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MICRO-STRUCTURAL ANALYSIS OF TIME-VARIANT EVOLUTION IN PORE GEOMETRY OF CEMENT MATERIALS DURING CARBONATION

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ABSTRACT

The purpose of this project was to gain a fundamental understanding of the carbonation-induced alterations in borehole grouts. This was approached by determining the relationship between the chemical denaturation of the minerals in the evolving pore network and its associated transport properties. These changes resulted from material processing under a range of simulated underground temperatures, pressures and pH. The pore network geometry and transport properties were examined as a function of the degree of structural and mineral alteration. These alterations were then macroscopically related to the depth evolution of the carbonation fronts under elevated temperature and pressure conditions.

The microstructure, pore geometry and transport properties were studied experimentally for class G cementitious grout samples immersed in CO₂ saturated brine at 60°C and 120°C (80 bar) for durations up to 5 months. The evolution of the carbonation depth was captured by means of X-ray computed tomography (XRCT), the compositional changes were detected using scanning electron microscopy (SEM) coupled with energy dispersive Xray analysis (EDXA) and X-ray diffraction (XRD) and finally the pore geometry was revealed using mercury intrusion porosimetry (MIP) and N₂-physisorption.

Temperature was the most sensitive variable to control the rate of alteration for both microstructure and pore network. Calcium leaching in the samples treated with N₂-saturated brine was found to be a thermally dependent process; in fact the activation energy for Ca transport was found to be higher when increasing temperature from 60°C to 120°C. At temperatures higher than 60°C full conversion of portlandite to other forms was justified on the grounds of activation energy and appeared to cause chemical instabilities within the grouts. Those instabilities where aggravated in the case of the carbonated brine.

The examined carbonated samples showed two clearly defined areas (inner core and carbonated region) for any duration, that were separated by a clear demarcation line, namely

the carbonation front. The time evolution of the carbonation depth was found to follow a power law equation that reflected the rate of diffusion for each temperature. At 60°C the higher rate of diffusion led to faster local supersaturation conditions in the pores (with respect to Ca^{2+} and HCO_3^-) justifying the growth of aragonite crystals. At 120°C, the slower rate of diffusion was reflected by the growth of calcite.

At 60°C and 120°C, both inner and carbonated parts exhibited a sealing stage (up to 1 month) and a dissolution stage (up to 5 and 3 months). The terms 'sealing' and 'dissolution' referred only for changes in the apparent porosity but in reality these changes were found to reflect the changes of the critical cavity to throat ratio due to different temperature and time. At 60°C the permeability was proved to be controlled by the critical throats (big values of cavity/ throat ratio) and at 120°C by the size of the critical cavity (small cavity/ throat ratio).

The critical size of the pores and throats at 120°C close to 12 nm, supported the unrestricted diffusion of calcium towards the outer and hence the faster buffering of the effluent bicarbonates. At 120°C, the buffering was found to take place at the surface sites of the C-S-H particles and thus from structural Ca²⁺. At 60°C the restricted transport of species due to the small critical throats (~4 nm) resulted in the big cavities which were the loci of aragonite crystallization from the free Ca²⁺. This distinction of 'diffusion' at 120°C and 'restricted transport' at 60°C, was the key point for the better fitting of the time evolution of the carbonation front to the $x_c = A \cdot t^{1/2}$ at 120°C.

At the inner parts of the CO₂ treated samples at 120°C, in order the throats and cavities to resemble in size, the silicate **matrix** was suggested to experience simultaneously localized expansion (decreasing the cavity size) and shrinkage (throat enlargement). At 60°C the preservation of the threshold diameter, the intensified ink-bottle phenomenon and same critical throats close to 3 nm, could have been caused due to: (1) the retarded pozzolanic reactions at 60°C that would have caused the throats to be mechanically stable due to the microsilica particles and, (2) the small activation energy for the C-S-H particles to re-organize their **structures** and to align them leading to silicate condensation and polymerization. The plethora of existing oilwells sealed with ordinary Portland cements globally, dictates that the permeability of the entire well to CO_2 fluids will rely on the diffusion among the pores of the C-S-H structures. The permeability values from this study (ranging from 70 µD to 0.1 µD) were found to allow for the efficient geological storage for CO_2 across the entire range of temperatures studied but with different mechanisms of diffusion.

The major significance of the present thesis was that it provided a better understanding of the relationship between the cement microstructure with its pore network parameters, a relationship that ultimately determined the permeability and extent of carbonation in the long term. In other words the aim of the thesis was fulfilled giving a more comprehensive image during carbonation of a class G oil well cement grout in a realistic scenario of geological storage of CO₂, with temperature and time to be the only variables. The implications of the studied temperatures (60°C and 120°C) and durations (1, 3 and 5 months) in real CO₂ injection wells, could provide better assessment of legacy injection wells (containing aged cement grouts) and more efficient design of new CO₂ injection wells.

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A command rings out within me: "Dig! What do you see?"

"Men and birds, water and stones." "Dig deeper! What do you see?" "Ideas and dreams, fantasies and lightening flashes!" "Dig deeper! What do you see?" "I see nothing! A mute Night, as thick as death. It must be death." "Dig deeper!" "Ah! I cannot penetrate the dark partition! I hear voices and weeping. I hear the flutter of wings on the other shore." "Don't weep! Don't weep! They are not on the other shore. The voices, the weeping, and the wings are your own heart."

