C) and pressure (5 Pa) for 24 hours, as proposed by Zhang and Scherer [73].

Chapter 3

Interaction between HGMS and the cement paste

3.1 Introduction

This chapter, the first one in which the experimental results are presented and discussed, focuses on the effects that the use of HGMS have on class G cement pastes. More specifically, it discusses the effects of HGMS on cement hydration in terms of HGMS' pozzolanic activity and filler effect.

As mentioned in Chapter 1, the rate and products of cement hydration are affected by several factors, among which the use of SCM stands out. Understanding this is important in order to further explore the effects of scCO_2 exposure on cements containing HGMS. In Chapter 1, it was also shown that upon exposure to scCO_2 , the hydration products of cement react chemically to form water, CaCO_3 crystals, and amorphous silica. Since the carbonation reactions presented in Equations 1.4.7 to 1.4.12 have different kinetics, the advancement of the cement paste carbonation will depend not only on its compactness, but also on its chemical composition.

Therefore, it is imperative to study the role of HGMS in the hydration reactions of cement in order to understand how they influence its chemical composition and compactness. This analysis lays the foundation for understanding the behaviour of HGMS cement pastes exposed to scCO_2 , which will be discussed in the following chapters.

On the one hand, the pozzolanic activity refers to the ability of certain materials to react with Ca(OH)_2 and water in the presence of cement, forming CSH. This is known to increase the strength and durability of the resulting material in traditional construction applications. The pozzolanic activity of HGMS was estimated based on the modified Chapelle test, the quantification of Ca(OH)_2 from TGA, and the I_{SA} obtained from UCS. Additionally, SEM images were obtained to analyse microstructural features.

On the other hand, the filler effect describes how finely ground additives can accelerate

cement hydration by providing additional nucleation sites [29]. It was discussed from TGA results and SEM images at short hydration time, in addition to isothermal calorimetry tests.

3.2 Direct measurement of the pozzolanic activity

As highlighted in the introduction of this chapter, pozzolanic activity involves the reaction of a material with $\text{Ca}(\text{OH})_2$ produced during cement hydration to form CSH. This chemical interaction is crucial as it is known to enhance the properties of cement pastes significantly. Utilizing cement with pozzolanic materials not only boosts strength and durability but also allows reducing the cement content. Furthermore, the pozzolanic activity influences the chemical composition and compactness of the cement paste, thereby impacting the mechanisms of supercritical carbonation.

Hence, in order to quantify the pozzolanic activity of HGMS, the modified Chapelle test was carried out. Following NF P18 – 513 [60], the modified Chapelle test can be performed to obtain a direct measurement of the pozzolanic activity of SCM by obtaining the amount of $\text{Ca}(\text{OH})_2$ consumed applying Equation 2.3.1.

The two classes of HGMS considered in the present study were tested. The results are shown in Figure 3.2.1. Given the conditions in which this test is performed, it can be assumed that it evidences the maximum pozzolanic activity potential of HGMS. It can be appreciated that the HGMS show a $\text{Ca}(\text{OH})_2$ consumption of 1107 mg/g and 1365 mg/g for HGMS41 and HGMS27, respectively. Given that the standard limit established in NF P18 – 513 [60] to consider a SCM as pozzolan is 700 $\text{Ca}(\text{OH})_2$ milligrams per SCM gram and that both HGMS overcome it, it is already possible to confirm their pozzolanic activity.

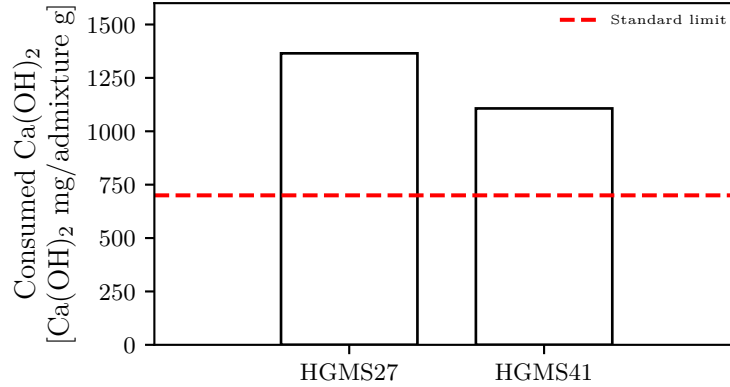


Figure 3.2.1: $\text{Ca}(\text{OH})_2$ consumed per gram of HGMS following the modified Chapelle test

Results of the modified Chapelle test obtained by Ali et al. [74] and Vejmelková et al. [75]

for pulverized fly ash and silica fume are, respectively, 550 and 1600 Ca(OH)_2 milligrams per SCM gram. Besides, for commercial metakaolin studied by Ferraz et al. [76], values ranging from 900 mg $\text{Ca(OH)}_2/\text{g}$ to 1600 mg $\text{Ca(OH)}_2/\text{g}$ were obtained. Considering these reference results, the HGMS studied in this research show a behaviour similar to that of commercial metakaolin, with a pozzolanic activity lower than that of silica fume.

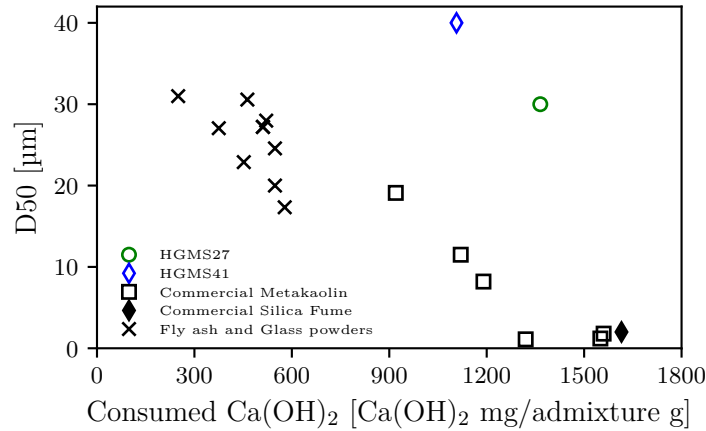


Figure 3.2.2: Modified Chapelle test results for HGMS and reference admixtures with varying D50

Ferraz et al. [76] established a correlation between the particle size and Ca(OH)_2 consumption: the smaller the particle size, the higher the Ca(OH)_2 consumption per SCM gram. This phenomenon is represented in Figure 3.2.2 for both HGMS, fly ash, silica fume, and commercial metakaolin studied by Ali et al., Vejmelková et al., and Ferraz et al. [75, 74, 76], respectively. The figure shows that the trend mentioned by Ferraz et al. is generally verified, including when considering the two classes of HGMS and their respective mean diameter, D50. Therefore, the variation of the Ca(OH)_2 consumption between HGMS41 and HGMS27 can be explained by their respective sizes. Finally, a greater reactivity of HGMS could explain the difference when comparing them with smaller sized fly ash and metakaolins in the cited studies.

3.3 Cement hydration heat release

This section examines the heat released during the hydration of cement pastes, which is important for understanding the behaviour of the material in the early stages. The aim is to see how the addition of HGMS affects this heat release through its filler effect. The results of the calorimetric tests showed differences in the heat patterns between pastes with and without HGMS, highlighting the role these materials play in the hydration of cement.

Understanding these variations in heat release is key to assessing the impact of HGMS on the final composition and microstructure of the cement, as these factors affect not only hydration but also the long-term performance of the material.

When a material presenting the filler effect is added into cement pastes, it accelerates the chemical reactions during hydration by providing additional nucleation sites for the formation of cement hydration products. Furthermore, this effect can improve the compactness of the material, making it more resistant to the exposure to conditions found in scCO_2 injection wells.

Cement hydration is the physico-chemical process resulting from mixing water and cement, from which cement hardening occurs, as explained in Chapter 1. The chemical reactions involved in this procedure are exothermic, i.e. releasing heat. By measuring this heat, the cement hydration reactions can be monitored. Isothermal calorimetry test was performed in three cement slurries: the reference one (CS0044C00), the cement slurry with 10% of HGMS27 (CS2744C00), and the cement slurry with 10% of HGMS41 (CS4144C00). Figure 3.3.1 shows the heat flow and the total heat normalized per gram of cement.

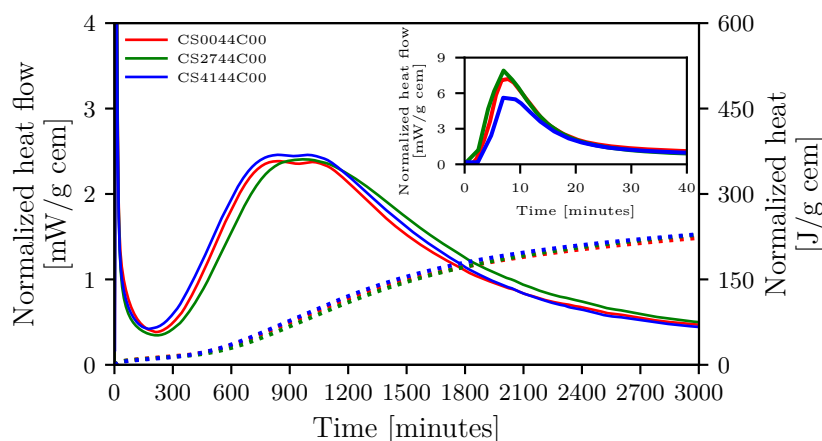


Figure 3.3.1: Heat flow (solid line) and cumulated heat (dotted line) normalized per gram of cement obtained following ASTM C 1679 [3] for each cement paste

As specified in ASTM C 1679 [3], the heat release curves are characterized by different zones: the initial heat flow related to the wetting and dissolution of cement and the beginning of its hydration, a dormant period, a heat flow increase associated with C_3S hydration reactions that contribute to setting and initial strength of cement slurries (related to the second heat flow maximum), a local minimum related to sulphate depletion and the third peak, which is associated to accelerated calcium aluminate activity. The third peak can be challenging to differentiate from the main hydration peak in some mixes containing SCM [3]. In these mixes, an overlap between the third peak, the depletion point, and the

calcium aluminate activity peak may occur.

As can be appreciated in the close-up view of Figure 3.3.1 and in Table 3.3.1, the initial heat release of all three slurries is high when water is mixed with anhydrous cement and HGMS. The heat flow reached a maximum value at 6 to 8 minutes for all slurries. In accordance with the research published by Hua et al. [77], CS2744C00 slurry yields the highest heat flow due to HGMS27's relatively high specific surface area, which is related to its low density and D50. The specific surface area of the SCM used influences the wetting and dissolution of the cement. The authors suggest that beyond a certain specific surface area, SCM can become well wetted, thereby increasing the initial heat flow. Given HGMS27's higher specific surface area, it explains why CS2744C00 exhibits greater initial heat flow compared to CS4144C00, and suggests that HGMS27 reaches the threshold where it is well wetted, enhancing the initial heat flow relative to CS0044C00. In contrast, the lower specific surface area of HGMS41, appears insufficient to meet this condition, resulting in initial heat flow values per gram of cement that are even lower than those of CS0044C00.

Table 3.3.1: Singular points of normalized heat flow and normalized heat of slurries CS0044C00, CS2744C00 and CS4144C00

	CS0044C00	CS2744C00	CS4144C00
Normalized heat flow local max 1 [mW/g cement]	7.19	7.91	5.61
Normalized heat flow local min 1 [mW/g cement]	0.38	0.34	0.42
Time for normalized heat flow local min 1 [min]	214.1	218.2	176.8
Normalized heat flow local max 2 [mW/g cement]	2.38	2.41	2.46
Time for normalized heat flow local max 2 [min]	842.8	972.0	842.5
Max normalized heat [J/g cement]	316.2	325.8	329.3

After the initial heat flow peak, the dormant period occurs. The behaviour of all three slurries is very similar in terms of minimum value of normalized heat flow [mW/g of cement], which is noteworthy since CS2744C00 and CS4144C00 have less cement per unit volume. The slurry with the minimum value is CS2744C00, followed by CS0044C00 and CS4144C00. Nevertheless, this minimum is reached about 30 minutes earlier for CS4144C00 when compared to CS0044C00 and CS2744C00, which is an indicator of the acceleration in the hydration induced by HGMS41.

As for the maxima corresponding to the main hydration peaks, the normalized heat

flow values are, once more, similar. However, there is a pronounced time variation between CS2744C00 and both CS0044C00 and CS4144C00. CS2744C00 reaches the maximum hydration peak approximately 130 minutes later than CS0044C00 and CS4144C00. According to ASTM C 1679 standard [3], this finds an explanation in the disappearance of the depletion and calcium aluminate peaks in slurry CS2744C00 as Figure 3.3.1 shows, in which only one peak is distinguishable after the dormant period for this cement paste.

Also, the slopes of the curves between the dormant period and the second peak, which can be appreciated in Figure 3.3.1, show a similar increase rate of the normalized heat flow between CS0044C00 and CS4144C00 slurries. On the other hand, the CS2744C00 slurry shows a slightly lower slope, which means a lower increase rate of the normalized heat flow and, consequently, slower hydration.

Finally, the maximum normalized released heat [J/g of cement] is higher for slurries CS4144C00 and CS2744C00 in comparison to CS0044C00, as stated in Table 3.3.1. These results indicate greater hydration per gram of cement within the first 190 hours for slurries with a 10% addition of HGMS27 and HGMS41.

The results found by Ouellet-Plamondon et al. [78] for mortars with the addition of 20% of calcined clay compared to reference mortar showed a significant decrease in the heat flow peaks and the slope of the curve between the dormant period and the second peak. This result is comparable to the behaviour appreciated in Figure 3.3.1 for CS2744C00. This behaviour changed with the addition of micro limestone and CSH seeds. Both admixtures, regardless of the added amount, reduced the dormancy to lower periods than those of reference mortar. The behaviour of micro limestone and CSH seeds is similar to that observed in Figure 3.3.1 for HGMS41, which could consequently induce an acceleration in the hydration kinetics.

Isothermal calorimetry was also used by Cordeiro et al. [61] to study the influence of sugar cane bagasse ash (SCBA) on hydration kinetics. They carried out calorimetry tests on three mixes: a reference mix and two mixes with 10% and 20% of SCBA by weight of cement. The heat flow results showed a delay in hydration reactions in mixes with SCBA. Furthermore, the greater its addition, the higher the delay, which was evidenced with a more extensive dormant period. SCBA had a D50 of about 10 μm and still produced a predominant dilution effect. Then, the composition of HGMS is likely to contribute to hydration at an early age. The alkalinity of the cement slurry may enhance the dissolution of HGMS, which releases more sodium into the solution and contributes to more dissolution and enhancement of hydration. Additional experiments in future work should prove this.

In the research of Pane and Hansen [62], silica fume (SF), which has a more similar chemical composition to HGMS than SCBA and limestone, is added to cement pastes. The heat of hydration of plain cement pastes and pastes with 10% by weight of cement replacement by SF are obtained at 23 °C with different water to binder ratios (w/b). When using a 0.45 w/b, the heat of hydration obtained for pastes with SF is lower than that obtained for plain cement pastes for the entire measurement period. This is certainly similar to the results of slurry CS2744C00 presented in Figure 3.3.1. As verified by Pane

and Hansen [62] when studying the heat of hydration with 0.35 w/b, this suggests that CS2744C00 may reach higher ultimate heat of hydration than CS0044C00. Therefore, HGMS27 might also be acting as nucleation agents.

From these researches and the obtained results, it can be appreciated that the addition of HGMS of different classes to cement slurries could affect hydration kinetics of cement during the first hours. It is highly probable that depending on physical properties (mainly D50), chemical composition, and percentage of HGMS, these could act as nucleation agents. Given the maximum normalized heat per gram of cement measured, the addition of both HGMS entail, to some extent, an increase in the final heat of hydration.

3.4 $\text{Ca}(\text{OH})_2$ consumption and changes in strength

This section aims at measuring the changes in the chemical composition of the cement pastes induced by the presence of HGMS. For this purpose, the TGA was used to measure the content of $\text{Ca}(\text{OH})_2$. The amount of $\text{Ca}(\text{OH})_2$ changes with time, due to the hydration of the cement, the filler effect, and the pozzolanic reaction of the HGMS. Therefore, determining the amount of $\text{Ca}(\text{OH})_2$ of cement pastes at different curing times can indicate the extent of both, the filler effect and the pozzolanic reaction induced by these SCM. Tests were carried out on CS0044C00, CS2744C00, and CS4144C00 pastes at different curing times (7, 28, and 56 days). The results are presented in Figure 3.4.1a.

Knowing the amount of $\text{Ca}(\text{OH})_2$, the fixed $\text{Ca}(\text{OH})_2$ can be calculated. It is defined as the relative difference between the amount of $\text{Ca}(\text{OH})_2$ in the reference cement pastes and the amount of $\text{Ca}(\text{OH})_2$ in the cement pastes with HGMS at a given curing time (Equation 3.4.1). This parameter is described by Ghoddousi and Adelzade Saadabadi [63] and by Velázquez et al. [79], and it is calculated using Equation 3.4.2.

$$C = (C_{\text{cement}})/(C_{\text{cement}} + C_{\text{HGMS}}) \quad (3.4.1)$$

$$\text{Ca}(\text{OH})_2^{f-i} = \frac{\text{Ca}(\text{OH})_2^{c-i}C - \text{Ca}(\text{OH})_2^{p-i}}{\text{Ca}(\text{OH})_2^{c-i}C} \quad (3.4.2)$$

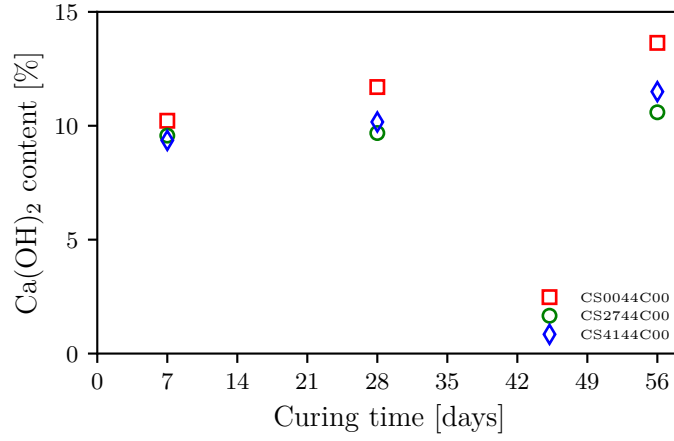
where C is the cement mass fraction (0.9 in these pastes), C_{cement} is the cement content, C_{HGMS} is the HGMS content, $\text{Ca}(\text{OH})_2^{f-i}$ is the fixed $\text{Ca}(\text{OH})_2$ content at a curing time “ i ” [%], $\text{Ca}(\text{OH})_2^{c-i}$ is the $\text{Ca}(\text{OH})_2$ content in the reference paste at curing time “ i ” [%] and $\text{Ca}(\text{OH})_2^{p-i}$ the $\text{Ca}(\text{OH})_2$ content in the paste with HGMS at curing time “ i ” [%].

The product $\text{Ca}(\text{OH})_2^{c-i}$ by C corresponds to the amount of $\text{Ca}(\text{OH})_2$ produced during the hydration of the cement present in pastes without any HGMS, scaled by the actual cement content in the pastes containing HGMS for meaningful comparisons. The difference between $(C\text{Ca}(\text{OH})_2^{c-i}C)$ and $\text{Ca}(\text{OH})_2^{p-i}$ quantifies the difference in $\text{Ca}(\text{OH})_2$ content at a curing time “ i ” between pastes with no HGMS and pastes containing HGMS. This difference can only be attributed to the presence of HGMS, all other parameters being equal. This

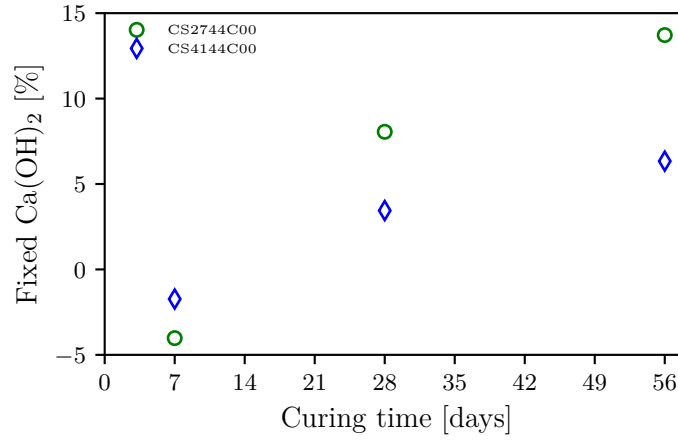
difference is finally normalized by the scaled amount of $\text{Ca}(\text{OH})_2$ produced in the reference paste. It is worthwhile noting that calculated values of the fixed $\text{Ca}(\text{OH})_2$ content could be either negative or positive.

Negative values of fixed $\text{Ca}(\text{OH})_2$ content correspond to higher $\text{Ca}(\text{OH})_2$ content in cement pastes containing HGMS, indicating an increase in the cement hydration [79], and demonstrating that the HGMS are acting as nucleation agents. This parameter could also adopt positive values, meaning that the amount of $\text{Ca}(\text{OH})_2$ measured by TGA in cements containing HGMS (or any other SCM) is lower than expected. In their research, Ghoddousi and Adelzade Saadabad [63] and Velázquez et al. established that positive values are indicators of pozzolanic activity, which consumes $\text{Ca}(\text{OH})_2$ [79]. It is important to note that $\text{Ca}(\text{OH})_2$ nucleation and pozzolanic reactions are two competing phenomena induced by the presence of HGMS, one possibly showing predominance over the other depending on the curing time.

The fixed $\text{Ca}(\text{OH})_2$ contents for CS2744C00 and CS4144C00 pastes at 7, 28, and 56 days are presented in Figure 3.4.1b. This figure illustrates the interest of using the fixed $\text{Ca}(\text{OH})_2$ content, as this parameter accounts for the actual content of cement in each paste, and thus allows to quantitatively determine which of the two phenomena mentioned above, namely $\text{Ca}(\text{OH})_2$ nucleation and pozzolanic reactions, is predominating.



(a) $\text{Ca}(\text{OH})_2$ content



(b) Fixed $\text{Ca}(\text{OH})_2$ content

Figure 3.4.1: TGA results for the three cement pastes at different curing times

After seven days of hydration, fixed $\text{Ca}(\text{OH})_2$ values are negative for both pastes with HGMS. This indicates that both HGMS are predominantly acting as nucleation agents for cement hydration products, and notably $\text{Ca}(\text{OH})_2$ content. This behaviour is a confirmation of the results obtained from the maximum normalized heat measured with isothermal calorimetry. When increasing the curing time, fixed $\text{Ca}(\text{OH})_2$ content increases. At curing times of 28 and 56 days, the values obtained for this parameter are positive, indicating the predominance of the pozzolanic activity of HGMS over the role it plays in creating more nucleation sites.

Velázquez et al. [79] obtained similar results for some combinations of fly ash and SCM.

These authors obtained negative values of around -20% after 3 and 7 days of curing time, and positive values of approximately 15% after 90 days. According to their results and conclusions, it is plausible to state that HGMS are mainly behaving as fly ash, transitioning from nucleation agents at low curing times to predominantly pozzolanic materials at high curing times.

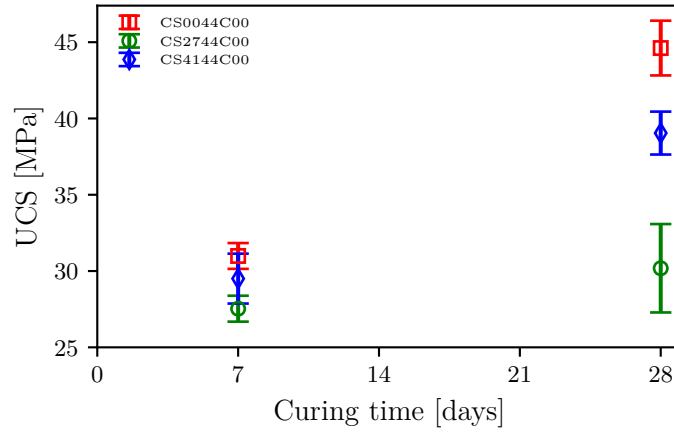
The chemical interactions between HGMS and cement hydration products discussed throughout this chapter are expected to significantly impact the strength and the durability of the resulting cement pastes. To quantify these mechanical aspects and to determine the pozzolanic activity of HGMS from another perspective, UCS tests were performed, and the I_{SA} proposed by ASTM C 311 [56] was calculated. The evolution of UCS has been used by many authors [80, 81, 82] to quantify the mechanical effects of SCM. The compressive strength of cement specimens with SCM should increase with increasing curing time. Furthermore, in accordance with Matos and Sousa-Coutinho [80] and Ismail et al. [82], a significant increase in UCS after 28 days means that pozzolanic activity occurred.

The UCS of the three pastes were measured at different curing times, as shown in Figure 3.4.2a. I_{SA} values were calculated using Equation 3.4.3 and plotted in Figure 3.4.2b:

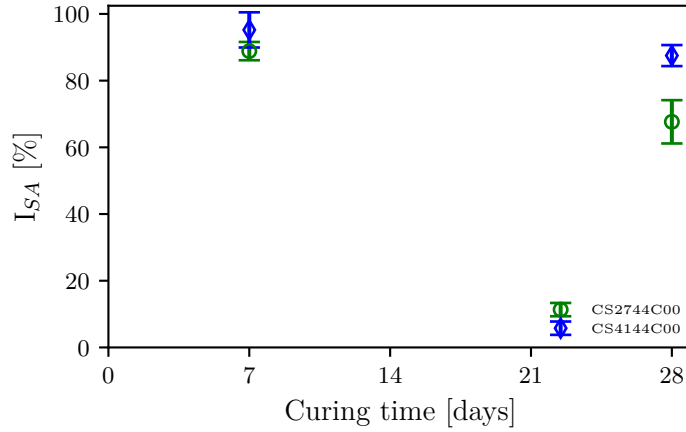
$$I_{SA} = \frac{RC_{a,i}}{RC_{p,i}} \quad (3.4.3)$$

where $RC_{a,i}$ is the UCS of cement paste with HGMS at curing time “ i ” (7, 28 or 90 days) and $RC_{p,i}$ the UCS of the reference cement paste at the same curing time “ i ”.

ASTM C 618 [83] establishes a lower bound for I_{SA} of pozzolans equal to 0.75 for a 20% replacement in cement mortar with a w/c ratio of 0.5. HGMS were added at only 10%, because of lack of workability at higher proportions, in a cement paste with a w/s ratio of 0.44. Despite the composition differences, this I_{SA} threshold could be considered a reference value. Both pastes, with 7 days of curing time, presented I_{SA} higher than 0.80, while at 28 days of curing time, this index is higher than 0.75 only for CS4144C00. According to these results, HGMS may exhibit some pozzolanic activity. Particularly, HGMS41 verifies the conditions established in ASTM C 618. However, while pozzolanic activity is typically associated with long curing times, the results for both HGMS indicate a decrease in I_{SA} as curing time increases.



(a) UCS of cubic specimens for the three cement pastes



(b) I_{SA} as obtained from UCS results

Figure 3.4.2: Uniaxial compressive test results at 7 and 28 days of curing time

As stated by Brooks et al. [84], among others, the UCS does not rely only on the SCM pozzolanic activity but also on other properties such as their particle size and mechanical properties, notably their crush strength. These authors studied the addition of lightweight fillers with low crush strength, such as expanded polystyrene spheres (EPS) and expanded thermoplastic spheres, demonstrating how such materials severely reduce the UCS of cement pastes. They compared these results to those obtained for cement pastes with HGMS and fly ash cenospheres, confirming that the shell properties of the SCM and its size affect the mechanical properties of cement pastes. Larger particle size and lower shell thickness decrease the crush strength and, therefore, decrease the UCS of cement pastes. Considering these results, the behaviour of the studied pastes could be explained, especially for

CS2744C00, since HGMS27 presents lower crush strength – and smaller shell thickness – than HGMS41.

Since HGMS are hollow, adding them increases the paste’s occluded porosity. This is evident from the reduction in density of the hardened cement pastes, which drops from 2.19 g/cm³ for CS0044C00 to 1.77 g/cm³ for CS4144C00 and 1.48 g/cm³ for CS2744C00. Additionally, because HGMS27 has a lower density than HGMS41, 10% of HGMS27 adds more volume and thus creates more occluded porosity compared to HGMS41.

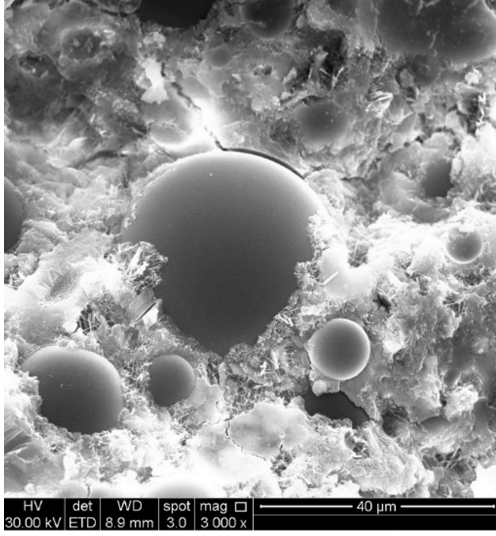
Based on the density reduction and increased occluded porosity caused by the HGMS, their impact on the UCS is more noticeably than their pozzolanic activity. The reduced density and the greater volume occupied by HGMS, due to their lower density and larger volume per unit weight, significantly influence the strength characteristics of the cement paste. Then, it can be concluded that when it comes to UCS, the shell properties of a hollow particle and the volume occupied by the SCM in the cement paste are more important than its pozzolanic activity. This observation lead us to propose an analytical homogenisation model to predict the mechanical properties of cement pastes of different HGMS classes, considering their geometry and the mechanical properties of the material forming their outer shell. This development is presented in Chapter 6 of this research.

As previously discussed, HGMS27 occupies a higher volume fraction in CS2744C00 than HGMS41 in CS4144C00. Additionally, HGMS27 has a lower crush strength than HGMS41. Hence, I_{SA} may not be an appropriate index when evaluating the pozzolanic activity of HGMS, since it does not consider these two properties that significantly affect the strength of cement pastes.

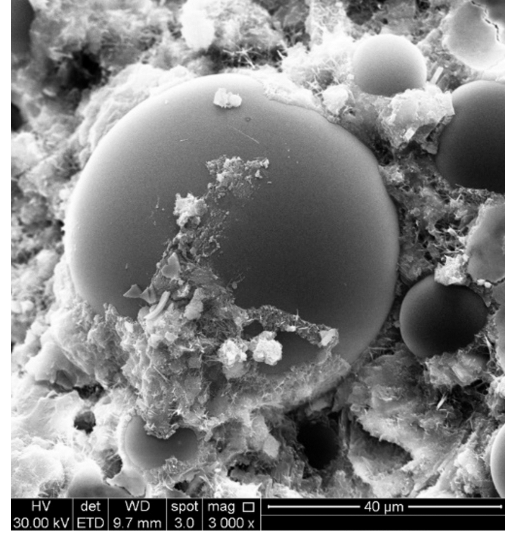
In the context of scCO₂ injection wells, where cement pastes are subjected to extreme conditions, the difference in strength obtained in cements with HGMS27 and HGMS41 compared to those without HGMS and the discussion on the importance of HGMS strength and the volume occupied by HGMS are of particular interest. First, the reduction in uniaxial strength exhibited by cement pastes with HGMS can be related to the durability of the pastes, as is common practice in the construction industry [85]. In the traditional construction industry it is generally accepted that the lower the strength, the lower the quality of the cement, which implies a reduction in durability. Second, and even more interesting, is the question of the occluded porosity that HGMS confer to cement pastes. The role played by this occluded porosity in the supercritical carbonation mechanisms of cement pastes with HGMS will be thoroughly discussed in Chapters 4 and 5.

Finally, SEM images obtained for cement pastes CS2744C00 and CS4144C00 after 7 and 28 days of curing time are presented in Figure 3.4.3. Figures 3.4.3a and 3.4.3b show the SEM images of CS2744C00 and CS4144C00 after 7 days of curing time. These already show the compatibility between cement and HGMS. A good interface between these materials exists. Moreover, some hydration products appear to have formed over the HGMS, confirming the filler effect of this material. Figures 3.4.3c and 3.4.3d show the SEM images of CS2744C00 and CS4144C00 after 28 days of curing time. The behaviour is roughly the same as that shown at 7 days of curing time, but an increased compactness

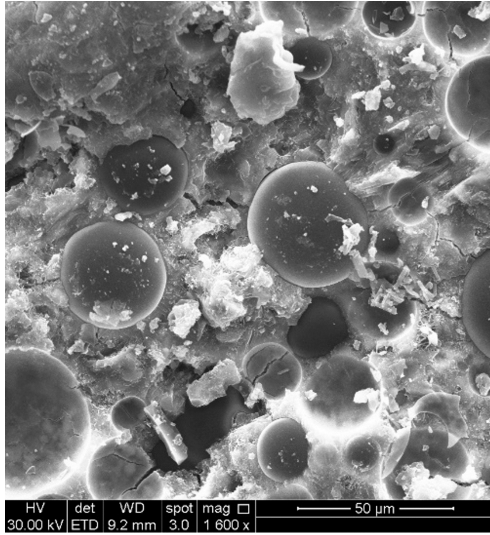
of the cement matrix and an even better interface between HGMS and cement hydration products is noticeable. It can be concluded that these images are consistent with the results previously discussed.



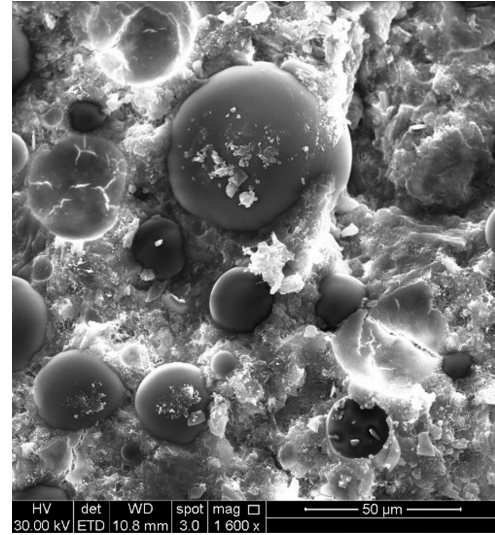
(a) CS2744C00 cured during 7 days



(b) CS4144C00 cured during 7 days



(c) CS2744C00 cured during 28 days



(d) CS4144C00 cured during 28 days

Figure 3.4.3: SEM images of CS2744C00 and CS4144C00 at 7 and 28 days of curing time

In order to comprehensively analyse the effects of the presence of HGMS on the cement pastes, the previous results are now jointly discussed.

To reach a general comparison of the filler effect and pozzolanic activity of HGMS27 and HGMS41, Figures 3.4.4 and 3.4.5 show the experimental results and the various calculated quantities introduced previously for both HGMS. The closer the value is to the external boundary, the higher is the corresponding property.

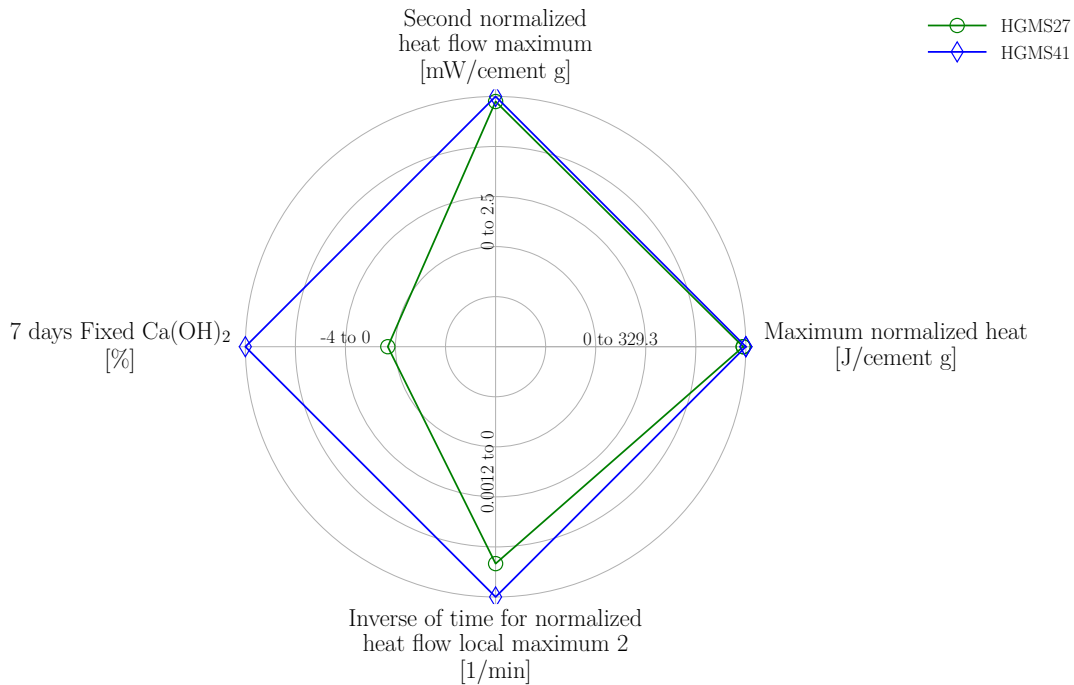


Figure 3.4.4: Filler effect comparison between HGMS27 and HGMS41

Figure 3.4.4 presents the main parameters that characterize the nucleation effect of HGMS. To begin with, the absolute fixed $\text{Ca}(\text{OH})_2$ value at seven days for HGMS41 is larger than for HGMS27, indicating more activity as a nucleation agent of the former. This result agrees with those obtained in the isothermal calorimetry test. Despite having almost the same normalized heat and second normalized heat flow maximum, the time for which the latter is reached is larger for CS2744C00 than for CS4144C00, which means a slower hydration reaction for CS2744C00.

Figure 3.4.5 shows a higher pozzolanic activity for HGMS41 compared to HGMS27, as observed from results of both TGA and I_{SA} . HGMS41 has, on the one hand, a higher density than HGMS27. Since HGMS were added to the pastes in the same proportion, the higher density of HGMS41 entails a smaller volume added to the paste than HGMS27. On the other hand, HGMS41 has higher crush strength than HGMS27. This might contribute to a higher compressive strength for CS4144C00 since, as aforementioned, the shell properties of the SCM could severely affect the results obtained in UCS. Given also the

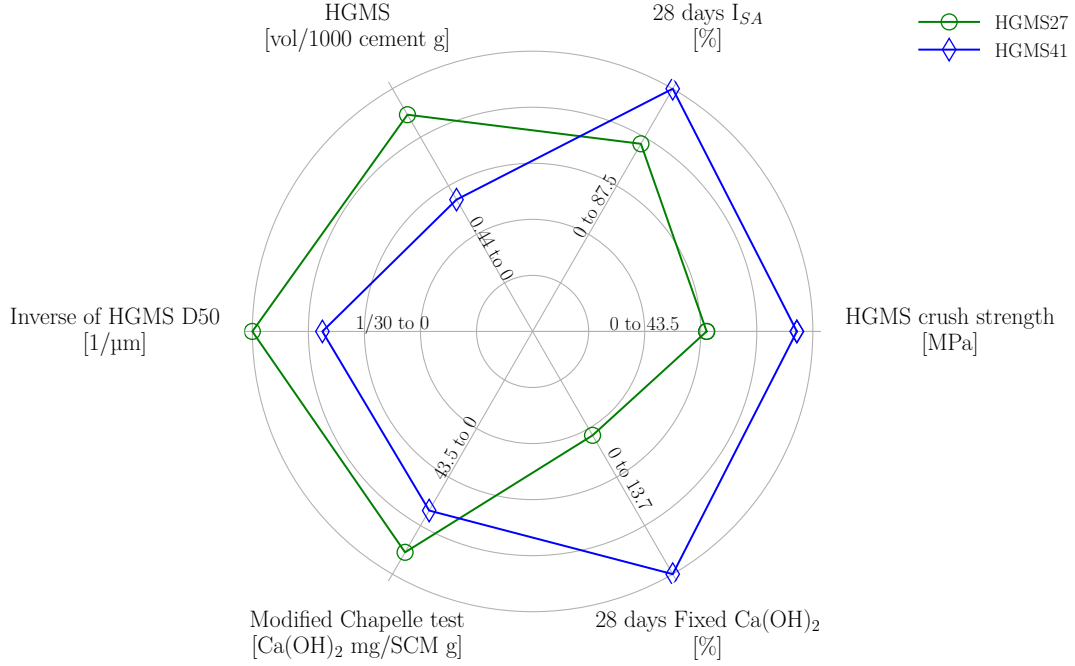


Figure 3.4.5: Pozzolanic activity comparison between HGMS27 and HGMS41

higher volume of HGMS27 in CS2744C00 than for HGMS41 in CS4144C00, the observed difference does represent not only the pozzolanic activity of the HGMS involved but also other properties that unintentionally (but necessarily) affect the mechanical properties and, particularly, the compressive strength.

Analysing the modified Chapelle test reveals that the results align with the findings of [76]: reactivity increases as the D50 decreases. HGMS27, which has a smaller D50, shows higher values for the "Inverse of HGMS D50" parameter and more pozzolanic activity in the modified Chapelle test compared to HGMS41. However, these results are inconsistent with the pozzolanic activity measured by TGA. TGA measurements suggest that HGMS41 is actually more reactive.

In order to understand this difference, special attention must be paid to the conditions at which both tests are performed. On the one hand, the modified Chapelle test is performed by exposing HGMS to a highly concentrated $Ca(OH)_2$ solution at high temperatures. In such conditions, the high temperature and the $Ca(OH)_2$ availability (which does not change regardless of the class of HGMS being evaluated) ensure that the reactivity of the SCM can be tested at its full potential. On the other hand, TGA is performed on cement pastes that were previously cured at room temperature. The $Ca(OH)_2$ availability is not the same on every paste mainly because of the higher volume fraction occupied by HGMS27 than HGMS41, implying a reduction in the cement volume fraction from paste

CS2744C00 to paste CS4144C00, thus, $\text{Ca}(\text{OH})_2$ availability.

Therefore, the modified Chapelle test evidence the reactivity potential of HGMS, while TGA measures their reactivity when added to cement pastes, with the corresponding $\text{Ca}(\text{OH})_2$ availability. These differences in testing conditions could explain why HGMS41 appears to be more reactive when tested using the Chapelle test than when using TGA. Nevertheless, from both tests it is concluded that both HGMS27 and HGMS41 interact with the cement paste with a pozzolanic reaction.

3.5 Conclusion

Understanding the behaviour of cement pastes containing HGMS is critical for their effective use in well cementing, particularly under scCO_2 exposure. This chapter has highlighted the significant influence of HGMS on the hydration process of class G cement pastes. By analysing both the pozzolanic activity and the filler effect, it is clear that HGMS play a key role in modifying the chemical composition and compactness of the paste. The following conclusions have been obtained:

- SEM images confirmed that HGMS41 and HGMS27 interact with cement paste hydration products. Furthermore, given the quantification obtained through the modified Chapelle test and TGA, it can be confirmed that both HGMS present a pozzolanic activity similar to that of smaller sized SCM, such as metakaolins or fly ash. The pozzolanic activity of HGMS leads to a decrease in $\text{Ca}(\text{OH})_2$ content.
- The studied HGMS also present a nucleation effect, since higher heat flow and heat maxima normalized per gram of cement were obtained for cement slurries with HGMS in the isothermal calorimetry test. For CS4144C00, these values were 3.4% and 4.1% higher than those for CS0044C00, respectively. For CS2744C00, they were 1.3% and 3.0% higher, respectively. These increases could indicate the formation of additional nucleation sites when adding any of the studied HGMS to cement slurries. This effect was slightly higher for HGMS41.
- Confirming these results, fixed $\text{Ca}(\text{OH})_2$ content measured by TGA at early curing times presented negative values of -1.7% for CS2744C00 to -4.1% for CS4144C00. It can then be concluded that both HGMS act as nucleation agents in the cement hydration reaction, and that HGMS41 characterizes by a larger effect than HGMS27.
- Regarding which class of HGMS is the most reactive, results were inconclusive. The reduction in the $\text{Ca}(\text{OH})_2$ content and the increase in the fixed $\text{Ca}(\text{OH})_2$ values measured with TGA for slurries with HGMS at different curing times evidenced pozzolanic activity. CS4144C00 slurry yielded, for 28 and 56 days of curing time, values of fixed $\text{Ca}(\text{OH})_2$ that were 57% and 54% higher than CS2744C00 slurry

respectively, indicating that HGMS41 is more reactive than HGMS27. Ca(OH)_2 consumption measured in terms of the modified Chapelle test for both HGMS overcame the standard limit of 700 Ca(OH)_2 mg per SCM gram, confirming their pozzolanic activity. However, the result obtained for HGMS27 was 23% higher than that of HGMS41, which indicates that HGMS27 are more reactive than HGMS41. Therefore, in the optimal conditions of the modified Chapelle test, HGMS41 presents the higher pozzolanic potential, though, in standard cement paste conditions, HGMS27 has a higher pozzolanic activity. Considering the operating conditions in CO_2 storage wells, which combine high temperatures with a limited availability of Ca(OH)_2 , the actual reactivity may fall between the results of these two tests

- The I_{SA} proved to be inconsistent for measuring the pozzolanic activity of these hollow SCM, since the compressive strength of both classes of HGMS strongly depends on their physical properties. At both 7 and 28 days of curing time, the compressive strength of cement pastes CS2744C00 and CS4144C00 was lower than for CS0044C00, CS2744C00 showing the lowest values. The compressive strength of CS2744C00 was 13% and 32% lower than for CS0044C00 at 7 and 28 days of curing time, respectively. The compressive strength of CS4144C00 was 5% and 11% lower than for CS0044C00 at 7 and 28 days of curing time, respectively. These variations are directly related to the lower crush strength and density of HGMS27 compared to HGMS41. Intrinsic properties of the HGMS are closely related to the overall strength of cements pastes to which they are added. This aspect will be further discussed in Chapter 6, where an analytical homogenisation model for estimating the elastic parameters of cement pastes with HGMS is developed.