Nikos Kazantzakis

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Appendix 2: Mercury intrusion porosimetry data

Appendix 3: Diffusion equations for the evolution of the carbonation front

LIST OF ACRONYMS

ΔFt	a laive triggelfa alveria eta hardeata
1 11 t	calcium trisultoaluminate nydrate
APEC	Asia-Pacific Economic Cooperation
API	American Petroleum Institute
AR	Alumina Ratio
B.P.	Before Present
BET	Brunauer–Emmett–Teller
BGS	British Geological Survey
BJH	Barrett-Joyner-Halenda
BSE	Back-Scattered Electrons
CCGS	Carbon dioxide Capture and Geological Storage
CCS	Carbon dioxide Capture and Storage
CCWs	Carbon dioxide Capture Wells
СН	Calcium Hydroxide
CR	Cement Rock (interface)
CS	Cement Steel (interface)
CSH	Calcium Silicate Hydrate (specific formula of known composition)
	Calcium Silicate Hydrate (general formula of unknown
C-S-H	composition)
EDXA	Energy Dispersive X-ray Analysis
EOR	Enhanced Oil Recovery
ET	Efficient Technologies
GERC	GeoEnergy Research Centre
GHG	GreenHouse Gas
IEAGHG	International Energy Agency of GreenHouse Gases
IGP	Interglobular Gel Pores
IPCC	Intergovernmental Panel of Climate Change
ITZ	Interfacial Transition Zone
LGP	Large Gel Pores
LSF	Lime Saturation Factor
MIP	Mercury Intrusion Porosimetry
ms	micro-silica
NERC	National Environmental Research Council
PTFE	PolyTetraFluoroEthylene
REV	Representative Elementary Volume
RH	Relative Humidity
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SGP	Small Gel Pores
SiC	Silicon Carbide
SPR	Safety Pressure Relief
SR	Silica Ratio
SSA _{bet}	Specific Surface Area (using Brunauer–Emmett–Teller equation)
TEM	Transmission Electron Microscopy
SGP SiC SPR SR SSA _{BET}	Small Gel Pores Silicon Carbide Safety Pressure Relief Silica Ratio Specific Surface Area (using Brunauer–Emmett–Teller equation)

USGS	United States Geological Survey
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- WRI World Resources Institute
- XRCT X-ray Computed Tomography
- XRD X-Ray Diffraction

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1.1 Scope of the problem

1.1.1 CCS technologies

1.1.2 Anthropogenic carbon emissions and associated problems

Carbon dioxide (CO₂) and methane (CH₄) constitute the main greenhouse gases (GHG's) that are naturally produced by the earth's geological processes, *e.g.* volcanic vapours or deglaciations. They provide necessary shielding of the atmosphere to the outbound radiation being reflected from the earth and accumulate sufficient heat to support life in the biosphere, *i.e.* the greenhouse effect. The earth's temperature has historically fluctuated across geological timescales due to phenomena such as tectonic plates shifts and volcanic eruptions [Caliro *et al.*, 2005]. The correlation between pre-industrial atmospheric CO₂ concentrations and the earth's surface temperatures has been established over the past 350,000 years by measurements of CO₂ bubbles found in Antarctic ice cores (Figure 1.1a). These trends started to deviate from their historic periodic profiles and in coincidence with the introduction of anthropogenic CO₂ emissions resulting from industrialisation (Figure 1.1b) [Ruddiman, 2003].

Increasing mean temperature, has accelerated the ice cap melting and is capable of reducing the land mass, with implications for an expanding population, due to penetration of salted waters to potable sources. The extreme weather events that are documented by the scientific community have a strong impact to the economy and seriously threaten the human lives, future generations and the preservation of endangered species [IPCC, 2007]. Since 1850 more than 330×10^9 metric tons of CO₂ from the burning of fossil fuels have been charged to the atmosphere [Canadell *et al.*, 2007]. The industrial era has also coincided with an increasing population (Figure 1.2) and transportation network, extensive urbanisation of land mass, and large-scale deforestation [Bin *et al.*, 2005], all of which have aggravated the

accumulation of CO_2 in the atmosphere. This has led to significant research effort over the last ~20 years [Moss *et al.*, 2010] in the understanding and prediction of risks associated future climate scenarios due to the predicted rise in CO_2 and its historic association with temperature.



Figure 1.1 (a) The natural trends of atmospheric CO_2 concentration 4×10^5 years before present (B.P.); source: Centre for Climate and Energy Solutions. (b) Anthropogenic emissions of CO_2 exhibit an increasing tendency since the industrial era; source: World Resources Institute (WRI).



Figure 1.2 The correspondence of the CO_2 emissions to the change in population. [IPPC, 2009] (Scenario: A1, fast economic growth and fast integration of efficient technologies (ET); A2, per capita economic growth and slow integration of ET; B1, economy based on services and implementation of clean ET; B2, medium economic development and varied technological shift)

The driver for carbon capture and storage (CCS) technology is not to reduce current concentrations of atmospheric CO₂, but to reduce current levels of CO₂ emissions from the major emitters ($m_{CO2} > 0.1$ Mt/yr [IPCC, 2005]) in secondary industry upon which the post-industrialised world has become dependent, *e.g.* coal and gas power, cement, iron & steel [IPCC, 2007], particularly for newly-industrialised nations such as China and India who have significantly increased their CO₂ emissions during the last two decades [Wei *et al.*, 2007]. Therefore, CCS can be categorised as a suite of transitional technologies that enable industries that are currently fossil fuel-dependent to maintain stability and flexibility in view of the CO₂ threat until the technological advancements (*e.g.* renewables, hydrogen, nuclear fusion) needed to move to a low carbon economy can be made, e.g. 50 year's time.

1.1.3 CCS technologies

<u>Capture:</u> CCS systems start with the separation of CO_2 from industrial flue gas streams. These streams are being selected so as the separation of carbon dioxide to be technically and economically achievable. Ammonia, hydrogen, methanol and ethylene oxide production and the processing of natural gas include reactions that are principal emitters of CO_2 as by-product. The capture of CO_2 can take place before (pre combustion), after (post combustion) or during a combustion process (*e.g.* oxyfuel). CO_2 can be isolated using solvents/sorbents, membranes and distillation of a gas stream being in the liquid phase [IPCC, 2005]. Several liquids can absorb the CO_2 from the CO_2 rich gas and release it in a different vessel through regeneration of the absorbing media. Capture of CO_2 with the production of biomass is another solution at the end of the chain of CCS systems [IPCC, 2005].

<u>Transport:</u> CO_2 after its separation can be transported as gas, liquid and solid. Appropriate pipes, vehicles and ships are employed for transporting CO_2 to specific sites for safe deposition (off-shore, on-shore) and reaction. IPCC (2005) states clearly the specifications of the CO_2 transport streams including maximum threshold levels at impurities like H₂S, S (total), N₂, hydrocarbons and glycol. Additionally, water content, temperature and oxygen concentration values are included in the specifications as well, due to their strong contribution to the corrosion in the pipes.

<u>Storage</u>: In order for CCS to be economically viable it is demanded that the operation of transport systems will allow for CO₂ to be stored safely. The safe storage implies zero emissions (from leakage) of CO₂ into the atmosphere. Mechanisms of storage include reaction of CO₂ with minerals and deposition of CO₂ at underground reservoirs or large depths like geological and oceanic storage respectively. Storage through mineralization is achieved when CO₂ reacts with naturally occurring minerals originating from mines, rich in Mg and Ca, for the production of carbonate or magnesium materials [Lackner *et al.*, 1995]. Otherwise, CO₂ can be accommodated in big depths (~2km) inside the ocean [IPCC 2005, chapter 6, p. 279] taking advantage of the precipitation of CO_2 when brought into contact with lower oceanic strata. Finally geological CCS is attained when CO_2 is injected in deep underground reservoirs for reaction with geological formations.

Geological storage is deemed as the most prominent CCS technology due to big existing reservoir volumes, proven storage capacities and no need for extensive miningmaterial transport [Huijgen *et al.*, 2003], high energy demands [IPCC 2005, chapter 7, p. 326] (mineralisation), or direct impact to the delicate and unknown natural ecosystems (oceanic storage) [Lackner *et al.*, 2009; Caulfield *et al.*, 1997]. To conclude with, carbon dioxide capture and geological storage (CCGS) is the most credibly and viably applicable technology and this tangible from the large body of existing work (USGS, BGS).

1.2 Geological storage

1.2.1 Loci and mechanisms of CCGS

 CO_2 has long been pumped in underground geological rocks on grounds of enhanced oil recovery (EOR) (Figure 1.3). The Weyburn field in Canada, [Verdon, 2012], is a successful example of CO_2 injection at 1300-1500m depth for EOR and has started its operation at 2000 [Emberley *et al.*, 2005]. Since then and until 2011 more than 15 Mt of CO_2 have been injected [White, 2011], while it is projected that the total storage volume of CO_2 will exceed the 20 Mt [Gozalpour *et al.*, 2006]. On the other hand, at the Sleipner field in the North Sea, CO_2 is been separated from the extracted natural gas and is injected at a saline aquifer, in a formation called Utsira located 800-1000m below the sea bottom [Boait *et al.*, 2012]. Sleipner operates since 1996 at an injection rate of 1Mt CO_2 /year approximately, with more than 10Mt CO_2 to be stored until 2012. Similar to the Sleipner field is the on-shore SACROC unit in West Texas where 68 Mt of CO_2 derived from the field of natural gas in the Val Verde have been pumped 2100 m below the surface since 1972 [Carey *et al.*, 2007].