Chapter 4

Microstructural insights into cement paste supercritical carbonation

4.1 Introduction

Throughout the CO₂ injection and subsequent storage process, evaluation of the integrity of the storage site is essential, and the cement sheath is a key component to ensure this integrity. The cement paste is continuously exposed to high pressure and high temperature conditions, and generally in the presence of water, before the initiation of scCO₂ injection. As explained in Chapter 1, H₂CO₃ is formed as a result of the reaction of CO₂ with water (cf. Equation 1.4.7), from which HCO₃⁻ and CO₃²⁻ are produced upon carbonic acid dissociation, which subsequently reacts chemically with certain cement hydration products, including Ca(OH)₂ and CSH, promoting cement paste carbonation. This chemical process yields CaCO₃ and water for Ca(OH)₂ carbonation, and CaCO₃ and amorphous SiO_xOH_x for CSH carbonation (cf. Equations 1.4.8 to 1.4.11).

Several studies have reported a decrease in porosity and permeability during the initial stages of supercritical carbonation due to the precipitation of CaCO₃ crystals [33, 42, 43]. Nevertheless, for longer exposure times there seems to be a considerable degradation of the cement paste characterised by increased porosity [42, 43]. This degradation is attributed to CaCO₃ dissolution (cf. Equation 1.4.12).

Furthermore, according to [44], Ca(OH)₂ depletion leads to CSH decalcification and increased CaCO₃ formation. CaCO₃ is stronger but bonds less effectively with the microstructure of the cement paste. The result is a significant reduction in porosity due to the degradation of CSH and dissolution of Ca(OH)₂, which reduces the mechanical properties of the cement paste after carbonation.

Regarding the use of cement replacement by HGMS in scCO₂ injection wells, there are

already some indications of how it may affect the performance of the cement paste [86, 87]. In Chapter 3, the effect of the incorporation of different classes of HGMS in class G cement pastes was studied, focusing on their chemical interaction with cement hydration products. HGMS will partially consume the $\text{Ca}(\text{OH})_2$ of the cement matrix to form secondary CSH, leading to a decrease in pH and facilitating the advance of the carbonation front into the cement matrix. This has been reported for other SCM exposed only to atmospheric carbonation [40].

In order to gain a better understanding of cement supercritical carbonation and its relationship with the pore structure of cement pastes, the effect of w/s ratio on supercritical carbonation is first studied. This will shed light on the relevance and implications of using lightweight materials (HGMS) to lighten cement pastes instead of increasing the w/s ratio.

The influence of the w/s ratio on cement pastes properties is a deeply studied and well-known subject. Increasing the amount of water in the mixture yields a higher porosity of the hardened material [88], which in turn affects its mechanical properties and durability [89]. The increased porosity results in a higher amount of interconnected porosity, which is positively correlated with permeability [88]. Hence, a higher w/s ratio results in a more permeable material.

In both fresh and hardened states, admixtures are also found to have a significant effect on the properties of cement pastes. While Chapter 3 dealt with the chemical aspects of these interactions, the influence of HGMS on the microstructural properties of hardened cement pastes, in particular pore structure and porosity, remains to be investigated and is therefore one of the main objectives of this chapter.

Finally, by understanding the differences in pore structure induced by varying w/s ratios and including HGMS in cement pastes, this chapter aims to characterise the behaviour of cement pastes with two different w/s ratios and two different classes of HGMS under scCO_2 injection well conditions. For this purpose, the results obtained from MIP, and SEM images are presented and thoroughly discussed. The carbonation mechanisms leading to alterations in pore structure are investigated at different w/s ratios in Section 4.2, and considering the influence of HGMS as cement replacement in Section 4.3.

4.2 Influence of the water to solid ratio

This section discusses the differences in carbonation mechanisms of class G cement paste under scCO_2 injection well conditions as the w/s ratio changes.

This is done by first studying the microstructural variations, focusing on the pore structure, exhibited by class G cement pastes when the w/s ratio is varied. To this end, porosity and pore size distribution are measured using MIP tests. These results, accompanied by SEM images and based on the discussions from Chapter 3, help to understand the changes in microstructure undergone by class G cement pastes when w/s ratio changes are made.

The section then continues with an examination of the effects of these changes on the

carbonation mechanisms of class G cement paste exposed to scCO_2 . The aim is to understand the rate of carbonation progression and the possible differences and/or similarities observed in the pore structure by MIP and in the microstructure by considering SEM and pH indicator results.

4.2.1 Effect on cement paste microstructure

Let us begin with the intrinsic differences in the porosity and pore structure that can be found between cement pastes with varying w/s ratios. The porosity obtained by MIP for these cement pastes is 28.5% and 39.8% for CS0044C00 and CS0060C00, respectively. This is a known phenomenon in the cement industry [90]. Leaving aside the effect of other variables, any increase in the amount of water used to produce the cement slurry will necessarily lead to an increase in the porosity of the resulting cement paste. This result is important in view of the porosity/permeability relationship and the durability of the cement paste, as mentioned in the introduction of this chapter.

Another important parameter for further understanding the influence of the w/s ratio on the carbonation mechanisms of class G cement paste is the pore structure. Figure 4.2.1 shows MIP test results for cement pastes prepared with the two considered w/s ratios, namely, 0.44 and 0.60. The figure shows two distinct pore entry size distributions for the two w/s ratios. For CS0044C00, a clear peak can be found around $3 \times 10^{-2} \mu\text{m}$ while for CS0060C00, the peak is not as clearly defined, and a wider pore entry size distribution is observed, with larger pores between $1.5 \times 10^{-2} \mu\text{m}$ and $6.5 \times 10^{-2} \mu\text{m}$ being detected.

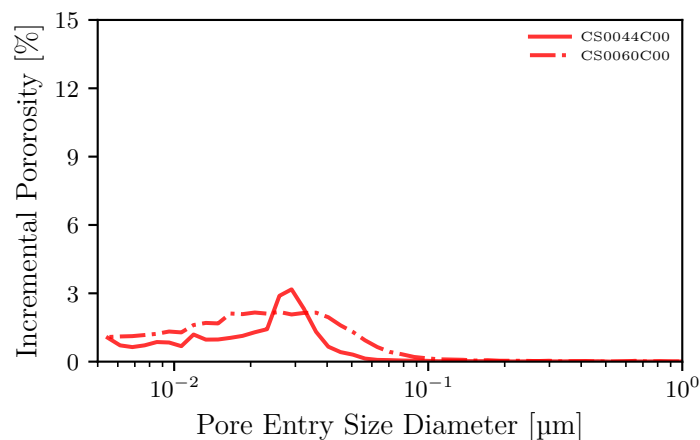


Figure 4.2.1: Pore entry size distribution of non-carbonated plain cement pastes

The durability of cement pastes, especially under carbonation, is closely related to their permeability and transport properties, both of which depend on the pore structure [91, 92, 93]. The porosity influences the diffusion of CO_2 [94], which is the primary focus of

this study, as well as ions diffusing in water that can also contribute to degradation [95]. The diffusion of CO_2 is particularly critical in carbonation processes, where it reacts with the cement matrix, altering the pore structure and long-term performance. Hence, given the differing pore entry size distributions for cement pastes with two distinct w/s ratios, variations in their resistance to carbonation are expected.

The results shown in Figure 4.2.1 align with the findings of Chen and Wu [96], which demonstrate that the threshold pore diameter – the point at which rapid mercury intrusion begins – increases with increasing w/s ratios. This threshold indicates the transition between low and high intrusion rates, suggesting a significant change in pore connectivity or size distribution that influences permeability. Higher w/s ratios result in larger pores, due to the greater initial spacing between cement particles. This leads to larger threshold diameters in high w/s ratios systems compared to those with lower w/s ratios.

The observed changes can also be analysed through SEM images of CS0044C00 and CS0060C00, as shown in Figure 4.2.2, where different w/s ratios correspond to significantly different CSH morphologies. The cement paste with a higher w/s ratio not only displays a fibrous and less dense CSH morphology but also reveals large fibres that may be ettringite embedded within the CSH matrix, as noted by Zhang et al. [97]. Conversely, the cement paste with a lower w/s ratio exhibits denser structures, as highlighted in Figure 4.2.2a, which aligns with the findings of Jennings et al. [98].

A lower w/s ratio induces densification of the hydration products, leading to a more compact CSH structure. In contrast, a higher w/s ratio provides more space, allowing for greater expansion of the hydration products. Previous studies have reported that CSH growing in cement pastes with higher w/s ratios tends to exhibit elongated shapes, with this elongation increasing as the w/s ratio does [99]. This expansion and elongation are consistent with the observed less dense and fibrous morphology in pastes with higher w/s ratios.

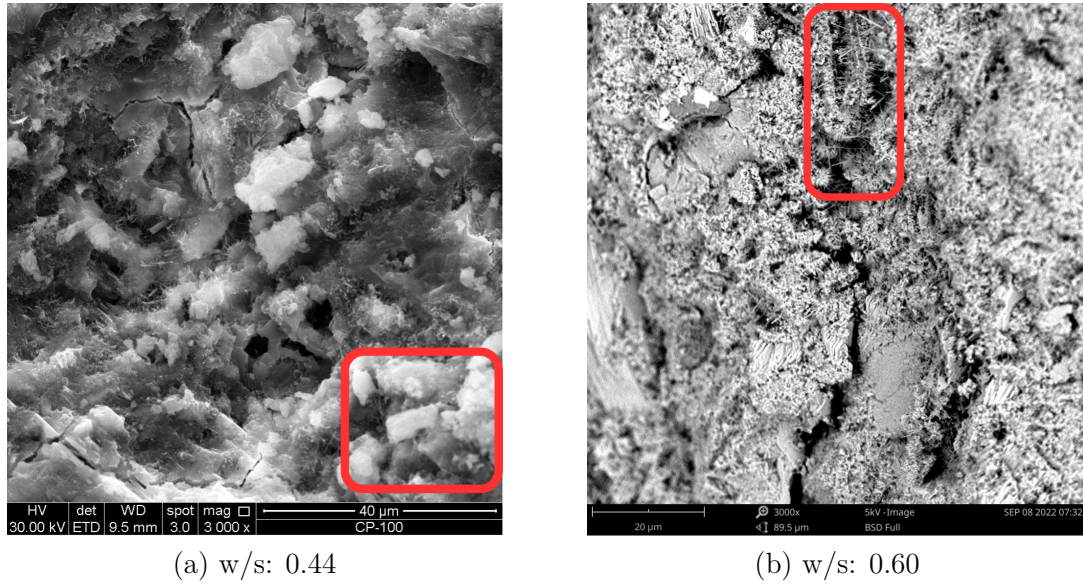


Figure 4.2.2: Scanning electron microscopy images comparing cement pastes with varying w/s ratios. Highlighted areas indicate regions demonstrating the shift in CSH morphology, corresponding to the different w/s ratios utilized in each cement paste. The images also reveal the presence of large fibres, potentially ettringite, embedded within the CSH matrix, particularly in pastes with higher w/s ratios.

4.2.2 Effect on cement carbonation

After having discussed the effects of w/s ratio on the porosity and pore structure of class G cement pastes, the focus will now shift to the evaluation of how these differences affect the carbonation of the cement pastes. Table 4.2.1 presents the porosity results obtained before and after carbonation for 60 days, for plain cement pastes with two different w/s ratios, as well as the results for carbonated samples with a w/s ratio of 0.44 after 120 days of carbonation. The table also highlights the porosity differences between internal and external parts of the carbonated specimens, reflecting the varying exposure levels to CO_2 . It is expected that the external parts, due to their greater exposure, will undergo more severe carbonation compared to the internal parts, affecting the extent of carbonation and the resulting porosity changes.

Table 4.2.1: MIP porosity results before and after carbonation of 60 on plain cement pastes with two w/s ratios, including results for carbonated samples with a w/s ratio of 0.44 after 120 days of carbonation

Specimen	MIP porosity [%]
CS0044C00	28.5
CS0044C60INT	35.9
CS0044C60EXT	31.7
CS0044C120INT	32.5
CS0044C120EXT	20.3
CS0060C00	39.8
CS0060C60INT	40.4
CS0060C60EXT	29.0

From these results, a first attempt on understanding the carbonation of cement pastes with different w/s ratios can be established. In the paste with a w/s ratio of 0.44, an increase in the porosity obtained by MIP is observed in the internal part of the specimens carbonated for 60 days (CS0044C60INT and CS0060C60INT) compared to the non-carbonated specimens (CS0044C00 and CS0060C00). In the paste with a w/s ratio of 0.60, the slightly larger porosity measured in CS0060C60INT might not be significant. As for the porosities of CS0044C60EXT and CS0060C60EXT samples, they are lower than those of CS0044C60INT and CS0060C60INT, respectively. The behaviour of the pastes with a w/s ratio of 0.44 carbonated for 120 days is similar to that of the pastes with a w/s ratio of 0.60 carbonated for 60 days, where the internal part (CS0044C120INT) shows a slight increase in porosity, while the external part (CS0044C120EXT) shows a decrease in porosity.

The volumetric consequences of carbonation in terms of porosity can be understood through the interplay between dissolution and precipitation processes that occur during carbonation. Initially, the dissolution of CO_2 in water (cf. Equation 1.4.7) allows for the diffusion of ions, such as HCO_3^- and CO_3^{2-} , into the cement matrix. These ions react with cement hydration products, such as $\text{Ca}(\text{OH})_2$ and CSH, as shown in Equations 1.4.8 to 1.4.11, leading to their dissolution. This dissolution results in a localized increase in porosity [44], as observed in the internal zones of carbonated specimens, particularly in CS0044C60INT, where the increase in porosity compared to CS0044C00 is significant.

As carbonation progresses, the dissolved calcium and carbonate ions precipitate as CaCO_3 , initially filling some of the created porosity. In systems with sufficient $\text{Ca}(\text{OH})_2$

and lower initial porosity, this precipitation may eventually lead to a reduction in overall porosity, as observed in samples CS0044C60EXT and CS0060C60EXT. This porosity decrease impacts the transport of species [100], as reduced porosity slows down the diffusion of HCO_3^- and CO_3^{2-} , thereby limiting further carbonation and transport phenomena. This is consistent with the observed differences in porosity between CS0044C60INT and CS0044C60EXT.

Hence, CS0044C60INT appears to be characterized by the effect of dissolution of cement hydration products due to the large increase in porosity observed compared to CS0044C00. However, the precipitation of CaCO_3 seems to be dominant in CS0044C60EXT, indicating a further extent of cement carbonation.

Regarding the cement paste with w/s ratio of 0.60 carbonated for 60 days, the dominance of dissolution or precipitation is not clear in CS0060C60INT. The porosity in CS0060C60INT is roughly the same as in CS0060C00, which could indicate that both dissolution of cement hydration products and precipitation of CaCO_3 are taking place. This suggests that carbonation advances more rapidly in this cement paste due to its high porosity, which increases species transport. CS0060C60EXT presents a lower porosity than both CS0060C00 and CS0060C60INT, indicating a predominance of CaCO_3 precipitation.

The behaviour of the paste with a w/s ratio of 0.44 carbonated for 120 days (CS0044C120INT and CS0044C120EXT) is similar to that of the paste with a w/s ratio of 0.60 carbonated for 60 days (CS0060C60INT and CS0060C60EXT). The slight difference in porosity between CS0044C120INT and CS0044C00, as well as between CS0060C60INT and CS0060C00, is attributed to the more advanced carbonation. In the former case, this is due to longer exposure (120 days), while in the latter, it results from higher porosity, which enhances transport properties and accelerates carbonation. CS0044C120EXT exhibits a similar trend to CS0060C60EXT, with lower porosity compared to both CS0044C00 and CS0044C120INT, reinforcing the notion of CaCO_3 precipitation predominance in the external part of the specimen.

These results are consistent with those reported by Barría et al. [44] for the external parts of the specimens, where precipitation of CaCO_3 crystals clearly dominates. However, the results for the internal parts do not align with their observations. Barría et al. note that the internal sections of specimens carbonated for 60 days show a reduction in porosity due to the dissolution of cement hydration products and the precipitation of CaCO_3 crystals. In contrast, the findings for the internal parts in this study differ, which may be attributed to differing criteria used to define the 'internal part' in each study.

To understand the differences in behaviour between CS0044C60INT and CS0060C60INT with respect to CS0044C00 and CS0060C00, respectively, it is interesting to note that carbonation reaction advances more rapidly in the paste with a w/s ratio of 0.60 than with a w/s ratio of 0.44 [44, 45, 101, 102]. This can be seen in Figure 4.2.3, which shows the cross-section of cylindrical cement specimens before and after carbonation.

The specimens were treated with phenolphthalein, a pH indicator that changes colour based on the alkalinity of the material. The purple colour appears when the pH is above

approximately 9.0, indicating the presence of $\text{Ca}(\text{OH})_2$ in the cement paste. Below this pH threshold, carbonation has likely occurred, resulting in the dissolution of the $\text{Ca}(\text{OH})_2$ and the loss of the purple colour due to the lower alkalinity. In paste CS0044C60, a subtle border lacking the characteristic purple colour was observed, suggesting that a minimal carbonation front with a lower pH was present in this sample. In contrast, paste CS0060C60 has a more pronounced border with low pH (not purple). This higher carbonation advance could explain why the porosities in CS0060C00 and CS0060C60INT are nearly the same. As mentioned earlier in this section, CS0060C60INT represents a condition where neither the dissolution nor the precipitation predominates. Instead, both processes are occurring simultaneously, resulting in similar porosity values between CS0060C00 and CS0060C60INT. This indicates that, only for these very particular specimen and carbonation conditions, the porosity remains almost unchanged due to the balance between dissolution and precipitation processes.

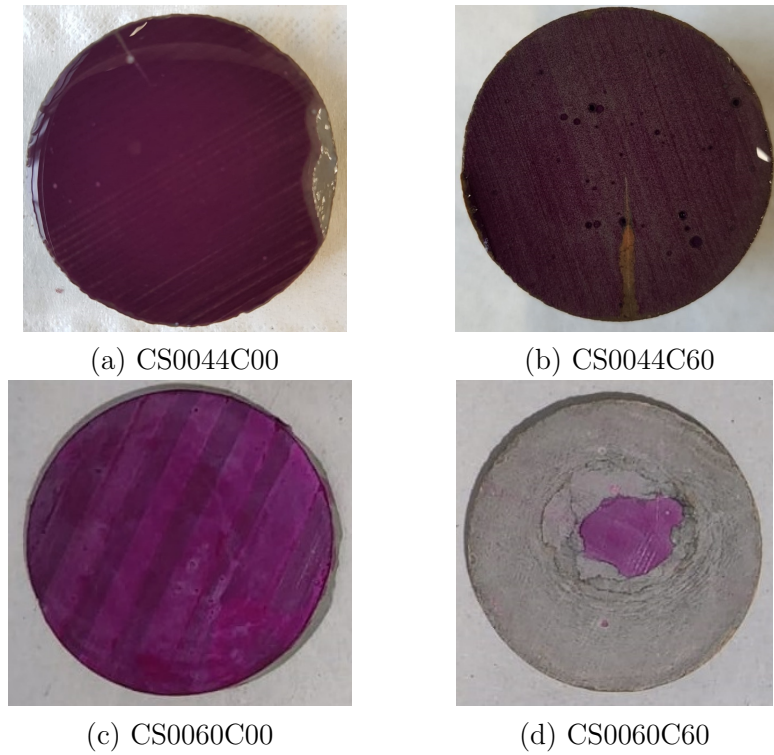
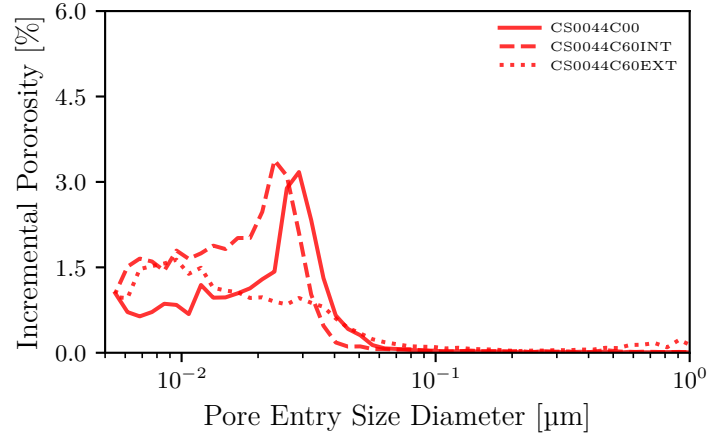


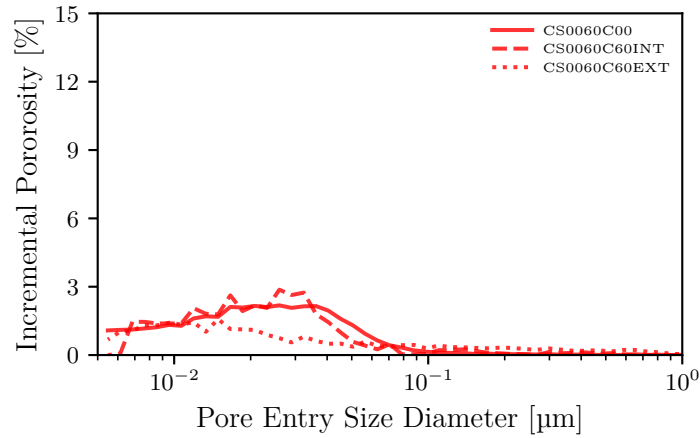
Figure 4.2.3: Cross-section of cement specimens with different w/s ratios before and after exposure to scCO_2 for 60 days treated with a pH indicator

Figure 4.2.4 shows the pore entry size distribution as obtained from the MIP tests on non-carbonated (CS0044C00 and CS0060C00) and carbonated for 60 days cement pastes.

For the specimens carbonated for 60 days, two samples were tested, one from the internal part of the specimens (CS0044C60INT and CS0060C60INT) and one from the external part of the specimens (CS0044C60EXT and CS0060C60EXT).



(a) w/s: 0.44



(b) w/s: 0.60

Figure 4.2.4: Pore entry size distribution of plain cement pastes, non-carbonated and after 60 days of carbonation

Comparing the non-carbonated samples with the external parts of the carbonated specimens, it is evident that there is a transition in the effects of carbonation. The transition goes from the least affected (non-carbonated), through the moderately affected (internal), to the most affected (external). As expected, the external parts of the specimens carbonated for 60 days, which are closest to the surface exposed to CO_2 , show the most

pronounced changes. In these external parts of the carbonated specimens, the peak in the pore size distribution, whether initially clearly defined or wider, has disappeared. The internal parts represent an intermediate case where the disappearance of the peak starts. For example, as shown in Figure 4.2.4a for the cement paste with a w/s ratio of 0.44, the peak in CS0044C00 shifts towards smaller pore entry sizes. A similar trend is seen in Figure 4.2.4b, although it is more difficult to distinguish due to the less pronounced peak.

In both cases, the peak, whether it was originally clearly defined or wider, disappeared. The pore entry size distribution for the most carbonated part of both specimens results in a wide distribution between $6 \times 10^{-3} \mu\text{m}$ and $6.5 \times 10^{-2} \mu\text{m}$. The disappearance of the peak could be related to the phenomenon shown in the research of Kuthcko [33] and confirmed in the research of Barria et al. [44] which shows that during $\text{Ca}(\text{OH})_2$ and CSH carbonation, the resulting CaCO_3 crystals precipitate in the larger pores, resulting in a reduction of the frequency of the largest pore sizes in the pore entry size distribution.

This aligns with the earlier discussion regarding the porosity in the external part of the cement paste specimens carbonated for 60 days. These external regions exhibited a reduction in porosity compared to the internal part, likely due to the predominance of CaCO_3 precipitation, which fills the larger pores and decreases overall porosity.

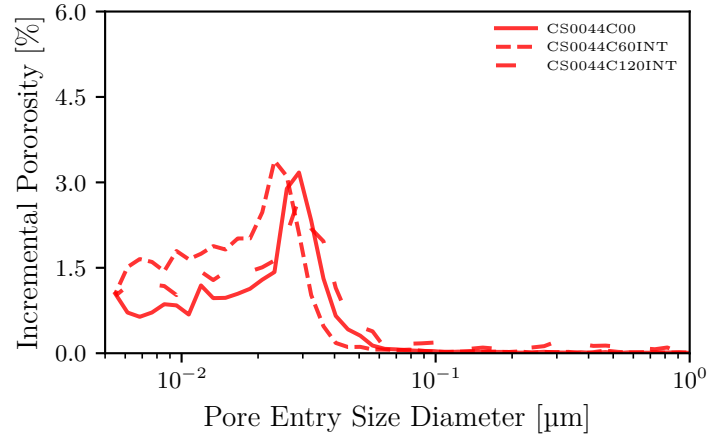
For CS0044C60EXT, a slight increase in the pore entry size distribution in the range of $6 \times 10^{-3} \mu\text{m}$ to $1.5 \times 10^{-2} \mu\text{m}$ pore entry size diameter can be observed. This increase likely reflects further changes in the pore structure compared to CS0044C60INT, due to the more extensive exposure of CS0044C60EXT to CO_2 . This exposure induces the precipitation of CaCO_3 crystals in the cement matrix pores, which may generate internal pressure and lead to cracks generation, as previously discussed in [103, 104]. However, this concept does not seem applicable to these samples.

Instead, the changes observed can be more straightforwardly explained by the chemical processes of dissolution of hydration products and the precipitation of CaCO_3 , combined with the effects on transport properties. As carbonation progresses, these processes modify the pore structure without necessarily leading to cracks generation.

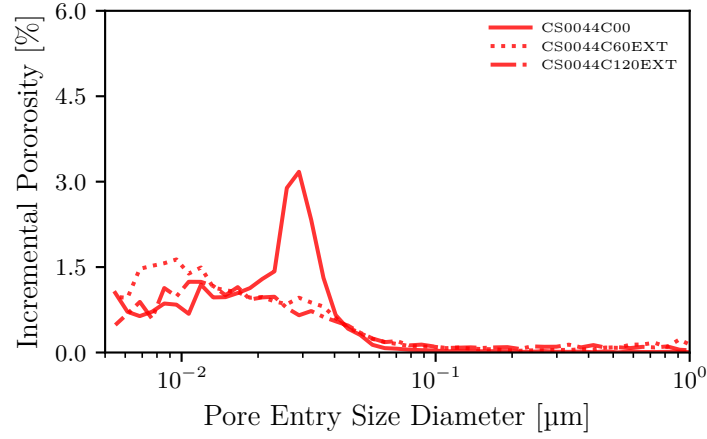
There exists differences between the non-carbonated and internal parts of the specimens carbonated for 60 days, but they are smaller than those observed in the external parts, as expected from the diffusive nature of carbonation [105, 106]. Both CS0044C60INT and CS0060C60INT show a shift in their peaks toward smaller pore entry sizes, particularly in CS0044C60INT, where an increase in pores smaller than $2 \times 10^{-2} \mu\text{m}$ is observed. This can be attributed to the dissolution of $\text{Ca}(\text{OH})_2$ and CSH and the subsequent precipitation of CaCO_3 .

The behaviour observed for specimens with a w/s ratio of 0.44 exposed to 60 days of carbonation can be confirmed by the pore entry size distributions obtained for specimens with the same w/s ratio exposed 120 days to carbonation, as shown in Figure 4.2.5. It can be appreciated that almost no change in the behaviour of the carbonated specimens occur when increasing the exposure time from 60 days to 120 days. For the results on the internal part of the specimen shown in Figure 4.2.5a, a slight decrease of the whole pore

entry size distribution can be noticed, while there also exists a slight offset of the main peak around $2.5 \times 10^{-2} \mu\text{m}$ (slighter than that between CS0044C00 and CS0044C60INT - Figure 4.2.4a). For the external part, a decrease in the pore entry size distribution is appreciated when transitioning from 60 to 120 days of carbonation for pore entry sizes smaller than $1 \times 10^{-2} \mu\text{m}$.



(a) CS0044C60INT and CS0044C120INT



(b) CS0044C60EXT and CS0044C120EXT

Figure 4.2.5: Pore entry size distribution of CS0044C00 after 60 and 120 days of carbonation

Figure 4.2.6 shows SEM images obtained from samples CS0044C60INT and CS0060C60INT. Comparing these images with those obtained for the corresponding non-carbonated samples in Figure 4.2.2, it is noticeable that exposure to scCO_2 results in a

much more disaggregated material. Furthermore, regardless of the w/s ratio, the relatively amorphous and compact structure of the cement paste is lost. CaCO_3 crystals can be seen in both images in Figure 4.2.6, although they are much more distinguishable in the CS0060C60INT sample.

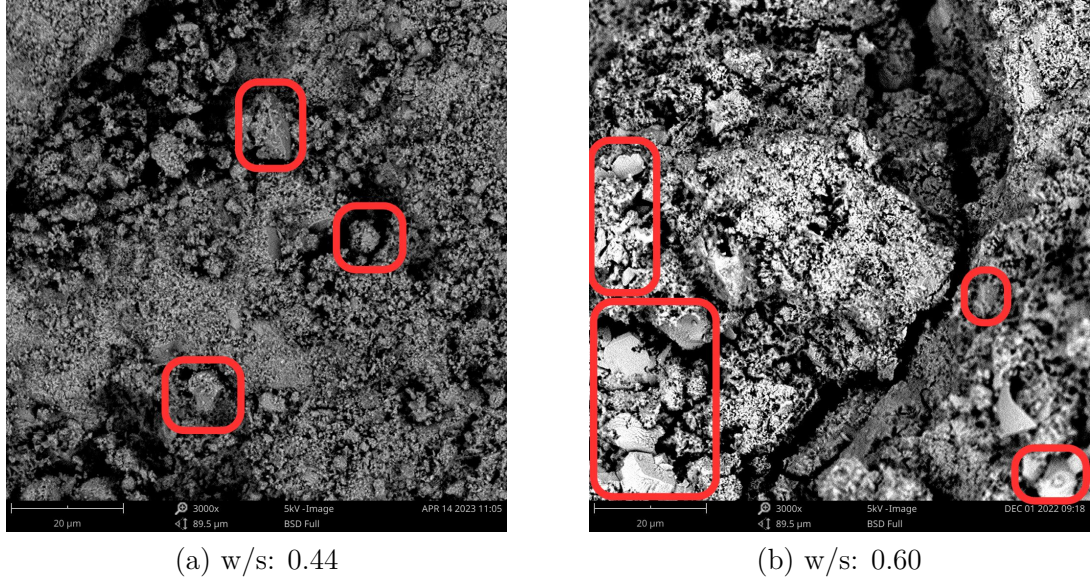


Figure 4.2.6: Scanning electron microscopy images of internal part of plain cement pastes after high pressure and high temperature carbonation for 60 days with highlighted CaCO_3 crystals

The precipitation of CaCO_3 crystals is clearly distinguishable in Figure 4.2.7a, which shows a SEM image of the external part of a specimen of cement paste CS0044C120. The identification of these crystals as CaCO_3 is based on similarities with previously reported crystal forms of vaterite, aragonite, and calcite [107, 108]. According to the work of Chang et al. [107], spherical shapes correspond to vaterite, cubic shapes to calcite, and elongated or 'rosette' shapes to aragonite. Additionally, needle-like structures can also be attributed to aragonite.

Furthermore, the cement paste shows a less defined matrix, with more visible loose particles compared to the corresponding non-carbonated cement specimens, suggesting a reduction in the presence of the continuous cement matrix. It is worth noting that this image exhibits a lower number of visible pores compared to Figure 4.2.2a, at the scale at which the images were captured. This may be related to the precipitation of CaCO_3 crystals within the pore space of the cement paste. The precipitation of these crystals in cement pastes with limited porosity will lead to pore filling.

Microstructural alterations are evident in Figure 4.2.7b, which shows the external part

of cement paste CS0060C60. However, the CaCO_3 crystals are not easily distinguishable, and detecting changes in porosity through SEM images alone remains challenging.

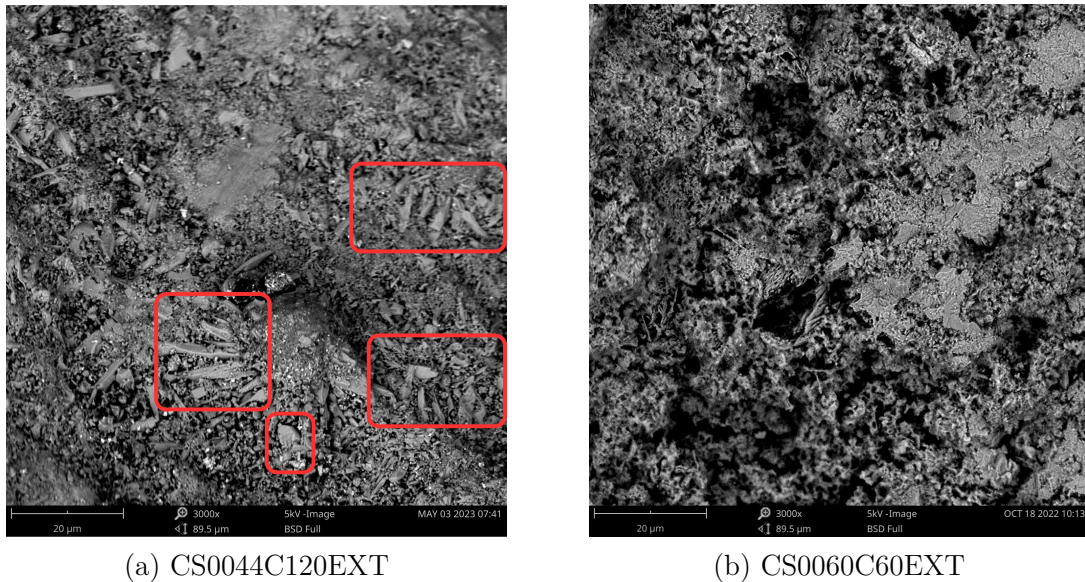


Figure 4.2.7: Scanning electron microscopy images of external part of plain cement pastes with two w/s ratios after carbonation, showing CaCO_3 precipitation

Given the results and discussions within this section, it is clear that the w/s ratio plays a crucial role in influencing the pore structure and durability of cement pastes. This highlights the importance of this parameter in understanding the material's long-term performance. Variations in the w/s ratio have a significant effect on the pore structure and therefore permeability. This, in turn, influences the carbonation mechanisms, primarily affecting the carbonation kinetics. For larger w/s ratios, enhanced carbonation kinetics can be attributed to increased porosity and permeability, which enhance the diffusion of CO_2 through the cement paste. This is consistent with the known correlation between diffusive properties and permeability, which influence the rate of carbonation, as further detailed in the works of Ghabezloo and Sulem [109] and Thiery et al. [110]. This supports the idea of a relationship between permeability and porosity and highlights the complex interplay of factors influencing the performance of class G cement pastes under scCO_2 injection well conditions.

4.3 Influence of HGMS

4.3.1 Effect on cement paste microstructure

In this section, the influence of HGMS on class G cement pastes for scCO₂ injection wells is analysed. As done in Section 4.2, the study initially focuses on the intrinsic differences in the microstructure due to the use of HGMS.

In this regard, Figure 4.3.1a shows the MIP results for CS0044C00, CS2744C00 and CS4144C00 specimens, showing mainly two important changes in the pore entry size distribution.

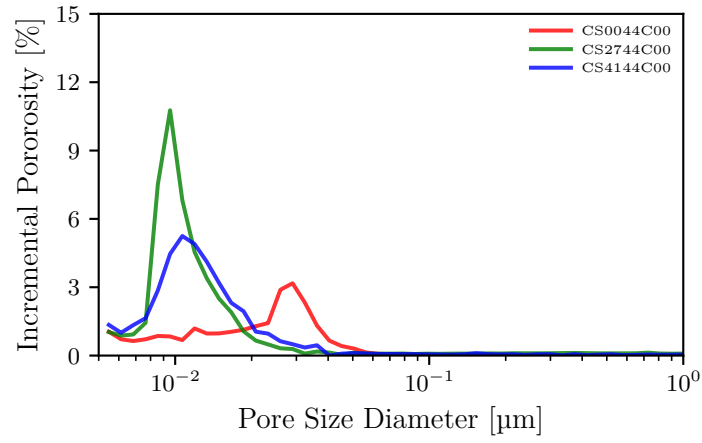
A first change is observed for pore entry sizes larger than 2×10^{-2} μm : cement pastes with HGMS present smaller entry pore sizes than CS0044C00. As discussed in Chapter 3, this effect on the cement matrix microstructure due to the cement replacement by HGMS is related to HGMS' pozzolanic activity and filler effect. A decrease in the porosity and a shift in the pore entry size distribution to smaller diameters is the expected behaviour for cement pastes modified with traditional pozzolanic and/or filler materials.

This phenomenon is confirmed in Figure 4.3.2 for cement pastes CS2744C00 and CS4144C00. This figure depicts a reduction in the pore volume of the cement matrix compared to the SEM image presented in Figure 4.2.2a.

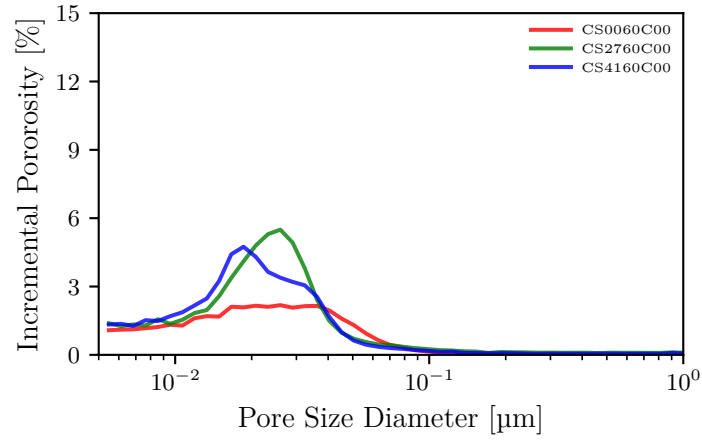
Furthermore, the location of the main peak obtained for each cement paste is also related to this first change. For CS0044C00, the main peak is around 3×10^{-2} μm , whereas for CS2744C00 and CS4144C00 it is around 1×10^{-2} μm . This indicates that the densification of the cement matrix due to the presence of both classes of HGMS (cf. Chapter 3) resulted in a similar shift of the pore size distribution for both cement pastes, in spite of their different properties.

At first sight, the aforementioned shift in the position of the main peak suggests that the most characteristic pore size of HGMS cement pastes is smaller than that of CS0044C00. However, this observation leads to what is referred to in this work as the second change in pore structure due to the use of HGMS. The second change corresponds to the difference in magnitude of the peak of those pore entry size distributions. In this regard, there are some comments that are worth mentioning related to the SEM images shown in Figure 4.3.2. This figure shows that the HGMS form a porous space within themselves. This is relevant because, even after the partial consumption of SiO₂ due to the pozzolanic reaction, the outer layer of HGMS remains recognizable. Therefore, this isolated porous space within the HGMS is not interconnected with the porosity of the cement matrix. This forms a occluded porosity that should not be measurable by the MIP technique.

From the above discussion, it can be argued that the increase in compactness of the cement matrix isolated the HGMS from the mercury, making it difficult for this fluid to find its way to reach them. In terms of pressure, this means that a higher pressure will be needed to let the mercury advance through the dense pore structure of the cement paste lightened with HGMS until the first contact between mercury and HGMS occurs.



(a) w/s: 0.44



(b) w/s: 0.60

Figure 4.3.1: Pore entry size distribution of cement pastes with and without cement replacement by HGMS, for two w/s ratios

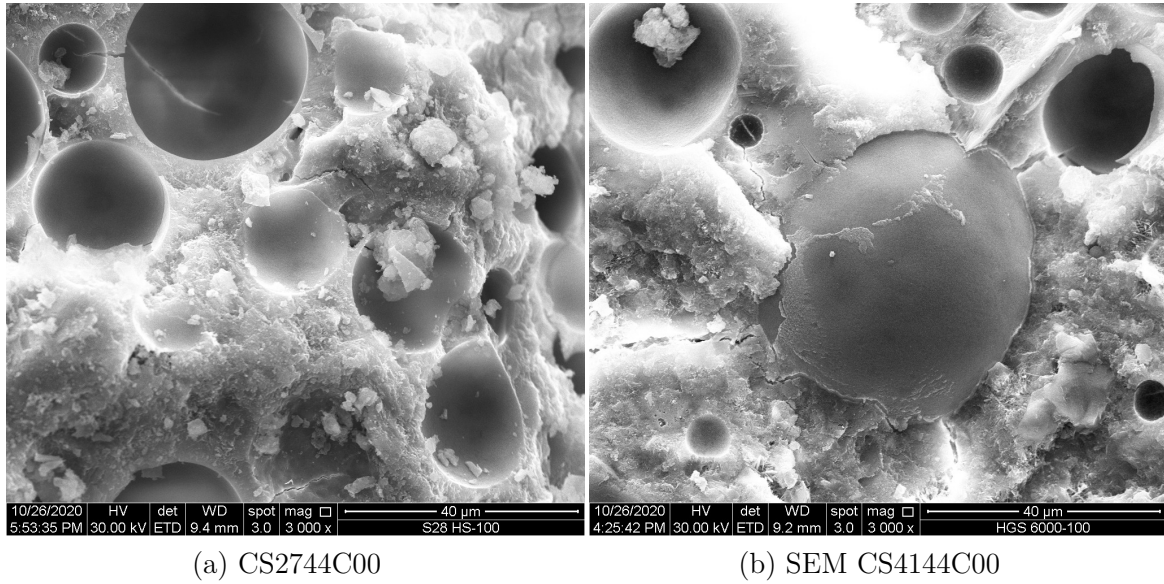


Figure 4.3.2: SEM images of cement pastes with a w/s ratio of 0.44 and partial cement replacement by HGMS

Figure 4.3.1a shows that the peaks for CS2744C00 and CS4144C00 both start at an entry pore size diameter of approximately $4 \times 10^{-2} \mu\text{m}$. According to Equation 2.3.3, this size corresponds to a mercury pressure of around 35 MPa. According to the manufacturer, both classes of HGMS present a crushing strength that is within the range of pressures achieved during mercury intrusion. Crushing strength is a common term used in the propants industry that refers to the ability to withstand high pressures without breaking down or fracturing during hydraulic fracturing operations [111]. According to the manufacturer, HGMS27 present a strength of 27 MPa with a minimum fractional survival of 80%, while HGMS41 yield a higher strength of 41 MPa with the same minimum fractional survival. Moreover, given the pozzolanic activity that HGMS were shown to present (cf. Chapter 3), one should expect a decrease in the thickness of their shell, resulting in a decrease in their strength.

Taking all of this into account, it can be argued that once the mercury comes into contact with HGMS, a pressure of 35 MPa is likely sufficient to break down the HGMS and enter the porosity they contained. As a result, an increase in incremental porosity corresponding to the vicinity of this pore entry size is expected, which is effectively observed. This hypothesis will be further developed and quantified later in this subsection, where a comparison between the porosity increment and the volume of HGMS in each cement paste will be presented to account for the effect of their rupture on the MIP results.

Similar results of pore entry size distributions were obtained by Hanif et al. [112] and Kabay et al. [113]. These authors show the refinement in the cement matrix pore structure,

followed by the rupture of the HGMS. Krakowiak et al. [114] also present results of MIP tests on cement pastes modified with HGMS. Their work states that at a pressure corresponding to the HGMS crushing strength, the mercury intrudes into the occluded porosity. It is argued that this could only be possible due to the rupture of the HGMS when its isostatic strength is reached during the mercury intrusion.

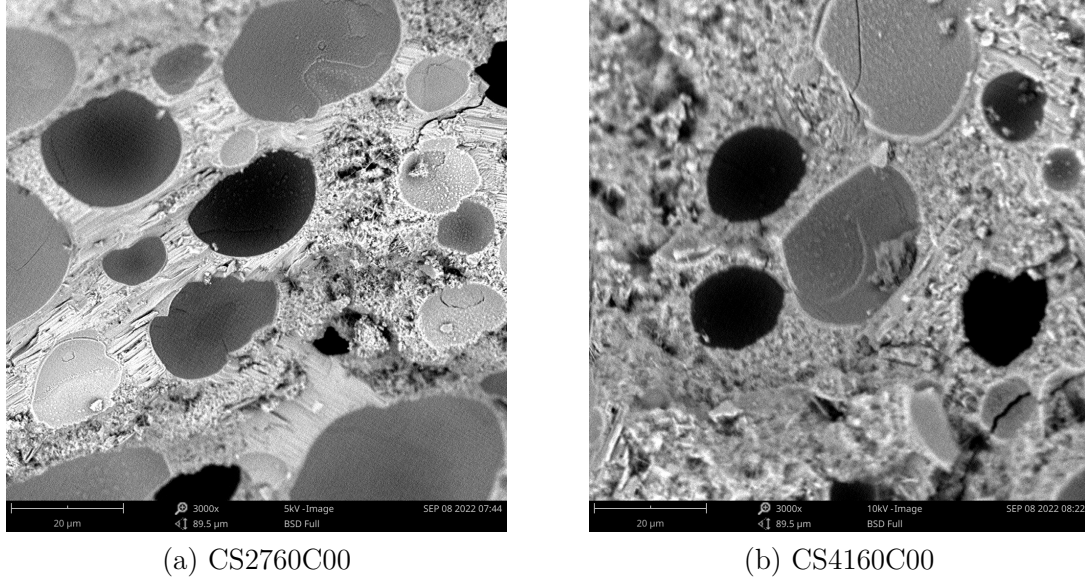


Figure 4.3.3: SEM images of cement pastes with a w/s ratio of 0.60 and partial cement replacement by HGMS

Let us now consider the effect of the w/s ratio coupled with the presence of HGMS of different classes. The differences in the results from Figures 4.3.1a and 4.3.1b can be analysed with this objective in mind. Recalling the discussion in Section 4.2, the peak in the pore entry size distribution of CS0060C00 is wider and less defined than the peak for CS0044C00. Also, the peak for CS0060C00 begins at around $7 \times 10^{-2} \mu\text{m}$, while for CS0044C00 it does at $3 \times 10^{-2} \mu\text{m}$.

In Figure 4.3.1, the coupled effect of the w/s ratio and the presence of HGMS can be appreciated. The increase in compactness on the cement matrix's pore structure due to the presence of HGMS exists regardless of the w/s ratio. As it happens in specimens with w/s ratios of 0.44, the pore size at which the peak starts in CS2760C00 and CS4160C00 is slightly shifted to smaller diameters when compared to CS0060C00. The reason is attributed to the increase in the compactness [2, 115] due to the presence of HGMS and is also shown in Figure 4.3.3. When comparing these figures with Figure 4.2.2b, a clear change in the microstructure of the cement paste is appreciated due to the presence of the HGMS. The microstructure of paste CS0060C00 shows higher porosity compared to pastes

CS2760C00 and CS4160C00. In pastes with HGMS and a w/s ratio of 0.60, the material becomes so compact that the expected increase in porosity due to the high w/s ratio is barely noticeable.