Figure 1.3 Mapping of the global CCWs according to their type and storage capacity of the corresponding reservoirs (Building capacity for CO₂ capture and storage in the APEC region)

CCGS technologies are comprised of the CO₂ injection well (or Carbon dioxide Capture Well-CCW) which penetrates vertically the earth's crust, through a sequence of geological zones (surrounding formations), leading CO₂ into an underground storage volume (Figure 1.4). The major target of CCGS is the flow of CO₂ into this volume which is located under particular stratifications with very low permeability that act as seals (caprock) to the upwards flow of CO₂ preventing seepage to the atmosphere. The subterranean formations are rocks, with certain porosity and transport properties soaked with several fluids or water/brines assembling a reservoir or an aquifer respectively [Bachu *et al.*, 2007], and are defined by the storage capacity and the geological storage formation materials [Keating *et al.*, 2011]. The injected CO₂ (being supercritical or gas) is distributed vertically and laterally according to interactions with the underground formations and fluids, generating a plume, and can be trapped physically (faults and folds, stratigraphic, residual trapping) [Bachu *et al.*, 2008] or chemically (solubility, ionic, mineral trapping) [Adamczyk *et al.*, 2009].



Figure 1.4 The overview of the CCGS technologies. The efficient injection and storage of CO_2 must be ensured from the sealing properties of geological formations by means of continuous monitoring

1.2.2 Risk-safety analysis in the CCGS applicability

CCGS technologies must guarantee that the CO_2 plume, during and after the injection period, remains trapped in the underground space, following a lateral pattern of flow (Figure 1.4) excluding any continuous upwards movement of CO_2 (leakage), fact dictating that no more than 0.1 % per year of the injected CO_2 is allowed flee to the atmosphere [Lotz *et al.*, 2008]. Possible leakage pathways [Zhang *et al.*, 2011] may be of natural origins, such as not compact caprock and discontinuities of the geological strata, or of man-made origins like abandoned or poorly sealed boreholes (Figure 1.5). Representative imprinting of the reservoir's structure (capacity, formation materials), proper injectivity (no overcoming of the maximum injection pressure) and ensuring confinement of the CO_2 in the reservoir are some preventive measures that target the minimization of the impact of natural causes in the CO_2 leakage.



Figure 1.5 Risk analysis and preventive actions from CO₂ migration [IPCC 2005, p35]

The main CO_2 leakage risk can be attributed to the increasing number of wells [EPA 2013], in comparison to the leakage from the caprock [Wollenweber *et al.*, 2010] or due to extreme phenomena, i.e. earthquakes. Since 1846, when the first shallow oilwell was drilled at Baku-Azerbaijan [Bommer, 2008], more than 350,000 wells have emerged for oil and gas extraction merely in Alberta at Canada [Bachu *et al.*, 2009] and more than 4500 wells are actively injecting CO_2 at the Weyburn-Midale field [Choi *et al.*, 2013]. Consequently, a further study of the wells as routes of CO_2 leakage is indispensable for the consolidation of the CCGS technologies and will act cumulatively to the existing expertise of countries like Canada, USA, UK and Australia that have already adopted specific regulations on CO_2 geological storage (or 'geosequestration') [Zakkour *et al.*, 2007] in which the importance of cementitious grouts for sealing the rock-borehole interface CCWs has been well defined.

1.3 CCS boreholes – leakage analysis

1.3.1 Interactions of grouts with underground environments

The grouts' reactivity is inherently coupled with the well that they are pumped. Whether the well was used for extraction of oil and gas and afterwards for CCS purposes or the well was designed exclusively for CO_2 injection are facts that predetermine the behaviour of the grout in its physical and chemical response to the CO_2 species. In principle the cementitious grouts are susceptible to the conditions of the underground reservoirs with temperatures ranging up to $150^{\circ}C$ and pressures ranging up to 500 bars. Under these T and P, CO_2 can be supercritical or wet; the former state is met at the top of the reservoir while the latter if CO_2 is diluted in brines.

Despite CO₂ several aggressive species are produced with the generation of acidic conditions (pH \approx 4). Other impurities like H₂S, NO_x, SO_x, O₂, CH₄, CO may be present in the stream of the injected CO₂ or in the underground fluids [IEAGHG, 2011]. Under particular specifications the quantity for each one of these species must not exceed established maximum limits [Visser *et al.*, 2008]. The reason is to inject a stream of CO₂ as pure as possible to minimise the impact of unforeseen circumstances of leakage to have the minimal impact in the aboveground living organisms and potable reserves. Otherwise, in the cases of CO₂ leakages the *in situ* monitoring tools should account only the CO₂ measurements excluding the impact of other secondary substances in the underground environments.

1.3.2 Assessment of cementitious grouts for CCGS

Carbon dioxide is mainly injected through a CCW as supercritical fluid. Due to buoyancy forces the CO_2 is restrained at the top of the reservoir [Damen *et al.*, 2006] and comes into contact with the CCW. CO_2 when diluted into water tends to form carbonic acid and other aggressive forms, and thus creating acidic environments. As with the reactions between CO_2 and the target underground rocks, the cementitious grouts also tend to react in the presence of CO_2 which alters their composition and functional properties.

The cementitious grouts must provide sealing of the annular space while providing adequate time for complete assimilation of CO_2 by the underground rocks, in a way such as the long-term durability of the grout will allow the complete isolation of the injected CO_2 in the subterranean environments (Figure 1.6).

Several faults can be observed at the borehole cement which might constitute precursors of favourable paths for CO_2 leakage [Celia *et al.*, 2004]. Potential pathways for leakage can occur (Figure 1.6) through the grout of the annular cement or the cement sheath, or via either the cement-rock (CR) [Gu *et al.*, 2012] or the cement-steel (CS) interfaces [Carey *et al.*, 2010]. As a consequence the assessment of the impact of carbon dioxide species in the grouts is imperative for the prediction of their long term behaviour at subterranean storage conditions.



Figure 1.6 Possible failures of the adhesion of cement can create migration pathways of CO₂ [Celia *et al.*, 2004]

1.4 Aim

The overall aim of the project was to gain a fundamental understanding of the carbonation-induced alterations in borehole grouts, and to determine the relationship between the chemical denaturation of the minerals in the evolving pore network and its associated transport properties. These changes result from material processing under a range of simulated underground temperatures, pressures and pH. The pore size distribution of the grout will be examined as a function of the hydration degree, the rate of the conversion of the minerals, the diffusivity of water, salts and CO_2 and the penetration of the carbonation fronts.

1.5 Objectives

In order to meet this aim, the following quantifiable objectives were initially set:

- 1. Identification and comparison of the cement minerals *a priori* and *a posteriori* of mixing and curing with salt and/ or CO₂ solutions
- Determination of the pore size distribution, surface area and other pore characteristics and connection with the grout design process parameters: water to cement ratio, cement type and type of aggregate.
- Specification and delineation of cement carbonation propagation routes and chemicalmineralogical transmutations of cement particles in these routes
- Determine the relationship between *in-situ* alternation processes –caused by CO₂ injection at elevated T-P- and the depth profile evolution of minerals
- 5. Experimental calculation of the amplification of the diffusion- associated transport phenomena due to the carbonation reactions
- 6. Quantification of the rate of carbonation for the purpose of extrapolation from accelerated to natural experiments. In what extent are results from the accelerated carbonation realistic when comparing them with data acquired from natural carbonated samples

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7. Quantifying the characteristics of the aged pore network with the pore fluid transport phenomena including the variable incoming and leached species due to carbonation of cement minerals.

1.6 Limitations of the research programme

In order to assess the stability of CO_2 injection wells it is necessary that the borehole cementitious seals to be examined for their chemical, mechanical and permeability properties. In this project only the chemical and permeability properties will be assessed. Even though the cementitious grouts are been subjected to pressures depending on the type of well (maximum depth, diameter, history, rock environment) the study of mechanical stress to strain relationships or possible cracks induced by mechanical loading will be left out of the current experiments. Additionally, although the thermal properties of the individual component of the cementitious grouts will be taken into consideration, possible cracks due to thermal expansion or contraction are areas out of the scope of the present project.

Furthermore, natural carbonation as performed in nature is a time demanding process that requires more than ten years correspondingly to levels of CO_2 concentrations equal to 0.03 %-0.04 % v/v [Ji et al., 2010]. Thus it is not feasible to produce samples directly from the raw materials in order to monitor the carbonation reactions within the range of the current project. However, this limitation will be resolved partly, on one hand from accelerated experiments and on the other hand from samples provided from the British Geological Survey. The assistance of existing naturally carbonated samples for comparison with the samples subjected to accelerated carbonation will provide the degree of reliability and validity for the last samples. In other words mineral transformations of existing carbonated samples with natural rates will be used as templates for assessing the validity of the accelerated conditions.
Additionally, any specific inherent limitations related with each instrument or technique will be taken under consideration and it will be attempted the use of methods which complement each other so as the aims and objectives to be as completed as possible. One important issue that must be mentioned beforehand is the constraints related with the size scale of the samples of the carbonation experiments. In other words, the experimental investigation of the carbonation-associated microstructural changes of the minerals in conjunction with the transport properties of the chemical species of the cement particles will be attained up to the scale that provides representative and meaningful results as shown in Figure 1.7.



Figure 1.7 The size scale limitations of the different microstructural levels of organization of concrete (after [Ulm, 2003]).

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2.1 Preface

2.1.1 Geological CCS technology

Carbon Capture and Storage Systems (CCS) are one kind of highly promising mitigation technologies (Figure 2.1) for tackling the high concentrations of carbon dioxide emitted from the industrial activity on condition of the acknowledgement of their technological background [Riahi *et al.*, 2004]. These "mitigation technologies" have been used for prediction of the long term levels of CO_2 and have already been implemented in fossil fuel-based societies in order to render them aware of the CCS technologies [Alphen *et al.*, 2007]. Geological CCS technologies constitute those sequestration techniques of capturing CO_2 in geological formations, after the CO_2 has been transported to the appropriate storage site. Other industrially implemented or experimental ways of capturing CO_2 are wet scrubbing with aqueous solutions of amines, pre-combustion or post-combustion capture [Gibbins *et al.*, 2008; Rai *et al.*, 2010] including CO_2 gas separation-absorption in membranes or ceramic materials, microbial fixation of CO_2 and other physical or chemical methods [Rubin *et al.*, 2012].