For both CS2760C00 and CS4160C00 the peaks begin at 5×10^{-2} μm of pore entry size which, according to Equation 2.3.3 corresponds approximately to a mercury pressure of 27 MPa. According to Krakowiak et al. [114], and confirmed by the results of Hanif et al. [112], and Kabay et al. [113], HGMS break during MIP tests once their strength is achieved. This observation is consistent with the appearance of peaks in the pore entry size distribution for cement pastes CS2760C00 and CS4160C00. The pressure of 27 MPa achieved likely exceeds the rupture strength of HGMS. The standalone MIP tests on HGMS powder detailed in Appendix A reveal rupture pressures of 15.9 MPa for HGMS27 and 34.4 MPa for HGMS41. Additionally, HGMS' pozzolanic activity (cf. Chapter 3) may weaken the borosilicate glass forming the outer shell of the HGMS. This weakening may reduce HGMS' strength, making it plausible that both, HGMS27 and HGMS41, break at around 27 MPa, which aligns with the observed peak in the pore entry size distributions.

Table 4.3.1: MIP porosity results on plain cement pastes and HGMS cement pastes with two w/s ratios

Paste	MIP porosity [%]
CS0044C00	28.5
CS2744C00	49.3
CS4144C00	42.1
CS0060C00	39.8
CS2760C00	62.6
CS4160C00	56.7

After discussing the impact of HGMS on the pore structure of the cement matrix at two w/s ratios, it is relevant to consider the effective porosity of the composite material. Preliminary results of porosity as obtained from the MIP tests are shown in Table 4.3.1.

It is expected that the porosity of the cement matrix would decrease both in quantity and pore size due to the presence of the filler/pozzolanic admixture. However, the preliminary porosity results indicate an increase in porosity of around 50% for cement pastes containing HGMS compared to cement pastes without HGMS.

These results can be explained by the rupture of the HGMS during the MIP test. Mercury intrudes into the voids within the HGMS once their crushing strength is reached. Therefore, the peaks observed in the cement pastes with HGMS are not only indicative of

the actual interconnected porosity of the cement matrix, but also (and possibly mainly) reflect the volume of broken HGMS particles.

Looking at the effect of HGMS on the pore structure and porosity of the cement matrix, it is clear that a thorough understanding of the true role of HGMS is essential. Porosity measurements of class G cement pastes containing HGMS will be affected if HGMS break. It is thus imperative to develop a method for the quantification of the interconnected porosity in these cement pastes that is independent of this particular effect.

One possible approach to determine the actual porosity of the cement matrix involves considering the effect of so-called ink-bottle pores. As a reminder, the MIP mainly consists of measuring the volume of mercury intruded to reach a given pressure. Also, given that each pressure is related not to an actual pore size but to an entry pore size according to Equation 2.3.3, the test provides a pore entry size distribution. This differs from the actual pore size distribution, as some pores may have entry diameters smaller than their actual diameters, as illustrated in Figure 4.3.4. The presence of larger pores inaccessible to mercury except through smaller ones leads to an overestimation of small pores and an underestimation of larger ones [72].

Many authors commonly link the differences between intrusion and extrusion curves in cementitious materials to the presence of ink-bottle pores [72]. However, the extrusion process is more complex, involving additional factors such as pore size interconnectivity and heterogeneities that complicate the ability of mercury to exit the pores [116].

During MIP tests, the HGMS present in the cement pastes appear to break, as their strength is exceeded. Therefore, a significant size difference between the large pores left behind by the broken HGMS and the smaller pores of the cement matrix results. This is supported by the HGMS' granulometry (Figure 2.1.2), the pore entry size distributions, SEM images of the cement pastes, and the increased compactness of the cement matrix with HGMS due to their filler effect and pozzolanic activity. Hence, the disparity in pore sizes may lead to the retention of mercury during the extrusion process, similar to what has been observed in the study of Wardlaw and McKellar [116].

The collapse of the thin outer shell of the HGMS during MIP tests would not significantly affect the size of the pore left behind when they break. Hence, the void space remains almost the same size as the HGMS. According to Equation 2.3.3, based on the HGMS' D50 (30 μm for HGMS27 and 40 μm for HGMS41), the pressure required to extrude mercury from within these pores is less than 0.05 MPa. However, the MIP machine used has a minimum extrusion pressure of 0.5 MPa, meaning it cannot fully extrude mercury from the interior of the HGMS. This explains the incomplete extrusion observed in the results.

For specimens containing HGMS, as shown in Figure 4.3.5, a significant gap between intrusion and extrusion curves is observed. This indicates that a considerable amount of mercury intruded during the intrusion phase does not withdraw during the extrusion phase. This phenomenon is likely due to the rupture of HGMS, which creates large voids in the cement matrix. While this phenomenon is more pronounced in cement pastes with HGMS, it is also observed to a lesser extent in plain cement pastes in Figure 4.3.6.

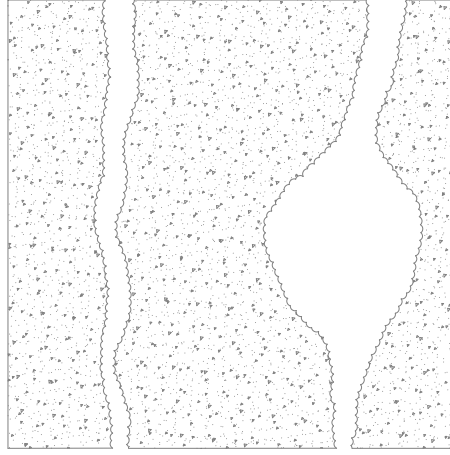
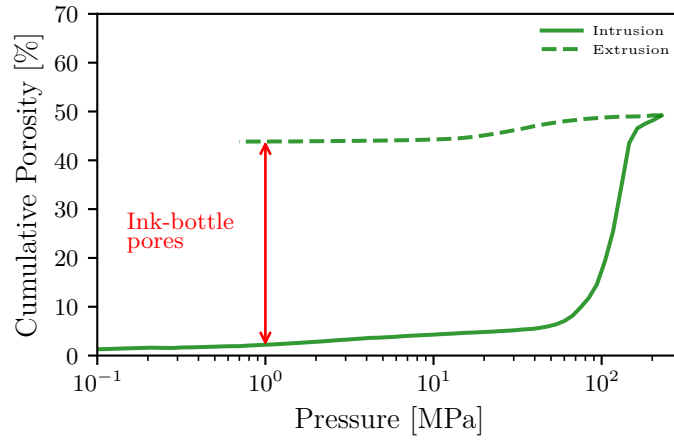


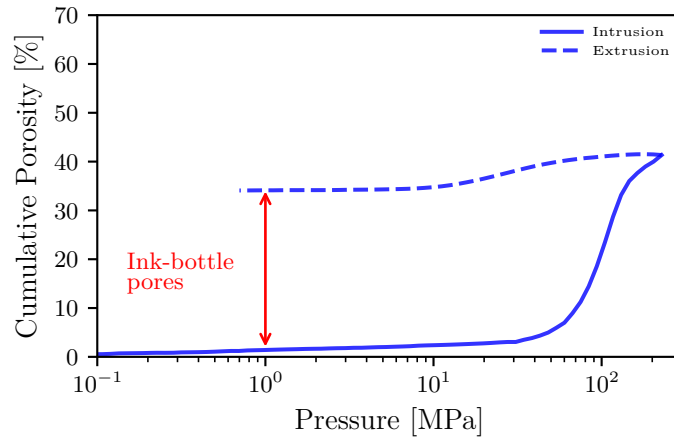
Figure 4.3.4: Cylindrical shaped pores (left) vs ink-bottle pores (right)

It is possible to consider the ink-bottle pores as those pores exclusively related to broken HGMS within the cement matrix [72]. By subtracting the volume of these ink-bottle pores measured as the volume shown in Figure 4.3.5 from the total porosity, the actual interconnected porosity of the cement matrix could possibly be obtained. However, it should be noticed that CS0044C00 and CS0060C00 also present some amount of ink-bottle pores related to the non-cylindrical shaped pores of the cement matrix [72, 117], which can be appreciated in Figure 4.3.6. Moreover, it was already argued that HGMS affect the microstructure of the cement matrix because of their filler effect, the pozzolanic reactions they induce, and the consequent influence in compactness. These changes likely reduce the total volume of larger pores. As a result, the proportion and distribution of ink-bottle pores in cement pastes with HGMS could differ significantly compared to pastes without HGMS. This change in pore structure may be similar to observations made with ground granulated blast furnace slag (BFG), as shown by Zhang et al. [117].

The study of Zhang et al. [117] reveals that BFG induces an augmentation in the volume of ink-bottle pores for short curing times, which goes up to 4%. This phenomenon is linked to the ongoing formation of hydration products, which reduces the connectivity of pores in certain areas. As a result, the decrease in local porosity can lead to the formation of new ink-bottle pores, increasing their overall volume. Nevertheless, the ink-bottle cumulative porosity of BFG cement pastes tends to a value similar to that presented by plain cement pastes, as the curing time increases. Particularly, for 100 days of curing time, the difference between plain and modified with BFG cement pastes results lower than 2%, making it almost negligible.



(a) CS2744C00



(b) CS4144C00

Figure 4.3.5: Intrusion and extrusion stages for cement pastes with HGMS

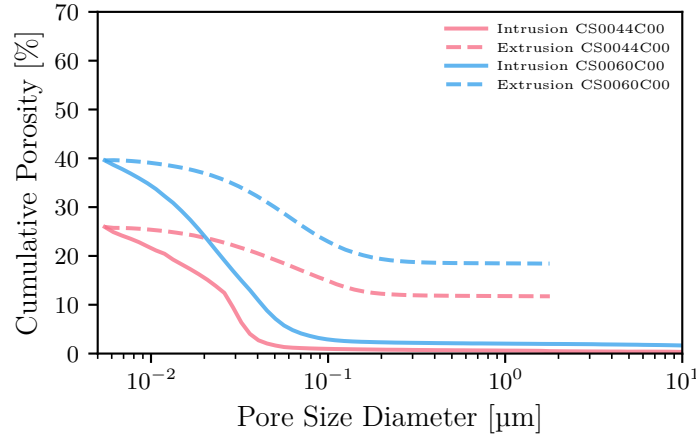


Figure 4.3.6: Intrusion and extrusion stages for CS0044C00 and CS0060C00

Zhang et al. [117] showed that the difference in ink-bottle pores between cement pastes with and without BFG is minimal. Hence, assuming that HGMS behave similarly, a simple approach to correct the porosity can be applied. This involves subtracting the volume of ink-bottle pores from the total porosity of each specimen. The corrected porosity is then obtained using Equation 4.3.1, where ϕ_{MIP} corresponds to the porosity obtained directly from the MIP tests, and $\phi_{InkBottlePores}$ represents the ink-bottle pores calculated as the difference between the extrusion and intrusion curves at the lowest pressure during the extrusion stage.

$$\phi_{CorrectedPorosity} = \phi_{MIP} - \phi_{InkBottlePores} \quad (4.3.1)$$

This method may slightly overestimate the actual interconnected porosity of specimens with HGMS because it does not account for potential differences in ink-bottle porosity between cement pastes. By subtracting the total ink-bottle porosity, the correction assumes that all ink-bottle pores are caused by the HGMS. However, if the cement matrix in the HGMS paste has a significantly higher volume of ink-bottle pores than the plain cement paste, this approach would incorrectly attribute the excess ink-bottle porosity to the HGMS alone, leading to an inaccurate correction. Nevertheless, this result is useful for the sake of comparing the interconnected porosity in the specimens with and without HGMS.

Another possible method to obtain a corrected porosity of specimens with partial cement replacement with HGMS without making the previous assumption consist of subtracting some amount of pore volume, which should be related to the volume of HGMS added to the specimen. Since the dosages (Table 2.2.1) and the HGMS density are defined, it is possible to know the volume fraction of HGMS, f_{HGMS} , used in each cement paste. Moreover, it is also possible to obtain the volume fraction of each phase from which HGMS are composed, meaning outer layer of borosilicate glass and inner void space. For this

calculation, it is assumed that the shell thickness of HGMS is not severely affected by the pozzolanic reactions.

The volume fraction of HGMS shell, f_{shell} , and that of HGMS inner void space, f_{void} , can be evaluated by knowing the HGMS internal and external radii as shown in Equation 4.3.2.

$$f_{\text{void}} = \left(\frac{r_1}{r_2}\right)^3 f_{\text{HGMS}} \quad ; \quad f_{\text{shell}} = \left[1 - \left(\frac{r_1}{r_2}\right)^3\right] f_{\text{HGMS}} \quad (4.3.2)$$

where r_1 and r_2 are the inner and outer radii of HGMS, respectively, from which r_2 could be deduced from the D50 of the HGMS and r_1 can thus be obtained from the density of the HGMS ($\rho_{\text{HGMS27}} = 0.28 \text{ g/cm}^3$ and $\rho_{\text{HGMS41}} = 0.46 \text{ g/cm}^3$) and the density of the borosilicate glass ($\rho_{\text{glass}} = 2.23 \text{ g/cm}^3$) as expressed in Equation 4.3.3.

$$r_1 = r_2 \left[1 - \frac{\rho_{\text{HGMS}}}{\rho_{\text{glass}}}\right]^{1/3} \quad (4.3.3)$$

For each cement specimen with HGMS, the volume fraction f_{void} can be subtracted from the MIP porosity to obtain a corrected porosity, assuming that this internal void volume corresponds entirely to the non-interconnected porosity of the cement paste with HGMS. Though this is a more straightforward method for obtaining the actual interconnected porosity of the cement matrix of specimens with HGMS, it shall be noticed that there are also some simplifications considered in this method. To begin with, it is assumed that the pozzolanic reaction was not enough to severely affect the size and shape of the HGMS so that both Equations 4.3.2 and 4.3.3 are valid. Also, if the total volume fraction f_{void} is to be subtracted from the MIP porosity results, it means both that the mercury was able to reach every HGMS within the cement matrix and that all of them resulted broken after this. Though it is not possible to know if the mercury actually got in contact with every HGMS, it is indeed possible to estimate the HGMS fraction that will reach its strength and break.

To address this issue, a method must be developed to estimate the proportion of HGMS that will reach their maximum strength and break under mercury pressure. In this regard, the research of Loubrieu et al. [118] investigates the strength of HGMS under hydrostatic loading. With a fluid, they applied hydrostatic pressure and measured the mechanical response of the admixture. For pressures up to 0.7 MPa, a linear response was observed, attributed to the elastic strain of the HGMS used in that research. For higher hydrostatic pressure, the rate of volume loss increased significantly, indicating the collapse of the HGMS induced by mechanical loading.

Therefore, a similar test using the MIP equipment was carried out on specimens containing only HGMS (in powder state). The detailed results and discussions of these tests are presented in Appendix A. The results indicate that HGMS rupture begins at fluid pressures of 6.51 MPa for HGMS27 and 17.77 MPa for HGMS41. Also, the main rupture

of HGMS occurs at 15.9 MPa for HGMS27 and 34.4 MPa for HGMS41. Both values support the previous discussions on HGMS rupture during MIP tests in cement specimens. The peak in the pore entry size distribution starts around 35 MPa for CS2744C00 and CS4144C00 (Figure 4.3.1a), and around 27 MPa for CS2760C00 and CS4160C00 (Figure 4.3.1b), both exceeding the initial rupture pressure of the HGMS from MIP tests on HGMS27 and HGMS41 samples.

In addition, it is confirmed in the Appendix A that not all HGMS break during the MIP test on HGMS alone, even at 230 MPa (the maximum pressure reached in all tests). This implies that the occluded pore volume fraction provided to the cement paste by HGMS, f_{void} , may not be fully accessible to mercury. To address this, a ratio between the volume intruded during MIP tests on each class of HGMS and the expected volume was calculated. This yielded 0.879 and 0.967 for HGMS27 and HGMS41, respectively.

The partial rupture of HGMS during MIP tests leads to an overestimation of the interconnected porosity. This experimental artifact results in the measurement of additional porosity due to the broken HGMS. Therefore, it is crucial to adjust the measured porosity to account for the volume that is attributable to the rupture of the HGMS. By doing so, a more accurate representation of the actual interconnected porosity in cement pastes with HGMS can be achieved.

Assuming that the mercury reached all the HGMS present in the cement pastes, it can be estimated that 87.9% of the total volume fraction f_{void} for HGMS27 and 96.7% of the total volume fraction f_{void} for HGMS41 could be subtracted from the MIP porosity measured for CS2744C00, CS2760C00, CS4144C00 and CS4160C00. The purpose of this adjustment is to obtain their true porosity.

The porosity results for non-carbonated cement specimens are presented in Table 4.3.2, including data from raw MIP measurements, ink-bottle pores correction, and HGMS volume fraction correction. These results allow for a comparison of the two distinct approaches used to address the impact of HGMS rupture and ink-bottle pores on porosity measurements. To begin with, it can be appreciated that the porosity obtained from the correction related to the volume fraction f_{void} called 'HGMS's void volume fraction correction' yields negative porosity results for the cement pastes with HGMS. These results do not have any physical sense on their own, but considering the calculus made to obtain it, it could be argued that the calculated volume fraction of inner void space of HGMS in the cement specimens is overestimated. This can only be explained by the fact that not all the HGMS within the cement specimens were accessible to the mercury. Moreover, it can be seen that the corrected values for cement pastes with a w/s ratio of 0.44 are more negative than for pastes with a w/s ratio of 0.60. The higher compactness of pastes with lower w/s ratios could possibly make it harder for the mercury to reach the HGMS than in pastes with higher w/s ratios. Then, the overestimation of the f_{void} is greater for a w/s ratio of 0.44 than for a w/s ratio of 0.60, and the corrected porosity results more negative.

Given the problem aroused from the method 'HGMS's void volume fraction correction', this research will focus and consider as valid the method of the 'Ink-bottle pores correction'.

It should be noted that the hypothesis underlying this application is that the ink-bottle pores in the cement matrix are assumed to be similar, or at least not significantly different, for pastes with the same w/s ratio, regardless of the presence of different classes of HGMS.

Table 4.3.2: MIP porosity and corrected porosity results of non-carbonated cement pastes with and without HGMS with two w/s ratios

Paste	MIP [%]	Ink-bottle pores correction [%]	HGMS's void volume fraction correction [%]
CS0044C00	28.5	16.3	28.5
CS2744C00	49.3	7.0	-11.1
CS4144C00	42.1	9.3	-32.4
CS0060C00	39.8	22.7	39.8
CS2760C00	62.6	17.8	-1.5
CS4160C00	56.7	20.9	-20.9

The lowest porosity as obtained from the raw data of the MIP tests and shown in Table 4.3.2 is related for each w/s ratio to the plain cement pastes, followed by cement pastes with HGMS41 and HGMS27, respectively. This has a relationship with the aforementioned rupture of HGMS during this test. Particularly, it should be noticed from Section 2.1 that HGMS27 are lighter than HGMS41 and also that both HGMS were added as 10% of cement weight replacement. This implies that cement pastes with HGMS27 had a larger volume of HGMS than cement pastes with HGMS41. Therefore, a larger volume of HGMS will be intruded by the mercury during MIP tests on cement pastes with HGMS27 than on those with HGMS41 which yields, as shown in the results, to higher porosity for specimens with HGMS27 than for those with HGMS41.

Table 4.3.2 shows interesting results for the porosity as obtained after the ink-bottle pores correction. To begin with, it is noticeable that plain cement pastes CS0044C00 and CS0060C00 both show a relative decrease in porosity of 43%, which indicates that there is no change in the proportion of the ink-bottle pores between cement pastes with different w/s ratios. Inspecting the influence of the presence of HGMS, it appears that cement pastes with HGMS27 yield the lowest porosity values for each w/s ratio, followed by cement pastes with HGMS41 and then plain cement pastes. These results are in agreement with the increase in compactness of cement pastes with HGMS, which is more noticeable for HGMS27 than for HGMS41 due to the larger specific surface of the former.

4.3.2 Effect on cement carbonation

After studying the effects of two classes of HGMS on the pore structure of class G cement pastes, it is crucial to understand how these changes affect cement pastes under scCO_2 injection well conditions. Connecting the dots between HGMS induced pore changes and their influence on supercritical carbonation provides a deeper understanding of how HGMS, pore structure, and carbonation interact in this context.

This analysis begins with Table 4.3.3, which presents a summary of all the MIP porosities, corrected porosities, and ink-bottle pores for each cement paste studied in this work. This includes cement pastes with HGMS27 and HGMS41, cement pastes with a w/s ratio of 0.44 and 0.60, and carbonated cement pastes both external and internal parts of the cylindrical specimens.

Based on the results presented in Table 4.3.3, as discussed in Section 4.2 of this chapter, the MIP porosity for non-carbonated cement pastes without HGMS (CS0044C00 and CS0060C00) is less than or equal to the porosity obtained for the same cement paste taken from the internal parts of specimens carbonated for 60 days. In addition, a decrease in MIP porosity can be observed when comparing CS0044C60INT with CS0044C60EXT and CS0060C60INT with CS0060C60EXT. A similar behaviour to that of cement pastes with a w/s ratio of 0.60 carbonated for 60 days is observed for cement pastes with a w/s ratio of 0.44 carbonated for 120 days. This trend is also observed in the corrected porosity values after applying the ink-bottle pores correction.

Cement pastes with HGMS and a w/s ratio of 0.44 show a similar trend to those without HGMS. However, this trend is less pronounced, as shown by the similar porosity values (both MIP and corrected) between CS4144C60INT and CS4144C60EXT. Furthermore, while the MIP porosity of CS2744C60INT is lower than that of CS2744C60EXT, the corrected porosity values show a less pronounced difference.

For cement pastes with HGMS and a w/s ratio of 0.60, the relationship between the non-carbonated specimens and the internal part of the specimens carbonated for 60 days differs for MIP porosity and ink-bottle corrected porosity. For MIP porosity, the non-carbonated specimens have higher porosity than the internal part, while ink-bottle corrected porosities show the opposite trend. However, in both cases, the internal part has a higher porosity than the external part of the specimens carbonated for 60 days.

Table 4.3.3: MIP porosity and corrected porosity results before and after carbonation of 60 days of cement pastes with and without HGMS with two w/s ratios, including 120-day carbonation results for cement pastes with a w/s ratio of 0.44

Paste	MIP porosity [%]	Corrected porosity [%]	Ink-bottle pores [%]
CS0044C00	28.5	16.3	12.2
CS0044C60INT	35.9	23.5	12.4
CS0044C60EXT	31.7	21.0	10.7
CS0044C120INT	32.5	19.5	13.0
CS0044C120EXT	20.3	13.4	6.9
CS2744C00	49.3	7.0	42.3
CS2744C60INT	33.1	15.1	18.0
CS2744C60EXT	43.7	20.5	23.2
CS2744C120INT	46.2	21.3	24.9
CS2744C120EXT	38.2	15.8	22.4
CS4144C00	42.1	9.3	32.8
CS4144C60INT	37.5	23.7	13.8
CS4144C60EXT	39.5	23.8	15.7
CS4144C120INT	34.0	18.5	15.5
CS4144C120EXT	35.2	19.8	15.4
CS0060C00	39.8	22.7	17.1
CS0060C60INT	40.4	26.6	13.8
CS0060C60EXT	29.0	20.1	8.9
CS2760C00	62.6	17.8	44.8
CS2760C60INT	53.2	29.4	23.8
CS2760C60EXT	42.2	17.5	24.7
CS4160C00	56.7	20.9	35.8
CS4160C60INT	39.2	22.5	16.7
CS4160C60EXT	35.9	18.5	17.4

For cement pastes carbonated for 120 days, the trends in porosity values reveal significant differences among the samples. For MIP porosity, the internal parts of the specimens carbonated for 120 days show comparable or even higher porosity compared to the non-carbonated samples, except for CS4144C120INT. In contrast, the external parts of the carbonated specimens display lower porosity values than their internal counterparts, except for CS4144C120EXT, which shows a roughly equal porosity than CS4144C120INT. In terms of ink-bottle corrected porosity, all samples show significantly lower values compared to their MIP counterparts. The internal parts of the carbonated specimens exhibit higher corrected porosity than the external parts for plain cement pastes and those with HGMS27. However, for cement pastes with HGMS41, the porosities on the internal and external parts of the carbonated for 120 days samples are nearly equal.

Table 4.3.3 also shows a notable change in the volume of ink-bottle pores after subjecting the cement specimens to scCO₂ conditions. This parameter seems suitable for measuring the progress of carbonation reactions within the cement specimens. The volume of ink-bottle pores remains relatively constant between CS0044C00 and CS0044C60INT, indicating that the pore structure of the CS0044C60INT samples is practically unaffected. However, the ink-bottle pore volume decreases by 1.7 points from CS0044C60EXT to CS0044C60INT, likely because the exposure to scCO₂ is more severe compared to CS0044C60INT. This reduction in the ink-bottle pores between external and internal parts is also observed in the pastes carbonated for 120 days.

For CS2744C00 and CS4144C00, the outcomes differ from those of CS0044C00. There is a significant reduction in ink-bottle pores from non-carbonated to carbonated specimens after 60 days, with a decrease of approximately 19 points for CS2744C00 and around 18 points for CS4144C00. Notably, the ink-bottle pore volume is greater in the external parts of the specimens carbonated for 60 days (i.e. CS2744C60EXT and CS4144C60EXT) compared to their internal counterparts (CS2744C60INT and CS4144C60INT). Additionally, the percentage of ink-bottle pores in the external parts of the specimens carbonated for 60 days (i.e. CS2744C60EXT and CS4144C60EXT) is equal to that of both the internal and external parts of the specimens carbonated for 120 days (i.e. CS2744C120INT, CS4144C120INT, CS2744C120EXT, and CS4144C120EXT). A similar trend is observed for cement pastes with a w/s ratio of 0.60 carbonated for 60 days, where the total ink-bottle pores are equal between the internal and external parts. This observation suggests that carbonation reactions advanced throughout the entire specimens during 120 days of scCO₂ exposure for cement pastes with HGMS and a w/s ratio of 0.44, and during 60 days of scCO₂ exposure for cement pastes with HGMS and a w/s ratio of 0.60.

The advancement of the carbonation reactions within the cement specimens also impacts their pore structure and the material properties. Following exposure, the cement matrix is expected to exhibit a coarser pore structure due to the consumption of cement hydration products. Also, CaCO₃ crystals are known to precipitate in the larger pores of the cement matrix [33, 44].

These two phenomena combined are shown to decrease the volume of ink-bottle pores.

On one hand, the consumption of cement hydration products increases the pore size of the smaller pores within the cement matrix. On the other hand, the precipitation of CaCO_3 crystals in the larger pores decreases their pore size.

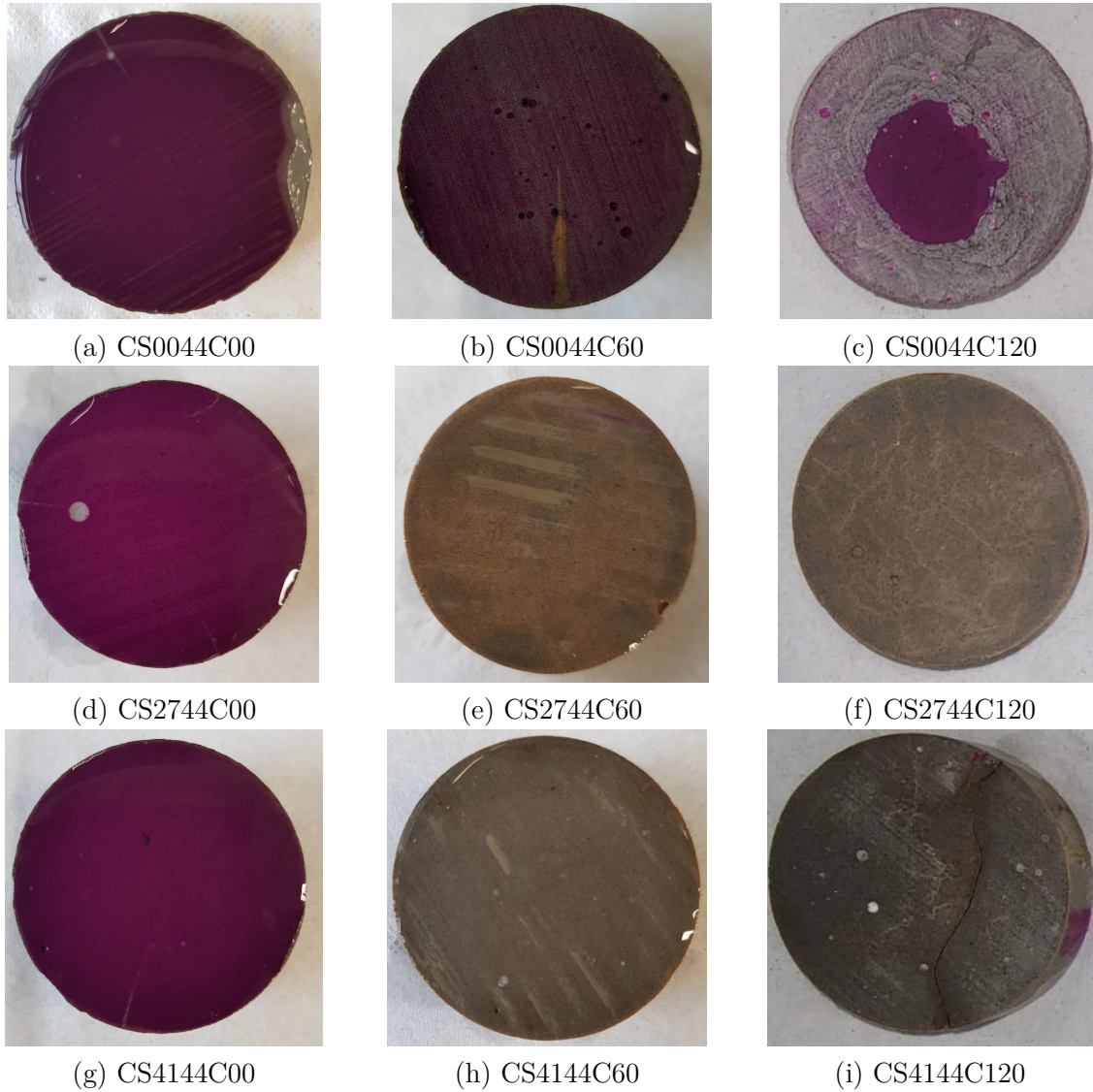


Figure 4.3.7: Cross-section of cement specimens with a w/s ratio of 0.44 before and after scCO_2 exposure for 60 and 120 days treated with a pH indicator

To gain further insights into the coupled influence of w/s ratios and HGMS on cement carbonation, Figures 4.3.7 and 4.3.8 display the cross-sections of each studied specimen

before and after 60 and 120 days of carbonation, with a phenolphthalein (pH indicator). As previously mentioned, carbonation consumes both $\text{Ca}(\text{OH})_2$ and CSH, making it possible to qualitatively assess the progress of the carbonation reaction by examining the pH of the cement paste specimen.

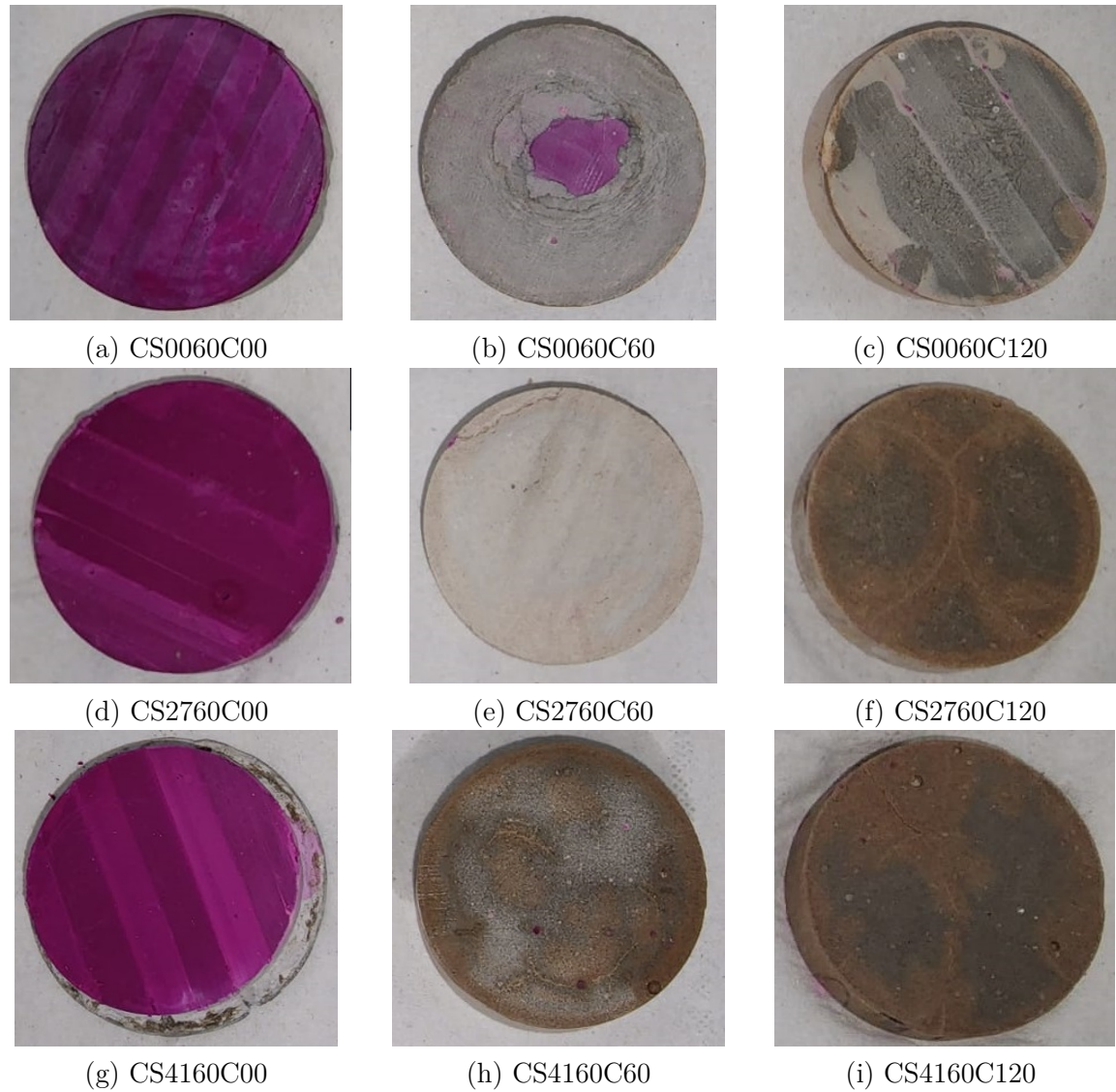


Figure 4.3.8: Cross-section of cement specimens with a w/s ratio of 0.60 before and after scCO_2 exposure for 60 and 120 days treated with a pH indicator

Figures 4.3.7 and 4.3.8 highlight the importance of studying both internal and ex-

ternal regions of cylindrical cement specimens subjected to the carbonation process. By examining variations in pH and pore structure across different regions of the specimens, a comprehensive understanding of the interplay between HGMS, pore morphology, and cement carbonation can be attained.

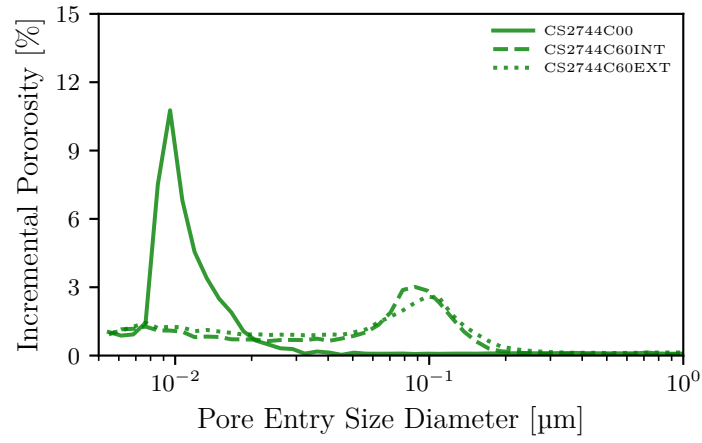
It is noteworthy that the pozzolanic reaction of HGMS consumes the $\text{Ca}(\text{OH})_2$, which could lead to a reduction of the pH of the cement matrix. However, regardless of the w/s ratio, cement pastes containing HGMS from both classes exhibit a consistent purple cross-section before carbonation. This suggests an even distribution of HGMS induced pH changes, with $\text{Ca}(\text{OH})_2$ content being high enough to maintain the pH above 9.

For cement specimens with a w/s ratio of 0.44, the presence of HGMS from both classes noticeably influences the carbonation progress within the specimen. While CS0044C60 shows minimal carbonation, with almost the entire cross-section appearing purple, CS2744C60 and CS4144C60 exhibit no indication of a pH exceeding 9. This discrepancy in carbonation progress at the specimen scale between specimens with and without HGMS underscores the importance of considering the specific characteristics of HGMS in cement paste formulations.

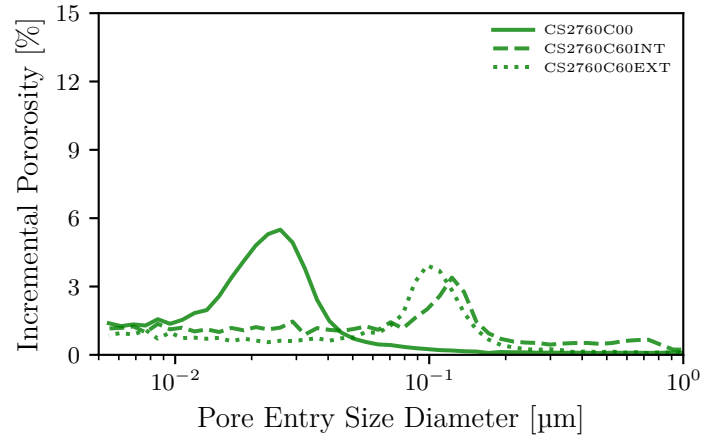
To understand the results for cement pastes with HGMS at different w/s ratios, several factors must be taken into account. The carbonation process involved high pressure and temperature conditions (20 MPa and 90 °C) in the presence of supercritical CO_2 and water. MIP tests on HGMS powder samples (cf. Appendix A) revealed that HGMS27 begin to break at a pressure of 15.9 MPa. This suggests that under the carbonation conditions considered in this study, the HGMS in cement pastes CS2744C00 and CS2760C00 break, leading to the transformation of their occluded porosity into interconnected porosity. Such a transformation alters the pore structure and may affect the transport properties of cement pastes containing HGMS27, thereby influencing the carbonation rate. In contrast, HGMS41 (CS4144C00 and CS4160C00) should not exhibit this behaviour, as they show a strength higher than 34 MPa. However, as discussed in Chapter 3, the outer shell of HGMS is partially consumed by pozzolanic activity, which likely decreases their crushing strength over time, resulting in similar behaviour between cement pastes with HGMS27 and those with HGMS41.

After 120 days of carbonation, CS0044C120 displays a significant advancement of the carbonation front, evidenced by a decrease in pH extending from the surface towards the core of the specimen. Conversely, CS2744C120 and CS4144C120 do not exhibit signs of elevated pH values, indicating a more uniform distribution of carbonation throughout the specimens.

Figures 4.3.9 and 4.3.10 show the pore entry size distribution obtained from MIP tests on cement pastes with HGMS27 and HGMS41 both before and after a carbonation stage of 60 days and with the two w/s ratios considered in this research. As done for the plain cement pastes in Subsection 4.2.2, internal and external parts of the cylindrical carbonated specimens were tested.

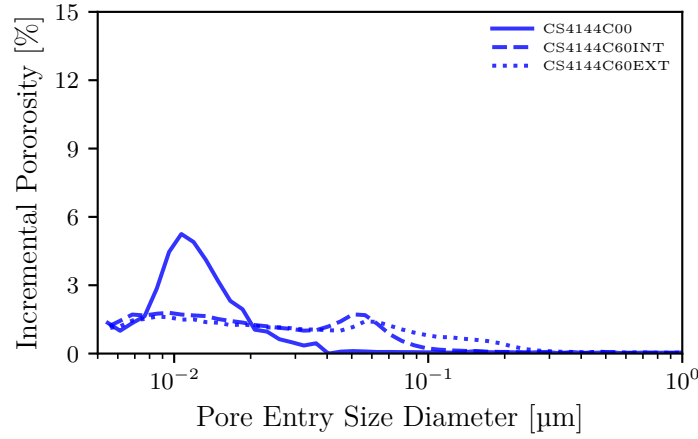


(a) w/s: 0.44

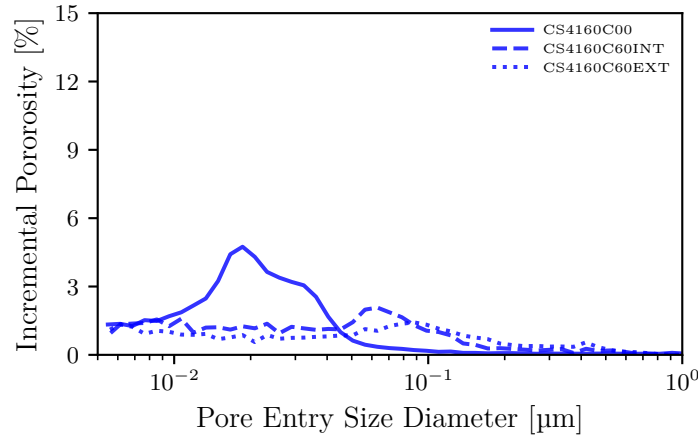


(b) w/s: 0.60

Figure 4.3.9: Pore entry size distribution of cement pastes with HGMS27 in non-carbonated state and after 60 days of carbonation



(a) w/s: 0.44



(b) w/s: 0.60

Figure 4.3.10: Pore entry size distribution of cement pastes with HGMS41 in non-carbonated state and after 60 days of carbonation

Some clear differences can be appreciated between the results before and after 60 days of carbonation for every specimen. It is noticeable that, differing from the results seen for plain cement pastes, the pore entry size distribution after carbonation of the internal and the external part of the specimens are almost the same or, at least, similar. This confirms the pH indicator results, which show a total dissolution of the $\text{Ca}(\text{OH})_2$ in HGMS cement pastes.

In every case, regardless of the class of HGMS and the w/s ratio, after carbonation the main peak significantly shifts to a larger pore entry size diameter. For cement pastes with

HGMS27 at both w/s ratios, the peak shifts to an approximate value of $1 \times 10^{-1} \mu\text{m}$, while for cement pastes with HGMS41 at both w/s ratios, the peak translates somewhere between $9 \times 10^{-2} \mu\text{m}$ and $5 \times 10^{-2} \mu\text{m}$. These peaks correspond to pressures of approximately 12 MPa for HGMS27 and between 14 and 25 MPa for HGMS41.

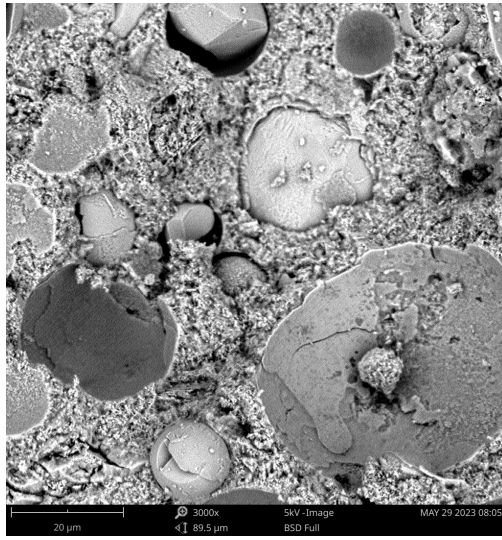
It is likely that these pressures reflect the rupture pressure of each class of HGMS after being partially consumed by pozzolanic activity. However, not all HGMS undergo rupture during this testing phase, as some had already broken during the carbonation process itself. Additionally, the degradation of the cement matrix now makes the HGMS more accessible for mercury intrusion, particularly in the broken ones.

At pressures beyond those previously mentioned, mercury begins to intrude into two distinct regions: first, into the remaining intact HGMS that survived the carbonation process, and second, into the interior of the HGMS that have already broken. In the latter case, access to these internal pores remains limited because many of these broken HGMS are not in direct contact with larger, interconnected pores, even after carbonation. This behaviour further influences the pore structure and contributes to the observed pore size distribution shifts.

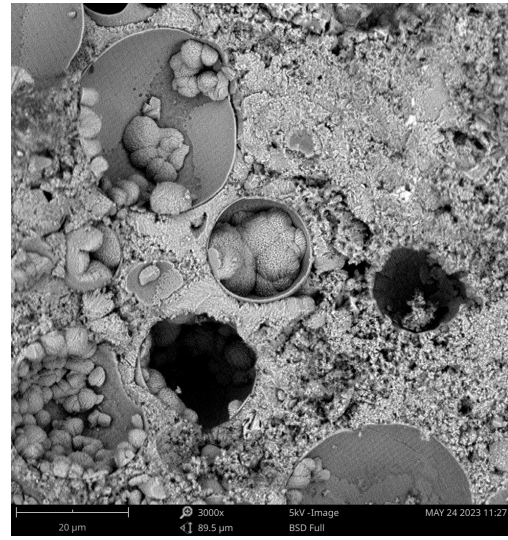
SEM images are shown in Figure 4.3.11 for cement pastes with a w/s ratio of 0.44 carbonated during 60 days, in Figure 4.3.12 for cement pastes with a w/s ratio of 0.60 carbonated during 60 days, and Figure 4.3.13 for the internal part of cement specimens with both w/s ratios carbonated for 120 days. These figures help understanding the mechanisms of degradation of lightweight cement pastes exposed to these conditions. It is initially noteworthy that in many of the presented SEM images the outer glass shell is still present, though HGMS present a decrease in the outer shell thickness due to the pozzolanic activity.

Then, the change in the microstructure really stands out. By comparing any of these images with those presented before carbonation in Figures 4.3.2 and 4.3.3, the degradation of the microstructure of the cement specimens with HGMS after carbonation (both 60 and 120 days) is noticeable. The material exhibits significant degradation of its microstructure, with a less prominent matrix contributing to an altered structural integrity.