Figure 2.1 The location of geological CCS technologies in the map of the overall management of anthropogenic CO_2 [Rubin *et al.*, 2012]

Oil wells, saline aquifers and coal mines are highly probable candidates for accommodating the excess amounts of CO₂ for geological storage [Alphen *et al.*, 2010]. An example of geological storage of carbon dioxide is shown in Figure 2.2. In brief, CO₂ can be transported either though pipes directly from the industry to the storage site (route $1\rightarrow3$), or by ship to storage sites and then pumping it into the subterranean formations (route $1\rightarrow2\rightarrow3$). Cementitious grouts are found to be compatible materials for isolating the injected CO₂ from fleeing to the atmosphere and are placed in the vacant circular ring in between the casing of the pipe and the surrounding rock formations. The main target of those grouts lies at the sealing of the storage sites in order to achieve the aim of the mitigation policies for as smooth a transition to clear forms of energy as possible and for long term reduction of the atmospheric CO₂ levels.



Figure 2.2 The main concept of injecting CO₂ for geological CCS applications. [CO₂ club Romania, 2008-2011]

However there are potential risks for leakage of CO_2 from the oilwells to the atmosphere, due to chemical or mechanical failure of the cement paste to secure the long term

storage of CO₂. Lack of substantial knowledge of the ways of alteration of cement properties with connection to its porosity upon cement carbonation is a major problem for predicting and securing the CO₂ storage. This may be attributed mainly to the gap that exists in the interpretation of the cement properties at a more fundamental point of view including the chemical reactions that occur in the range of pores of cementitious materials and the driving force behind their propagation. Carbonation of cement and associated phenomena need to be examined in depth for a better sealing and design of the cement grout systems [Fabbri *et al.*, 2012; Gherardi *et al.*, 2012].

2.1.2 Performance of borehole grouts

Cement paste is a complex system of minerals and hydrated products with variable chemical composition and heterogeneous distribution within the paste mainly with reference to commercial applications [Poyet *et al.*, 2013]. When the paste is applied in aggressive environments with various T, P and chemistries of the host-rock formations [Zivica *et al.*, 2001], then serious chemical transformations can occur. Chemical attacking species like CO₂, chlorides and sulphates [Müllauer *et al.*, 2012] undermine the stability of the cement particles with the production of potentially unstable chemical formations like carbonates. These products may occupy more space, so as the surface area to be decreased (*e.g.* Figure 2.3; after Thomas *et al.*, 2009), and due to their low solubility [Johannesson *et al.*, 2001] to decelerate the leaching process. These alterations have been found one the one hand to depend on the type of interface of cement (cement steel, [Carey *et al.*, 2010] or cement rock [Newell *et al.*, 2013] interfaces) and on the other hand to be related with mechanical stresses that induce fractures in the paste [Wigand *et al.*, 2009].

When anhydrous cement powder is mixed with water, several paths are created between the hydrated particles, which upon normal conditions they contain water and other ions from the hydration process. The amount of water that is present within the pore network determines the mechanical properties of the hardened cement paste [Felekoğlu *et al.*, 2007]. The consolidation of a cement paste is intensely affected by a range of attacking factors, like CO₂, which undermine the stability of minerals and denature the pore network leading possibly to the higher rates of reaction and failure of the cement paste [Fabbri *et al.*, 2012]. Pure CO₂, carbonated brine, acids, sulphates and other T, P environments [Jacquemet *et al.*, 2008; Jacquemet *et al.*, 2006] need to be correlated with the parameter of porosity when designing and implementing a project of injection cement in a borehole for CCS purposes.



Figure 2.3 An example of the impact of water in the modification of the surface area during the process of cement carbonation [Thomas *et al.*, 2009]; a description of the D-drying method is given at Korpa *et al.*, 2006.

Despite the numerous studies on the integrity of cement applications for geological CCS storage [Kutchko *et al.*, 2007; Rimmelé *et al.*, 2008], the role and the contribution of porosity in the transport and mechanical properties of cement have not been studied yet with the appropriate rigor. First and foremost, numerical simulations of the permeability of wells

used for CO_2 injection and prediction of leakages [Ghabezloo *et al.*, 2009] do not incorporate the variability of the porosity parameters. Additionally, chemical reaction modelling and simulations of the cement interactions with the steel and surrounding rocks [Gherardi *et al.*, 2012] provide incomplete data due to inherent thermodynamic and reactive limitations of the models. Finally, kinetics of the carbonation reactions and simple mineralogical identification [Celia *et al.*, 2004] require the connection of the changes over the porous network to mineralogical alterations along the network.

2.2 Cement chemistry

2.2.1 Introduction

The use of cement nowadays is steadily increasing (Figure 2.4) [Schneider *et al.*, 2011], with most predictive scenarios to underestimate the demand of cement for various applications comparing to real data that have been recorded up to this moment. A cement processing plant (Figure 2.5) can be characterized by high temperature ceramic processes that lead from the calcareous and argillaceous raw materials to the final cement clinker.



Figure 2.4 Cement production according to optimistic and pessimistic scenarios [Schneider *et al.*, 2011]

2.2.2 Cement clinker and processing

• Overview of the cement plant

It took cement a lot of time since 1824 when Joseph Aspdin patented a product entitled as Portland cement [Bogue, 1947]. Numerous civilizations used cement or premature forms of cement for constructive purposes. Nowadays the cement production is conducted in plants similar to that of Figure 2.5. Initially, the proper raw materials like limestone, clay, shale and marl are extracted from the appropriate quarry. Then they are crushed to fine powder, which enters to the rotary kiln where it melts in temperatures up to 1600°C, cools under controlled conditions and then crushed again in order to obtain the final cement. In order the grey powder of cement clinker to be created, calcium oxides and silicon oxides must react and create the calcium silicates. Calcium oxides are produced from the calcination of limestone while the sources of silicon oxides are clays [Elimbi *et al.*, 2011]. Marl clay is used as a source of both CaO and SiO₂ [Hughes *et al.*, 2007].