It is interesting to note that some CaCO_3 crystals appear to have formed within the large voids of the HGMS. This observation confirms that during exposure to CO_2 , some HGMS broke, allowing carbonation products to precipitate within these large, accessible voids. These results are particularly noteworthy and support previous considerations regarding the supercritical carbonation process of cement paste [32, 119].



(a) CS2744C60INT



(b) CS2744C60EXT

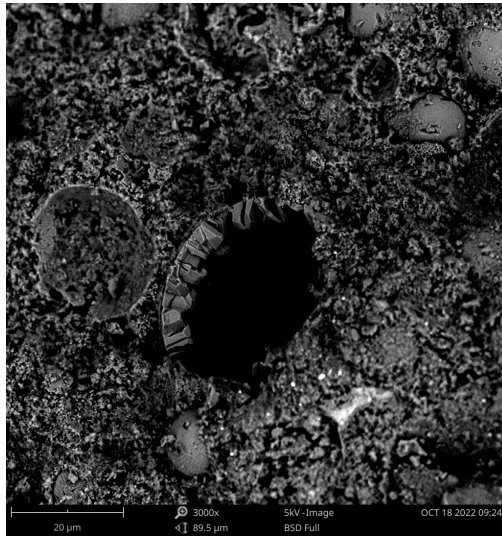


(c) CS4144C60INT

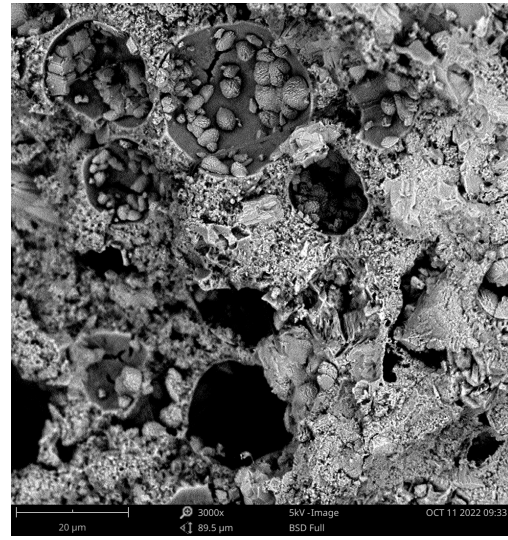


(d) CS4144C60EXT

Figure 4.3.11: SEM images of internal and external parts of cylindrical specimens with HGMS and w/s ratio of 0.44 after 60 days of carbonation



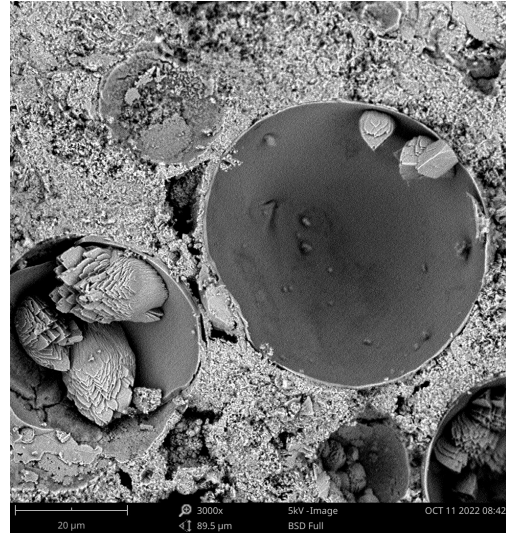
(a) CS2760C60INT



(b) CS2760C60EXT

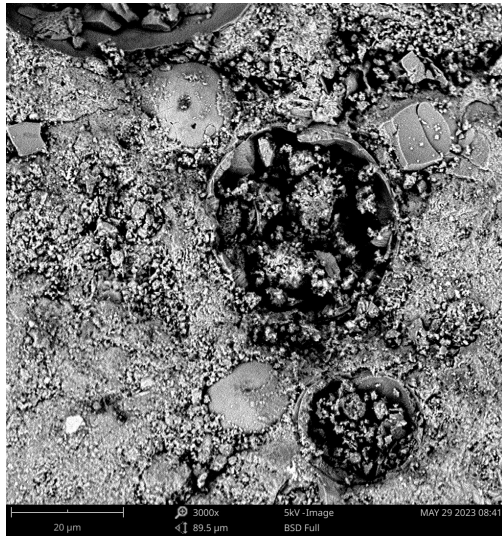


(c) CS4160C60INT

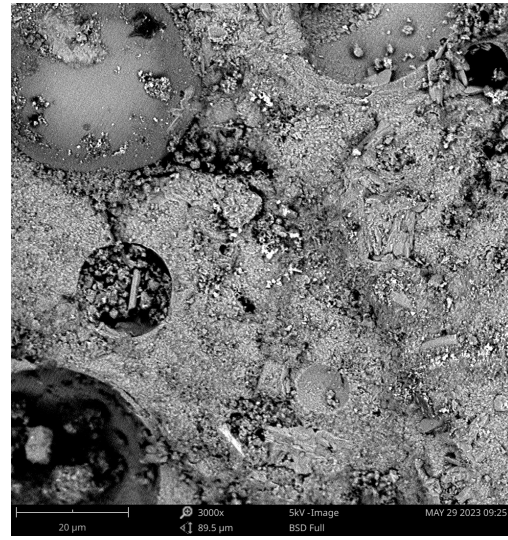


(d) CS4160C60EXT

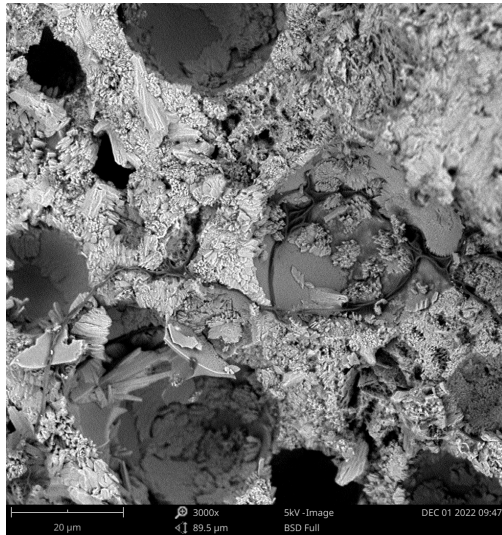
Figure 4.3.12: SEM images of internal and external parts of cylindrical specimens with HGMS and w/s ratio of 0.60 after 60 days of carbonation



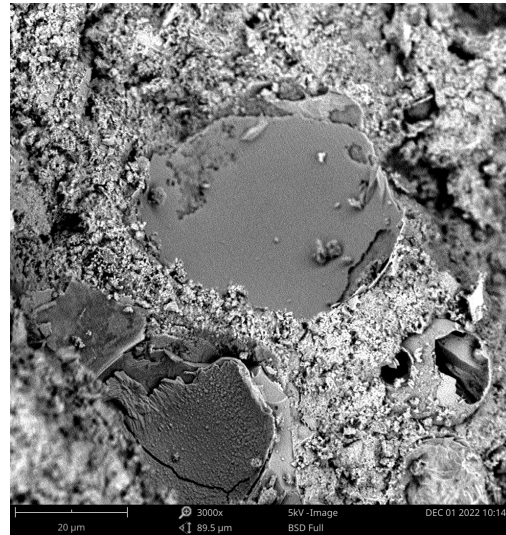
(a) CS2744C120INT



(b) CS4144C120INT



(c) CS2760C120INT



(d) CS4160C120INT

Figure 4.3.13: SEM images of internal parts of cement paste with HGMS and both w/s ratios cylindrical specimens after 120 days of carbonation

Overall, cement paste lightened with HGMS is affected similarly to cement pastes without HGMS. By disregarding the peaks of pore size distribution associated with this admixture in both non-carbonated and carbonated specimens, the trend observed in Figure 4.2.4 can also be noticed in Figures 4.3.9 and 4.3.10. Initially, there is a relatively well-defined peak (depending on the w/s ratio), which completely disappears after carbon-

ation, resulting in a relatively uniform pore size distribution. Additionally, it should be noted that the entire process of lightened cement paste carbonation depends on the properties of the HGMS used, particularly their chemical interaction with the cement paste and their crushing strength.

4.4 Conclusion

Variations in the microstructure of the class G cement pastes studied in this research have been analysed. In particular, the effects of w/s ratio, the presence of HGMS and supercritical carbonation were discussed. This was done on the basis of an exhaustive analysis of the results obtained from MIP tests, SEM observations and the carbonation progress measured qualitatively with phenolphthalein.

It is highlighted that, as expected, the w/s ratio and the presence of HGMS significantly affect the microstructure of the class G cement pastes. These factors influence the carbonation mechanisms when the cement pastes are exposed to scCO₂ injection well conditions.

In particular, the following conclusions can be derived from this chapter:

- The w/s ratio affects the porosity of class G cement pastes. Higher w/s ratios induce higher porosity.
- The w/s ratio also affects the pore structure of cement pastes. According to the MIP results, the lower the w/s ratio, the smaller the pore entry size and the more pronounced the peak of the pore entry size distribution. Similarly, the SEM images show the changes in the microstructure associated with the smaller space available in the cement paste with a w/s ratio of 0.44, resulting in a much more compact cement matrix.
- The pH indicator results indicate that carbonation of cement pastes at greater w/s ratios is accelerated during exposure to scCO₂. Under the specific pressure and temperature conditions of 20 MPa and 90 °C, the external parts of the carbonated specimens for both w/s ratios show predominant CaCO₃ crystal precipitation, which reduces the MIP porosity. For the internal parts of the carbonated specimens the behaviour varies slightly with the w/s ratio. Specimen CS0044C60INT shows mainly dissolution of cement hydration products (Ca(OH)₂ and CSH), while specimen CS0060C60INT shows combined dissolution and precipitation.
- Exposure to scCO₂ results in a reduction of the pore entry size independent of the w/s ratio. Specifically, for the external part of the carbonated specimens, the reduction is significant enough to cause the peak observed in the pore entry size distribution of the non-carbonated specimens to disappear.

- The pozzolanic activity and filler effect of HGMS causes the pore entry size distribution to shift towards smaller values. This indicates an increase in the compactness of the cement matrix, which can be verified from SEM images.
- HGMS initially confer occluded porosity to cement pastes. However, the results and discussion presented in this chapter are valuable in understanding their potential influence on the interconnected porosity of cement pastes under certain stress conditions. The pressures achieved during the MIP tests exceed the strength of the HGMS used. Therefore, as soon as the applied pressure reaches the strength of the HGMS, they break, resulting in an increase in the interconnected porosity, as indicated by the very sharp peak in the corresponding pore entry size distributions.
- Correction by measuring the ink-bottle pores made it possible to quantify the interconnected porosity of the cement matrix independently of the presence of HGMS. In this way, the reduction in the interconnected porosity of the cement matrix due to the use of HGMS could be assessed.
- The high pressure used to expose the cement specimens to scCO_2 injection well conditions produced a similar effect to that of the MIP test. During exposure, the HGMS broke. This led to an increase in interconnected porosity, which in turn favoured a more rapid advancement of carbonation along the HGMS cement specimens. The MIP results support this claim, as the pore entry size distribution in C60EXT and C60INT specimens are almost identical. The pH indicator yielded additional evidence, as it could be seen that the pH decreased throughout the whole specimen, indicating that the Ca(OH)_2 was completely consumed. The SEM images confirm this accelerated progress of carbonation, as even in the C60INT specimens CaCO_3 crystals could be observed.

Chapter 5

Mechanical properties

5.1 Introduction

The mechanical integrity of the cement paste is critical to ensure the stability of injection wells during CO₂ injection and subsequent storage. Various factors, such as the w/s ratio, the incorporation of HGMS, and exposure to CO₂ injection well conditions, can significantly influence the mechanical performance of cement pastes. As discussed in Chapter 1, the cement sheath must withstand the combined effects of high pressure, temperature, and chemical interactions within the storage site environment. These interactions, including carbonation, induce microstructural changes that directly affect mechanical properties.

The relationship between cement paste porosity and mechanical properties is well-established. Chapter 4 presented a detailed examination of how the w/s ratio and HGMS content influence the pore structure, with important implications for durability and mechanical response. Specifically, the inclusion of HGMS and their potential rupture under elevated pressures introduces a challenge, as their mechanical failure not only affects the structural integrity of the cement paste but also accelerates the carbonation process. These factors will be further explored in this chapter to understand how they contribute to the changes in mechanical performance of cement pastes under CO₂ injection well conditions.

This chapter is divided into three sections. The first section investigates the impact of the w/s ratio on the mechanical properties of cement pastes, with a focus on the relationship between porosity and strength. The second section examines the effect of HGMS incorporation on mechanical performance, emphasizing how the strength and volume fraction of different HGMS classes (HGMS27 and HGMS41) influence the results of UCS tests and drained triaxial compression tests. Finally, the third section discusses the role of supercritical carbonation in altering the mechanical behaviour of cement pastes, particularly through the rupture of HGMS and the resulting microstructural changes.

By examining the results of UCS tests, triaxial compression tests, and dynamic elastic properties, this chapter aims to characterize the mechanical behaviour in cement pastes.

The conclusions drawn from this analysis, together with those from Chapters 3 and 4, will provide a foundation for the homogenisation model developed in Chapter 6 and the finite element modelling in Chapter 7.

5.2 Impact of water to solid ratio

This section discusses the effects of the w/s ratio on the mechanical properties of class G plain cement pastes subjected to scCO₂ injection well conditions.

Following the structure established in Chapter 4, the discussion first focuses on the mechanical behaviour in the reference state, i.e. before carbonation. To this end, the results from ultrasonic wave velocity measurements are analysed to determine the dynamic Young moduli. These findings, along with data from UCS tests, and isotropic and triaxial compression tests, provide a comprehensive understanding of the effects of the w/s ratio on the mechanical behaviour of the cement pastes considered in this research.

This section then examines how exposition to scCO₂ affects the mechanical properties of class G plain cement pastes prepared at different w/s ratios. By analysing the results of ultrasonic wave velocity measurements, UCS, and triaxial tests, we gain insight into the mechanical performance and suitability of cement pastes with different w/s ratios for scCO₂ injection wells.

The dynamic Young moduli were calculated by measuring the transit speed of an ultrasonic pulse through the cylindrical cement specimens. The investigation results revealed notable changes in the p- and s-wave velocities due to variations in the w/s ratio. Specifically, for CS0044C00, V_p was measured at 3800 m/s and V_s was recorded at 2210 m/s. For CS0060C00, the corresponding values were found to be 3370 m/s for V_p and 1880 m/s for V_s . These results are consistent with the higher porosity obtained for CS0060C00 when compared to CS0044C00 (cf. Section 4.2).

In accordance with Equation 2.3.6, the bulk and shear moduli can be easily obtained by knowing the densities of each paste, which are 1.99 g/cm³ for CS044C00 and 1.80 g/cm³ for CS0060C00. Moreover, by applying Equation 2.3.7, the Young modulus and the Poisson coefficient can also be calculated. The elastic properties of the two cement pastes are summarised in Table 5.2.1. The decrease in the V_p and V_s velocities for the paste with a w/s ratio of 0.60 corresponds to a decrease of K, G and E ranging from 23% to 34% depending on the parameter, while the Poisson coefficient increased around 12%.

Additionally, the UCS was determined for the cylindrical cement paste specimens. The results indicate a clear correlation with the w/s ratio. Cement pastes with higher w/s ratios show a reduced UCS compared to those with a lower w/s ratio. For CS0044C00, the UCS results in 52 MPa while CS0060C00 yields a UCS of 40 MPa, corresponding to a reduction of 23% for an increase in the w/s ratio from 0.44 to 0.60.

Table 5.2.1: UCS and dynamic elastic parameters of plain cement pastes with different w/s ratios

Cement paste	UCS [MPa]	K [GPa]	G [GPa]	E [GPa]	ν
CS0044C00	52.0	15.7	9.7	24.1	0.24
CS0060C00	33.7	12.0	6.4	16.3	0.27

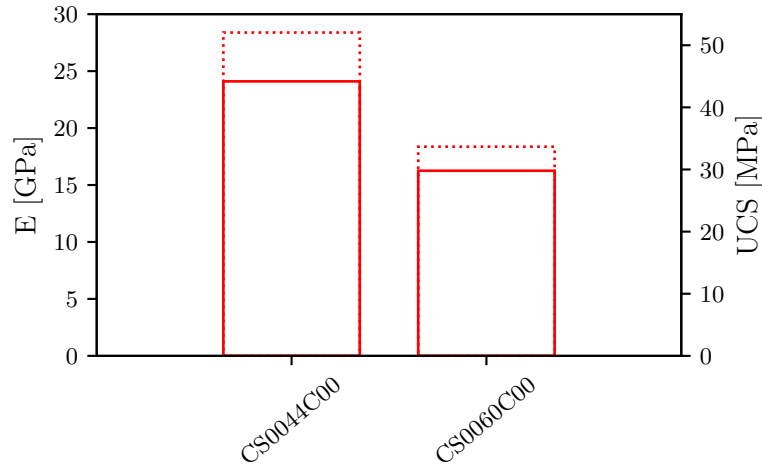


Figure 5.2.1: Young modulus (solid line) and UCS (dotted line) of plain cement pastes with different w/s ratios

As previously discussed (cf. Chapter 4), increasing the w/s ratio leads to higher porosity in cement pastes [90]. An increased porosity reduces the compactness of the hydrated cement structure [58]. A less compact structure directly impacts the mechanical behaviour of the material, leading to a reduction in its strength and stiffness. As a result, both the elastic properties, such as the Young, bulk, and shear moduli, and the UCS are diminished as the w/s ratio increases [120, 121, 122, 123]. Moreover, the strong correlation between the elastic properties, measured using ultrasonic wave velocity, and the UCS results shown in Figure 5.2.1 aligns with the results of Kaplan [124].

5.3 Impact of HGMS

Chapters 3 and 4 thoroughly investigated the effect of HGMS on the microstructure of class G cement pastes. It was observed that HGMS not only contribute to a higher compactness of the cement matrix, thereby reducing the porosity, but also play a crucial role in improving

the pore size distribution.

However, to arrive at these results, two main properties of HGMS were considered: strength and geometry. The strength of the HGMS is crucial, if exceeded mechanical damage occurs. Additionally, the geometry of the HGMS is characterized by a significant internal void space. Hence, during high confining pressure tests HGMS may break, as it happened during MIP tests, leading to changes in the initially improved pore structure and possibly affecting the mechanical properties of the cement pastes.

The dynamic Young moduli were measured for cement pastes CS2744C00, CS4144C00, CS2760C00, and CS4160C00 using Equation 2.3.6. However, it is important to note that this equation assumes that the material behaves as homogeneous and isotropic.

Despite the material not being perfectly homogeneous, it is still possible to make use of the measured velocities presented in Table 5.3.1 if the separation of scales requirement ($d \ll \lambda$) is satisfied, where d stands for the size of the Representative Elementary Volume (REV) of the heterogeneous material and λ for the wavelength of the ultrasonic pulse [69].

Table 5.3.1: Measured ultrasonic wave velocities on cement pastes with different w/s ratios and with HGMS27 and HGMS41

Paste	V_p [m/s]		V_s [m/s]	
	Mean	SD	Mean	SD
CS0044C00	3800	41.80	2210	70.34
CS2744C00	3340	32.56	1980	11.88
CS4144C00	3580	15.20	2070	22.68
CS0060C00	3370	28.04	1880	22.17
CS2760C00	3090	15.05	1760	7.86
CS4160C00	3270	25.65	1840	6.73

Based on the ultrasonic pulse frequency of 500 kHz and the velocities presented in Table 5.3.1, the wavelength is at least 3.5 mm. This is significantly larger than both the HGMS and the REV of the material (see Figures 4.3.2 and 4.3.3). Even by considering a REV 10 to 20 times larger than the HGMS, which have a D50 of 30 and 40 μm , the use of Equation 2.3.6 for these cement pastes is justified due to the scale separation between the wavelength and the characteristic size of the REV.

The dynamic elastic properties obtained through ultrasonic wave velocities gathered in Table 5.3.2 demonstrate the influence of HGMS. For each w/s ratio, the plain cement pastes yield the highest moduli, followed by cement paste with HGMS41 and with HGMS27, respectively.

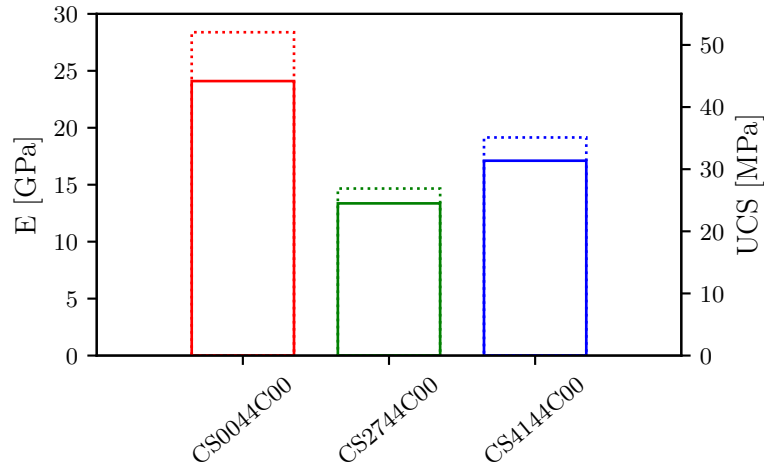
This observation aligns with expectations, as HGMS41 presents a higher density than HGMS27, leading to a thicker outer shell and reduced inner void space. It is crucial to

Table 5.3.2: UCS and dynamic elastic parameters of cement pastes with different w/s ratios and with HGMS27 and HGMS41

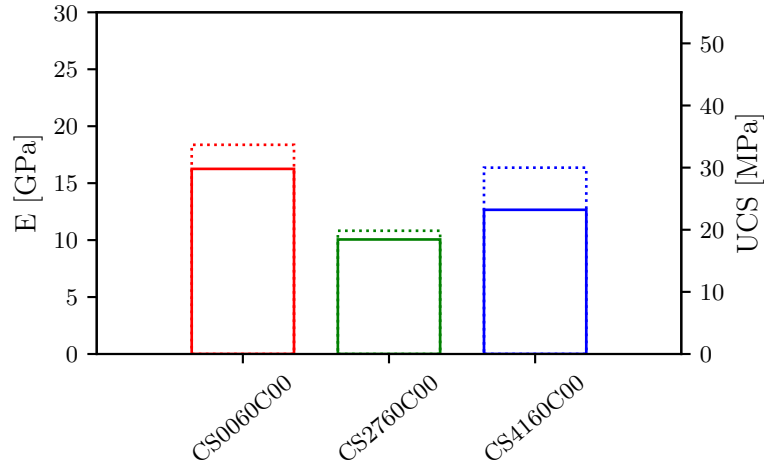
Cement paste	UCS [MPa]	K [GPa]	G [GPa]	E [GPa]	ν
CS0044C00	52.0	15.7	9.7	24.1	0.24
CS2744C00	26.9	8.3	5.4	13.4	0.23
CS4144C00	35.1	11.4	6.8	17.1	0.25
CS0060C00	33.7	12.0	6.4	16.3	0.27
CS2760C00	19.8	6.9	4.0	10.1	0.26
CS4160C00	30.0	9.1	5.0	12.7	0.27

emphasize that the dosages were derived by replacing 10% with HGMS from each class. Consequently, the density of the respective class of HGMS directly impacts the volume fraction of the HGMS used. HGMS27, with its lower density, exhibits both larger volume fraction and larger inner void space in comparison to HGMS41. This translates into a significantly larger inner void space for cement pastes with HGMS27 than for those with HGMS41.

Additionally, the UCS results are depicted in Figure 5.3.1, and they are also compared with the dynamic Young moduli. As observed previously for different w/s ratios in Section 5.2, a clear relationship exists between the UCS and dynamic Young modulus values. Higher dynamic Young modulus values correspond to higher UCS values.



(a) $w/s=0.44$



(b) $w/s=0.60$

Figure 5.3.1: Young modulus (solid line) and UCS (dotted line) of cement pastes with and without cement replacement by HGMS

To gain insight into these results, the physical properties of HGMS are crucial [49, 84], as the UCS test measures the compressive strength of the cement paste as a whole, including the contribution of HGMS. HGMS41 has a higher density and thicker outer shell compared to HGMS27, which translates to greater strength as informed by the manufacturer. The difference in strength is verified through MIP tests on powder samples (Appendix A). During these MIP tests, the rupture pressure observed for each class of HGMS is less than

or equal to the UCS measured in the respective cement pastes. This suggests that, under the compressive loads applied during the UCS test, the HGMS likely surpass their rupture strength.

Therefore, given the higher strength and lower volume fraction of HGMS41 within the cement paste (both attributed to its higher density), the UCS results were expected. The cement paste with the lowest amount of void space presented the highest UCS, followed by cement paste with HGMS41, which yields higher strength and lesser HGMS volume fraction. Lastly, cement paste with HGMS27 yields the lowest UCS since HGMS27 presents higher volume fraction, greater inner void space, and lower strength.

Figures 5.3.2 and 5.3.3 show the plots of dynamic Young modulus and UCS against absolute porosity, respectively. As expected, there is a clear relationship between these mechanical properties and the total porosity, regardless of whether this porosity is interconnected or occluded within the HGMS. The occluded porosity inside the HGMS also influences the overall behaviour of the cement paste. Additionally, the dynamic elastic properties are closely related to the material's density, which depends on the inner void space of the HGMS. Similarly, UCS values are not solely determined by the compactness of the cement matrix but also by the strength and void space of the HGMS.

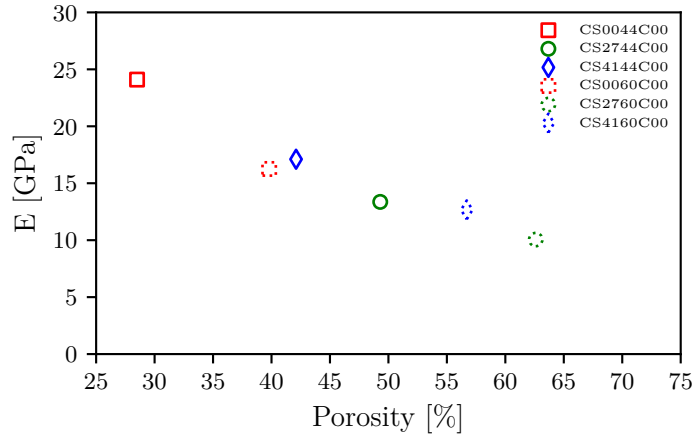


Figure 5.3.2: Young modulus as a function of porosity of plain cement pastes and cement pastes with HGMS with different w/s ratios

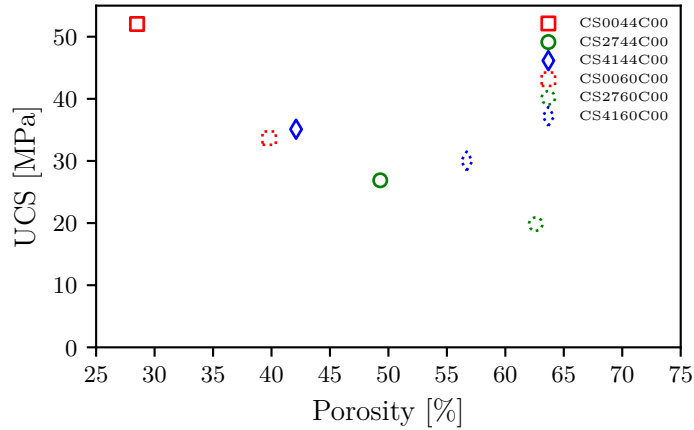


Figure 5.3.3: UCS as a function of porosity of plain cement pastes and cement pastes with HGMS with different w/s ratios

It is expected that cement pastes with the highest porosity for each w/s ratio are the ones with the largest volume fraction of HGMS and inner void space per HGMS (CS2744C00 and CS2760C00), which effectively yield the lowest Young moduli and UCS. For CS4144C00 and CS4160C00, an increase in both mechanical parameters is observed. This is possibly due to the reduced volume fraction of HGMS41 in the cement pastes and the higher strength of this class of HGMS compared to HGMS27.

Though an increase in compactness is granted to the cement matrix by the presence of HGMS of both classes, their strength still appears to be a limiting factor. It could be expected that cement pastes with partial cement replacement by HGMS of higher strength than that of the plain cement paste could possibly yield higher UCS, since the compactness increases and the material would start failing through the cement matrix instead of doing so through some weakness points granted by the HGMS. This concept can be further analysed by quantifying, for each w/s ratio, the differences in porosity and mechanical properties obtained for cement pastes with HGMS with respect to plain cement pastes, as shown in Table 5.3.3.

It is noticeable that the trend in the differences presented in Table 5.3.3 change with the w/s ratio. The change in porosity due to cement replacement by each HGMS slightly increases from cement pastes with a w/s ratio of 0.44 to those with a w/s ratio of 0.60. This would indicate that the decrease in the informed mechanical parameters shall be more important for cement pastes with a w/s ratio of 0.60 than for those with a w/s ratio of 0.44. However, the absolute difference of both the Young modulus and the UCS due to the influence of HGMS is lower for cement pastes with a w/s ratio of 0.60 than for those with a w/s ratio of 0.44.

This behaviour could be related to the decrease in the mechanical properties of the

Table 5.3.3: Porosity and mechanical parameters difference compared to plain cement pastes

Cement paste	E [GPa] / [%]	UCS [MPa] / [%]	Porosity [%] / [%]
CS0044C00	0	0	0
CS2744C00	-10.7 / -44	-25.2 / -48	20.8 / 73
CS4144C00	-7.0 / -29	-16.9 / -33	13.6 / 48
CS0060C00	0	0	0
CS2760C00	-6.2 / -38	-13.8 / -41	22.8 / 54
CS4160C00	-3.6 / -22	-3.7 / -11	16.9 / 40

cement matrix due to the increase in the w/s ratio, as informed in Section 5.2. This decrease could also be understood as an increase of the relative mechanical properties of HGMS27 and HGMS41 with respect to the cement matrix. Therefore, instead of granting weakness points to the cement matrix prepared at a w/s ratio of 0.6, the HGMS start to behave as inclusions that are both relatively more rigid and have a relatively higher strength with respect to the cement matrix than those within cement pastes with a w/s ratio of 0.44. Hence, the decrease in the mechanical properties due to the influence of HGMS is less noticeable. Moreover, it can be seen that for CS4160C00 the difference is close to being null, which indicates that effectively this class of HGMS is achieving both the rigidity and the strength of the cement matrix in paste CS4160C00.

Bringing the focus of the discussion to the results of the triaxial tests, Figure 5.3.4 shows the behaviour of each non-carbonated cement paste when subjected to an isotropic compression. There are two clearly distinguishable behaviours to outline.

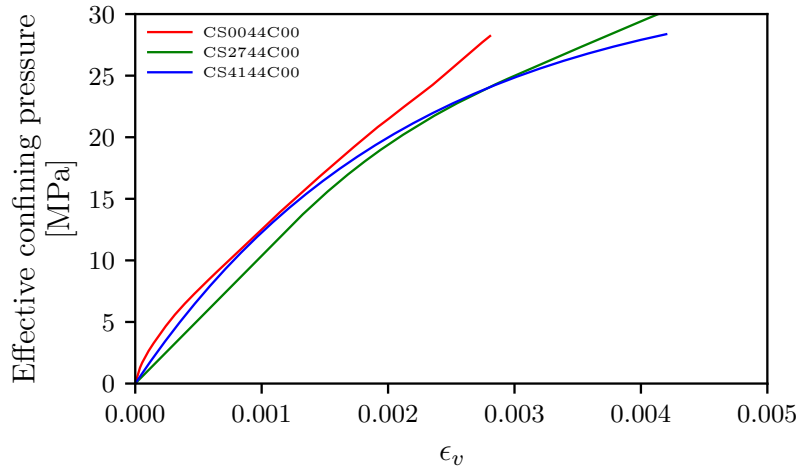


Figure 5.3.4: Cement pastes behaviour under high effective confining stress

A confining pressure results in a shift in the behaviour of the cement pastes, but the pressure at which this change occurs varies between samples. For CS0044C00, a noticeable change in slope occurs before 10 MPa of confinement. In contrast, for CS2744C00, the change in slope is observed before 18 MPa, and for CS4144C00, it occurs before 15 MPa. The observed decrease in the slope in cement pastes with HGMS could be related to both damage and elastoplastic behaviour.

The cement pastes exhibit a non-linear elastic behaviour. To quantify their compressibility, the secant drained bulk modulus (K_d) was measured over a range of 0 MPa to 5 MPa of effective confining pressure. The term secant modulus is used to describe the average value of the tangent modulus over this pressure interval. Unlike the tangent modulus, which represents the slope of the stress-strain curve at a specific point, the secant modulus provides a broader measure of stiffness that accounts for the material's overall response within the specified pressure range [71]. This approach helps to characterize and compare the cement pastes' compressibility despite their non-linear behaviour. These results are consistent with the dynamic elastic parameters shown in Table 5.3.2. The highest K_d corresponds to CS0044C00, followed by CS4144C00 and CS2744C00, respectively.

Lima et al. [125] studied two alternative mixtures of class G cement pastes. The first one is a plain cement paste while the second one is a stabilized one, in which a defoamer was used at 0.1% by weight of cement to reduce its porosity. A significant porosity decrease in stabilized cement pastes when compared to traditional ones was measured through both helium expansion and MIP. The authors performed triaxial compression tests with confining pressures ranging from 0 MPa to 20 MPa. Among the obtained results, the increased stiffness of the stabilized cement paste when compared to plain cement pastes is noteworthy. This is an expected result, since the mechanical properties of cement paste/mortar/concrete

is well-known in the industry to be affected by its porosity [24].

In the research of Zhang et al. [126], an analysis of the mechanical properties of cement mortars with different compositions and porosities was performed. They compare the behaviour of mortars with different amounts of alcohol-based shrink-reducing admixture (ASRA). Three different mixtures were prepared with varying amounts of ASRA: 0%, 1%, and 2%. The inclusion of ASRA influenced the porosity of the mixtures, resulting in porosities of 3.89%, 4.13%, and 5.90%, respectively, corresponding to the increasing ASRA content. With these mixtures, they prepared cylindrical specimens and performed triaxial compression tests at different confining pressures, ranging from 0 MPa to 40 MPa. These tests also showed the decrease in stiffness of the mortars related to a higher porosity.

The behaviour of cement pastes containing HGMS in isotropic compression tests is directly linked to their porosity as measured by MIP, before considering any corrections for the rupture of HGMS. Cement pastes with HGMS exhibit characteristics similar to cementitious mixtures with higher porosity, as observed in previous studies [125, 126, 127]. CS0044C00, with the lowest total porosity (including both interconnected and occluded porosity), demonstrates the highest stiffness. Among the cement pastes containing HGMS, CS4144C00, due to the higher density of HGMS41 compared to HGMS27, contains a smaller volume of HGMS, leading to lower total porosity and consequently greater stiffness than CS2744C00. This trend aligns with previous findings that higher porosity leads to lower stiffness and strength [120, 121, 122, 123].

Furthermore, the results for the cement pastes used in this research are in accordance with those of class G cement pastes modified with ground tire rubber (GTR) used in the research of Cheng et al. [128]. The authors performed both, MIP tests to assess the pore entry size distribution, and triaxial compression tests at confining pressure of 16 MPa.

Similar to the changes observed between CS2744C00 and CS4144C00, the most probable pore entry size shifts when comparing traditional class G cement paste with GTR-modified cement paste. According to Cheng et al. [128], this shift is attributed to the enhanced compactness of the cement matrix. They suggest that this effect is due to the GTR particles reducing the presence of larger pores and contributing to the densification of the cement paste. However, considering the significant difference in size between the GTR particles (average size of 120 μm) and the pore size distribution of plain cement pastes (ranging from 30 to 80 nanometres), it is more plausible that the GTR particles exhibit a filler effect, enhancing the compactness of the cement paste.

As for the triaxial compression tests, traditional and GTR-modified cement pastes exhibited notable differences in behaviour under a maximum deviatoric stress of 16 MPa. Plain cement paste displayed a completely linear elastic response throughout the test. In contrast, the GTR-modified cement paste exhibited a two-phase behaviour: an initial linear elastic phase up to approximately 6 MPa, followed by a plastic phase characterized by a decrease in stiffness and the appearance of irreversible strains. This change in behaviour, where GTR cement paste shows reduced stiffness in the linear elastic phase compared to plain cement paste, mirrors the trends observed in cement pastes with HGMS.

The similarity in behaviour between cement pastes containing GTR – shown in the research of Cheng et al. [128] – and HGMS – shown in Figure 5.3.4 – can be attributed to their similar effects on the cement matrix’s microstructure. Both GTR and HGMS lead to a shift in the pore size distribution of the plain cement paste to smaller diameters, indicating an increase in the matrix’s compactness. Moreover, the HGMS and GTR particles themselves appear to be acting as weak points within the cement matrix. Although the interfaces between the GTR or HGMS and the cement matrix differ –HGMS shows a stronger interface due to its pozzolanic activity and filler effect (cf. Chapter 3) while GTR has a weaker interface [128] – both result in a comparable reduction in elastic properties.

Figure 5.3.5 shows the results of these triaxial compression tests in terms of shear stress (q) versus shear strain (ϵ_s) for non-carbonated cement pastes. These results showed different characteristics depending on the presence of HGMS. CS0044C00 showed the highest stiffness, followed by CS4144C00 and CS2744C00. In addition, all three pastes exhibited changes in the slope of the plotted data, which might indicate a combination of mechanical damage and irreversible strain.

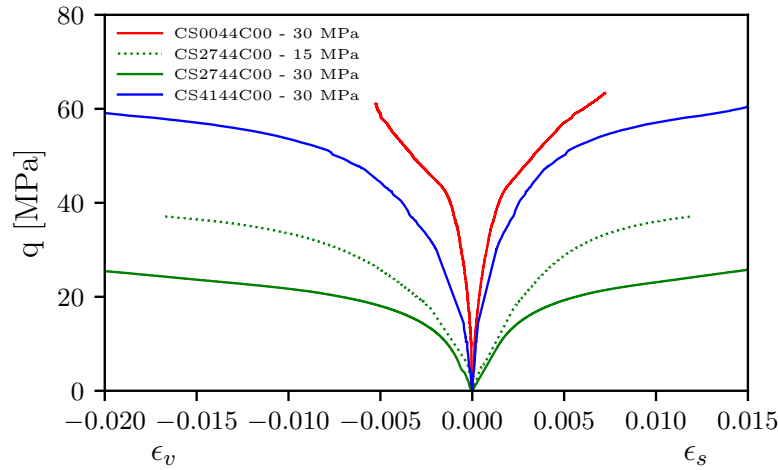


Figure 5.3.5: q versus ϵ_s and ϵ_v obtained for cement pastes with a w/s ratio 0.44 and cement replacement with HGMS. Data are shown for effective confining pressures of 30 MPa for CS0044C00, CS2744C00, and CS4144C00, and 15 MPa for CS2744C00. For q versus ϵ_v , results are available for CS0044C00 and CS2744C00 under 30 MPa effective confining pressure.

For cement paste CS2744C00, Figure 5.3.5 illustrates that the test with an effective confining pressure of 15 MPa yields higher stiffness than that with an effective confining pressure of 30 MPa. This unexpected behaviour may be linked to the mechanical properties of HGMS27 within the cement paste. The MIP tests on powder indicate that the rupture

pressure of HGMS27 is around 15 MPa (cf. Appendix A), suggesting that higher confining pressures increase the probability of breaking the HGMS27 in CS2744C00. Additionally, the pozzolanic activity of HGMS27 contributes to a reduction in the strength of these HGMS by consuming part of their outer shell (cf. Chapter 3). Supporting this hypothesis, the volumetric strain data reveals a significant increase when the confining pressure rises from 15 MPa to 30 MPa, with the volume strain under 15 MPa remaining low and escalating approximately threefold to around 0.00431 at 30 MPa. This substantial increase in volume strain may serve as evidence of extensive damage to the HGMS, indicating that the elevated confining pressure not only contributes to their failure but also impacts the mechanical properties of the cement paste, resulting in a decrease in stiffness with increasing effective confining pressures.

Besides, the behaviour of all the cement pastes under confinement presents three main zones. Initially, the materials show an elastic part, the largest being that of CS0044C00, followed by CS4144C00, and CS2744C00, respectively. This is followed by a transition phase where the material appears to exhibit signs of the beginning of both damage and plastic strains. The end of the elastic behaviour occurs at lower stress for CS2744C00, followed by CS4144C00 and then CS0044C00. Finally, an almost linear hardening zone exists, which is more pronounced for CS0044C00, but ends abruptly with material failure. For CS2744C00 and CS4144C00, this hardening zone continues up to larger strains.

In the aforementioned researches of Lima et al. and Zhang et al. [125, 126] the strength dependency on the porosity of cement pastes is also studied.

On the one hand, Lima et al. [125] focused on the type of rupture presented by each material. In terms of behaviour, the stabilized cement paste (less porous) presented a more brittle behaviour, even at relatively high confining pressures. For 10 and 20 MPa of confining pressure, the plain cement paste presents two clearly defined zones. The first one is denoted as linear elastic behaviour, which is sustained until reaching a damage zone, characterized by a decreased stiffness of the material. Moreover, the stabilized cement paste presented a much higher strength than the traditional one.

On the other hand, Zhang et al. [126] noticed in their work a decrease in the compressive strength for every confining pressure when the porosity increases. The authors divide the behaviour of the cement mortars into zones. The linear elastic zone, which corresponds to the elastic behaviour of the material in which no damage occurs. The elastoplastic and damage zone, in which the material experiences inelastic deformation as it reaches its yield point. The stress-strain curve exhibits nonlinearity, particularly under uniaxial loading and in specimens with low internal porosity. Within this zone, internal damage starts to accumulate as mesocracks that cause discontinuities in the solid matrix. This damage is characterized by irreversible strains and changes in the material's internal structure. The presence of mesocracks results in localized stress concentrations, which accelerate the progression of internal damage. Finally, the post-peak softening zone corresponds to the formation of macroscopic shearing planes. Regarding the strength attained by each of these pastes, the trend is similar to that of the stiffness. The most porous cement paste exhibited

the lowest strengths across all confining pressures, followed by the paste with intermediate porosity, and finally, the paste with the least porosity.

The results in Figure 5.3.5 further confirm the behaviour of HGMS cement pastes. The void space within HGMS appears to be playing a significant role in the mechanical performance of CS2744C00 and CS4144C00. Both cement pastes exhibit a more ductile behaviour and a lower strength than CS0044C00. By comparing the results of HGMS cement pastes with those observed in the studies of Lima et al. and Zhang et al. [125, 126], it can be further confirmed that the use of HGMS leads to mechanical behaviour akin to an increase in the total porosity of the material.

In addition, Figure 5.3.6 presents the relationship between effective axial stress (σ'_1) and effective confining pressure (σ'_3) for cement pastes CS0044C00, CS2744C00, and CS4144C00. These results were obtained from UCS tests and drained triaxial tests conducted at effective confining pressures of 30 MPa and 15 MPa (only for CS2744C00), with a constant pore pressure of 5 MPa. The UCS tests are performed in accordance with standard procedures for cement characterization (cf. Chapter 2), while the triaxial tests are designed to assess the material properties under well conditions, considering both pore and confining pressures. Each data point reflects the effective stress state at failure for each paste.

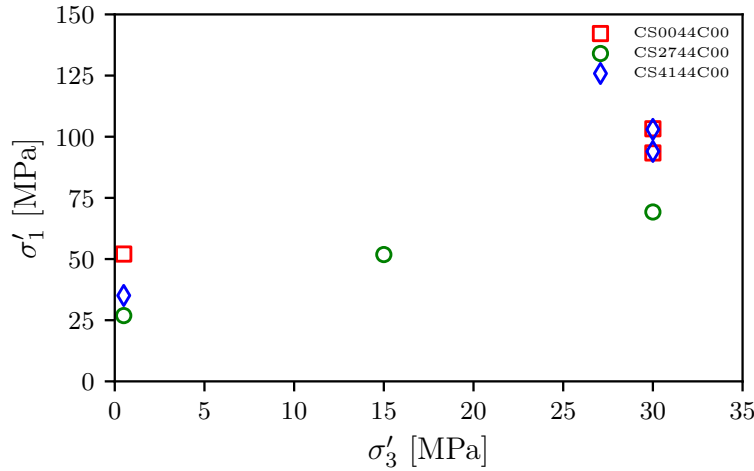


Figure 5.3.6: σ'_1 vs. σ'_3 obtained from drained triaxial tests with 15 MPa and 30 MPa of effective confining pressure and 5 MPa of pore pressure. Cement pastes with a w/s ratio 0.44 and partial cement replacement with HGMS

The results reveal significant differences in the strength of the three cement pastes. CS0044C00 demonstrates the highest axial stress reached by the specimen (σ'_1) at low effective confining pressures (σ'_3), likely due to the absence of HGMS. In contrast, CS2744C00 exhibits a marked reduction in strength at low σ'_3 , reflecting the influence of the weak points

granted by HGMS27. This trend is also observed in CS4144C00, which uses HGMS41 – stronger than HGMS27 – but still shows a decrease in strength at low σ'_3 compared to CS0044C00.

In terms of the increase in q_{max} at high σ'_3 , CS4144C00 exhibits a greater increment compared to the other pastes, suggesting a more frictional behaviour. This enhancement may be attributed to the strong interaction between the cement matrix and HGMS41. In contrast, CS2744C00 displays a lower increment in q_{max} at high σ'_3 , likely due to the increased likelihood of HGMS27 rupture under elevated confining pressures in contrast to HGMS41.

It is interesting to note that σ'_1 does not increase in CS2744C00 between 15 MPa and 30 MPa of σ'_3 . One possible way of understanding this phenomenon is by considering the strength of HGMS27 and the confining pressure to which it was subjected. CS2744C00 strength was obtained for two effective confining pressures, i.e. 15 MPa and 30 MPa. HGMS27 has a strength of 27 MPa as informed by the manufacturer, which could be lower in accordance to the results obtained in Appendix A, Figure A.2. It is therefore possible that during this test, the pore structure of this cement paste resulted severely affected only due to the increase in confining pressure, which would have affected the mechanical properties of the material.