Figure 2.5 A modern plant consists of several units which accommodate all the necessary processes to create a cement powder for several applications [CMI, 2003].

• Cement kilns and reactions

Kilns are these reactors (Figure 2.6) used for the chemical reactions of the two kinds of oxides by supplying heat at high temperatures up to 1600°C [Ranade *et al.*, 2007]. Several fuels are burned at the flame located at the end of kiln so as to overcome the energetic barrier of disruption and junction of the oxides [Rahman *et al.*, 2013]. Modern cement industries encompass provisions, like preheaters and precalciners, for a better efficiency of the kiln and a smaller size of the kiln (Figure 2.5) [Ranade *et al.*, 2007].

The reactions within the kiln take place at specific ranges of temperatures which happen to increase as the materials flow to the outlet of the kiln (Figure 2.6; Figure 2.7). Volatiles, gas and liquid phases are the means for the clinker reactions, with the liquid phase to play a major role in the production of alite, belite, aluminate and ferrite phases [Mastorakos *et al.*, 1999]. Finally cooling, is another important factor which determines the quality of the produced powder of cement clinker. Rapid cooling of the cement clinker is known to give to the clinker high quality characteristics as the main phase of cement, C_3S , is not embedded into the precipitated C_2S and C_3A and thus allowing higher values of long term hardening [Hong *et al.*, 2001].



Figure 2.6 The formation of belite (a) and alite (e) in the different zones of the kiln. The other letters correspond alphabetically to the formation of aluminate and ferrite phases (b), to the melt formation (c) and finally to the formation of aggregates (d) [Telschow *et al.*, 2012]. In cases like a, b and e the diffusion of Ca^{2+} is evident (Mosci, 2012).

• Phase diagrams during cement production

The phase diagram of conversion of the raw materials to the final clinker describes the changes in composition for the cement clinker (Figure 2.7). In the latter figure the formation temperatures for alite and belite are 1250°C and 700°C correspondingly. The occurrence of high temperatures for the formation of alite is essential in order to obtain the desired polymorph that would lead to better performance of the final hardened cement. In other words the formation of alite as described in Figure 2.6 (e) not only implies that the diffusion of the Ca²⁺ to occur for the formation of tricalcium silicates but with a particular crystallographic profile. Both time and temperature should be sufficient to generate the proper melting mixture that would lead to the desired diffusion of the elements (primarily Ca²⁺) from the calcareous grains to the siliceous and argillaceous phases. For belite to be created the temperature is lower as two Ca²⁺ are required for the formation of the dicalcium silicate. For both alite and belite, the desired crystal structures of the final product are essential, since other crystallographic orientations, although thermodynamically favorable, in fact they do not possess hydraulic properties.

For the formation of alite and belite the molten mixture should have the appropriate flow characteristics inside the kiln that would allow the diffusion from phase to phase. The presence of C_3A and C_4AF is essential for these phase to phase transformations. These phases melt at lower temperatures (700°C) than the main polymorphs of alite and belite and give particular characteristics for the molten mixture so as diffusion to be feasible in higher temperatures. From the discussion above, it is important to state the critical parameters for the creation of the proper clinker:

- 1. Physical and chemical properties of the raw materials
- 2. Pretreatment of the raw materials
- 3. Time and temperature of reactions inside the kiln
- 4. Cooling and grinding



Figure 2.7 The sequence of products inside the cement kiln: from the raw materials of calcareous and argillaceous nature to the final phases of cement powder [Moir, 2003]

The changes of the clinker can be predicted by using empirical formulas like the Bogue equations [Bogue, 1889] but more accurate models have been proposed [Kural *et al.*, 2004]. The produced composition of the clinker can be assessed in qualitative terms using the indices of lime saturation factor, silica ratio and alumina ratio (Table 2.1). Finally, the grinding technique has been proved of major importance since properties like strength depend on the liberation of the main phases which will lead to the desired hydration products [Celik *et al.*, 2006].

Lime saturation factor, LSF	Silica ratio, SR	Alumina ratio, AR
CaO	SiO ₂	Al_2O_3
$\overline{2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3}$	$\overline{Al_2O_3 + Fe_2O_3}$	$\overline{Fe_2O_3}$

Table 2.1 Indices for assessment for the quality of cement clinker [Neville, 2011]

2.2.3 Hydration reactions

To begin with, Neville (2011) differentiates the systems of cement that are mixed with water. In the first category are encountered the closed systems (in example the ones that are used in some laboratory practices) which are isolated systems which are mixed without interactions with their environment. These interactions may be bleeding and contraction of the paste or other environmental factors which lead to transport phenomena through the boundaries of the system. The last systems are called open systems. Open systems can be found anywhere in the world a cement grout is currently placing or setting.