5.4 Impact of carbonation

The discussion now focuses on the influence of the w/s ratio and presence of HGMS on the mechanical behaviour after supercritical carbonation. This analysis will be related to the effects already shown on the pore structure.

In this regard, it is worth noting that the integrity of some specimens was affected during the carbonation process. The carbonation, conducted under high pressure and high temperature conditions, subjected the specimens to a total confining pressure that, as discussed in Chapter 4, led to the rupture of the HGMS. This damage to the HGMS had a significant impact on the behaviour of the cement paste as carbonation advanced, potentially affecting the mechanical properties.

Another source of damage relies on the process of dismantling the carbonation cell. As explained in Subsection 2.3.4, this process needs to be carefully done since the decrease in the CO₂ pressure will generate some pressure gradient between the inside of the specimen and the cell. This induces tensile stresses which could overpass the tensile strength of the material and break it.

These phenomena could be considered physical effects on the integrity of the cement specimens, solely due to the high pressure involved in the scCO₂ exposure. Moreover, the changes in the microstructure due to the cement paste supercritical carbonation also affect the integrity of the specimens, as shown in Chapter 4. The alteration of the cement matrix, where the well-defined structure is replaced by loosely bound particles, further contributes

to the reduction in material integrity.

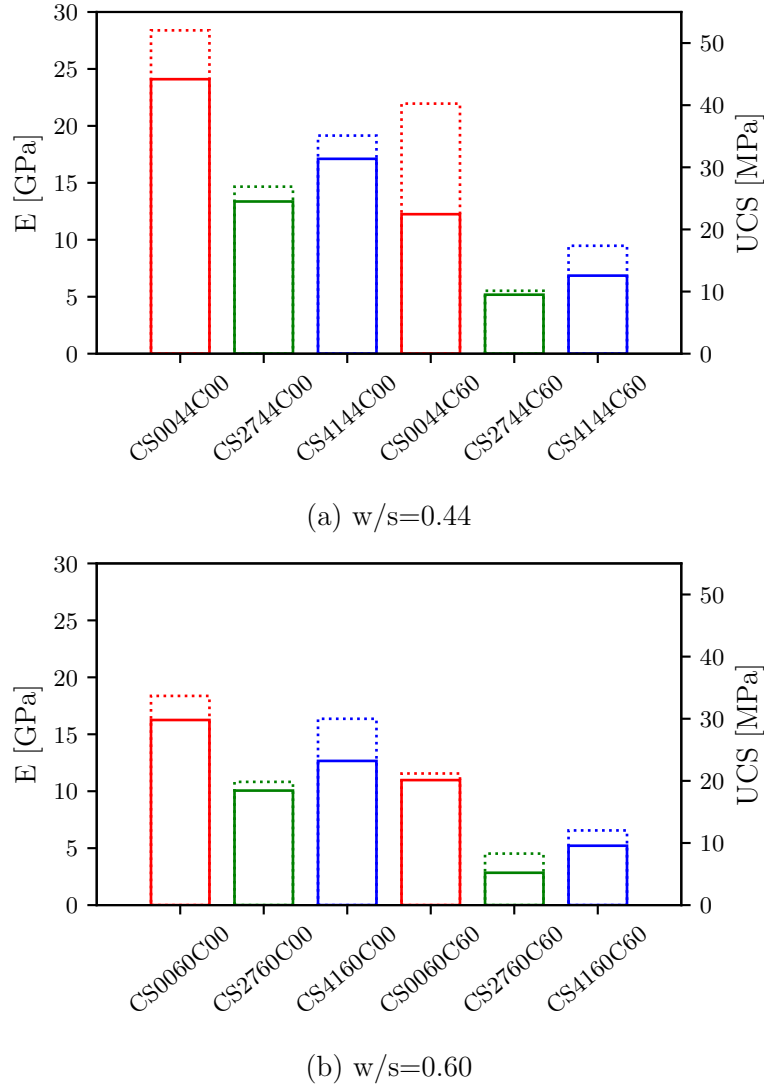


Figure 5.4.1: Young modulus (solid line) and UCS (dotted line) of cement pastes with and without cement replacement by HGMS before and after carbonation for 60 days

Hence, in terms of mechanical properties, the total damage related to the $scCO_2$ exposure can be measured as a decrease in the dynamic Young moduli. A decrease in the ultrasonic wave velocity was observed for all the specimens, regardless of the w/s ratio or the class of HGMS used. These results are presented in solid line in Figure 5.4.1, which shows a comparison between the results before and after carbonation for cement pastes

with a w/s ratio of 0.44 in Figure 5.4.1a and for those with a w/s ratio of 0.60 in Figure 5.4.1b. Additionally, Figure 5.4.1 also shows the UCS results for each cement paste in dotted line.

It is interesting to study the relative decrease obtained in both the Young modulus and the UCS due to carbonation, which is shown in Table 5.4.1. The most significant decrease in the Young modulus due to carbonation corresponds to the cement paste with HGMS27 for both w/s ratios, i.e. CS2744C60 and CS2760C60, while the lowest decrease corresponds to cement pastes without HGMS, i.e. CS0044C60 and CS0060C60. As for the UCS, the trend is similar, though a much lower decrease is observed in CS2760C60. Both CS2760C60 and CS4160C60 yield a roughly equal decrease of the UCS after 60 days of carbonation.

Additionally, the relationship between the Young modulus and the UCS can be verified for all the cement pastes after carbonation. However, it is remarkable that the UCS of CS0044C60 does not appear to be as affected as the Young modulus. This trend only occurs with the plain cement paste with a w/s ratio of 0.44, since CS0060C60 does not present the same phenomenon.

This difference may be explained by the occurrence of incomplete carbonation in certain specimens. As discussed in Chapter 4, pH indicator tests revealed that the consumption of $\text{Ca}(\text{OH})_2$ is not uniform across all specimens. For instance, CS0044C60 exhibited a pH above 9 throughout its entire section, indicating that there was little to no consumption of $\text{Ca}(\text{OH})_2$. In contrast, CS0060C60 showed two distinct zones: one with a pH below 9 and another with a pH above 9. These clearly defined zones in specimens with higher w/s ratios leads to a more heterogeneous material, which impacts the mechanical properties, particularly the UCS. In these cases, the material tends to fail due to the detachment of the outer zone, where pH is lower than 9, resulting in a failure at lower stresses.

Table 5.4.1: Decrease in the Young modulus and the UCS after carbonation for 60 days

Paste	E [%]	UCS [%]
CS0044C60	49.2	22.7
CS2744C60	61.2	62.3
CS4144C60	59.9	50.5
CS0060C60	32.5	37.1
CS2760C60	71.8	58.2
CS4160C60	58.8	59.9

Figure 5.4.2 shows the volumetric strain against effective confining pressure before and after scCO_2 exposure. It is important to note that while we refer to the confining pressure as effective, this assumption may not be entirely guaranteed due to the uncertainty around the drained condition. After 60 days of carbonation, the heterogeneity of the specimens,

leading to variations in porosity and permeability, could affect the drainage conditions. In this study, the same loading rates used for non-carbonated pastes were applied, with the assumption that they would be sufficient to maintain drained conditions.

The decrease in K_d for each cement paste after carbonation is noteworthy. The decrease in stiffness for the plain cement paste (CS0044C60) is relatively small compared to cement pastes with HGMS. This smaller reduction may be related to the absence of HGMS, as their rupture during carbonation likely contributes to the greater stiffness loss observed in CS2744C60 and CS4144C60.

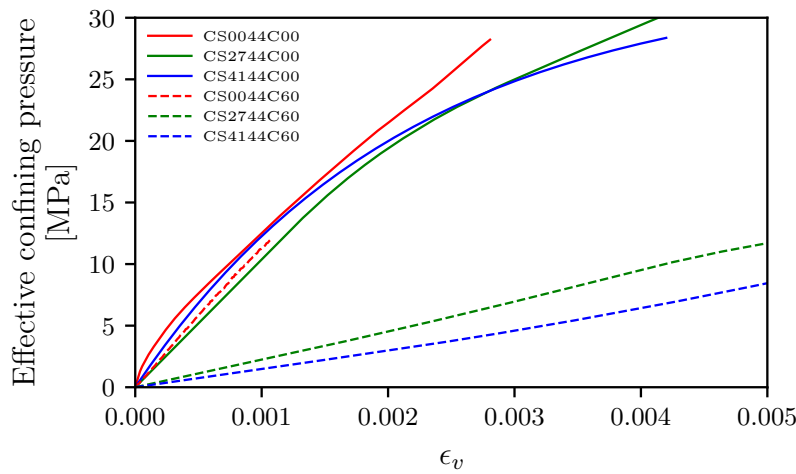


Figure 5.4.2: Drained bulk modulus of cement pastes before and after scCO_2 exposure

Some similar trend can be noticed in Figure 5.4.3. In this case, the confining pressure increase speed was such that it did not allow the complete release of the pore pressure, leading to the measurement of the undrained bulk modulus (K_u) of the cement pastes. However, due to the aforementioned heterogeneity introduced by the carbonation exposure, it is challenging to guarantee fully undrained conditions. There may have been some degree of pore pressure dissipation during the tests, meaning that the measured K_u might not represent a truly undrained state. The variability in permeability after carbonation exposure, coupled with the fact that the loading rates were the same as those used for non-carbonated specimens, may have resulted in an intermediate condition, somewhere between drained and undrained.

K_u presents a similar behaviour to K_d , with the highest K_u before scCO_2 exposure corresponding to CS0044C60, followed by CS4144C60 and CS2744C60, respectively. After carbonation, the loss of stiffness is more pronounced in CS4144C60 compared to CS2744C60, resulting in CS0044C60 retaining the highest K_u , followed by CS2744C60 and finally CS4144C60. This deviation from the trend observed with K_d could be linked to

the uncertainty about drainage conditions. It is possible that K_u and K_d reflect different states of drainage, which complicates a direct theoretical relationship between the two.

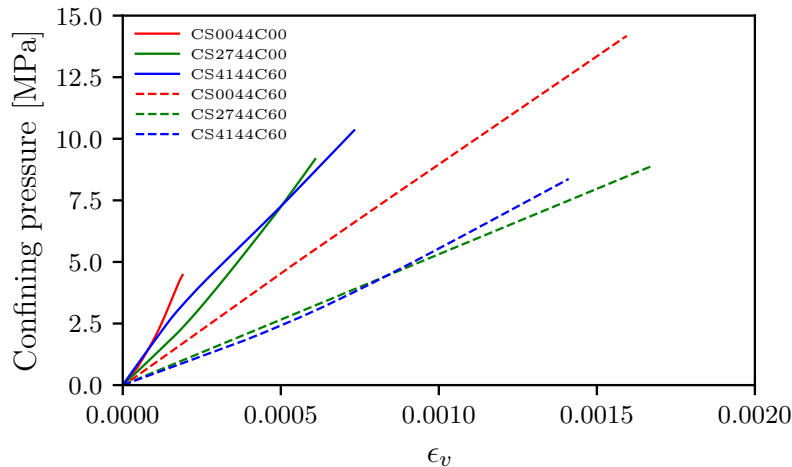


Figure 5.4.3: Undrained bulk modulus of cement pastes before and after scCO_2 exposure

In their research, Takla et al. [129] focus on studying the behaviour of carbonated and calcium-leached oil-well cement pastes. They use traditional class G cement pastes with a w/c ratio of 0.4 from which cylindrical specimens were obtained and cured at 90 °C for a month. Then, they prepared 4 groups of specimens. Two of them were non-carbonated specimens, from which only one was subjected to a calcium leaching procedure with ammonium nitrate. The other two correspond to carbonated specimens also divided in two groups, from which one was subjected to the calcium leaching procedure. This results in the following groups of specimens: sound specimens, leached specimens, carbonated specimens, and carbonated leached specimens. It is worth noting that the curing conditions and the carbonation procedure followed in this research were sufficient to reach full carbonation of the cement specimens.

Among the results presented in this research, the Young modulus was measured for each group using micro-indentation tests. The highest stiffness corresponds to the carbonated specimens and the lowest to leached specimens. Leached carbonated specimens showed a nearly 50% reduction in the Young modulus compared to the sound specimens.

In the research of Yurtdas et al. [130], a comprehensive study of the mechanical behaviour of oil-well cement pastes is performed. The cement paste considered is a traditional class G cement paste with a w/c ratio of 0.44. It was cured at 90 °C for one month, after which the cylindrical specimens were divided into two groups. Each group was kept in different fluids at 90 °C before being tested. One group of specimens was kept in a neutral fluid, while the other was subjected to chemical degradation by exposure to ammonium

nitrate.

The authors assessed the drained bulk modulus and highlighted a difference between the sound and degraded specimens. The bulk modulus of degraded specimens resulted lower than that of sound specimens. Moreover, damage appeared in degraded specimens for confining pressures greater than 3 MPa. The authors state that the chemical degradation induces this elastoplastic behaviour of the material.

According to the research of Takla et al. [129], the solely carbonated specimens yield a higher stiffness than the sound specimens. However, both researches of Takla et al. and Yurtdas et al. [129, 130] agreed that leached/chemically degraded specimens have a lower stiffness.

Based on the findings displayed in Figures 5.4.2 and 5.4.3, it appears that cement pastes tested in the present research not only present some extent of carbonation due to the scCO_2 exposure, but also a chemical degradation. In this regard, carbonation is known for producing a similar effect to that of ammonium nitrate, as described in the studies by Takla et al. and Yurtdas et al. [129, 130]. The exposure to ammonium nitrate leads to the dissolution of $\text{Ca}(\text{OH})_2$, which results in a decrease in pH, and the dissolution of CSH [131, 132]. Unlike carbonation, where the precipitation of CaCO_3 crystals occurs, the resulting mineral from ammonium nitrate exposure, calcium nitrate, remains dissolved due to its high solubility, preventing its crystallization [132].

The mechanical damage observed in HGMS cement pastes primarily results from the rupture of the HGMS. This aspect was discussed in Section 5.3, where a reduction in stiffness of the cement pastes with HGMS was attributed to the rupture of these inclusions. Additionally, Chapter 4 highlighted that HGMS break due to the pressure experienced during exposure to scCO_2 . The chemical degradation associated with carbonation also plays a significant role. As shown in Figures 5.4.2 and 5.4.3, there is a notable decrease in stiffness due to the carbonation of the cement pastes. Furthermore, the results obtained may be influenced by the heterogeneities introduced by the incomplete carbonation of the specimens that were carbonated for 60 days.

For CS0044C00, and as already stated in Chapter 4, chemical damage appears to be the primary factor to affect the porosity and pore structure of the cement paste, resulting in stiffness reduction. However, the damage mechanisms observed in CS2744C00 and CS4144C00 are more intricate. In accordance with the MIP results, exerting 20 MPa of fluid pressure on the specimens was enough to cause the rupture of the HGMS. This mechanical damage exacerbated the effects of exposure to scCO_2 by significantly altering the pore structure, resulting in increased interconnected porosity. As a result, the cement matrix, initially enhanced by the presence of HGMS due to its pozzolanic activity and filler effect (cf. Chapter 3), is heavily affected by the increase in interconnected porosity due to HGMS rupture, resulting in more severe consequences than anticipated during scCO_2 exposure, as discussed in Chapter 4.

The analysis will now focus on the stress-strain curves, namely the results of shear stress (q) in relation to shear strain (ϵ_s). Figure 5.4.4 shows these curves for specimens non-

carbonated and carbonated for 60 days, on which drained triaxial compression tests were performed, with an effective confining pressure of 30 MPa for CS0044C60 and CS4144C60, and of 15 MPa for CS2744C60 and CS4144C60.

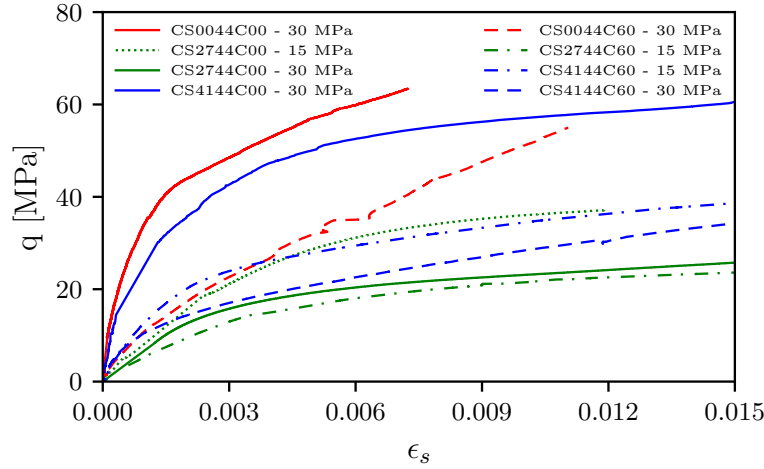


Figure 5.4.4: Deviatoric stress vs. deviatoric strain obtained from drained triaxial tests with 15 MPa and 30 MPa of effective confining pressure and 5 MPa of pore pressure. Cement pastes with a w/s ratio 0.44 and partial cement replacement with HGMS before and after 60 days of carbonation.

After carbonation, the trend in stiffness remained consistent with observations prior to the exposure of specimens to scCO_2 . However, the stiffness of CS4144C60 and CS2744C60 became almost identical. This indicates that CS4144C60 was more degraded than CS2744C60. This observation aligns with the results shown in Figure 5.3.4. Specifically, for confining pressures greater than 15/20 MPa, which are similar to those experienced in the carbonation cell, the cement paste CS4144C00 exhibited greater damage compared to CS2744C00. This suggests that the specimens may have sustained mechanical damage due to the pressure applied in the carbonation cell prior to carbonation and subsequent testing in the triaxial cell. Therefore, the observed differences in damage levels can be attributed to the initial conditions experienced by each specimen before the carbonation process.

Overall, all the cement pastes demonstrated increased ductility after the scCO_2 exposure, indicative of damage. All pastes reached the change in slope from the elastic behaviour to the damaged zone at lower stress levels compared to non-carbonated ones.

Triaxial drained compression tests were performed on carbonated cement specimens to obtain the σ'_1 at different σ'_3 . By also considering the results obtained from UCS tests, Figure 5.4.5 shows the relationship between σ'_1 at different σ'_3 , obtained from UCS and 30 MPa σ'_3 results for CS0044C60; UCS and 15 MPa σ'_3 results for CS2744C60; and UCS,

15 MPa, and 30 MPa σ'_3 results for CS4144C60.

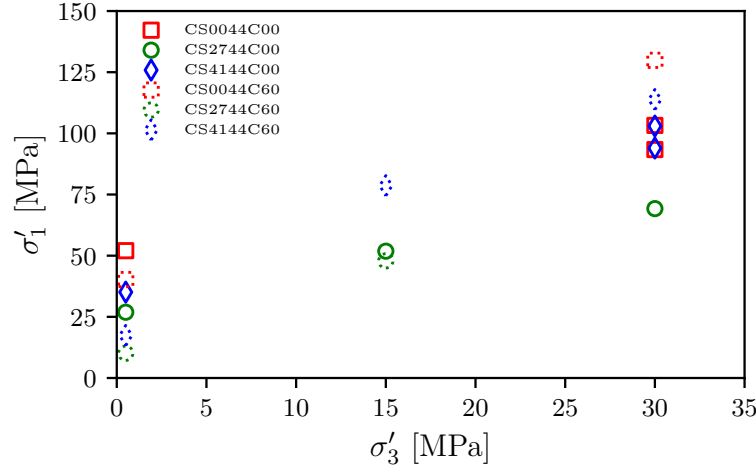


Figure 5.4.5: σ'_1 vs. σ'_3 obtained from drained triaxial tests with 15 MPa and 30 MPa of effective confining pressure and 5 MPa of pore pressure. Cement pastes with a w/s ratio 0.44 and partial cement replacement with HGMS before and after 60 days of carbonation

Based on these results, a notable shift in the behaviour of all cement pastes is evident after exposure to scCO_2 . A lower q_{max} is observed with low p' in carbonated cement pastes. Furthermore, within the effective pressure range explored in this study – relevant to realistic conditions encountered in CO_2 storage wells – it appears that q_{max} increases more significantly with rising p' in cement pastes exposed to scCO_2 compared to those not exposed. This suggests a more frictional behaviour in the carbonated pastes, which can be attributed to the microstructural changes induced by carbonation. As discussed in Chapter 4, the SEM images illustrate a reduced presence of the cement matrix and an abundance of precipitated CaCO_3 crystals, likely contributing to the increased frictional behaviour observed in the samples carbonated for 60 days.

Takla et al. [129] performed triaxial compression tests on sound, carbonated, leached, and carbonated leached specimens. The strength of each group of cement specimens was obtained at four confining pressures 0 MPa, 3 MPa, 10 MPa, and 20 MPa. It is interesting to note that the carbonated cement paste yielded the highest strength at every confining pressure. This cement paste presented the highest cohesion and frictional behaviour. Furthermore, the leached cement paste resulted the one with the lowest strength for each confining pressure used. Then, intermediate results were obtained for groups of sound specimens and leached carbonated specimens. The compressive strength for these last two groups was roughly the same regardless of the confining pressure.

In their work, Takla et al. [133] also focuses on the changes that oil-well cement pastes

undergo when subjected to scCO_2 conditions. In this case, they used a traditional class G cement paste with a w/c ratio of 0.44 with defoamer and dispersant additives. It is worth noting that the curing of the specimens was performed at 90 °C for 72 hours. The carbonation exposure in that research consisted in introducing the specimens in a chamber with temperature and humidity control. The temperature was set at 90 °C, while the relative humidity was kept at 65%. In these conditions, a flow of 100 cm^3/min of CO_2 was injected to achieve the complete carbonation of the specimens after 28 days.

Specimens with different carbonation degrees were subjected to triaxial compression tests, with confining pressures ranging from 0 MPa to 20 MPa. Moreover, these tests were performed at a controlled temperature of 90 °C. The authors observed, regardless of the confining pressure, an increase in the compressive strength with increasing depths of carbonation of the cement specimens. The fully carbonated specimens presented both a higher strength at 0 MPa confining pressure, indicating an increase in cohesion. Moreover, the increase in the compressive strength with the confining pressure is greater in carbonated specimens than in sound specimens, indicating larger frictional properties.

Furthermore, Yurtdas et al. [130] performed triaxial compression tests at 3, 10, and 20 MPa of confining pressure on sound and leached specimens. For every confining pressure, a decrease in the compressive strength was noticed for degraded specimens when compared to sound specimens. Moreover, the authors reported that the increase in the compressive strength with the confining pressure is more important for sound specimens than for degraded ones, indicating that the former present a more frictional behaviour than the latter. In the research of Heukamp et al. [134], similar results were obtained. However, the research of Xie et al. [135] reported a decrease in the cohesive behaviour and an increase in the frictional behaviour from degraded specimens to sound ones. These differences could be related to the different curing and exposure conditions, since both Yurtdas et al. and Heukamp et al. subjected the cement pastes to a curing procedure and chemical degradation at 90 °C while Xie et al. considered a temperature of 20 °C. It is noteworthy that the degradation rate is significantly amplified at higher temperatures [136, 137] and that the porosity also increases with the curing temperature [138]. This results in a greater advancement of degradation due to the elevated temperature.

The triaxial compression tests conducted on cement pastes before and after different types of chemical degradation, as previously reported, revealed notable variations in the results. While some studies informed an increase in strength for carbonated specimens, attributed to enhanced cohesion and frictional behaviour, others indicated a general deterioration in cement paste strength after chemical damage. Additionally, intermediate behaviours were also reported.

Considering the results of Takla et al., Yurtdas et al., Heukamp et al. and Xie et al. mentioned above, the results of this work, shown in Figure 5.4.5, can provide more information. The cement pastes show less σ'_1 at low σ'_3 and more frictional behaviour after carbonation, due to the specific type of exposure adopted in this research. The carbonation of $\text{Ca}(\text{OH})_2$ and CSH and the consequent precipitation of CaCO_3 crystals leads, according

to the references, to an increase in all mechanical parameters. However, the prolonged exposure to scCO_2 conditions in this work appeared to result in the dissolution of CaCO_3 crystals, contributing to the degradation of the cement matrix and a subsequent decrease in the stiffness and UCS of the pastes. Yet, SEM images presented in Chapter 4 reveal a microstructure with a reduced presence of the cement matrix and a considerable amount of precipitated CaCO_3 crystals. Moreover, the rupture of HGMS during carbonation adds complexity to the interpretation of the mechanical degradation, potentially causing more significant changes than carbonation alone might induce.

5.5 Conclusion

The investigation into the mechanical properties of cement pastes revealed significant insights into the influence of the w/s ratio, cement replacement by HGMS, and supercritical carbonation.

The chapter leads to the following conclusions:

- A reduction in the dynamic elastic properties and in the UCS results from increasing the w/s ratio. This is related to the increase in porosity.
- The inner porosity of HGMS significantly affects the mechanical properties and carbonation progression of cement pastes, primarily due to their rupture at elevated pressures. This failure influences the mechanical properties and the degradation mechanisms of the cement pastes.
- The dynamic elastic properties and the UCS of cement pastes with HGMS27 are the lowest for both w/s ratios, due to the low strength and high volume fraction of this class of HGMS in cement pastes.
- The mechanical performance of the cement pastes is significantly influenced by the relative stiffness and strength of the HGMS in comparison to the cement matrix. CS0060C00 and CS4160C00 show almost the same dynamic elastic properties and UCS because of the similarity between stiffness and strength of HGMS41 and cement paste with a w/s ratio of 0.60.
- Drained isotropic compression tests show that damage occurs in cement pastes with HGMS27 and HGMS41 for pressures higher than 10 MPa.
- Every cement paste presents signs of damage during the deviatoric tests. CS2744C00 shows more damage in the deviatoric test at 30 MPa confining pressure than at 15 MPa. This leads to the specimen achieving higher strength and stiffness at 15 MPa compared to 30 MPa.

- The use of HGMS leads to a more ductile material, showing a behaviour similar to that of high porosity cement pastes.
- After exposure to scCO_2 , the dynamic Young moduli and UCS of all cement pastes experience a decline. In HGMS cement pastes, this reduction is influenced by the rupture of HGMS during carbonation, which results in both mechanical damage and an accelerated carbonation process compared to plain cement pastes. For each w/s ratio, the most affected are the cement pastes with HGMS27, followed by those with HGMS41, with the least impact observed in the cement pastes without HGMS.
- The mechanical properties determined experimentally indicate a strong advance of the carbonation. For cement pastes with HGMS, the greater extent of the carbonation due to the rupture of the HGMS leads to a further degradation of the mechanical properties.
- Carbonated cement pastes present a further increase in shear strength for increasing confining pressures than non-carbonated ones. This is indicative of a more frictional behaviour in carbonated than in non-carbonated cement pastes. This can be attributed to the microstructural changes observed in Chapter 4, where SEM images revealed a microstructure with reduced cement matrix presence and a significant amount of CaCO_3 crystals precipitated during the carbonation process.

Part II

Modelling

Introduction to Part II

This second part of the thesis focuses on the numerical modelling of the behaviour of cement pastes, both with and without HGMS, under conditions representative of CO₂ geological storage wells. A coupled chemo-poromechanical model is used to account for cement carbonation using the finite element method. The model is calibrated using laboratory experimental data, allowing it to accurately represent the performance of cement pastes under real well conditions.

The aim of this modelling is to improve our understanding of how these cement pastes behave in the environments encountered in CO₂ storage facilities. By integrating chemical and mechanical interactions, this approach facilitates the extrapolation of laboratory results to predict the durability and integrity of cement in CO₂ injection well applications.

Chapter 6

Homogenisation of the elastic parameters

6.1 Introduction

The mechanical integrity of cement pastes used in CO₂ storage wells plays a critical role in ensuring fluid containment and overall well durability. In particular, lightweight cement pastes with HGMS are being investigated for their ability to modify the density of cement pastes while maintaining adequate mechanical properties compared to other traditional solutions (cf. Chapter 1). However, the use of HGMS in cement pastes does result in changes in their mechanical behaviour (cf. Chapter 5). While the compressive strength of these pastes is often studied, the elastic parameters are equally important as they govern the interaction between the cement sheath, the surrounding rock formation and the casing. Lower elastic moduli can reduce stresses in the cement sheath during thermal or mechanical loading, thereby reducing the risk of failure or plastic strains [139, 140, 141].

In the experimental part of this work (cf. Part I), the mechanical behaviour of HGMS cement pastes was characterised, including their elastic properties. To complement and extend these measurements, this chapter presents an analytical micromechanical model designed to estimate the elastic parameters of HGMS lightweight cement pastes. The proposed model is based on established micromechanical modelling approaches, as those developed by Hervé and Zaoui [142] for perfect interfaces and Ghabezloo [143] for imperfect interfaces. These frameworks allow the prediction of the elastic properties of HGMS cement pastes using available inputs such as the elastic properties of the cement matrix, the dimensions of the HGMS, and the volume fraction of HGMS.

Micromechanical modelling has previously been successfully applied to cementitious materials for the evaluation of macroscale properties and the study of hydration progress, w/s ratio and the influence of additives [144, 145, 146, 147, 148, 149]. Using this approach, the model presented here provides a relatively simple yet accurate method for estimating

the mechanical response of HGMS cement pastes.

This micromechanical model is initially validated and verified with experimental data and will subsequently be implemented in the finite element model used in Chapter 7. This integration allows for the simulation of the mechanical behaviour of HGMS cement pastes under well conditions, providing a comprehensive understanding of their performance in real-world applications.

6.2 Basic considerations and choice of REV

The development of the micromechanical model for HGMS cement pastes requires first the definition of an adequate REV to represent the microstructure of the material. Based on the SEM images, the considered REV for the HGMS cement paste is presented schematically in Figure 6.2.1. It consists of HGMS inclusions embedded in a cement paste matrix. The relative simplicity of the chosen REV is of great practical importance in what concerns the number of model parameters and the facility and accessibility of their experimental evaluation. The cement matrix mechanical parameters can be measured on a hardened specimen of a paste prepared with the same composition, without HGMS. The HGMS dimensions, composition, and mechanical parameters are usually provided by the manufacturer or can be obtained as shown in Chapter 2 for dimensions and composition, and in Appendix A for strength. The information related to the volume fraction of the phases can be easily calculated from the slurry formulation.

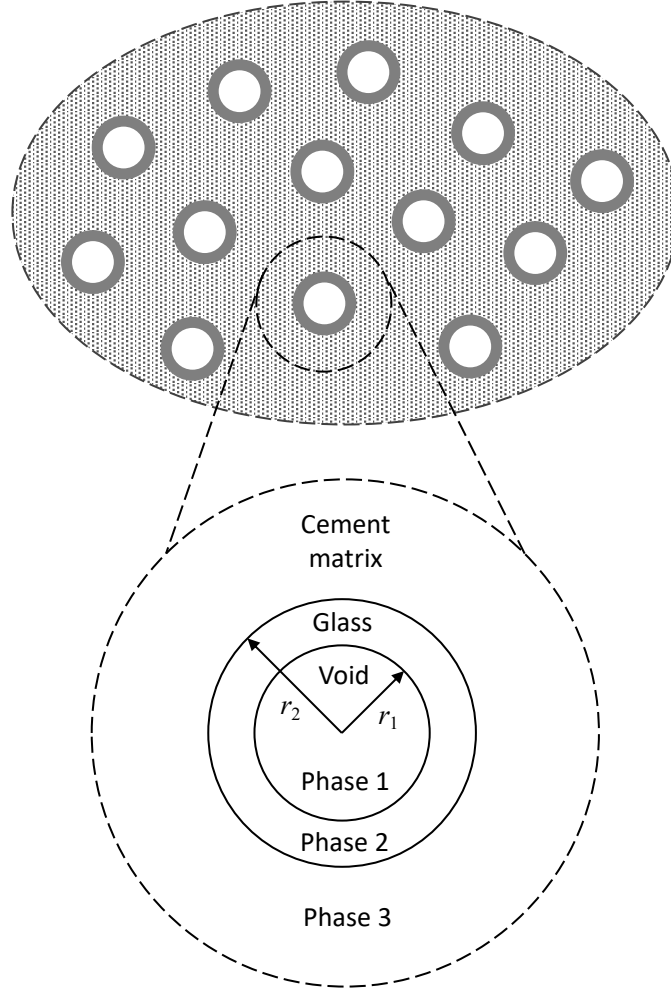


Figure 6.2.1: Top: Schematic representation of the REV of the lightweight cement paste based on HGMS, Bottom: multi-layer spherical geometry used for evaluation of the strain localization coefficients

It has been shown in Chapter 3 that there is a chemical interaction between HGMS and cement matrix. HGMS are acting as nucleation agents, which implies that cement hydration products are forming on their surface. Furthermore, HGMS present pozzolanic activity, which make them react with the $\text{Ca}(\text{OH})_2$ formed during cement hydration to form further CSH. For these reasons, considering a perfect interface between the HGMS and cement matrix does not seem to be a strong assumption for the precision needed for most practical applications. This being said, the effect of imperfect interfaces between HGMS and cement matrix will also be presented and briefly studied in the paper.

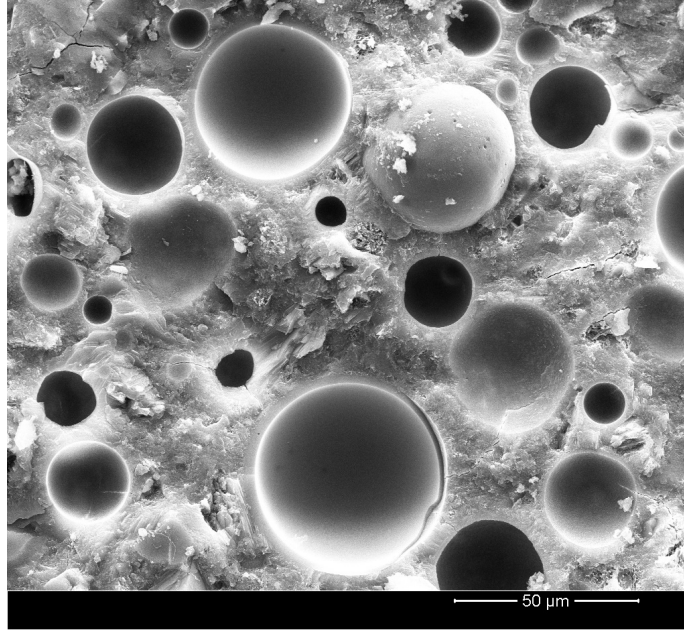


Figure 6.2.2: SEM image of HGMS cement paste after 100 days of curing time

Another point that should be mentioned in relation to the pozzolanic activity of HGMS is that it will consume the glass outer shell to some extent, decreasing its thickness and affecting the chemical composition, microstructure and, eventually, the mechanical parameters of the cement matrix in the vicinity of the HGMS. It should be noted that, in general terms, the degree of pozzolanic reaction is not 100% but rather less than 50% for most cases [150, 151]. This results in the pozzolanic additions not being completely consumed by this reaction, a matter that can be verified in Figure 6.2.2, where the presence of HGMS in the cement pastes tested in this work can still be appreciated. To adequately take into account the influence of pozzolanic reactions in the micromechanical model it is necessary to obtain precise information on the zone influenced by the pozzolanic reactions, including the kinetics of the reaction and its effect on the HGMS thickness, the area of the influence zone in the cement matrix and resulting changes in mechanical properties. The mechanical properties of the influenced zone may be evaluated by experimental methods like nanoindentation. It is then possible to adapt the REV to take into account the modifications resulted from pozzolanic reactions in the model. This is however out of the scope of this work, and both the HGMS and the cement matrix are assumed to keep their initial dimensions and properties.

The evaluation of the homogenised elastic parameters from Equation 6.2.1 needs the knowledge of the volume fraction of different microstructure phases of the REV. The volume fraction of HGMS in the paste, f_{HGMS} , can be evaluated by knowing the HGMS mass per

unit volume of the paste and the HGMS density. The necessary volume fraction of the three microstructure phases of the REV (void, glass, and cement matrix), can then be evaluated by knowing the HGMS internal and external radii.

$$K^{\text{hom}} = \sum_{k=1}^n f_k k_k A_k^v \quad ; \quad G^{\text{hom}} = \sum_{k=1}^n f_k g_k A_k^d \quad (6.2.1)$$

$$f_1 = \left(\frac{r_1}{r_2}\right)^3 f_{HGMS} \quad ; \quad f_2 = \left[1 - \left(\frac{r_1}{r_2}\right)^3\right] f_{HGMS} \quad ; \quad f_3 = 1 - f_1 - f_2 = 1 - f_{HGMS} \quad (6.2.2)$$

The density of the lightweight cement paste can be evaluated as:

$$\frac{\rho}{\rho_3} = 1 - f_{HGMS} \left[1 - \frac{\rho_2}{\rho_3} \left(1 - \left(\frac{r_1}{r_2}\right)^3\right)\right] \quad (6.2.3)$$

where ρ_2 and ρ_3 are respectively the glass and cement matrix densities.

6.3 Strain localization coefficients

Due to the particular geometry of the inclusions, i.e. HGMS, the strain localization coefficients can not be evaluated based on the classical Eshelby's solution [152]. Instead, the multi-layer spheres solution developed by Hervé and Zaoui [142] is adapted based on the three layer geometry shown in the bottom part of Figure 6.2.1. This solution is based on the assumption of the linear elastic behaviour of the cement matrix and the glass material, as well as the existence of a perfect contact between the HGMS and the cement matrix. The presence of an imperfect interface between the cement matrix and HGMS inclusions will be taken into account based on an extension of Hervé and Zaoui [142] model by Ghabezloo [143].

A detailed mathematical development of the strain localization coefficients is given in the appendix of the paper. The essential final equations for a numerical application of the model are presented below, in a way that the strain localization coefficients can be calculated without referring to the appendix. The presentation is done first by assuming perfect interfaces between HGMS and cement matrix. An extension is then presented to take into account the influence of imperfect interfaces.

6.4 Perfect interface between HGMS and cement matrix

The coefficients A_k^v and A_k^d to be used in Equation 6.2.1 are given by the following expressions:

$$A_k^v = \frac{H_k^v}{\sum_{k=1}^n f_k H_k^v} \quad ; \quad A_k^d = \frac{H_k^d}{\sum_{k=1}^n f_k H_k^d} \quad (6.4.1)$$

The coefficients H_k^v and H_k^d can be evaluated by knowing the geometrical properties of the REV, mainly the radii r_1 and r_2 (cf. Figure 6.2.1), and the elastic properties of glass and cement matrix, respectively referred to by superscripts 2 and 3 (e.g. k_2 is the bulk modulus of glass and g_3 is the shear modulus of the matrix). The coefficients H_k^v are given by the following expressions:

$$H_1^v = \frac{(4g_2 + 3k_2)(4g_3 + 3k_3)}{12 \left(\frac{r_1}{r_2}\right)^3 k_2 (g_3 - g_2) + 4g_2 (4g_3 + 3k_2)} \quad (6.4.2)$$

$$H_2^v = \frac{4g_2}{(4g_2 + 3k_2)} H_1^v \quad (6.4.3)$$

$$H_3^v = 1 \quad (6.4.4)$$

It is interesting to note that the H_k^v parameters, and consequently the homogenised bulk modulus evaluated from Equation 6.2.1, depend only on the ratio r_2/r_1 of the HGMS and are independent of the actual values of r_1 and r_2 . For obtaining the expressions of H_k^d , it is necessary to calculate the $\mathbf{P}^{(2)}$ matrix, which is a 4×4 matrix given by:

$$\mathbf{P}^{(2)} = \mathbf{L}_3^{-1}(r_2) \mathbf{L}_2(r_2) \mathbf{L}_2^{-1}(r_1) \mathbf{L}_1(r_1) \quad (6.4.5)$$

where the matrices $\mathbf{L}_k(r)$ are given by:

$$\mathbf{L}_k(r) = \begin{bmatrix} r & -\frac{6\nu_k}{1-2\nu_k} r^3 & \frac{3}{r^4} & \frac{5-4\nu_k}{1-2\nu_k} \frac{1}{r^2} \\ r & -\frac{7-4\nu_k}{1-2\nu_k} r^3 & -\frac{2}{r^4} & \frac{2}{r^2} \\ g_k & \frac{3\nu_k}{1-2\nu_k} g_k r^2 & -\frac{12}{r^5} g_k & \frac{2(\nu_k-5)}{1-2\nu_k} \frac{g_k}{r^3} \\ g_k & -\frac{7+2\nu_k}{1-2\nu_k} g_k r^2 & \frac{8}{r^5} g_k & \frac{2(1+\nu_k)}{1-2\nu_k} \frac{g_k}{r^3} \end{bmatrix} \quad (6.4.6)$$

Note that the superscript (2) in $\mathbf{P}^{(2)}$ is not a power. In accordance with the notations of Hervé and Zaoui [142], it is used to attribute the matrix to the phase 2. The mathematical expressions obtained by calculating each of the components of the $\mathbf{P}^{(2)}$ matrix are considerably long. Since they are obtained from a multiplication of matrices, the equations of the H_k^d can be expressed in terms of the components of matrix $\mathbf{P}^{(2)}$, $P_{11}^{(2)}$, $P_{12}^{(2)}$, $P_{21}^{(2)}$, $P_{22}^{(2)}$, as presented below. It should be noted that these components do not all have the same physical unit. $P_{11}^{(2)}$ and $P_{22}^{(2)}$ have no unit, while $P_{12}^{(2)}$ has unit L^2 and $P_{21}^{(2)}$ has unit L^{-2} .

$$H_1^d = \frac{21P_{21}^{(2)}r_1^2 + 5P_{22}^{(2)}}{5(P_{11}^{(2)}P_{22}^{(2)} - P_{12}^{(2)}P_{21}^{(2)})} \quad (6.4.7)$$

$$H_2^d = \frac{P_{21}^{(2)}}{5(\nu_2 - 1)(P_{11}^{(2)}P_{22}^{(2)} - P_{12}^{(2)}P_{21}^{(2)})} \left[\frac{P_{22}^{(2)}(5\nu_2 - 7)}{3P_{21}^{(2)}} + 7r_1^2(\nu_2 - 1) - \frac{84(r_1^5 - r_2^5)}{5(r_1^3 - r_2^3)} \right] \quad (6.4.8)$$

$$H_3^d = 1 \quad (6.4.9)$$

In the above equations, r_1 and r_2 are respectively the internal and external radii of HGMS. k_k , g_k and ν_k stand respectively for bulk modulus, shear modulus and Poisson's ratio of the k phase (with void space, silicate glass and cement matrix indexed from 1 to 3, respectively). Note that the elastic parameters of the phase 1 (void space) should be considered equal to zero.

Considering the complexity of the equations of H_k^d parameters, one can numerically verify that, similarly to what was mentioned above for H_k^v parameters, these coefficients and consequently the homogenised shear modulus evaluated using Equation 6.2.1 are independent of the numerical values of r_1 and r_2 and depend only on the ratio r_2/r_1 . It can also be verified that by considering similar elastic parameters for phases 2 and 3, the above equations are reduced to the ones given by classical Eshelby solution for a simple porous medium.

It should be noted that considering the phase number 3 as the cement matrix corresponds to the Mori-Tanaka homogenisation scheme. A different choice could be the self-consistent scheme in which the reference medium is the homogenised medium. In this latter case, the elastic parameters of the matrix are not known in advance. Consequently, iterative calculations should be used to evaluate the homogenised elastic parameters. Considering the microstructure of the HGMS lightweight cement, Mori-Tanaka scheme seems to be more appropriate. However, comparison tests were performed between the two methods for a variety of parameters. For usual volume fractions of HGMS, the results of these two methods are extremely close together. Therefore, in the following, Mori-Tanaka scheme is used for the calculations since it has the advantage of being easier to apply, in accordance with the main objective of obtaining an easy to apply model for estimating the elastic properties of lightweight cement pastes based on HGMS.

6.5 Imperfect interface between HGMS and cement matrix

The above mathematical framework can be extended to take into account the presence of an imperfect interface between the HGMS and the cement matrix. The imperfect interface,

characterized by its compliances, results in displacement jumps across the interface. The micromechanical models with imperfect interface has been previously developed and used in the literature [153, 154, 155, 156, 157]. Ghabezloo [143] presented an extension of the micromechanical model of Hervé and Zaoui [142] to take into account imperfect interfaces between phases. This model is used in the following.

The displacement jump at the interface is assumed to be proportional to the traction vector, $\sigma_{ij}n_j$ which is continuous across the interface. The following general equation is postulated for the displacement jump across the interface [154, 158, 159]:

$$\Delta u_i = \eta_{ij} \sigma_{jk} n_k \quad (6.5.1)$$

where η_{ij} is a second-order tensor representing the compliances of the interface. $\eta_{ij} = 0$ corresponds to a perfectly bounded interface. A simple form of η_{ij} with one tangential and one normal compliance, η^t and η^n respectively, can be given as [154, 158, 159]:

$$\eta_{ij} = \eta^t \delta_{ij} + (\eta^n - \eta^t) n_i n_j \quad (6.5.2)$$

In the presence of imperfect interfaces, the strain localization coefficients of each phase A_k^v and A_k^d can be written as [143]:

$$A_k^v = \frac{H_k^v}{\sum_{k=1}^n f_k (1 + 3\lambda_k) H_k^v} \quad (6.5.3)$$

$$A_k^d = \frac{H_k^d}{\sum_{k=1}^n f_k \left(1 + 2\xi_k \frac{2\psi_k + 3}{5}\right) H_k^d} \quad (6.5.4)$$

The following dimensionless parameters have been introduced to simplify the presentation of the equations:

$$\lambda_k = \frac{k_k \eta_k^n}{r_k}; \quad \xi_k = \frac{g_k \eta_k^t}{r_k}; \quad \psi_k = \frac{\eta_k^n}{\eta_k^t} \quad (6.5.5)$$

The coefficient H_1^v is given by the following expression:

$$H_1^v = \frac{(4g_2 + 3k_2)(4g_3 + 3k_3)}{12 \left(\frac{r_1}{r_2}\right)^3 k_2 [g_3 (1 - 4\xi_2 \psi_2) - g_2] + 4g_2 [4g_3 (1 + 3\lambda_2) + 3k_2]} \quad (6.5.6)$$

The coefficients H_2^v and can be evaluated as a function of H_1^v using Equation 6.4.3 and $H_3^v = 1$, same as Equation 6.4.4. One can easily verify that for a perfect bounding between the HGMS and cement matrix, i.e. $\lambda_2 = \xi_2 = 0$, Equation 6.5.6 is reduced to Equation 6.4.2. To evaluate H^d coefficients, the matrix $\mathbf{P}^{(2)}$ can be evaluated as follows:

$$\mathbf{P}^{(2)} = \mathbf{L}_3^{-1}(r_2) [\mathbf{L}_2(r_2) + \mathbf{L}'_2(r_2)] \mathbf{L}_2^{-1}(r_1) \mathbf{L}_1(r_1) \quad (6.5.7)$$

where the matrix $\mathbf{L}'_k(r)$ is given by:

$$\mathbf{L}'_k(r) = \begin{bmatrix} g_k \eta_k^n & \frac{3\nu_k}{1-2\nu_k} g_k r^2 \eta_k^n & -\frac{12}{r^5} g_k \eta_k^n & \frac{2(\nu_k-5)}{1-2\nu_k} \frac{1}{r^3} g_k \eta_k^n \\ g_k \eta_k^t & \frac{7+2\nu_k}{1-2\nu_k} g_k r^2 \eta_k^t & \frac{8}{r^5} g_k \eta_k^t & \frac{2(\nu_k+1)}{1-2\nu_k} \frac{1}{r^3} g_k \eta_k^t \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (6.5.8)$$

The matrices $\mathbf{L}_k(r)$ are given by Equation 6.4.6. The coefficients H_1^d , H_2^d and H_3^d are then evaluated using Equations 6.4.7, 6.4.8 and 6.4.9 respectively.

6.6 Sensitivity analysis

To understand the model parameters and their influence on the evaluated elastic parameters, a sensitivity analysis is undertaken. For this purpose, it is useful to recall Equation 6.2.1 showing that the homogenised elastic parameters will depend on the volume fraction of each phase, f_k , the elastic properties of each phase, k_k and g_k , and the localization coefficients, A_k^v and A_k^d , which play the role of some weighting factors. As shown in Equations 6.4.2 to 6.4.9, these parameters depend on the elastic properties of each phase and on the radii ratio r_2/r_1 . It is obvious that using a cement matrix with higher elastic parameters results directly in a cement paste with higher parameters. This is the same for the HGMS material, an increase in its elastic parameters is directly reflected on the elastic parameters of the paste, though with a less important effect as compared to cement paste due to its lower volume fraction.

It is interesting to see the effect of the ratio r_2/r_1 and HGMS volume fraction on the homogenised elastic parameters of the HGMS lightweight cement paste while keeping constant the other parameters. The Young's modulus and the Poisson's ratio of the silica glass and the cement matrix are given the values of $E_2 = 64$ GPa, $\nu_2 = 0.2$, $E_3 = 24.1$ GPa and $\nu_3 = 0.24$ (cf. Chapter 5, Table 5.2.1). The needed values of bulk and shear moduli can be evaluated using $K = E/[3(1-2\nu)]$ and $G = E/[2(1+\nu)]$. A perfect interface is assumed between the cement matrix and HGMS. The results of sensitivity analysis are presented as contour graphs in Figure 6.6.3 for the bulk modulus and in Figure 6.6.4 for the shear modulus for different values of f_{HGMS} and r_2/r_1 ratio. The homogenised elastic parameters are normalized with respect to the elastic parameters of the cement matrix. The normalized cement paste density corresponding to each case can be evaluated using Equation 6.2.3.

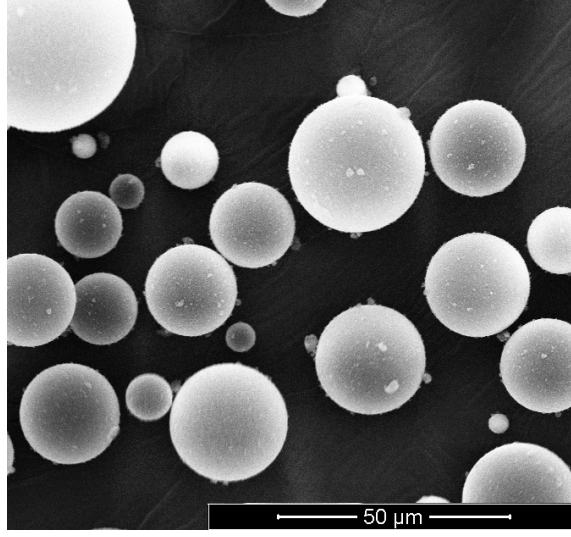


Figure 6.6.1: SEM image of HGMS

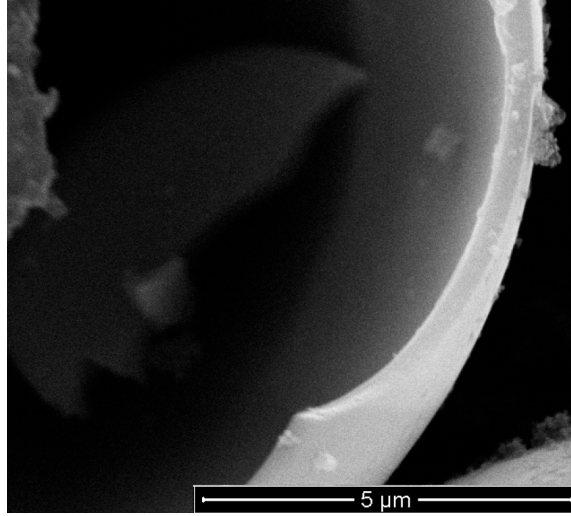


Figure 6.6.2: SEM image of broken HGMS

One can see in Figures 6.6.3 and 6.6.4 that the results are in agreement with expectations. For constant HGMS volume fraction, both bulk and shear moduli increase with increasing r_2/r_1 ratio, which implies increasing the glass (phase 2) to void (phase 1) proportion in the composite medium. If the volume fraction of glass increases and the void volume fraction decreases, greater amounts of stiff material will increase the stiffness of the composite material. Therefore, using thicker HGMS results in higher Young moduli,

but also, in higher density of the cement paste, which is less desirable. At constant HGMS dimensions, higher HGMS volume fraction results in a lighter cement paste, but also in lower elastic parameters. From Figures 6.6.1 and 6.6.2, it is clear that HGMS's void volume fraction is much larger than the borosilicate glass volume fraction. Increasing the HGMS volume fraction implies increasing the void space, which decreases the homogenised elastic parameters.

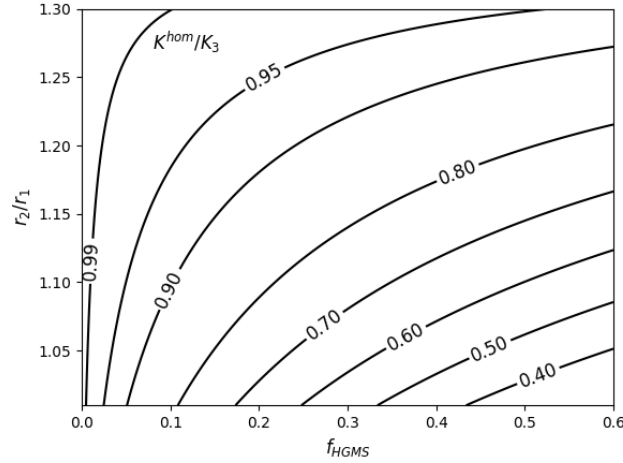


Figure 6.6.3: Effect of HGMS volume fraction and the radii ratio r_2/r_1 of HGMS on the homogenised bulk modulus (perfect interface is assumed between HGMS and cement matrix)

It is also interesting to see how the existence of an imperfect interface between the cement matrix and HGMS can influence the evaluated Young moduli. For this analysis, the internal and external radii of the HGMS are fixed respectively equal to $r_1 = 18 \mu\text{m}$ and $r_2 = 20 \mu\text{m}$. HGMS volume fraction is taken equal to 0.24. The homogenised bulk and shear moduli are evaluated for a wide range of interface normal and tangential compliances. The homogenised bulk modulus depends only on the normal compliance and is independent of the tangential compliance. Its variations with the normal compliance are plotted in Figure 6.6.5. The evaluated bulk moduli are normalized with respect to the matrix bulk modulus. $\eta^n = 0$ corresponds to a perfect interface. The results show that the bulk modulus decreases by increasing the interface compliance, but tends towards an asymptotic value. Generally, it seems that the presence of an imperfect interface between HGMS and cement matrix has a limited influence on the bulk modulus. For the parameters used in the sensitivity analysis, the ratio K^{hom}/K_3 is reduced from 0.736 for the perfect interface to 0.696 for a highly compliant interface.

The influence of interface normal and tangential compliances on the homogenised shear

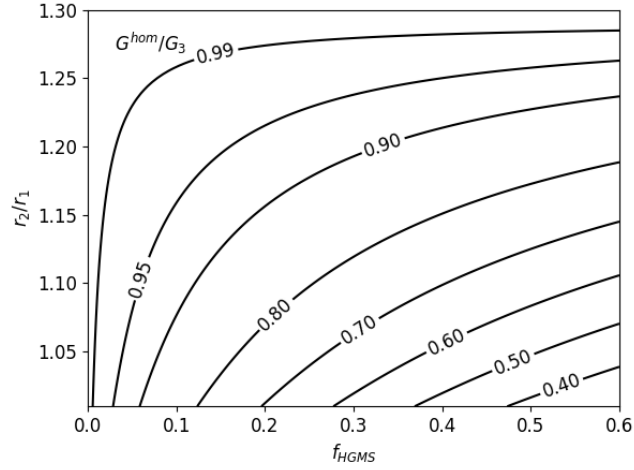


Figure 6.6.4: Effect of HGMS volume fraction and the radii ratio r_2/r_1 of HGMS on the homogenised shear modulus (perfect interface is assumed between HGMS and cement matrix)

modulus is presented in Figure 6.6.6 in the form of a contour plot. One can see a complex interaction between the effects of normal and tangential compliances on the homogenised shear modulus. An important difference between the two compliances, e.g. big η^n and small η^t or inverse, results in lower shear modulus. In the particular case of $\eta^n = \eta^t$ an asymptotic influence can be observed. For the parameters used in the sensitivity analysis, the ratio G^{hom}/G_3 is reduced from 0.76 for the perfect interface to an 0.54 for a highly compliant interface.

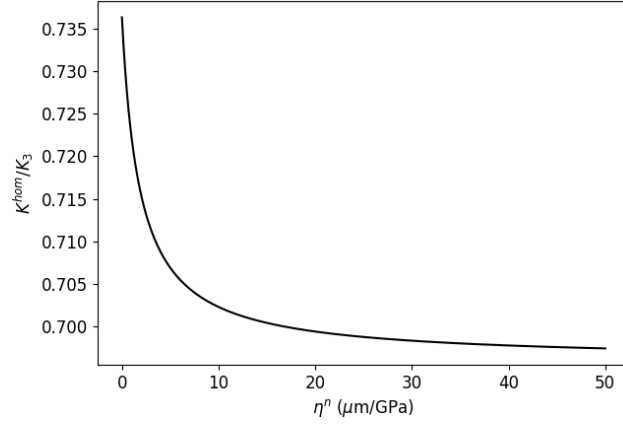


Figure 6.6.5: Effect of interface normal compliance on the homogenised bulk modulus

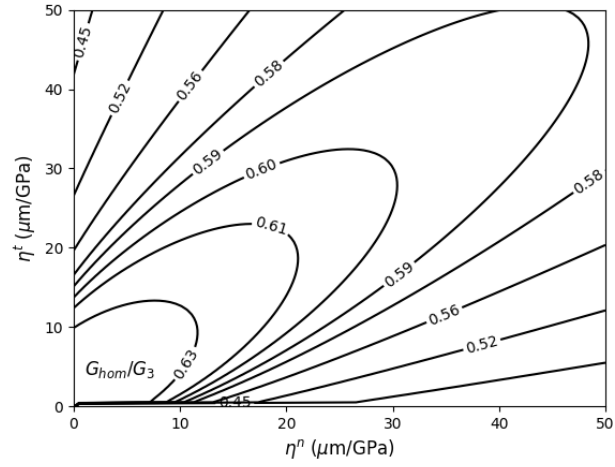


Figure 6.6.6: Effect of interface normal and tangential compliances on the homogenised shear modulus

6.7 Model predictions considering perfect interface

For applying this homogenisation model to cement pastes with HGMS, it was considered that their matrix was composed of cement paste with the same elastic properties as those of CS0044C00 and CS0060C00 for each w/s ratio. In addition, Table 6.7.1 shows all the necessary parameters for different cement pastes. The HGMS volume fractions are evaluated from the pastes' composition, specified in Table 2.2.1 and the density of each component. The volume fractions of phases are then evaluated using Equation 6.2.2. The outer radius r_2 is given as the D_{50} of the HGMS, while the inner radius r_1 is determined by knowing the density of the HGMS ($\rho_{\text{HGMS}} = 0.28 \text{ g/cm}^3$) and the borosilicate glass ($\rho_2 = 2.23 \text{ g/cm}^3$) using the following equation:

$$r_1 = r_2 \left[1 - \frac{\rho_{\text{HGMS}}}{\rho_2} \right]^{1/3} \quad (6.7.1)$$

Finally, the properties of the borosilicate glass forming the outer shell are obtained from the literature [160, 161]. It should be emphasized that no parameter calibration or fitting is done.

Table 6.7.1: Model parameters for different cement pastes

Parameter	CS2744C00	CS4144C00	CS2760C00	CS4160C00
r_1 (μm)	14.344	18.518	14.344	18.518
r_2 (μm)	15.000	20.000	15.000	20.000
f_{HGMS}	0.329	0.230	0.287	0.197
f_1	0.288	0.183	0.251	0.156
f_2	0.041	0.047	0.036	0.041
f_3	0.671	0.770	0.713	0.803
E_2 (GPa)	64.0	64.0	64.0	64.0
E_3 (GPa)	24.1	24.1	16.3	16.3
ν_2	0.20	0.20	0.20	0.20
ν_3	0.24	0.24	0.27	0.27

A perfect interface is first assumed between the HGMS and the cement matrix. Figures 6.7.1 and 6.7.2 present comparisons between the evaluated and experimentally measured bulk and shear moduli for different cement pastes. It can be appreciated that the model predictions assuming the perfect interface, needless of any calibration, are in quite good agreement with those of laboratory tests, with differences lower than 15%. The biggest difference between the model prediction and experimental results is related to cement paste CS2760C00, which is the lightest paste among all that were studied, given the higher w/s ratio and the lower specific weight of HGMS27 as compared to HGMS41. It

is interesting to notice that the model predictions for all the studied pastes are slightly higher than the laboratory results.

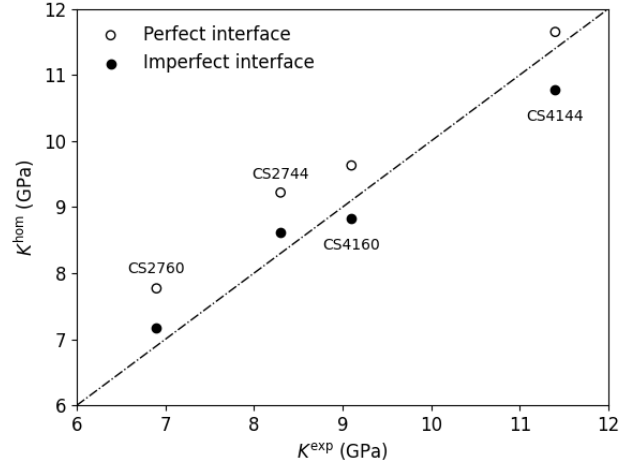


Figure 6.7.1: Comparison between experimentally evaluated bulk moduli of different specimens and model predictions considering perfect and imperfect interfaces

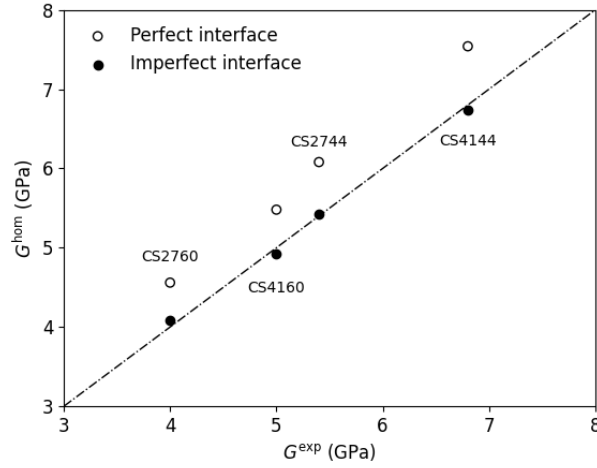


Figure 6.7.2: Comparison between experimentally evaluated shear moduli of different specimens and model predictions considering perfect and imperfect interfaces

6.8 Effect of interface

The difference between the model predictions and the experimental results, which is less than 15% for the studied specimens, is probably negligible for most practical applications. This difference can be due to simultaneous effects of various factors and simplifications assumptions related to the homogenisation method, the configuration of the REV, and the perfect interface between HGMS and cement matrix. Considering the over-estimation of the elastic parameters compared to the measured values, as can be seen in Figures 6.7.1 and 6.7.2, it is interesting to see if the model predictions can be improved by considering an imperfect interface between the HGMS and the cement matrix. The interface parameters can be fitted to minimize the error between the model predictions and experimental results. The studied specimens have different w/s ratios and different HGMS dimensions. Consequently, the interfaces in these specimens are not necessarily similar. However, for the sake of simplicity, it is assumed that the interfaces in all specimens have the same normal and tangential compliances.

The fitting of interface parameters is done by evaluating the error, defined in Equation 6.8.1, between the model predictions and experimental results by varying the interface parameters, η^n and η^t , in a large span.

$$\text{Error} = \sum_{i=1}^4 \left[\left(\frac{K_i^{\text{hom}} - K_i^{\text{exp}}}{K_i^{\text{exp}}} \right)^2 + \left(\frac{G_i^{\text{hom}} - G_i^{\text{exp}}}{G_i^{\text{exp}}} \right)^2 \right] \quad (6.8.1)$$

The results are presented in the contour plot of Figure 6.8.1. The minimum error is

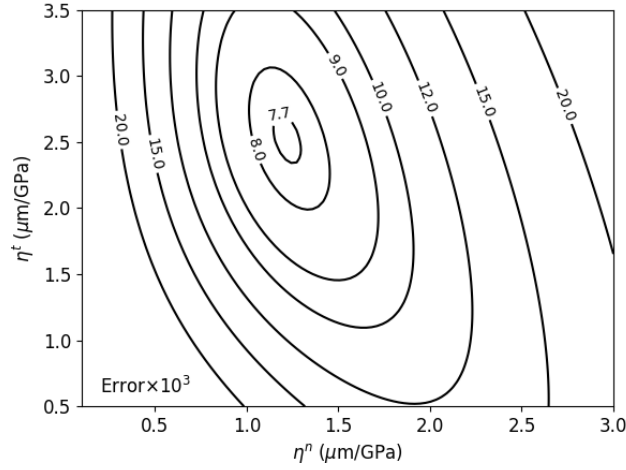


Figure 6.8.1: Fitting of the interface parameters. Contour plot of error for different values of normal and tangential compliances

found equal to 7.66×10^{-3} for the interface parameters $\eta^n = 1.215 \mu\text{m/GPa}$ and $\eta^t = 2.527 \mu\text{m/GPa}$. The fact that for the fitted values $\eta^n < \eta^t$ is compatible with the available information in the literature [158, 162, 163]. It is interesting to mention that the evaluated error for the case of perfect interfaces is 115×10^{-3} .

Figures 6.7.1 and 6.7.2 present the model predictions for the fitted interface parameters. Obviously, the predictions are much closer to the experimental values, with very small differences in bulk modulus and almost perfect predictions for shear modulus.

6.9 Conclusion

The micromechanical model presented in this chapter aims to predict the elastic properties of lightweight cement pastes containing HGMS. The model provides a simplified yet effective tool, allowing for the estimation of mechanical parameters with minimal input data, including the elastic properties of the cement matrix and the HGMS themselves. While the model makes certain simplifying assumptions, its results show good agreement with experimental data, making it suitable for practical applications in the design of cement paste formulations for CO₂ storage wells.

- An analytical model based on homogenisation theory has been developed to predict the elastic properties of HGMS cement pastes. The model requires knowledge of the elastic properties of the cement matrix, as well as the volume fraction of HGMS, their dimensions, and elastic properties.

- Despite evidence of interaction between the HGMS and the cement matrix, the model assumes that the effects of this interaction, including pozzolanic activity and filler effects, are negligible for calculating elastic moduli. While this simplification is reasonable for most practical applications, it remains a limitation of the model.
- Although the assumption of scale separation between the cement matrix and the HGMS is not strictly accurate, it appears to have minimal impact on the predictions for hardened cement pastes with a low volume fraction of clinker grains (assuming complete hydration). However, it is important to note that a more robust model could involve a multiscale approach, accounting for the interaction between the HGMS and the clinker grains, as well as changes in the matrix microstructure due to the pozzolanic activity of the HGMS.
- The sensitivity analysis revealed that the model's results are particularly dependent on changes in the ratio of the external to internal radii of the HGMS and on the properties of the cement matrix. The presence of an imperfect interface between the HGMS and the cement matrix has a limited effect on the predicted bulk modulus, but depending on the interface parameters, can have a more significant effect on the predicted shear modulus.
- The model's predictions were compared with experimental data obtained in Chapter 5, showing a strong correlation. Without any parameter calibration for the case of a perfect interface, the model's predictions, with a discrepancy of less than 15% from experimental values, are suitable for most practical applications. Calibrating a single pair of interface parameters (normal and tangential compliances) for all tested pastes significantly improved the model's predictions.
- This model serves as a valuable tool for engineers designing lightweight cement paste formulations incorporating HGMS. It provides a relatively simple and accurate method for estimating elastic properties using readily available parameters, making it suitable for a range of practical applications in the field of well cementing.
- The micromechanical model developed in this chapter will serve as the foundation for the chemo-poromechanical model that will be implemented in Chapter 7. This subsequent model will incorporate the effects of chemical reactions, such as carbonation and pozzolanic activity, alongside mechanical deformation and pore structure evolution. The initial validation and verification of the micromechanical model presented here provide a solid basis for the more complex finite element model to be introduced in the next chapter.

Chapter 7

Chemo-poromechanical model

7.1 Introduction

This chapter presents the numerical modelling of class G cement pastes containing HGMS under scCO₂ injection well conditions. Building upon the experimental results discussed in Part I, the main objective is to predict the mechanical and chemical behaviour of these cement pastes, using a refined poromechanical model. The simulations in this chapter serve as a means to apply the knowledge gained on the chemical interaction, microstructure, and mechanical properties of the materials, allowing for the assessment of their behaviour in realistic well conditions.

The original model, developed to simulate the progression of carbonation in cement pastes in scCO₂ environments, relies on fundamental balance equations of mass and momentum conservation in porous media. However, to account for the distinct behaviour introduced by the presence of HGMS, modifications have been made. The analytical homogenisation model for elastic properties, discussed in Chapter 6, has been incorporated to enhance the accuracy of mechanical predictions. In addition, the rupture of HGMS under pressure, as observed in the laboratory and mainly discussed in Chapter 4, has been included in the model. This phenomenon impacts both the mechanical and species transport properties of the material, which in turn influence the progression of carbonation.

These refinements make the model more representative of the actual behaviour of HGMS cement pastes under well conditions. A comparative analysis is performed between the original and improved models, illustrating the advantages of each modification. Sensitivity analyses highlight the importance of each parameter on the overall prediction accuracy. The validation of the model is supported by experimental data, with clear initial and boundary conditions. Finally, the refined model is applied to simulate the behaviour of HGMS cement pastes under realistic injection well conditions, demonstrating its practical value in predicting their performance in geological CO₂ storage applications.

7.2 Fundamentals

Developed by Vallin within her research [164], the computational model integrated into the finite element software BIL (<http://perso.lcpc.fr/dangla.patrick/bil/>) was specifically developed to analyse the effects of scCO₂ on cement pastes, considering various aspects including both chemical reactions and poromechanical phenomena.

The model conceptualizes the cement paste as a saturated porous material. The skeleton, as currently defined, consists of different phases, i.e. Ca(OH)₂, CSH, aluminates, and CaCO₃. Within this model, a system of equations is employed to describe the material's behaviour. Among these equations, Equation 7.2.1 governs fluid mass conservation.

$$\frac{\rho_f \Phi_f}{K_f} \frac{\partial p_f}{\partial t} + \frac{\rho_f}{N_{ff}} \frac{\partial p_f}{\partial t} + \rho_f b \operatorname{div} \left(\frac{\partial u}{\partial t} \right) + \rho_f \sum_{R_i} Y_{R_i} \frac{\partial \xi_{R_i}}{\partial t} - \operatorname{div} \left[\rho_f \frac{\kappa}{\eta} \operatorname{grad} (p_f) \right] = 0 \quad (7.2.1)$$

where ρ_f represents fluid density, Φ_f denotes porosity, K_f signifies fluid compressibility modulus, p_f is the fluid pressure, N_{ff} stands for fluid-fluid coupling coefficient, b represents Biot's coefficient, u indicates the displacement of the solid skeleton, Y_{R_i} represents the molar flow of reactant R_i , ξ_{R_i} denotes the advancement of the reaction of reactant R_i , κ represents fluid permeability, and η signifies fluid dynamic viscosity.

Equation 7.2.1 comprises five terms. The first corresponds to fluid compressibility. The second and third terms correspond to porous medium deformation. The fourth term reflects chemical reactions generating water as a by product. The fifth term is associated with fluid transport, governed by Darcy's law.

Then, Equation 7.2.2 is the second equation of the system, describing CO₂ mass conservation.

$$\frac{\partial (\Phi_f C_{\text{CO}_2})}{\partial t} + \sum a_{R_i} \frac{\partial \xi_{R_i}}{\partial t} - \operatorname{div} \left[d_{eff} \operatorname{grad} (C_{\text{CO}_2}) + C_{\text{CO}_2} \frac{\kappa}{\eta} \operatorname{grad} (p_f) \right] = 0 \quad (7.2.2)$$

where C_{CO_2} represents CO₂ concentration, a_{R_i} denotes stoichiometric coefficient of reaction R_i , and d_{eff} signifies the effective diffusion coefficient.

This equation consists of four terms, where the first accounts for the mass variation of CO₂ within the porous medium over time, the second reflects chemical reactions consuming CO₂. The third and fourth terms relate to CO₂ transported by diffusion or advection, respectively.

The system of equations also includes both mechanical equilibrium and a constitutive relation describing the material's response. The mechanical equilibrium is expressed through Equation 7.2.3 (balance equation), while the total stress is related to the state variables via Equation 7.2.4 (constitutive relation).

$$\operatorname{div}(\boldsymbol{\sigma}) + \boldsymbol{\gamma} = 0 \quad (7.2.3)$$

$$\boldsymbol{\sigma} - \boldsymbol{\sigma}_0 = 2G\boldsymbol{\varepsilon} + \left(K - \frac{2}{3}G\right)\text{tr}(\boldsymbol{\varepsilon}) - b(p_f - p_{f,0}) \quad (7.2.4)$$

where $\boldsymbol{\gamma}$ represents the body force vector, $\boldsymbol{\sigma}$ represents the stress tensor, $\boldsymbol{\sigma}_0$ denotes the initial stress tensor, G is the shear modulus, $\boldsymbol{\varepsilon}$ denotes the strain tensor, K represents the bulk modulus, p_f stands for fluid pressure, and $p_{f,0}$ indicates the initial fluid pressure.

In this system, chemical reactions drive the carbonation process of Ca(OH)_2 and CSH, as described in Equations 1.4.8 to 1.4.11 in Chapter 1. Furthermore, the model tracks the advancement of carbonation reactions by incrementing ξ until it reaches ξ_{max} . At each increment, the model adjusts the mole amounts of reactants (Ca(OH)_2 or CSH) and products (CaCO_3) accordingly.

It shall be noticed that sudden changes in material composition at each step create a discontinuity front of an unknown variable. Finite elements struggle to model such behaviour, especially with the Galerkin formulation used in BIL. When the exact solution exhibits jumps or discontinuities, the approached solution becomes contaminated with spurious oscillations. Dvorkin [165] highlights that the Galerkin technique can lead to ill-posed formulations for certain source terms, causing the stiffness matrix of the problem to become non-symmetric and indefinite.

To address this, the chosen approach is to smooth the carbonation front, resulting in the equation for the chemical reaction advancement rate shown in Equation 7.2.5.

$$\frac{\partial \xi}{\partial t} - \frac{(\xi_{max} - \xi)}{\tau} \frac{C_{CO_2}}{S_{CO_2}} = 0 \quad (7.2.5)$$

where C_{CO_2} is the CO_2 concentration and S_{CO_2} is a minimum CO_2 threshold above which chemical reactions can be triggered.

With this regularisation approach, in the presence of CO_2 , Ca(OH)_2 and CSH do not react immediately, and the reaction kinetics are smoothed by the time constant τ .

The chemical reactions representing Ca(OH)_2 and CSH carbonation yield changes in the volume fraction of each phase of the cement paste, i.e. Ca(OH)_2 , CSH, aluminates, and CaCO_3 . Moreover, the model considers changes in porosity resulting from cement carbonation. Consumed moles of reactants increase porosity due to lixiviation, while produced moles of CaCO_3 reduce porosity due to precipitation.

Moreover, these chemical reactions affect both the transport and mechanical properties of the cement paste. Carbonation advances through diffusion and permeability, which are influenced by changes in porosity. Equations 7.2.6 and 7.2.7 show the relationship found by Ghabezloo et al. [166] for class G cements.

$$\kappa = \kappa^0 \left(\frac{\Phi_F}{\Phi_0} \right)^{11} 10^{-19} \quad (7.2.6)$$

$$d_{eff} = d_{eff}^0 e^{(9.95\Phi_F - 29.08)} \quad (7.2.7)$$

where κ^0 and d_{eff}^0 are parameters to calibrate, Φ_0 is the initial porosity of the cement paste, and Φ_F is the porosity at a given time during the test.

Furthermore, the changes in the volume fractions also play a key role in the determination of the elastic parameters of the cement paste. In the model, this is performed through a classical homogenisation method that aims at replacing an actual heterogeneous complex body with a fictitious homogeneous one that behaves macroscopically in the same way.

The main equations needed for the particular studied application are presented in scalar form. The homogenisation equations are developed for the REV of a heterogeneous material which is composed of n different phases, each phase k having a volume fraction f_k . In the case of isotropy of the solid phases, the elastic bulk and shear moduli of a phase k are represented by k_k and g_k , respectively. Still, in the isotropic case, the homogenised macro-scale bulk and shear moduli of the material can be evaluated by the following relations (see derivation in Appendix B):

$$K^{\text{hom}} = \sum_{k=1}^n f_k k_k A_k^v \quad ; \quad G^{\text{hom}} = \sum_{k=1}^n f_k g_k A_k^d \quad (6.2.1)$$

Equation 6.2.1 shows that the effective elastic moduli are determined as a weighted average of the moduli of the individual constituents. The coefficients A_k^v and A_k^d , which depend on the elastic properties and geometry of each phase and its surrounding matrix, act as weighting factors for the volumetric and deviatoric strain localization of each phase. These coefficients can be evaluated using Eshelby's solution [152] for elastic inclusions with ellipsoidal geometry perfectly embedded in a reference medium.

At this stage, the model considers the homogenisation of the cement paste matrix itself, which consists of phases like $\text{Ca}(\text{OH})_2$, CSH, aluminates, CaCO_3 , and porosity. However, the inclusion of HGMS will be introduced as a second phase, which requires a two-step homogenisation approach. The first step deals with obtaining the effective elastic properties of the cement paste without HGMS, as described here. In the second step, these properties are then used to account for the impact of the HGMS. This two-step process will be detailed further later in this chapter.

With the elastic parameters of the cement pastes determined, the model is capable of determining the stress - strain conditions under which each point of the material is being subjected. Under these circumstances, it is possible that for a given set of initial and/or boundary conditions, the material will reach a stress that overpasses its strength. The strength of the material is defined by the Drucker-Prager criterion, which is expressed in Equation 7.2.8.

$$f(\sigma) = q - (c_c + f_c p') \quad (7.2.8)$$

where c_c is the constant associated with the material's cohesion, f_c is the constant associated with the material's friction angle, and p' is the mean effective stress. q refers to

deviatoric stress. These are related to the stress state that accounts for the internal pore pressure within a material. It is defined by the equation:

$$\boldsymbol{\sigma}' = \boldsymbol{\sigma} - u \mathbf{I} \quad (7.2.9)$$

where $\boldsymbol{\sigma}'$ represents the effective stress tensor, $\boldsymbol{\sigma}$ denotes the total stress tensor, and u is the pore water pressure.

The expressions for f_c and c_c are derived by considering the Drucker-Prager criterion in the context of the Mohr-Coulomb failure surface. The resulting formulations reflect how cohesion and the friction angle influence the material's strength. The values of f_c and c_c are determined by the relationships expressed in Equation 7.2.10.

$$\begin{cases} f_c = \frac{6 \sin(\phi)}{3 - \sin(\phi)} \\ c_c = c \frac{6 \cos(\phi)}{3 - \sin(\phi)} \end{cases} \quad (7.2.10)$$

where ϕ is the friction angle and c is the cohesion of the material.

Then, Equations 7.2.11 to 7.2.14 represent the parameters calculated at each computational step in the chemo-poromechanical model. The subscript "0" denotes variables calculated based on initial conditions, while those without the subscript represent values under applied boundary conditions.

Here, p'_0 and q_0 denote the average and deviatoric stresses obtained from initial conditions, respectively. p' and q represent the corresponding stresses under applied boundary conditions. Similarly, $J_1(\boldsymbol{\epsilon})$, $J_1(\boldsymbol{\epsilon}_0)$, $J_2(\boldsymbol{\epsilon})$, and $J_2(\boldsymbol{\epsilon}_0)$ are the first and second invariants of the strain tensor obtained for initial and boundary conditions.

These equations and Equation 7.2.8 collectively describe the stress-strain behaviour of the material.

$$p' = p'_0 + K \Delta \epsilon_v \quad (7.2.11)$$

$$q = q_0 + 3G \Delta \epsilon_s \quad (7.2.12)$$

$$\Delta \epsilon_v = J_1(\boldsymbol{\epsilon}) - J_1(\boldsymbol{\epsilon}_0) \quad (7.2.13)$$

$$\Delta \epsilon_s = \frac{2}{3} \left[(3J_2(\boldsymbol{\epsilon}))^{0.5} - (3J_2(\boldsymbol{\epsilon}_0))^{0.5} \right] \quad (7.2.14)$$

For the conditions of the problem to be solved using this model, for a given computational step, an increment in the volumetric and deviatoric strains ϵ_v and ϵ_s is obtained. With those, the corresponding average and deviatoric stresses increments are obtained. If these stress values do not satisfy the criterion established in Equation 7.2.8, the model considers damage to represent the actual behaviour of the material.

A damage model quantifies the degradation of a material and its effect on the performance under mechanical loads. A damage variable d is introduced, which value can vary between 0 and 1, representing undamaged and fully damaged conditions, respectively. Any value of d between 0 and 1 reflects a partially damaged state [167].

The mechanical behaviour of damaged materials is often characterized by two fundamental hypotheses. First, the principle of strain equivalence states that the state of deformation of a damaged material can be translated by the laws of behaviour of a sound material, in which the field of usual stresses is replaced by the field of damaged stresses [168]. Second, the principle of equivalence in elastic energy assumes that the elastic energy of the damaged material is the same as that of the sound material, except that the stress is replaced by the damaged stress [169].

The damage law itself can be defined as a function of several parameters that define the material's strength, as well as parameters related to the applied loads on the material. The equation adopted to define this damage is presented in Equation 7.2.15 [164].

$$d = 1 - \frac{c_c - q_0 - f_c \sigma_0}{3G_0 \Delta \epsilon_s + f_c K_0 \Delta \epsilon_v} \quad (7.2.15)$$

The damage is applied in a way that results in a loss of stiffness of the material according to Equation 7.2.16 in which K_0 and G_0 stand for the initial bulk and shear moduli, and K and G for the damaged (or apparent) Young moduli.

$$\begin{cases} K = K_0(1 - d) \\ G = G_0(1 - d) \end{cases} \quad (7.2.16)$$

From Equation 7.2.16, it is clear that an increase in damage implies a decrease in the resulting Young moduli. Moreover, damage could induce material anisotropy due to the presence of microcracks and their heterogeneous distribution. However, as can be noticed in Equation 7.2.16, for simplicity, only isotropic damage will be addressed in this discussion.

This section provided an overview of the chemo-poromechanical model utilized in this research. The subsequent sections will focus on the modifications made to the model to better suit our requirements, specifically its adaptation to incorporate HGMS and introduce new considerations. By implementing these changes, the aim is to develop a model that accurately predicts the behaviour of the material under the specific conditions observed in laboratory measurements, including its performance in real CO₂ injection well conditions.

7.3 Model improvement

This section presents the implementation of the improvements included in the model to account for the presence of HGMS. These improvements include the homogenisation model developed in Chapter 6, which aims to predict the elastic properties of lightweight cement

pastes containing HGMS, and the effects of HGMS rupture under mechanical stress, crucial for accurately characterizing the behaviour of these materials (cf. Chapters 4 and 5).

7.3.1 Homogenisation model implementation

The original homogenisation approach focuses exclusively on the cement matrix, achieving homogenisation based on the volume fractions and elastic parameters of the various phases within the composite, as outlined in Section 7.2. This part of the homogenisation model was used as a first stage to estimate the elastic parameters of the cement matrix.

A second stage was then introduced, which incorporates the contributions of HGMS into the elastic properties of the cement pastes. This second stage is based on the model presented in Chapter 6 and acknowledges that the mechanical performance of the cement pastes is influenced by HGMS' geometry, volume fraction, and stiffness. By integrating the effects of HGMS, the model can more accurately reflect the interactions within the composite material, leading to improved estimations of elastic properties and overall material behaviour (cf. Chapter 6).

The input parameters considered for the homogenisation model applied to cement pastes CS0044C00, CS2744C00, and CS4144C00 are presented in Table 7.3.1. These parameters include the initial volume fractions of the main cement phases such as $\text{Ca}(\text{OH})_2$ (f_{ch0}), CSH (f_{csh0}), and aluminates (f_{al0}), as well as the initial volume fraction of HGMS (f_{HGMS0}) and the total porosity at the initial state (Φ_0). Furthermore, the values of r_1 and r_2 correspond to the inner and outer radii of the HGMS, respectively.

Table 7.3.1: Input parameters considered for the homogenisation model

Parameter	CS0044C00	CS2744C00	CS4144C00
f_{ch0}	0.137	0.083	0.100
f_{csh0}	0.601	0.447	0.496
f_{al0}	0.099	0.071	0.081
f_{HGMS0}	-	0.329	0.230
Porosity ₀	0.163	0.070	0.093
r_1	-	14.344	18.518
r_2	-	15.000	20.000

The values for f_{HGMS0} were determined based on the mix designs presented in Chapter 2. The values for f_{ch0} were obtained from the experimental results described in Chapter 3, while the porosity values were derived from corrected MIP results presented in Chapter 4. The internal and external radii r_1 and r_2 were determined as established in Chapter 6.

The remaining volume fractions, f_{csh0} and f_{al0} , were calibrated to match the elastic properties of the cement matrix as estimated by the first stage of the homogenisation model. This calibration process aimed to obtain values that align closely with those derived from the homogenisation results presented in Chapter 6.

Table 7.3.2 presents a comparison between the elastic properties obtained experimentally and those predicted by the two-stages homogenisation model for the three cement pastes considered: CS0044C00, CS2744C00, and CS4144C00. The elastic parameters include K and G , expressed in GPa. Both experimental data from ultrasonic wave velocity measurements and model predictions are displayed.

Table 7.3.2: Elastic parameters' comparison between experimental results and model predictions

Elastic parameter		CS0044C00	CS2744C00	CS4144C00
K [GPa]	Experimental	15.7	8.3	11.4
	Model	16.8	10.9	13.1
G [GPa]	Experimental	9.7	5.4	6.8
	Model	10.4	6.9	8.1

The implementation of the model yielded consistently higher results than those obtained experimentally via ultrasonic wave velocity measurements. However, the trend observed in both the model and laboratory results is the same, with CS0044C00 presenting the highest elastic moduli, followed by CS4144C00 and CS2744C00, respectively.

The homogenisation model was also used to account for the effect of carbonation on the elastic properties of the cement pastes within the chemo-poromechanical model. Specifically, the model incorporates changes in the chemical composition due to carbonation, where the decrease in $\text{Ca}(\text{OH})_2$ and CSH phases results in the formation of CaCO_3 and amorphous SiO_xOH_x . These changes are accounted for by adjusting the volume fractions of $\text{Ca}(\text{OH})_2$ and CSH within the model according to the degree of carbonation, allowing for a more accurate prediction of the elastic behaviour as the material carbonates. This aspect of the model is essential for understanding the mechanical performance of cement in CO_2 -rich environments, as the changes in chemical composition have a significant effect on the stiffness of the material.

7.3.2 HGMS rupture

The incorporation of the rupture of HGMS into the model represents a critical improvement. As discussed in Chapter 4 and confirmed by MIP tests on powder specimens of HGMS (cf. Appendix A), HGMS are susceptible to rupture under mechanical stress, which can significantly influence the interconnected porosity of the cement pastes, thereby affecting their performance when subjected to CO_2 injection well conditions.

The following steps outline the approach used to estimate the volume fraction of broken HGMS under a given target pressure. This method incorporates laboratory data from MIP tests on powder samples to approximate the porosity changes resulting from HGMS rupture.

1. **Define the target pressure:** The target pressure is set based on the mean effective stress and fluid pressure (p_f and p').
2. **Identify the closest pressure values:** From the laboratory results presented in Appendix A and shown in Figure 7.3.1, the two pressure values obtained from the MIP on powder samples closest to the target pressure are selected.
3. **Perform linear interpolation:** Linear interpolation is applied between these two values to determine the volume fraction of broken HGMS at the target pressure, as illustrated in Figure 7.3.1.
4. **Update the porosity:** It is assumed that the total volume of broken HGMS transforms into additional porosity.

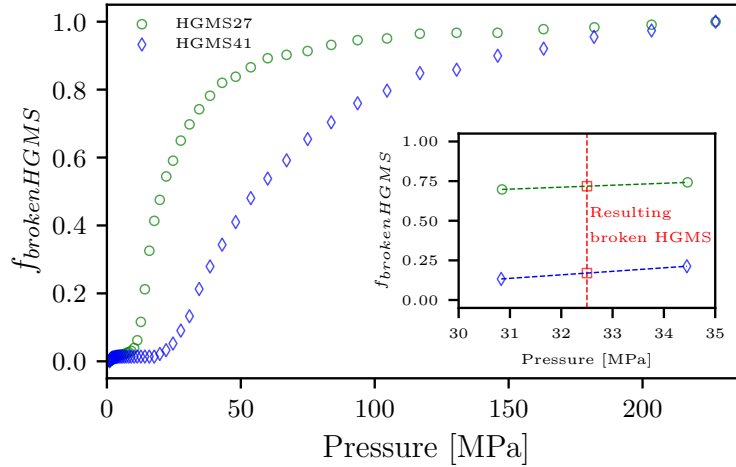


Figure 7.3.1: Volume fraction of broken HGMS vs. pressure resulting from MIP results on powder specimens (Appendix A). The zoomed area shows the linear interpolation used.

The changes in phases f_{HGMS} and porosity induced by the rupture of HGMS impact the results of the homogenisation model. When HGMS break, the volume fraction of broken HGMS is converted into porosity within the model. This adjustment effectively captures the loss of the HGMS' shell, resulting in a more accurate representation of the elastic properties.

Figure 7.3.2 illustrate the relationship between the fraction of HGMS and porosity with increasing mean effective stress for cement paste CS2744C00. It demonstrates that as the mean effective stress increases, the proportion of broken HGMS also rises. This results in a decrease in the fraction of intact HGMS and an increase in porosity.

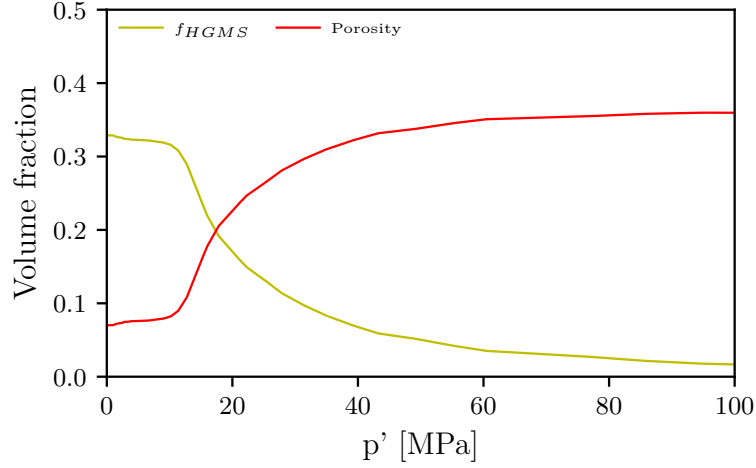


Figure 7.3.2: Modelled impact of confining pressure on the volume fractions of HGMS and porosity in cement paste CS2744C00, considering the rupture of HGMS

Additionally, Figure 7.3.3 presents the variations in K and G as the mean effective stress increases for cement paste CS2744C00. As a consequence of the decrease in f_{HGMS} and the increase in porosity, a decrease in the elastic moduli results from the homogenisation model.

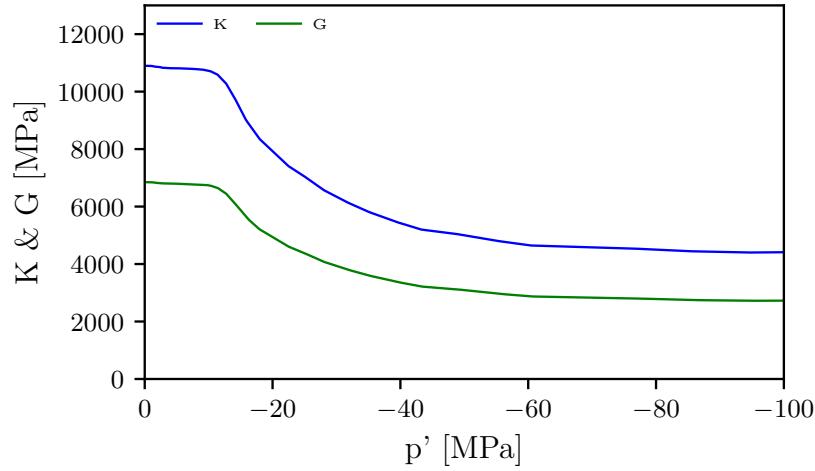


Figure 7.3.3: Modelled variation of K and G as a function of mean effective stress, considering the rupture of HGMS

Moreover, the new source of interconnected porosity introduced by the inclusion of broken HGMS must be accounted for in the model's calculations of the material transport properties. While the model's governing equations for permeability and diffusivity, shown in Equations 7.2.6 and 7.2.7 remain unchanged, the increase in interconnected porosity resulting from HGMS rupture leads to higher values of these parameters. Hence, a significant influence in the carbonation rate of cement pastes containing HGMS is expected.

7.4 Validation with laboratory tests

The results presented in this section focus on the validation of the model by comparing its predictions with laboratory test results. The three cement pastes were modelled using axisymmetric conditions in a quarter of the specimen. The mesh used in this study is structured and consists of 341 rectangular elements with 4 nodes, as show in Figure 7.4.1. The figure also shows the regions considered to apply boundary conditions effectively.

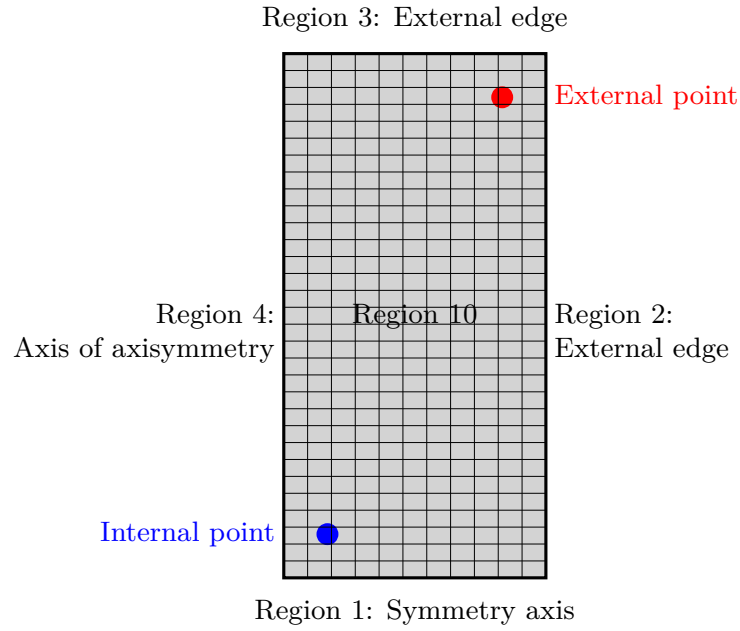


Figure 7.4.1: Geometry, mesh, and boundary condition regions for cement specimen modelling

The initial boundary conditions for the model were established as shown in Table 7.4.1.

Table 7.4.1: Initial boundary conditions

Region	Initial Conditions
1	Vertical displacement restriction
4	Horizontal displacement restriction
10	Zero fluid pressure

Two conditions were considered: carbonated and non-carbonated cement pastes. The carbonation process involved incrementing the fluid pressure and confining pressure to 20 MPa with a CO_2 concentration of 1200 mol/m^3 [64], reflecting the conditions achieved in the laboratory carbonation cell. Hence, for modelling the carbonation process, the boundary conditions described in Table 7.4.2 were applied.

Table 7.4.2: Boundary conditions for carbonation

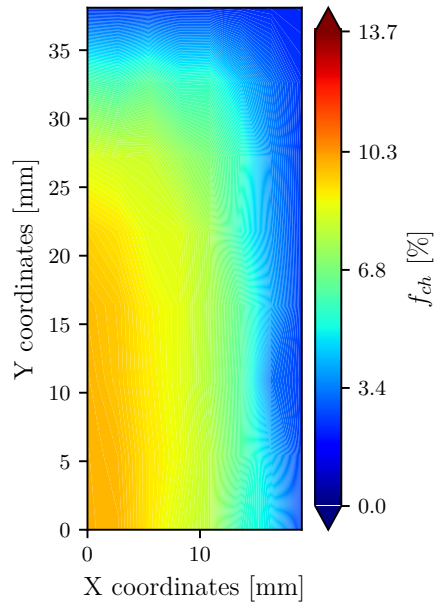
Region	Boundary Conditions
1	Vertical displacement restriction
4	Horizontal displacement restriction
2 & 3	In contact with CO ₂
2 & 3	Fluid pressure applied
2 & 3	Confining pressure applied

Table 7.4.3 shows the input parameters used related to the kinetics of the carbonation process (i.e. τ and d_{eff}^0). These parameters were calibrated to ensure that the model results of carbonation advancement align with the experimental outcomes from the laboratory tests discussed in Part I.

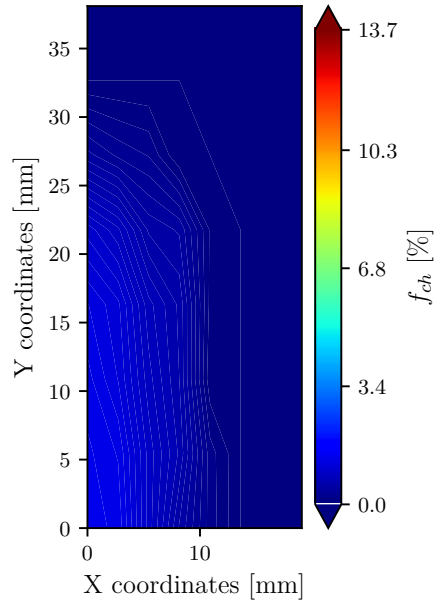
Table 7.4.3: Input calibrated parameters considered for modelling the carbonation advancement

Parameter	CS0044C00	CS2744C00	CS4144C00
τ [s]	1000	1000	1000
d_{eff}^0 [m ² s ⁻¹]	40	40	40

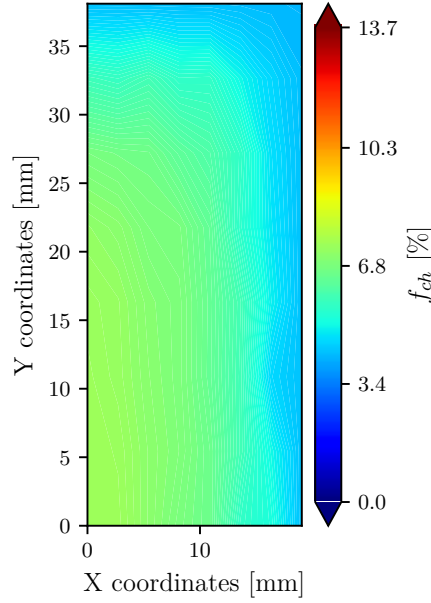
To visualize the impact of cement carbonation on the volume fraction of Ca(OH)₂ as obtained from the model, colour maps were generated and are shown in Figure 7.4.2. These maps illustrate the distribution of Ca(OH)₂ volume fraction in the cement specimens following carbonation for 60 days, taking into account the rupture of HGMS.



(a) Volume fraction of $\text{Ca}(\text{OH})_2$ in CS0044C60



(b) Volume fraction of $\text{Ca}(\text{OH})_2$ in CS2744C60



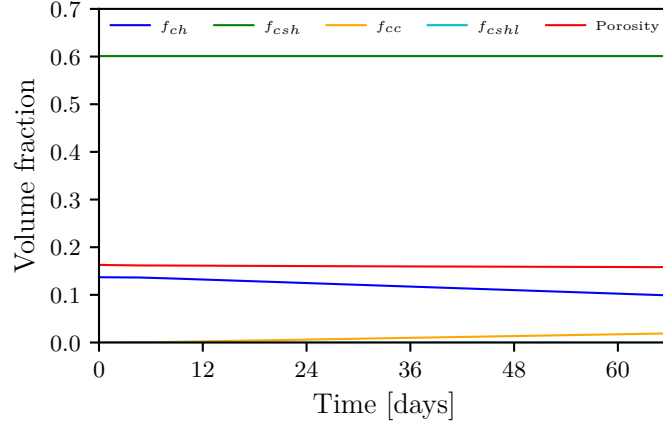
(c) Volume fraction of $\text{Ca}(\text{OH})_2$ in CS4144C60

Figure 7.4.2: Colour maps illustrating the volume fraction of $\text{Ca}(\text{OH})_2$ in cement pastes after carbonation of 60 days, accounting for HGMS rupture

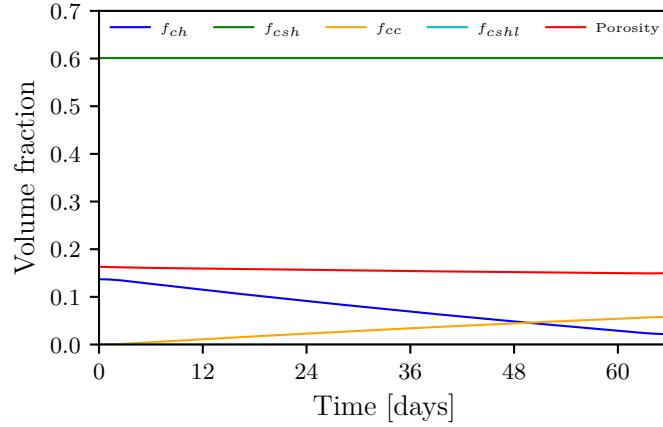
With the model considering the rupture of the HGMS, CS2744C60 presents an almost complete consumption of $\text{Ca}(\text{OH})_2$ due to the increase in porosity, which leads to higher diffusivity and consequently a greater advancement of carbonation. In contrast, CS4144C60 shows little difference compared to CS0044C60. The difference in the behaviour between CS2744C60 and CS4144C60 is attributed to the results of MIP on HGMS powder, which indicate that at the 20 MPa pressure reached in the carbonation cell, there is almost no rupture of HGMS41. This result contradicts the laboratory results presented in Chapter 4, where the pH indicator test in CS4144C60 showed an almost complete consumption of $\text{Ca}(\text{OH})_2$, likely due to the rupture of HGMS41. This observation emphasizes a critical point: the model does not currently account for the pozzolanic activity of HGMS, which, as discussed in Part I, can consume the outer shell of the HGMS and reduce their strength. If the pozzolanic activity and the resulting decrease in strength were taken into account, a similar outcome would likely have been achieved between CS4144C60 and CS2744C60.

To show the effects of carbonation over time for a exposure of 60 days – with an additional 3 days for loading and 3 days for unloading the carbonation cell – obtained through the modelling, the volume fractions of all phases in cement pastes CS0044C60 and CS2744C60 are shown at both internal and external points (cf. Figure 7.4.1) in Figure 7.4.3. This examination provides insight into how carbonation influences the evolution of phase

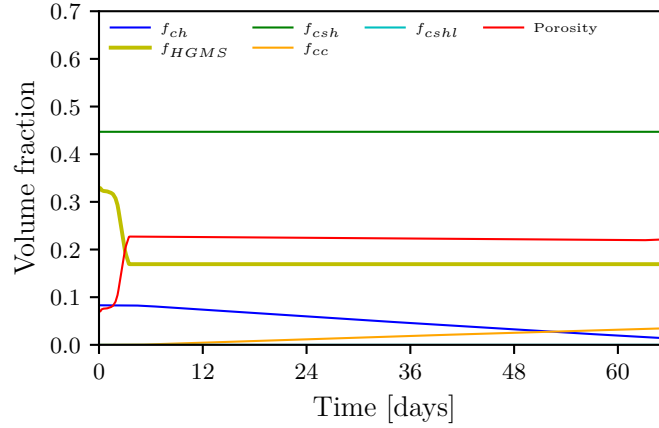
compositions over time in the studied cement pastes. The results for CS4144C60 are excluded from this analysis due to the lack of HGMS41 rupture during carbonation, as previously mentioned.



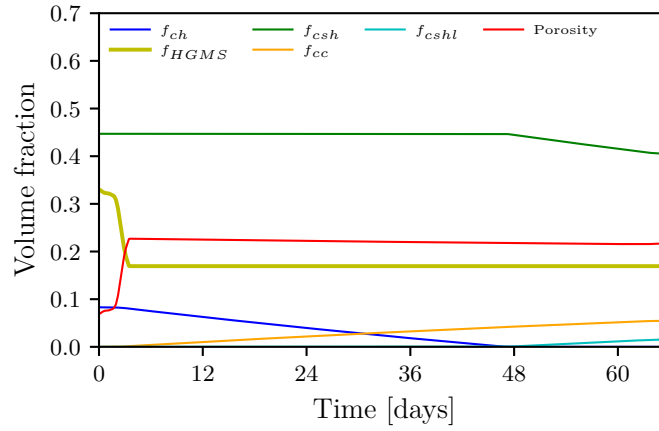
(a) Changes in phases volume fractions in plain cement paste at the internal point



(b) Changes in phases volume fractions in plain cement paste at the external point



(c) Changes in phases volume fractions in cement paste with HGMS27 at the internal point



(d) Changes in phases volume fractions in cement paste with HGMS27 at the external point

Figure 7.4.3: Changes in phases volume fractions in plain cement pastes and cement paste with HGMS27 as a function of time during carbonation of 60 days at internal and external points

The analysis of the volume fractions of phases in cement pastes reveals distinct behaviours between the plain cement paste and the cement paste with HGMS27 during carbonation. The plain cement paste shows consumption of $\text{Ca}(\text{OH})_2$ at both the internal and external points, but no consumption of CSH is observed. The consumption of $\text{Ca}(\text{OH})_2$ at the internal point is significantly lower than that at the external point, where a non-zero concentration of $\text{Ca}(\text{OH})_2$ remains. This observation is consistent with laboratory results

obtained using pH indicator. Additionally, the overall porosity experiences a slight decrease due to the larger molar volume of CaCO_3 compared to Ca(OH)_2 .

Cement paste with HGMS27 exhibits initially a marked variation in the volume fractions of HGMS and porosity at both points, which is attributed to the initial increase in fluid and confining pressures imposed during carbonation. The degree of carbonation in this paste is considerably higher than that seen in CS0044C60, due to the increased porosity resulting from the rupture of HGMS. At the internal point, the consumption of Ca(OH)_2 is virtually complete at both the internal and external points. At the external point there is also partial consumption of CSH. Once more, these chemical phenomena result in a slight decrease in porosity, associated with the greater molar volume of CaCO_3 .

To complete the analysis, UCS and triaxial compression tests on both non-carbonated and carbonated cement pastes were modelled to assess the effect of carbonation and HGMS fracture. Boundary conditions were defined for these compressive strength simulations as shown in Table 7.4.4.

Table 7.4.4: Boundary conditions for UCS and triaxial compression strength testing

Region	Boundary Conditions
1	Vertical displacement restriction
4	Horizontal displacement restriction
3	Fluid pressure applied
2 & 3	Confining pressure applied
3	Deviatoric pressure applied

Furthermore, Tables 7.4.5 and 7.4.6 show the input strength parameters for applying the Drucker-Prager criterion for cement pastes before and after carbonation of 60 days, respectively. Both parameters for each cement paste were obtained from the results of Chapter 5.

Table 7.4.5: Input calibrated strength parameters for non-carbonated cement pastes

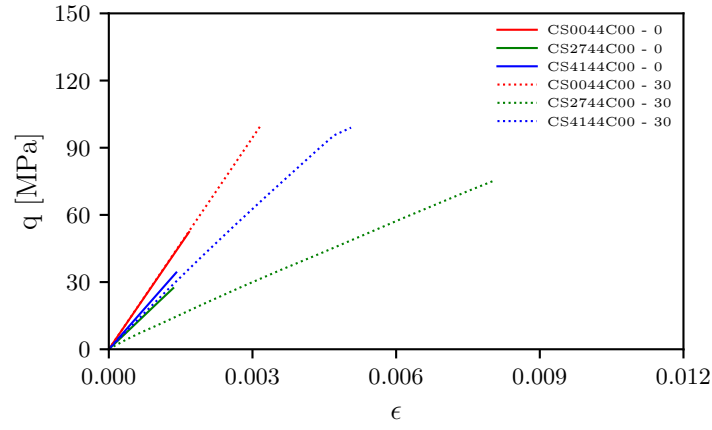
Parameter	CS0044C00	CS2744C00	CS4144C00
ϕ [°]	12.0	9.8	20.0
c [MPa]	21.2	11.5	12.0

Table 7.4.6: Input calibrated strength parameters for carbonated for 60 days cement pastes

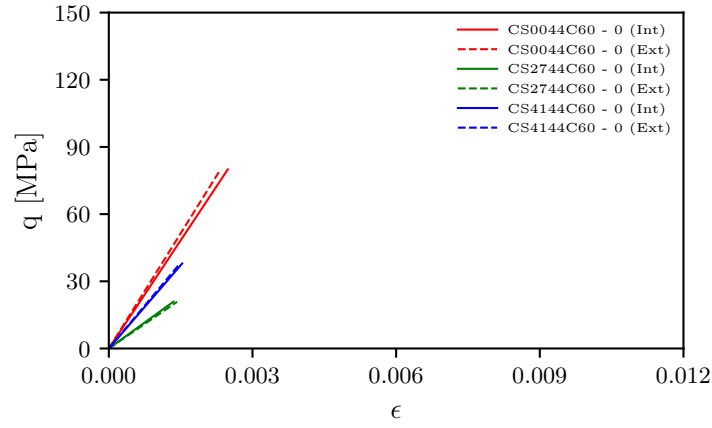
Parameter	CS0044C60	CS2744C60	CS4144C60
ϕ [°]	11.5	3.2	4.7
c [MPa]	35.0	30.0	43.8

For the triaxial compression strength test, the pressures were gradually applied to properly represent the conditions attained in the laboratory. Initially, the confining pressure was increased to 6 MPa; next, the pore pressure was raised to 5 MPa. These confining and pore pressures were maintained for a duration that matched the time used in the laboratory test to ensure specimen saturation. Following this, the effective confining pressure was increased to 30 MPa at a rate that adhered to the "drained" condition used in laboratory tests. Finally, the deviatoric pressure was gradually increased at the same rate until the material's strength was reached. For UCS tests, both the confining pressure and fluid pressure were set to zero.

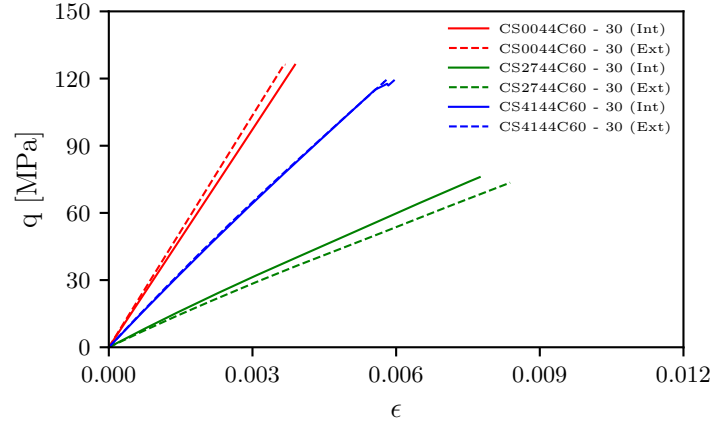
Figure 7.4.4 shows the modelled strain evolution during UCS and triaxial compression tests on non-carbonated and carbonated cement pastes. The results shown in Subfigure 7.4.4a demonstrate a decrease in Young's modulus from UCS to triaxial compression tests in cement pastes containing HGMS of both classes. This phenomenon is due to the rupture of the HGMS initiating at the achieved effective confining pressure of 30 MPa. Subfigure 7.4.4b shows differences between the stiffness of the inner and outer points on carbonated specimens during the UCS test. In CS0044C60, this is due to the heterogeneous nature of the specimen, which is represented in the external point by the abundance of CaCO_3 resulting from the carbonation of the $\text{Ca}(\text{OH})_2$. Since CaCO_3 is stiffer than $\text{Ca}(\text{OH})_2$, the outer point has a higher stiffness than the inner point. For CS2744C60, the trend is the opposite, giving a higher stiffness in the inner point than in the outer point due to the rupture of HGMS27 during the UCS test. Finally, Subfigure 7.4.4c shows similar trends to those of Subfigure 7.4.4b.



(a) Modelled strain evolution during UCS (solid line) and triaxial compression (dotted line) tests on non-carbonated cement pastes



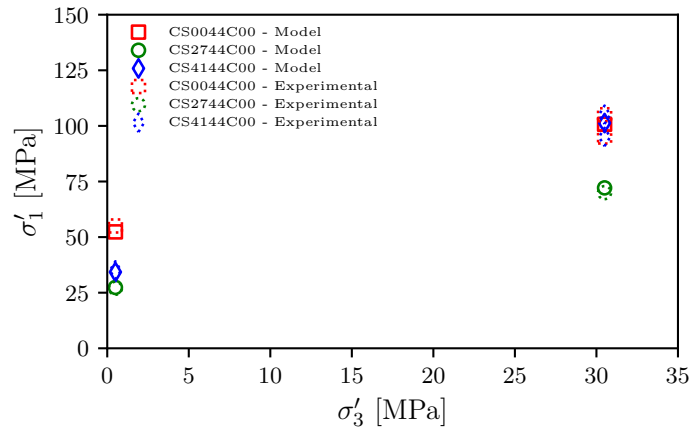
(b) Modelled strain evolution during UCS tests on carbonated cement pastes at internal (solid line) and external points (dashed line)



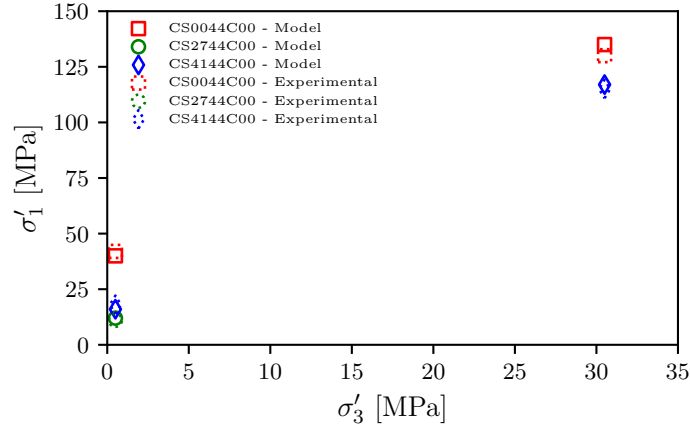
(c) Modelled strain evolution during triaxial compression tests on carbonated cement pastes at internal (solid line) and external points (dashed line)

Figure 7.4.4: Modelled strain evolution during UCS and triaxial compression tests on cement pastes, both non-carbonated and carbonated for 60 days. For the carbonated specimens, the curves are displayed for both internal and external points of the specimen

Finally, Figure 7.4.5 compares the strength of cement pastes obtained from UCS tests and triaxial compression tests with 30 MPa confinement, as determined by both the model and laboratory tests for non-carbonated samples and those carbonated for 60 days. The cohesion and friction angle parameters selected for each condition show good agreement between model predictions and experimental results.



(a) σ'_1 vs. σ'_3 at 0 MPa and 30 MPa effective confining pressure and 5 MPa of pore pressure before carbonation



(b) σ'_1 vs. σ'_3 at 0 MPa and 30 MPa effective confining pressure and 5 MPa of pore pressure after carbonation of 60 days

Figure 7.4.5: σ'_1 vs. σ'_3 at 0 MPa and 30 MPa effective confining pressure and 5 MPa of pore pressure before and after carbonation of 60 days. Comparison between modelled and experimental results

7.5 Modelling of cement pastes under real well conditions

This section focuses on the modelling of cement pastes under actual well conditions. By incorporating the developed homogenisation model along with the effects of HGMS rupture, the simulation can effectively represent the material behaviour in environments similar to those found in CO₂ geological storage wells. This predictive approach not only enhances the understanding of how lightweight cement pastes with HGMS respond to varying conditions but also aids in optimizing formulations to ensure durability and reliability in critical applications.

The mesh used to model the slice of the cement annulus is structured and consists of 1276 rectangular elements of 4 nodes each. To apply boundary conditions effectively, the regions of the model were defined as indicated in Figure 7.5.1.

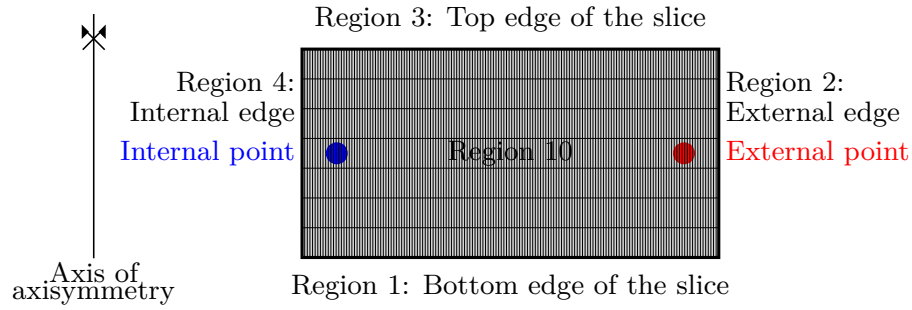


Figure 7.5.1: Geometry, mesh, and boundary condition regions for CO₂ injection well cement annulus modelling (note: radial distance from the axis of axisymmetry is not to scale)

The initial boundary conditions for the model were established as shown in Table 7.5.1.

Table 7.5.1: Initial boundary conditions for the well model

Region	Initial Conditions
2	Zero CO ₂ concentration
4	Horizontal displacement restriction
4	Vertical displacement restriction
10	Fluid pressure of 10 MPa
1	Confining pressure of 25 MPa
2	Confining pressure of 25 MPa
3	Confining pressure of 25 MPa

Then, for modelling the carbonation process in well conditions, the boundary conditions described in Table 7.5.2 were applied.

Table 7.5.2: Boundary conditions for carbonation in well conditions

Region	Boundary Conditions
2	In contact with CO ₂
4	Horizontal displacement restriction
4	Vertical displacement restriction
10	Fluid pressure of 10 MPa
1	Confining pressure of 25 MPa
2	Confining pressure of 25 MPa
3	Confining pressure of 25 MPa

The application of boundary conditions in the well model follows the physical characteristics and interactions expected at a depth of 1000 meters. The cement paste is confined between the casing and the surrounding rock, and its behaviour is governed by mechanical, hydraulic, and chemical interactions with the environment. These boundary conditions aim to simulate the confinement pressures and the gradual income of CO₂ from the outer regions of the cement ring, reflecting the conditions typically encountered in CO₂ geological storage wells.

Regarding the pressure exerted by the rock mass on the cement, this creates a confinement on the cement that occupies the annular region between the rock mass and the casing. This confinement is defined by Equation 7.5.1.

$$p_{\text{conf}} = K_0 (\gamma_s z - \gamma_w z) + \gamma_w z \quad (7.5.1)$$

where K_0 is the coefficient of earth pressure at rest (considered as 1), γ_s is the specific weight of the rock (assumed to be 25 kN/m³ as an average), γ_w is the specific weight of water (10 kN/m³), and z is the depth (1000 m). This confinement pressure is applied to the right edge of the cement ring slice modelled.

Horizontal and vertical displacements are restricted in region 4, corresponding to the left edge of the cement ring slice (or inner radius), where the cement paste is in contact with the casing. This assumption reflects both an assumption of perfect adhesion between the cement paste and the casing and an assumption that the casing is more rigid than the cement paste.

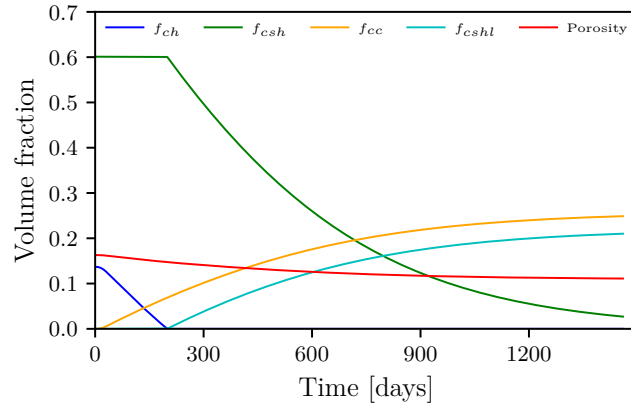
The initial state of the model assumes no CO₂ concentration throughout the system. The concentration of CO₂ is then gradually increased at the right edge of the cement ring (Region 2), which is the only part in direct contact with the injected gas. This setup mirrors the exposure conditions during CO₂ injection, where the cement must withstand the income of CO₂ from the surrounding geological storage.

Table 7.5.3 shows the input parameters used to model the cement pastes under CO₂ injection well conditions, including the initial volume fraction of each phase (i.e. Ca(OH)₂, CSH, aluminates, HGMS and porosity), the radii of HGMS27 and HGMS41, the parameters related to carbonation kinetics and the parameters related to the strength of the cement pastes before carbonation.

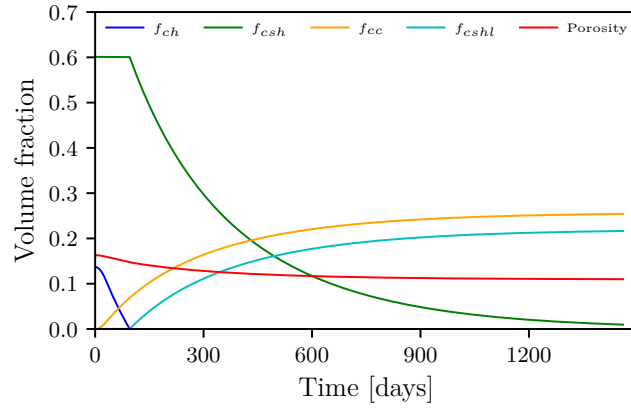
Table 7.5.3: Input parameters for cement pastes subjected to CO₂ injection well conditions

Parameter	CS0044C00	CS2744C00	CS4144C00
f_{ch0}	0.137	0.083	0.100
f_{csh0}	0.601	0.447	0.496
f_{al0}	0.099	0.071	0.081
f_{HGMS0}	-	0.329	0.230
Porosity ₀	0.163	0.070	0.093
r_1	-	14.344	18.518
r_2	-	15.000	20.000
τ [s]	1000	1000	1000
d_{eff}^0 [m ² s ⁻¹]	40	40	40
ϕ [°]	12.0	9.8	20.0
c [MPa]	21.2	11.5	12.0

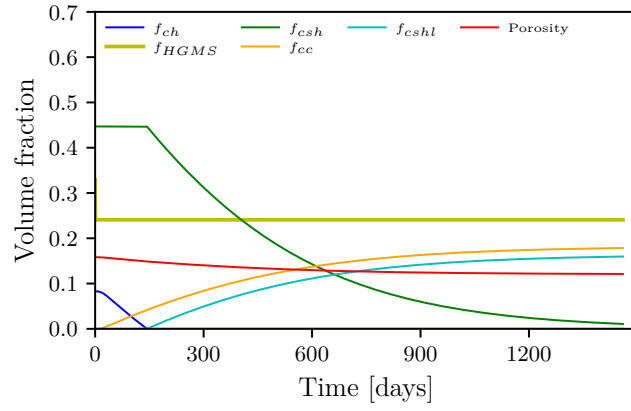
Following the presentation of the regions and the input parameters and the boundary conditions, the results of the change in the phases volume fractions during the carbonation process of 4 years in the CO₂ injection well are presented in Figure 7.5.2. This figure illustrates the temporal evolution of phase compositions in plain cement paste, as well as in cement pastes incorporating both classes of HGMS (HGMS27 and HGMS41), at both internal and external points of the cement ring. The internal point represents the region in close contact with the casing, while the external point reflects the area directly exposed to the incoming CO₂.



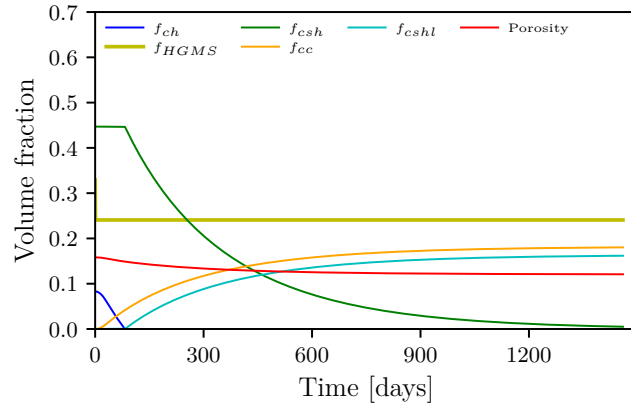
(a) Changes in phases volume fractions in plain cement paste at the internal point



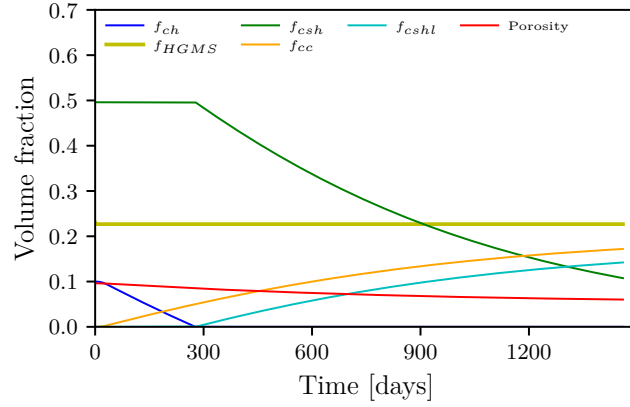
(b) Changes in phases volume fractions in plain cement paste at the external point



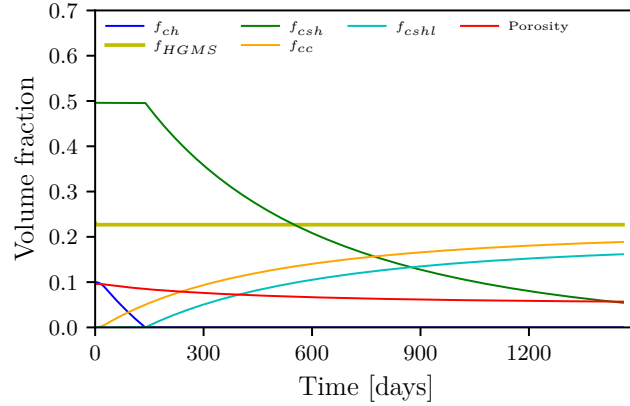
(c) Changes in phases volume fractions in cement paste with HGMS27 at the internal point



(d) Changes in phases volume fractions in cement paste with HGMS27 at the external point



(e) Changes in phases volume fractions in cement paste with HGMS41 at the external point



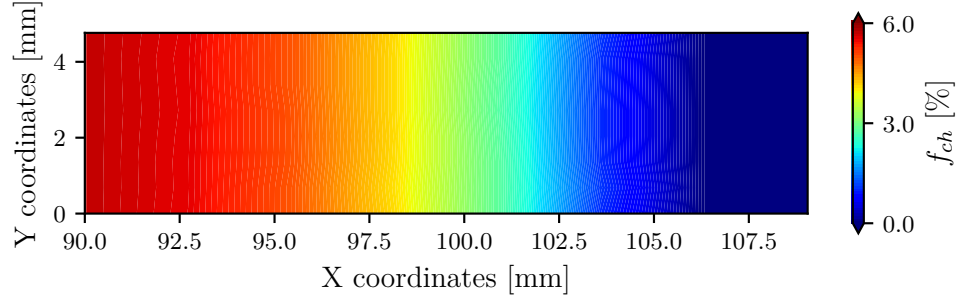
(f) Changes in phases volume fractions in cement paste with HGMS41 at the external point

Figure 7.5.2: Changes in phases volume fractions in plain cement paste, cement paste containing HGMS27, and cement paste containing HGMS41 as a function of time during carbonation in CO₂ injection well at internal and external points

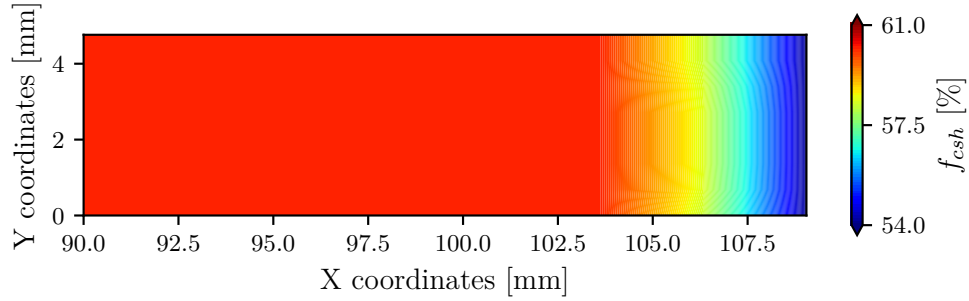
The results presented in Figure 7.5.2 reveal the behaviour of the cement pastes when exposed to CO₂. As outlined in Section 7.2, the initial reaction involves the consumption of Ca(OH)₂ in the cement pastes, leading to the formation of CaCO₃. In scenarios where all Ca(OH)₂ is fully consumed, the carbonation process then shifts towards the consumption of CSH, further producing CaCO₃. Both chemical reactions contribute to a reduction in porosity due to the greater molar volume of CaCO₃ compared to both Ca(OH)₂ and CSH.

As illustrated in Figure 7.5.3, which shows the colour maps of the volume fractions of Ca(OH)₂, CSH, and CaCO₃ for plain cement paste after 120 days of exposure, it becomes

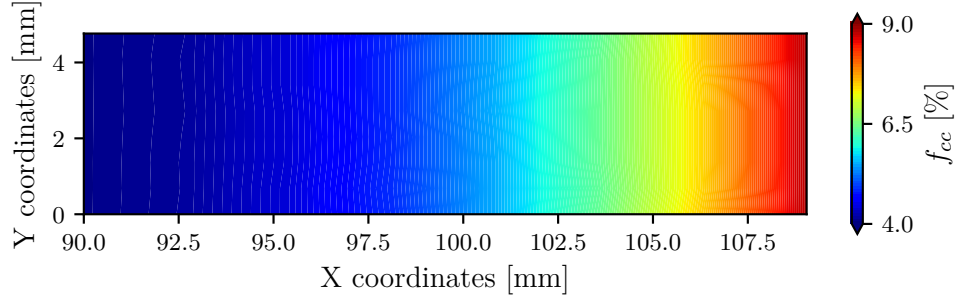
evident that carbonation faces greater difficulty in reaching the internal point compared to the external point, primarily due to the latter's higher exposure to the injected CO_2 . Notably, the plain cement paste and the cement paste with HGMS27 exhibit similar porosities resulting from the rupture of HGMS, which yields an approximately equal rate of CO_2 diffusivity in both types of cement. Consequently, the advancement of carbonation occurs at a similar pace in both cement pastes. However, the cement paste with HGMS27 has lower contents of $\text{Ca}(\text{OH})_2$ and CSH, leading to a faster complete carbonation process than that of plain cement paste.



(a) Volume fraction of $\text{Ca}(\text{OH})_2$ in CS0044C120



(b) Volume fraction of CSH in CS0044C120



(c) Volume fraction of CaCO_3 in CS0044C120

Figure 7.5.3: Colour maps illustrating the volume fraction of $\text{Ca}(\text{OH})_2$, CSH, and CaCO_3 in plain cement paste after being subjected to CO_2 injection well conditions for 120 days

On the other hand, the cement paste with HGMS41, which contains the strongest class of HGMS of the two used, does not experience rupture during exposure to CO_2 , maintaining its initial porosity. This results in the lowest initial porosity under the proposed conditions. Hence, this cement paste exhibits the slowest carbonation rate among the pastes modelled.

The findings underscore the critical importance of selecting appropriate HGMS for cement formulations. While the pozzolanic activity of HGMS is not accounted for in this analysis, the results indicate that the cement paste with HGMS27 presents a carbonation advancement behaviour comparable to that of the plain cement paste. Notably, the density of the cement paste with HGMS27 is 1388 kg/m^3 , while the plain cement paste stands at 1988 kg/m^3 (cf. Chapter 2). This implies that, while maintaining similar performance against carbonation, a significant reduction in density can be achieved, which is essential for optimizing well cementing operations. Alternatively, choosing the cement paste with HGMS41, which has an intermediate density of 1601 kg/m^3 , would result in lower carbonation advancement while still achieving a controlled density, thereby facilitating efficient well cementation.

7.6 Conclusion

This chapter presented a comprehensive analysis of the chemo-poromechanical model used to simulate the behaviour of cement pastes under conditions relevant to CO_2 geological storage. The fundamentals of the model were first outlined, emphasising its theoretical basis, which is critical to understanding the interactions within cementitious materials.

Improvements to the original model were then discussed, including the implementation of the homogenisation model and the HGMS rupture. Regarding the homogenisation model, a two-stages approach was used. The first stage focuses on the homogenisation of the cement matrix, while the second stage addresses the integration of HGMS into the model. This dual approach allows for a precise estimation of the material elastic properties

accounting for the presence of HGMS. Additionally, incorporating the rupture of HGMS into the model represented a significant enhancement. This consideration enables the model to account for the stiffness loss and its impact on transport properties, both related to the decrease in f_{HGMS} and the increase in porosity. As a result, the model provides a more accurate representation of the carbonation process in cement pastes containing HGMS.

Validation of the model with laboratory tests confirmed the effectiveness of the proposed enhancements. By calibrating the volume fractions of CSH and aluminates in the cement pastes, the elastic properties obtained from the model were aligned with experimental measurements. Furthermore, the parameters τ and d_{eff}^0 were adjusted to ensure that the carbonation advancement predicted by the model closely matched the laboratory results, particularly from pH tests.

Finally, the modelling of cement pastes under realistic well conditions demonstrated the potential benefits of using HGMS. It was found that the performance of these cement pastes is highly dependent on careful selection, considering the mechanical loads they will face to minimize the likelihood of HGMS rupture. Additionally, the pozzolanic activity of the HGMS, which can influence their integrity, is crucial for optimizing cement paste formulations. Overall, this chapter highlights the importance of refining modelling approaches to enhance the durability and reliability of cement pastes containing HGMS in the context of CO₂ injection wells.

Chapter 8

Final considerations

8.1 General conclusions

This thesis has investigated the mechanical properties and microstructure of lightweight class G cement pastes modified with HGMS, with a view to their potential application in CO₂ geological storage wells. A combination of laboratory testing and numerical modelling was employed to examine the behaviour of these cement pastes under injection well conditions. In particular, experimental tests were conducted to assess the impact of HGMS on the cement paste's strength and durability, while numerical simulations provided insights into the long-term stability of these materials when exposed to CO₂ injection well environments.

In the first part, the research examined how varying the w/s ratio, incorporating different HGMS classes, and exposing cement pastes to supercritical carbonation affected their properties. The analysis centred on the chemical interactions between the HGMS and the cement matrix, the modifications induced in the microstructure, and how these factors collectively influenced the mechanical behaviour of the cement pastes.

Cement pastes with 10% cement replacement by HGMS27 and HGMS41 and two w/s ratios (0.44 and 0.60) were studied. Modified Chapelle, granulometry and pycnometry tests were carried out on class G cement and HGMS. Isothermal calorimetry, TGA, UCS on cubic and cylindrical specimens, and triaxial compression tests (with isotropic and deviatoric loading) were performed on class G cement specimens with and without HGMS. Cylindrical specimens of each class G cement paste were subjected to supercritical carbonation conditions (90 °C, 20 MPa, CO₂ saturated atmosphere in the presence of water) for 60 and 120 days. Then, it was possible to quantify the changes in the various properties of class G cement pastes due to this exposure.

Building on the findings of the first part of this research project, the second part focused on modelling the behaviour of cement pastes with HGMS under conditions of CO₂ injection well. This involved enhancing an existing model by incorporating a novel homogenisation

method to estimate the elastic properties of cement pastes with HGMS, and accounting for HGMS rupture and its impact on the material's elastic and transport properties. The model was subsequently validated with respect to laboratory results, thereby supporting its utility in the analysis of the material's response to scCO₂ exposure.

The conclusions drawn from each topic covered in this work are presented below:

Interaction between HGMS and cement paste

A physico-chemical interaction exists between the HGMS and the class G cement paste. This interaction includes both a filler effect and the pozzolanic activity of the HGMS.

The filler effect refers to the ability of HGMS to act as nucleation sites for cement hydration products. This was confirmed and quantified through SEM images, isothermal calorimetry tests, and TGA on specimens with short curing times. These studies demonstrated that, in cement pastes containing HGMS, the matrix became more compact, the rate and degree of hydration increased, and the Ca(OH)₂ content was higher compared to plain cement pastes.

Pozzolanic activity refers to the chemical interaction between high silica admixtures and the Ca(OH)₂ resulting from the hydration of the cement. According to the modified Chapelle test, both HGMS27 and HGMS41 have sufficient pozzolanic activity to be considered as pozzolanic admixtures. These results were verified by other tests, such as SEM images to verify the increase in compactness produced by this interaction, and TGA on specimens with long curing times to verify the decrease in Ca(OH)₂ content.

Microstructural insights into cement carbonation

The interaction between HGMS and cement paste, the w/s ratio and the supercritical carbonation affected the microstructure of the cement pastes.

MIP tests confirmed that increasing the w/s ratio resulted in greater absolute porosity and larger pore sizes in the class G cement pastes. SEM images showed that the plain cement paste with a w/s ratio of 0.44 has a denser and more compact microstructure compared to the one with a w/s ratio of 0.60. A greater advancement of the carbonation front was measured with phenolphthalein, indicating that the more porous structure of the cement paste with a w/s ratio of 0.60 makes it more susceptible to the effects of carbonation. Additionally, MIP test results revealed that in both types of cement pastes exposed to supercritical carbonation, there was a decrease in pore entry size due to the precipitation of CaCO₃.

The increase in compactness due to the use of HGMS is evident from SEM images. MIP tests confirm that the pore entry size becomes smaller. From the analysis of changes in microstructure, combined with the results obtained from the rupture of HGMS, it can be concluded that the large peak observed in the MIP tests corresponds to the rupture of the HGMS, which consequently confer occluded porosity.

In the supercritical carbonation used in this work, with a pressure of 20 MPa, the rupture of the HGMS occurs as in the MIP test. Upon rupture, the occluded porosity conferred by HGMS to the paste becomes interconnected, and carbonation front advance is greater than expected. This is verified by the pH indicator test and by the results obtained from the MIP in external and internal samples of carbonated cement pastes with HGMS, which show a high degree of homogeneity in the carbonation of the cement pastes containing HGMS.

Effects of carbonation on the microstructure and the mechanical properties

Changes in the microstructure resulted in changes in the mechanical behaviour of the cement pastes. The three variables studied in this work, w/s ratio, HGMS and supercritical carbonation, have an influence on the mechanical properties.

An increase in the w/s ratio results in a decrease in the dynamic elastic properties and UCS. This is due to the increase in porosity in cement pastes with increasing w/s ratios. The additional porosity leads to reduced stiffness and strength of the material.

Cement pastes containing HGMS27 have the lowest dynamic elastic properties and UCS for each w/s ratio, due to the low strength and high volume fraction of HGMS27 in CS2744C00 and CS2760C00. The relative stiffness and strength between the HGMS and the cement paste has a significant effect on these properties. For example, pastes CS0060C00 and CS4160C00 have very similar elastic properties and UCS due to the similar stiffness and strength between HGMS41 and the paste with a w/s ratio of 0.60. In addition, drained isotropic tests show that CS2744C00 and CS4144C00 pastes are damaged at isotropic pressures above 10 MPa and all cement pastes show signs of damage in deviatoric tests.

Exposure to supercritical carbonation reduces the dynamic Young moduli and UCS of all cement pastes. Pastes with HGMS27 are most affected, followed by those with HGMS41 and finally those without HGMS. The experimental results indicate a strong advance of carbonation, which dissolves the CaCO_3 and affects more the pastes with HGMS due to their rupture.

Homogenisation of the elastic parameters of lightweight cement

Chapter 6 proposes an analytical model based on the Eshelby rigid inclusion theory to predict the elastic properties of cement pastes with HGMS.

The model requires knowledge of the elastic properties of the cement matrix as well as the volume fraction of HGMS, its dimensions and elastic properties. The model can also take into account an imperfect interface between the HGMS and the cement matrix. The results of the model depend on the ratio between the outer and inner radii of the HGMS, and the mechanical properties of the cement matrix and the material forming the HGMS. The imperfect interface between the microspheres and the cement matrix has a limited

effect on the bulk modulus, but can have a more significant effect on the shear modulus, depending on the interface parameters.

The model predictions have been compared with experimental data and show a very good agreement. Without any parameter calibration for the perfect interface case, the model predictions, with less than 15% deviation from the experimental values, are adequate for most practical applications. By adjusting a single pair of interface parameters for both HGMS classes used in this study, the model predictions significantly improved.

Chemo-poromechanical model considering carbonation

Finally, a chemo-poromechanical model was implemented to represent the behaviour of the cement pastes used in this work under CO₂ injection well conditions. This model is complex and has been improved to correctly represent the behaviour of cement pastes with HGMS.

Improvements to the original model included a two-stage homogenisation approach: first, homogenisation of the cement matrix and second, integration of the HGMS. This approach allowed a more accurate estimation of the elastic properties of the material in the presence of HGMS. In addition, the inclusion of HGMS rupture allowed the model to capture the effects of stiffness reduction and increased porosity on transport properties.

The results obtained with the new model are consistent with those obtained from laboratory tests, although there are certain limitations. The model takes into account the rupture of the HGMS and its influence on homogenisation, which allows a reasonable representation of the behaviour observed in laboratory tests. However, it should be noted that the model does not address, among other possible phenomena, the effects of pozzolanic activity and the resulting reduction in strength of the HGMS.

8.2 Perspectives

Several improvements and future perspectives can be considered to better understand the interaction between HGMS and cement paste. Although the data are conclusive, and it is now known that HGMS have filler effect and pozzolanic activity, quantitative chemical analyses such as XRD with Rietveld quantification including the amorphous content could be carried out. In this way, the variation in Ca(OH)₂ content would be known more precisely and, more importantly, the amount of CSH produced by the pozzolanic reaction would be known. Similarly, the extent of the consumption of the HGMS by this reaction could be known by carrying out specific tests such as nanoindentation in the HGMS-cement paste contact zone. Furthermore, in order to relate this to the homogenisation of the elastic parameters, the properties of the interface between the HGMS and the cement paste could be accurately measured in order to properly calibrate the model.

With regard to the microstructure study, the results obtained were sufficiently con-

clusive. Given the difficulty of quantifying the porosity of the pastes using MIP, another method could be used for this purpose. It should be remembered that the aim of measuring porosity is to understand the extent to which CO_2 affects the cement pastes. For this reason, it may be more interesting to make direct measurements of the permeability and diffusivity of CO_2 in cement pastes. One could also investigate the chemical composition by XRD tests with Rietveld quantification, including the amorphous content.

Mechanical characterization is one of the most laborious parts of the laboratory, especially for drained triaxial tests. In order to ensure the drained condition, the tests must be run very slowly. This makes obtaining failure surfaces a complex task. A more detailed characterization would be useful to fully understand the behaviour of the materials under study. This, in addition to the previous comments, can help to understand the reason for the more frictional behaviour of carbonated cement pastes compared to the behaviour of non-carbonated ones.

Finally, the modelling carried out was able to correctly reproduce the behaviour of the cement pastes. In any case, it could be of interest to modify the constitutive model used, which currently considers an elastic period followed by pure damage, to a model that includes damage coupled with plasticity. Damage related to chemical changes in the cement paste due to supercritical carbonation could also be added.

Appendix A

Analysis of HGMS rupture during the MIP test

This appendix presents the analysis of HGMS rupture during the MIP test. The focus is on quantifying the extent to which HGMS particles break under the increasing pressure applied during the MIP process. By analysing the results of the MIP test on HGMS powder, insight is gained into the behaviour of cement pastes containing these HGMS and their contribution to the overall porosity measurements.

To measure the actual strength of HGMS subjected to isotropic stress conditions, MIP tests were performed on two sets of powder specimens consisting only of HGMS27 and HGMS41. Since the specimen is desegregated, the interpretation of the results obtained may vary slightly. Mercury porosimetry measurements on similar non-porous solid powders, such as polymer and glass beads, have demonstrated a characteristic pattern where rapid mercury intrusion occurs at a specific low pressure, followed by minimal further intrusion at higher pressures [5]. This phenomenon is governed by the breakthrough pressure, defined as the pressure required to force mercury into the interparticle voids, which is determined by factors such as surface tension, particle geometry, and the constricted regions between solid particles [6]. In our tests, a similar pattern was observed, with the initial breakthrough pressure, corresponding to the intrusion into the interparticle spaces, occurring in a low and restricted range of pressures. This behaviour aligns with the findings of Carli and Motta [4], who attributed this pressure range to the intrusion of mercury into interparticle voids. Similarly, Emeruwa et al. [7] reported a breakthrough pressure for similar packed powders typically around 0.1 MPa, characterized by a distinct change in the slope of the cumulative mercury intrusion volume. This phenomenon is shown in Figure A.1, where Figure A.1a shows the initial state of the powder in which all the particles tend to agglomerate without allowing the entrance of mercury to the space between them and Figure A.1b illustrates the state of the powder after the breakthrough pressure has been exceeded, where mercury fully infiltrates the interparticle spaces.

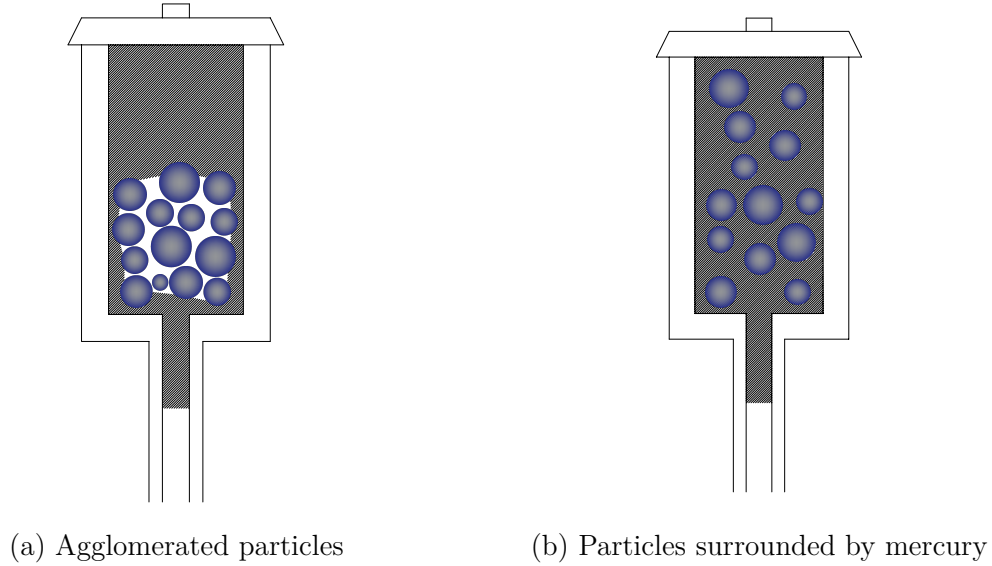
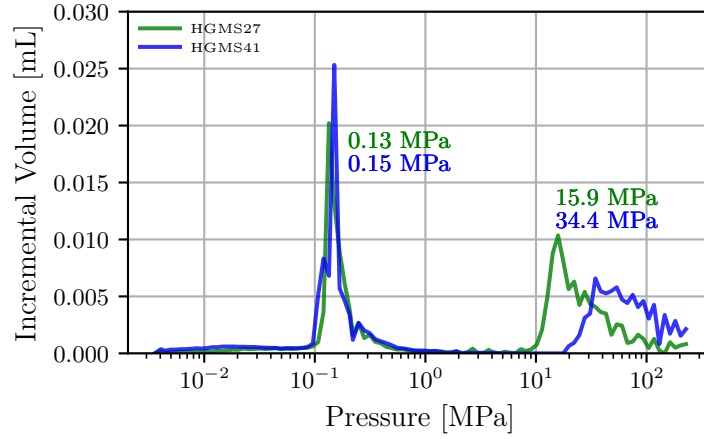


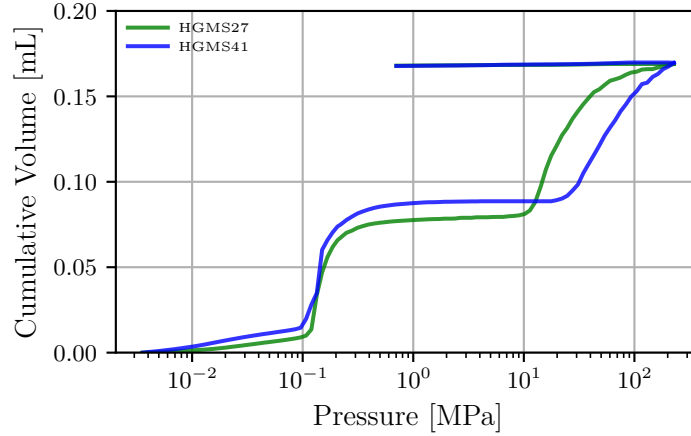
Figure A.1: MIP test on desegregated particles illustrating the state of the powder sample after the breakthrough pressure is reached, allowing mercury infiltration into interparticle spaces [4, 5, 6, 7]

Figure A.2 shows the incremental and cumulative volume of mercury per gram of specimen intruding for each imposed pressure during the powder MIP tests performed on HGMS27 and HGMS41. Figure A.2a shows the incremental mercury intrusion volume, while Figure A.2b shows the cumulative mercury intrusion volume. In both cases, the increase in the slope that can be appreciated at 0.13 MPa and 0.15 MPa could be easily related to the overpass of the particles' agglomeration strength. After this, another important and wider change in the incremental volume is observed for pressures higher than 10 MPa. Though it is typically expected that further increases in cumulative volume during MIP tests would correspond to the intrinsic porosity of the particles, in the case of HGMS, their perfect spherical shape suggests no porosity, as supported by the MIP results and consistent with Palmer's findings on non-porous glass beads [5]. Furthermore, SEM images of HGMS27 and HGMS41, shown in Figure 2.1.1 (cf. Chapter 2, Section 2.1), confirm the absence of porosity in the HGMS shells. Instead, increasing the mercury pressure at this point will only result in increasing the stress to which the particles are subjected. According to the manufacturer, the strengths of HGMS are specified as 27 MPa for HGMS27 and 41 MPa for HGMS41. So, at some given pressure, HGMS are expected to break, leading to this increase in the incremental volume and in the slope of the cumulative volume. With this test, it is possible to measure in a relatively easy way the actual strength of the HGMS,

which is already an interesting issue. Furthermore, it can be seen that this material do not present a given strength, but instead there exists a distribution of strength, which can be obtained from these results. In Figure A.2a, the informed pressures of 15.9 MPa for HGMS27 and 34.4 MPa for HGMS41 correspond to the pressures at which the highest peak is found within this distribution. The proximity of the obtained values for the main peak and the crush strength informed by the manufacturer is noticeable.



(a) Incremental



(b) Cumulative

Figure A.2: Incremental and cumulative mercury intrusion volume for HGMS27 and HGMS41 vs. pressure applied

In addition, from Figure A.2b, the total volume intruded as a result of the rupture of HGMS could be obtained following Equation A.1. Initially, the total volume of mercury

that entered the penetrometer during the whole test (V_{Hg-Max}) is 0.169 ml for HGMS27 and 0.170 ml for HGMS41. These volumes include both the volume intruded into the HGMS and the volume between the particles forming the HGMS powder. The latter can be subtracted by considering the cumulative mercury volume just before the first HGMS breaks ($V_{1^{st}break}$) for each class of HGMS. It was found that the pressure just before the rupture of the first HGMS is 6.51 MPa for HGMS27 and 17.77 MPa for HGMS41, resulting in the $V_{1^{st}break}$ of 0.089 ml and 0.081 ml for HGMS27 and HGMS41, respectively. Hence, by applying Equation A.1, the mercury intruded into the HGMS ($V_{Hg-Void}$) results 0.080 ml for HGMS27 and 0.089 ml for HGMS41. Furthermore, by knowing the mass of the powder specimens, the density of the HGMS (0.28 g/cm³ and 0.46 g/cm³ for HGMS27 and HGMS41, respectively) and considering Equation A.2 one can obtain the total volume of HGMS in the specimen, which is 0.104 cm³ and 0.116 cm³, respectively for HGMS27 and HGMS41. Similarly, knowing the density of glass (2.23 g/cm³) it is possible to calculate the volume of glass present in the specimens by applying Equation A.3, which corresponds to 0.0131 cm³ for HGMS27 and 0.024 cm³ for HGMS41. The difference between V_{HGMS} and V_{glass} in Equation A.4 results in the volume of void inside the outer shell forming the HGMS, i.e. 0.091 cm³ and 0.092 cm³, respectively for HGMS27 and HGMS41. All these volume values are presented in Table A.1 for the sake of clarity.

$$V_{Hg-Void} = V_{Hg-Max} - V_{1^{st}break} \quad (A.1)$$

$$V_{HGMS} = \frac{M_{specimen}}{\rho_{HGMS}} \quad (A.2)$$

$$V_{glass} = \frac{M_{specimen}}{\rho_{glass}} \quad (A.3)$$

$$V_{void} = V_{HGMS} - V_{glass} \quad (A.4)$$

Table A.1: Volumes representing the MIP test on HGMS powder specimens

Class of HGMS	V_{Hg-Max} ml	$V_{1^{st}break}$ ml	$V_{Hg-Void}$ ml	V_{HGMS} ml	V_{glass} ml	V_{void} ml
HGMS27	0.169	0.089	0.080	0.104	0.013	0.091
HGMS41	0.170	0.081	0.089	0.116	0.024	0.092

In Table A.1, one can observe that the calculated void volume inside the HGMS (V_{void}) is larger than that obtained through the MIP test ($V_{Hg-Void}$) for both classes. This discrepancy could be attributed to variations in the strength of the HGMS, as they are not perfectly uniform. Some HGMS may have a higher strength than initially reported by

the manufacturer. Interestingly, HGMS27 shows a greater difference between the expected and obtained void space compared to HGMS41.

However, upon examining Figure A.2a, this finding seems counterintuitive. HGMS27 exhibits near-null incremental volume distribution at 200 MPa of mercury pressure, while HGMS41 shows higher incremental volumes throughout the pressure range of the test. However, upon examining Figure A.2a, this finding seems counterintuitive. HGMS27 exhibits near-null incremental volume distribution at 200 MPa of mercury pressure, while HGMS41 shows higher incremental volumes throughout the pressure range of the test. Moreover, according to the manufacturer, HGMS27 has a lower strength than HGMS41, suggesting that HGMS27 should be closer to reaching the calculated void volume V_{void} . It is also possible that a non-negligible fraction of the HGMS are not completely hollow or have thicker walls, which could contribute to their observed performance. Therefore, establishing a clear relationship between crush strength and the percentage of broken HGMS proves challenging.

To address this, the aim is to calculate the ratio between the expected void volume and the MIP void volume, which could serve as a useful parameter when studying cement pastes with HGMS. The void volume obtained through the MIP test ($V_{Hg-Void}$) and the calculated void volume inside the HGMS (V_{void}) were determined for both HGMS27 and HGMS41. Specifically, $V_{Hg-Void}$ for HGMS27 is 0.080, while V_{void} is 0.091. For HGMS41, $V_{Hg-Void}$ is 0.089 and V_{void} is 0.092. By dividing $V_{Hg-Void}$ by V_{void} , the resulting ratios are 0.879 for HGMS27 and 0.967 for HGMS41, as detailed in Table A.1.

Appendix B

Theoretical framework of the homogenisation model

This appendix is dedicated to the presentation of the theoretical framework of the model. The final equations are presented in the main text, in a way that the model can be used without referring to the appendix. The purpose of this appendix is to provide a unified presentation of the framework of the homogenisation model that permits the mathematical formulation to be easier to read and understand. The model framework is presented for a general case, including the effect of imperfect interface between phases. It can be reduced to the case with perfect interfaces by setting the interface compliances equal to zero.

Homogenisation method

The aim of classical homogenisation method is to replace an actual heterogeneous complex body by a fictitious homogeneous one that behaves globally in the same way. The theoretical framework of micromechanics modelling and homogenisation method has been presented in different papers and textbooks, e.g. [144, 170]. The principles and main equations of this framework are presented briefly in the following.

The volume V_0 of the REV (Representative Elementary Volume) of a heterogeneous material is composed of n different phases with volumes V_k , $r = 1 \dots n$, and volume fractions $f_k = V_k/V_0$. The tensors of Young moduli of each phase is denoted by $\mathbf{c}_k$. In the case of isotropy of the solid phases, the tensor of Young moduli can be written as the sum of a volumetric and a deviatoric part, $\mathbf{C}_k = 3k_k\mathbf{J} + 2g_k\mathbf{K}$, where k_k and g_k are the bulk modulus and shear modulus of the phase k respectively. $\mathbf{J}_{pqrs} = \frac{1}{3}\delta_{pq}\delta_{rs}$ is the volumetric part of the fourth-order symmetric unit tensor, $\mathbf{I}$ and $\mathbf{K} = \mathbf{I} - \mathbf{J}$ is the deviatoric part. $\mathbf{I}$ is defined as $\mathbf{I}_{pqrs} = \frac{1}{2}(\delta_{pr}\delta_{qs} + \delta_{ps}\delta_{qr})$ and δ_{pq} stands for the Kronecker delta. The homogenisation equations for the effective elastic properties can be derived on a REV submitted to a

homogeneous strain boundary conditions. The homogeneous strain boundary conditions are associated to prescribed displacements $\underline{u}$ at the boundary of the REV as $\underline{u} = \mathbf{E} : \underline{x}$, where $\underline{x}$ is the microscopic position vector and $\mathbf{E}$ is the macroscopic strain tensor. It can be shown that $\mathbf{E}$ is equal to the volume average of the microscopic compatible (i.e. derived from a displacement field) strain field $\varepsilon(\underline{x})$ in the REV [170], $\mathbf{E} = \langle \varepsilon \rangle_V$ where $\langle z \rangle_V = (1/V) \int_V z(\underline{x}) dV$ stands for the volume average of quantity z over domain V .

In the framework of linear elasticity, the local strain field $\varepsilon(\underline{x})$ is related to macroscopic strain $\mathbf{E}$ through fourth-order localization tensor $\mathbf{A}(\underline{x})$:

$$\varepsilon(\underline{x}) = \mathbf{A}(\underline{x}) : \mathbf{E} \quad (\text{B.1})$$

Using the equality $\mathbf{E} = \langle \varepsilon \rangle$, one obtains $\langle \mathbf{A} \rangle = \mathbf{I}$. The tensor of overall effective moduli $\mathbf{C}^{\text{hom}}$ of the heterogeneous porous material is given as:

$$\mathbf{C}^{\text{hom}} = \langle \mathbf{c} : \mathbf{A} \rangle \quad (\text{B.2})$$

The above equation is classical and has been presented in many papers [170, 144]. In the isotropic case, this equation is reduced to the following forms:

$$K^{\text{hom}} = \sum_{k=1}^m f_k k_k A_k^v \quad ; \quad G^{\text{hom}} = \sum_{k=1}^m f_k g_k A_k^d \quad (\text{B.3})$$

The evaluation of the effective Young moduli needs an estimation of the strain localization tensor $\mathbf{A}$. This needs the knowledge of the stress and strain fields in an inclusion embedded in an infinite medium and subjected to homogeneous strain $\mathbf{E}_0$ at infinity. The general form of the solution can be considered as follows:

$$\varepsilon^{(k)} = \mathbf{H}_k : \mathbf{E}_0 \quad (\text{B.4})$$

where the tensor $\mathbf{H}_k$ is a function of the Young moduli of the inhomogeneity and the reference medium, $\mathbf{C}_k$ and $\mathbf{C}_0$, respectively, and the geometry of the inclusion. Eshelby [152] gives the solution for the stress and strain fields inside an ellipsoidal inhomogeneity perfectly bounded to an infinite elastic reference medium.

As explained by Zaoui [170], the strain localization tensor can be estimated by estimating the average mechanical state in each phase k of the RVE subjected to the macroscopic strain $\mathbf{E}$ as that of an ellipsoidal inhomogeneity with the same moduli, embedded in an infinite matrix with arbitrary moduli $\mathbf{C}_0$ subjected to some adequate uniform strain at infinity $\mathbf{E}_0$. The stress and strain field in the phase k are thus estimated by Equation B.4. The strain tensor $\mathbf{E}_0$ can be determined knowing that $\mathbf{E} = \langle \varepsilon \rangle$:

$$\mathbf{E} = \langle \varepsilon \rangle = \langle \mathbf{H} \rangle : \mathbf{E}_0 \quad (\text{B.5})$$

Inserting $\mathbf{E}_0$ from this relation in Equation B.4 and comparing with Equation B.1, the strain localization tensor of the phase k can be identified:

$$\mathbf{A}_k = \mathbf{H}_k : \langle \mathbf{H} \rangle^{-1} \quad (\text{B.6})$$

Average strain in a REV with imperfect interfaces

This approach could be extended by considering the existence of an imperfect interface between a phase, and its surrounding medium. The presence of imperfect interface results in a displacement jump given by $\Delta u_i = \eta_{ij} \sigma_{jk} n_k$, where η_{ij} is interface compliance tensor. η_{ij} can be expressed in terms of η^n and η^t , which are respectively normal and tangential compliances. [154, 159, 143].

$$\eta_{ij} = \eta^t \delta_{ij} + (\eta^n - \eta^t) n_i n_j \quad (\text{B.7})$$

The average strain over the REV, considering displacement jumps at the interfaces, is given by:

$$\langle \varepsilon \rangle_V = \frac{1}{V} \int_V \varepsilon(\underline{x}) dV = \sum_{k=1}^m f_k \varepsilon_k + \frac{1}{2V} \sum_{k=1}^m \int_s (\Delta u_i n_j + \Delta u_j n_i) ds \quad (\text{B.8})$$

The strain tensor $\mathbf{E}_0$ can be determined knowing that $\mathbf{E} = \langle \varepsilon \rangle$, by inserting Equation B.4 in Equation B.8:

$$\mathbf{E} = \langle \varepsilon \rangle_V = \sum_{r=1}^n f_k \mathbf{H}_k : \mathbf{E}_0 + \frac{1}{2V} \sum_{k=1}^m \int_s (\Delta u_i n_j + \Delta u_j n_i) ds \quad (\text{B.9})$$

The term Δu in Equation B.9 can be replaced with the expression of the displacement jump to find:

$$\mathbf{E} = \sum_{k=1}^m f_k \mathbf{H}_k : \mathbf{E}_0 + \frac{1}{2V} \sum_{k=1}^m \int_s (\eta_{im} \sigma_{mk} n_k n_j + \eta_{jm} \sigma_{mk} n_k n_i) ds \quad (\text{B.10})$$

Considering the difficulty of the evaluation of the integral term in the above equation, an *ad hoc* approximation can be formulated by replacing the stress on the interface by its average over the inclusion [154, 159, 157, 143].

$$\int_s (\eta_{im} \sigma_{mk} n_k n_j + \eta_{jm} \sigma_{mk} n_k n_i) ds \simeq \bar{\sigma}_{mk} \int_s (\eta_{im} n_k n_j + \eta_{jm} n_k n_i) ds \quad (\text{B.11})$$

The calculation of the integral in Equation B.11 needs the evaluation of the integral $\int_s \eta_{ij} n_k n_l ds$. Using Equation B.7 this can be written as:

$$\int_s \eta_{ij} n_k n_l ds = \int_s \left[\eta^t \delta_{ij} + (\eta^n - \eta^t) n_i n_j \right] n_k n_l ds \quad (\text{B.12})$$

The above integral can be calculated using the following two integrals evaluated over a spherical inclusion:

$$\frac{1}{s} \int_s n_i n_j ds = \frac{1}{3} \delta_{ij}; \quad \frac{1}{s} \int_s n_i n_j n_k n_l ds = \frac{1}{15} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad (\text{B.13})$$

Using Equations B.13 and B.12, the integral term in Equation B.11 can be written as:

$$\int_s (\eta_{im} n_k n_j + \eta_{jm} n_k n_i) ds = \frac{s}{15} \left[(2\eta^n + 3\eta^t) (\delta_{im} \delta_{jk} + \delta_{ik} \delta_{mj}) + 2(\eta^n - \eta^t) \delta_{ij} \delta_{mk} \right] \quad (\text{B.14})$$

Knowing that $\mathbf{I}_{ijmk} = \frac{1}{2} (\delta_{im} \delta_{jk} + \delta_{ik} \delta_{jm})$ and $\mathbf{J}_{ijmk} = \frac{1}{3} \delta_{ij} \delta_{mk}$, the above equation can be re-written as:

$$\int_s (\eta_{im} n_k n_j + \eta_{jm} n_k n_i) ds = s \left[\frac{2\eta^n}{3} \mathbf{J} + \frac{4\eta^n + 6\eta^t}{15} \mathbf{K} \right] \quad (\text{B.15})$$

Using Equations B.15 and B.11, $s = 4\pi r^2$, $V = \frac{4}{3}\pi r^3$ for a spherical inclusion of radius r and $1/V = f_k/V_k$, Equation B.10 can be re-written as:

$$\mathbf{E} = \sum_{k=1}^m f_k \left(\mathbf{H}_k : \mathbf{E}_0 + \sigma^{(k)} : \mathbf{P}^{(k)} \right) \quad (\text{B.16})$$

where

$$\mathbf{P}^{(k)} = \frac{1}{r} \left[\eta_k^n \mathbf{J} + \frac{4\eta_k^n + 3\eta_k^t}{5} \mathbf{K} \right] \quad (\text{B.17})$$

By knowing that $\sigma^{(k)} = \mathbf{C}_k : \varepsilon^{(k)}$ and $\varepsilon^{(k)} = \mathbf{H}^{(k)} : \mathbf{E}_0$ the following can be obtained:

$$\mathbf{E} = \sum_{k=1}^m f_k \left(\mathbf{I} + \mathbf{C}_k : \mathbf{P}^{(k)} \right) : \mathbf{H}_k : \mathbf{E}_0 = \left\langle \left(\mathbf{I} + \mathbf{C}_k : \mathbf{P}^{(k)} \right) : \mathbf{H}_k \right\rangle : \mathbf{E}_0 \quad (\text{B.18})$$

Inserting $\mathbf{E}_0$ from this equation into the $\varepsilon^{(k)} = \mathbf{H}_k : \mathbf{E}_0$ the strain localisation tensor of the phase k is identified as:

$$\mathbf{A}_k = \mathbf{H}_k : \left\langle \left(\mathbf{I} + \mathbf{C}_k : \mathbf{P}^{(k)} \right) : \mathbf{H}_k \right\rangle^{-1} \quad (\text{B.19})$$

Using Equations B.19 and B.17 the strain localization coefficients A_k^v and A_k^d in Equations 6.5.3 and 6.5.4 are found.

The following section is dedicated to its evaluation of the coefficients H^v and H^d for the REV considered in this study.

Evaluation of strain localization parameters

This part is dedicated to the derivation of the elastic strain field in an infinite medium constituted of a 2-layered spherical inclusion, embedded with an imperfect interface, in a matrix subjected to uniform strain conditions at infinity. This solution is used to calculate the strain localization coefficients for the proposed micromechanical model. The considered model is presented in Figure B.1. A spherical coordinate system (r, θ, ϕ) is used. The presentation of the equations follows the same steps as in the original formulations of Hervé and Zaoui [142] and their extension to consider imperfect interfaces by Ghabezloo [143], but in a relatively concise manner. The interested reader may refer to the original papers for more details.

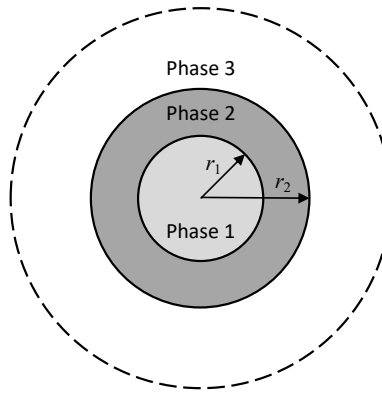


Figure B.1: The 2-layered spherical inclusion embedded in an infinite matrix

Considering the isotropy and spherical symmetry of the model, the general solution can be obtained by superposing the solutions of two elementary problems: hydrostatic pressure and simple shear applied at infinity

Hydrostatic pressure

A displacement in the following form is applied to the boundary of the model:

$$\underline{u}^0 = \frac{\theta_0}{3} r \underline{n} \quad (\text{B.20})$$

where $\underline{n}$ is the outward normal vector to the boundary. Due to the spherical symmetry, the problem is one-dimensional. The solution of the displacement component u_r is given in each phase by the following form, in which F_k and G_k ($k = 1, 2$) are constants which should be determined for each layer:

$$u_r^{(k)}(r) = F_k r + \frac{G_k}{r^2} \quad (\text{B.21})$$

The non-zero components of the stress tensor are thus found to be:

$$\sigma_{rr}^{(k)} = 3k_k F_k - 4g_k \frac{G_k}{r^3} \quad (\text{B.22})$$

$$\sigma_{\theta\theta}^{(k)} = \sigma_{\phi\phi}^{(k)} = 3k_k F_k + 2g_k \frac{G_k}{r^3} \quad (\text{B.23})$$

The continuity of the radial stress and displacement at the interface between phases k and $k+1$ with radius r , considering a compliant interface given by the tensor $\mathbf{J}'_k$, implies that ($k = 1, 2$):

$$[\mathbf{J}_k(r_k) + \mathbf{J}'_k(r_k)] \mathbf{V}_k = \mathbf{J}_{k+1}(r_k) \mathbf{V}_{k+1} \quad (\text{B.24})$$

where

$$\mathbf{V}_k = [F_k, G_k]^T; \quad \mathbf{J}_k(r) = \begin{bmatrix} r & \frac{1}{r^2} \\ 3k_k & -4\frac{g_k}{r^3} \end{bmatrix}; \quad \mathbf{J}'_k(r) = \begin{bmatrix} 3k_k \eta_k^n & -\frac{4}{r^3} g_k \eta_k^n \\ 0 & 0 \end{bmatrix} \quad (\text{B.25})$$

The relation between vectors $\mathbf{V}_{k+1}$ and $\mathbf{V}_k$ is given by:

$$\mathbf{V}_{k+1} = \mathbf{N}^{(k)} \mathbf{V}_k; \quad \mathbf{N}^{(k)} = \mathbf{J}_{k+1}^{-1}(r_k) [\mathbf{J}_k(r_k) + \mathbf{J}'_k(r_k)] \quad (\text{B.26})$$

The vectors $\mathbf{V}_{k+1}$ are related to the vector $\mathbf{V}_k$ by:

$$\mathbf{V}_{k+1} = \mathbf{Q}^{(k)} \mathbf{V}_k; \quad \mathbf{Q}^{(k)} = \prod_{l=1}^k \mathbf{N}^{(l)} \quad (\text{B.27})$$

Given that in the particular case of this research there only potentially exists an imperfect interface between phases 2 and 3 (HGMS and cement matrix), $\mathbf{J}'_k(r_k)$ will be a non-zero tensor only for $k = 2$, which stands for the contact between these phases:

$$\mathbf{N}^{(1)} = \begin{bmatrix} \frac{4g_2 + 3k_1}{4g_2 + 3k_2} & -\frac{4(g_1 - g_2)}{r_1^3(4g_2 + 3k_2)} \\ -\frac{3r_1^3(k_1 - k_2)}{4g_2 + 3k_2} & \frac{4g_1 + 3k_2}{4g_2 + 3k_2} \end{bmatrix} \quad (\text{B.28})$$

$$\mathbf{N}^{(2)} = \begin{bmatrix} \frac{4g_3 r_2 + 3k_2 r_2 + 12g_3 k_2 \eta_2^n}{r_2(4g_3 + 3k_3)} & -\frac{4(g_2 r_2 - g_3 r_2 + 4g_2 g_3 \eta_2^n)}{r_2^4(4g_3 + 3k_3)} \\ \frac{3r_2^2(k_3 r_2 - k_2 r_2 + 3k_2 k_3 \eta_2^n)}{4g_3 + 3k_3} & \frac{4g_2 r_2 + 3k_3 r_2 - 12g_2 k_3 \eta_2^n}{r_2(4g_3 + 3k_3)} \end{bmatrix} \quad (\text{B.29})$$

To avoid a singularity at $r = 0$, $G_1 = 0$ should be used. Also, given the applied displacement at infinity, $F_3 = \frac{\theta}{3}$. It permits to find:

$$F_1 = \frac{1}{Q_{11}^{(2)}} F_3; \quad F_2 = \frac{Q_{11}^{(1)}}{Q_{11}^{(2)}} F_3 \quad (\text{B.30})$$

$$G_2 = \frac{Q_{21}^{(1)}}{Q_{11}^{(2)}} F_3; \quad F_3 = \frac{Q_{21}^{(2)}}{Q_{11}^{(2)}} F_3 \quad (\text{B.31})$$

Simple shear

New boundary displacements are applied for this condition, reading in spherical coordinates:

$$u_r^0 = \gamma r \sin^2 \theta \cos 2\phi \quad (\text{B.32})$$

$$u_\theta^0 = \gamma r \sin \theta \cos \theta \cos 2\phi \quad (\text{B.33})$$

$$u_\phi^0 = -\gamma r \sin \theta \sin 2\phi \quad (\text{B.34})$$

The displacement field in phase i is given by:

$$u_r^{(k)} = u_r^{(k)}(r) \sin^2 \theta \cos 2\phi \quad (\text{B.35})$$

$$u_\theta^{(k)} = U_\theta^{(k)}(r) \sin \theta \cos \theta \cos 2\phi \quad (\text{B.36})$$

$$u_\phi^{(k)} = U_\phi^{(k)}(r) \sin \theta \sin 2\phi \quad (\text{B.37})$$

where U_r , U_θ and U_ϕ , given below, are functions of r :

$$u_r^{(k)}(r) = A_k r - 6 \frac{\nu_k}{1 - 2\nu_k} B_k r^3 + 3 \frac{C_k}{r^4} + \frac{5 - 4\nu_k}{1 - 2\nu_k} \frac{D_k}{r^2} \quad (\text{B.38})$$

$$U_\theta^{(k)}(r) = A_k r - \frac{7 - 4\nu_k}{1 - 2\nu_k} B_k r^3 - 2 \frac{C_k}{r^4} + 2 \frac{D_k}{r^2} \quad (\text{B.39})$$

$$U_\phi^{(k)}(r) = -U_\theta^{(k)}(r) \quad (\text{B.40})$$

Equations B.35 to B.40 represent the boundary displacement for the simple shear condition and the resulting displacement in each phase as a function of radius r . In these equations, the terms associated with the constants C_k and D_k are divided by the radius r .

For phase 1, the initial value of the radius ($r = 0$) would lead to a singularity, so $C_1 = 0$ and $D_1 = 0$ to avoid this singularity. Moreover, in phase $n + 1$ the radius tends to infinity, so the displacement values also tend to infinity, unless $B_{n+1} = 0$. Then $A_{n+1} = \gamma$, so, it is possible to represent the displacement imposed in the boundary region by applying Equations B.35 to B.37. The interface conditions between phases k and $k + 1$ imply the continuity of $u_r, u_\theta, u_\phi, \sigma_{rr}, \sigma_{r\theta}, \sigma_{r\phi}$, but only four of these conditions are independent. The continuity conditions are written as:

$$[\mathbf{L}_k(r_k) + \mathbf{L}'_k(r_k)] \mathbf{W}_k = \mathbf{L}_{k+1}(r_k) \mathbf{W}_{k+1} \quad (\text{B.41})$$

where

$$\mathbf{W}_k = [A_k, B_k, C_k, D_k]^T; \quad \mathbf{L}_k(r) = \begin{bmatrix} r & -\frac{6\nu_k}{1-2\nu_k}r^3 & \frac{3}{r^4} & \frac{5-4\nu_k}{1-2\nu_k}\frac{1}{r^2} \\ r & -\frac{1-2\nu_k}{7+4\nu_k}r^3 & -\frac{r^4}{2} & \frac{r^2}{2} \\ g_k & \frac{3\nu_k}{1-2\nu_k}g_k r^2 & -\frac{12}{r^5}g_k & \frac{2(\nu_k-5)}{1-2\nu_k}\frac{g_k}{r^3} \\ g_k & -\frac{7+2\nu_k}{1-2\nu_k}g_k r^2 & \frac{8}{r^5}g_k & \frac{2(1+\nu_k)}{1-2\nu_k}\frac{g_k}{r^3} \end{bmatrix} \quad (\text{B.42})$$

and $\mathbf{L}'_k$ stands for the compliant interface between two phases and can be defined as:

$$\mathbf{L}'_k(r) = \begin{bmatrix} g_k \eta_k^n & \frac{3\nu_k}{1-2\nu_k}g_k r^2 \eta_k^n & -\frac{12}{r^5}g_k \eta_k^n & \frac{2(\nu_k-5)}{1-2\nu_k}\frac{1}{r^3}g_k \eta_k^n \\ g_k \eta_k^t & \frac{7+2\nu_k}{1-2\nu_k}g_k r^2 \eta_k^t & \frac{8}{r^5}g_k \eta_k^t & \frac{2(\nu_k+1)}{1-2\nu_k}\frac{1}{r^3}g_k \eta_k^t \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (\text{B.43})$$

Once more, by considering the imperfect interface between phases 2 and 3 (HGMS and cement matrix), the tensor $\mathbf{L}'_k(r)$ will be not-zero only for the contact between them (i.e. $r = r_2, k = 2$). Then, the relationships between vectors $\mathbf{W}_{k+1}$ and $\mathbf{W}_k$ are given by:

$$\mathbf{W}_{k+1} = \mathbf{M}^{(k)} \mathbf{W}_k; \quad \mathbf{M}^{(k)} = \mathbf{L}_{k+1}^{-1}(r_k) [\mathbf{L}_k(r_k) + \mathbf{L}'_k(r_k)] \quad (\text{B.44})$$

The vectors $\mathbf{W}_{k+1}$ are related to $\mathbf{W}_1$ by:

$$\mathbf{W}_{k+1} = \mathbf{P}^{(k)} \mathbf{W}_1; \quad \mathbf{P}^{(k)} = \prod_{l=1}^k \mathbf{M}^{(l)} \quad (\text{B.45})$$

As mentioned before, the parameters with known values are $C_1 = 0, D_1 = 0, B_3 = 0$ and $A_3 = \gamma$. Therefore, one can obtain:

$$A_1 = \frac{P_{22}^{(2)} A_3}{P_{11}^{(2)} P_{22}^{(2)} - P_{12}^{(2)} P_{21}^{(2)}} \quad (\text{B.46})$$

$$B_1 = -\frac{P_{21}^{(2)} A_3}{P_{11}^{(2)} P_{22}^{(2)} - P_{12}^{(2)} P_{21}^{(2)}} \quad (\text{B.47})$$

and one can obtain W_2 as:

$$\mathbf{W}^{(2)} = \frac{A_3}{P_{22}^{(2)} P_{11}^{(2)} - P_{12}^{(2)} P_{21}^{(2)}} \mathbf{P}^{(1)} \begin{bmatrix} P_{22}^{(2)} \\ -P_{21}^{(2)} \\ 0 \\ 0 \end{bmatrix} \quad (\text{B.48})$$

Average strains in phase k

When uniform strain conditions $\varepsilon_0 = \frac{\theta_0}{3} \mathbf{I} + \mathbf{e}_0$ apply at infinity, the following volume and deviatoric strains in each phase write as follows:

$$\bar{\theta}^{(k)} = \frac{F_k}{F_{n+1}} \bar{\theta}_0 \quad (\text{B.49})$$

$$\bar{\mathbf{e}}^{(k)} = \frac{1}{A_{n+1}} \left[A_k - \frac{21}{5} \frac{r_k^5 - r_{k-1}^5}{(1 - 2\nu_k)(r_k^3 - r_{k-1}^3)} B_k \right] \bar{\mathbf{e}}_0 \quad (\text{B.50})$$

By developing Equations B.49 and B.50 the following equations are obtained:

$$\bar{\theta}^{(1)} = \frac{(4g_2 + 3k_2)(4g_3 + 3k_3)}{X} \bar{\theta}_0 \quad (\text{B.51})$$

$$\bar{\theta}^{(2)} = \frac{(4g_2 + 3k_1)(4g_3 + 3k_3)}{X} \bar{\theta}_0 \quad (\text{B.52})$$

$$\bar{\theta}^{(3)} = \bar{\theta}_0 \quad (\text{B.53})$$

$$X = (4g_2 + 3k_1) \left(4g_3 + 3k_2 + \frac{12g_3 k_2 \eta_2^n}{r_2} \right) + 3(k_1 - k_2) \left(4g_2 - 4g_3 + \frac{16g_2 g_3 \eta_2^n}{r_2} \right) \left(\frac{r_1}{r_2} \right)^3 \quad (\text{B.54})$$

$$\bar{\mathbf{e}}^{(1)} = \frac{21P_{21}^{(2)} r_1^2 - 10\nu_1 P_{22}^{(2)} + 5P_{22}^{(2)}}{(5 - 10\nu_1)(P_{11}^{(2)} P_{22}^{(2)} - P_{12}^{(2)} P_{21}^{(2)})} \bar{\mathbf{e}}_0 \quad (\text{B.55})$$

$$\bar{\mathbf{e}}^{(2)} = \frac{-\frac{P_{22}^{(2)}}{3}Y_1 - \frac{P_{21}^{(2)}}{2\nu_1 - 1}Y_2 + \frac{3(r_1^5 - r_2^5)}{5(r_1^3 - r_2^3)}P_{21}^{(2)}Y_3}{5g_2(P_{11}^{(2)}P_{22}^{(2)} - P_{12}^{(2)}P_{21}^{(2)})(\nu_2 - 1)}\bar{\mathbf{e}}_0 \quad (\text{B.56})$$

$$\bar{\mathbf{e}}^{(3)} = \bar{\mathbf{e}}_0 \quad (\text{B.57})$$

$$Y_1 = 8g_1 + 7g_2 - 5\nu_2(2g_1 + g_2) \quad (\text{B.58})$$

$$Y_2 = r_1^2[-7(g_1 - g_2) + 7\nu_2(2g_1 + g_2) + 3\nu_1(3g_1 - 24g_2)] \quad (\text{B.59})$$

$$Y_3 = 7(g_1 + 4g_2) + 5\nu_1(g_1 - 8g_2) \quad (\text{B.60})$$

By replacing the elastic properties of phase 1 with 0 (corresponding to the void space inside the HGMS), one can obtain some reduced expressions of H_k^v and H_k^d for the REV considered in the lower part of Figure 6.2.1.

$$\bar{\theta}^{(1)} = \frac{(4g_2 + 3k_2)(4g_3 + 3k_3)}{X}\bar{\theta}_0 \quad (\text{B.61})$$

$$\bar{\theta}^{(2)} = \frac{4g_2(4g_3 + 3k_3)}{X}\bar{\theta}_0 \quad (\text{B.62})$$

$$\bar{\theta}^{(3)} = \bar{\theta}_0 \quad (\text{B.63})$$

$$X = 4g_2\left(4g_3 + 3k_2 + \frac{12g_3k_2\eta_2^n}{r_2}\right) - 3k_2\left(4g_2 - 4g_3 + \frac{16g_2g_3\eta_2^n}{r_2}\right)\left(\frac{r_1}{r_2}\right)^3 \quad (\text{B.64})$$

$$\bar{\mathbf{e}}^{(1)} = \frac{21P_{21}^{(2)}r_1^2 + 5P_{22}^{(2)}}{5(P_{11}^{(2)}P_{22}^{(2)} - P_{12}^{(2)}P_{21}^{(2)})}\bar{\mathbf{e}}_0 \quad (\text{B.65})$$

$$\bar{\mathbf{e}}^{(2)} = \frac{P_{21}^{(2)}}{5(\nu_2 - 1)(P_{11}^{(2)}P_{22}^{(2)} - P_{12}^{(2)}P_{21}^{(2)})}\left[\frac{P_{22}^{(2)}(5\nu_2 - 7)}{3P_{21}^{(2)}} + 7r_1^2(\nu_2 - 1) - \frac{84(r_1^5 - r_2^5)}{5(r_1^3 - r_2^3)}\right]\bar{\mathbf{e}}_0 \quad (\text{B.66})$$

$$\bar{\mathbf{e}}^{(3)} = \bar{\mathbf{e}}_0 \quad (\text{B.67})$$

Finally, having obtained the expressions of H_k^v and H_k^d , by considering Equation B.19 and recalling the definition of $\mathbf{C}_k = 3k_k\mathbf{J} + 2g_k\mathbf{K}$, it is possible to obtain $\mathbf{A}_k$ as shown in Equations 6.5.3 and 6.5.4. Thus, the homogenised parameters of the composite material can be obtained by using Equation 6.2.1.

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