The hydration of cement is not an outdated issue, but rather a very complicated and unresolved phenomenon. When mixing the cement powder with water by means of hand mixing or mechanical mixing several phenomena take place. Paulini (1994), considered the hydration of cement as an issue strongly related with the nature of C-S-H as a crystal and as colloid. The term C-S-H is described extensively at section 2.3.2, but for the time being it is sufficient to state that it is the product of C_3S after it has reacted with water. Paulini proposed that when a critical volume of cement comes into contact with water then this volume expands due to repulsive forces which are reflected to a rise in the activation energy (Figure 2.8). The moment in which the mixture reaches a maximum energy level the first hydrated products appear, with a subsequent decline of the free energy due to the collapse of the repulsive forces. This continual decrease in the energy of the system grain-water is the natal principle of the hardening of cement. The macroscopic evidence for the hardening is the chemical shrinkage of the cement paste [Tazawa *et al.*, 1995].



Figure 2.8 The system of cement grain-water must overcome an energy barrier before the creation of the final cement products.

Despite the type of the reference system, open or closed, the mixture of cement powder with water needs to overcome an activation barrier due to kinetics restrictions [Paulini, 1994]. Those restrictions have to do with re-distribution of the cement crystals in order to accommodate the incoming molecules of water. The necessary energy for the instant increase in the free energy of the system is supplied by the mixing process and by the dissociation of the oxides of the cement powder as shown below (Figure 2.9a, b).

The theory of Browers, 2004 provide the necessary theoretical tools for calculating the volume of the hydrated products in terms of quantitative approach as shown below.

$$V_{initial \ paste} = v_{w0}m_{w0} + v_c m_{c0} = \frac{m_c(w/c)}{\rho_w} + \frac{m_c}{\rho_c}$$
 Eq. 2.1

 $V_{hardened \ paste} = V_{initial \ paste} + \sum_{i} (V_{hydration \ product} - V_{reactant})$ Eq.2.2



Figure 2.9 (I-IV) The hydration of alite; (a, b, c) Dissolution mechanisms of alite [Juilland *et al.*, 2010]

There are five stages (Figure 2.9) that lead to the formation of hardened cement paste [Juilland *et al.*, 2010; Thomas *et al.*, 2009]:

- I. Rapid dissolution- Initial hydration processes
- II. Induction period-Lag phase
- III. Massive precipitation of C-S-H and CH
- IV. Deceleration period
- V. Curing

Calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H), and hydrated ferrite (C-A-F-H) phases are the products of the hydration levels. The previous (C, S, A, F) are abbreviations of (CaO, SiO₂, Al₂O₃, Fe₂O₃), correspondingly [Neville, 2011]. The terms AFt and AFm are the official nomenclature in cement chemistry for tri-substituted and mono-substituted aluminoferrite phases. Further information for those phases can be found elsewhere [Rilem, 1986; Matschei et al., 2007].

The first namely with the generic term C-S-H are of colloidal nature [Jennings *et al.*, 2006;Jennings, 2008] and not essentially crystalline products as testified by the secondary hysteresis of their water isotherm [Feldman, 1968; Helmuth, 1965]. The mode of formation of C-S-H is shown in Figure 2.10 [Baglioni et al. 2011]. During the hydration reactions the function of gypsum is to provide **sulphate** anions $-SO_4^{2-}$ in order to prevent the premature stiffening of the paste which results in low long-term strength of the cement. If proper quantity of gypsum is used, then sufficient concentration of SO_4^{2-} will prevent the fast growth of calcium aluminate hydrates (C-A-H) (which causes flash set) and also the growth of gypsum crystals within the hydrated cement will be inhibited (preventing false set of cement). The first action of gypsum produces initially ettringite (tri-sulfoaluminate) and later monosulfoaluminate. On the actual mechanism of the induction period in a real cement paste Minard et al. (2007) concluded that, when CaSO₄ is present, neither the formation of ettringite nor the AFm appearance at the end of the dissolution period reduce the rate of C₃A reaction, but rather the inhibition due to adsorption of calcium or sulfate ions to the active dissolution sites of C₃A grains.



Figure 2.10 An overall representation of the C-S-H formation [Baglioni et al., 2011]

In Figure 2.10 the reactions leading to the formation of C-S-H and portlandite are not independent as thought previously [Sideris, 2000], but influence the mode of reaction of each other [Goñi *et al.*, 2011]. The composition of the final cement paste relies heavily on the

availability of water for hydration, the C/S ratio and of the drying method that is employed for the treatment of the cementitious materials (especially in the experimental scale).

Regarding the previous reactions the stoichiometric variable "x" represents the C/S ratio and its value determines the quantity of produced portlandite [Brouwers, 2004].

2.2.4 A review of the properties of cementitious materials

The majority of cement types requires the mixing with water for the production of the cement paste. These types represent hydraulic cements from their ability to harden by the action emanated from hydration. Cementitious grouts or commonly cements are the products after hydration of the cement clinker with various additives to be added in order to control the final properties of the hardened materials according to the each individual application [Neville, 2011]. The term "cement clinker" refers to the product of high temperature treatment at kilns up to 1,500°C [Telschow *et al.*, 2012], of calcareous and argillaceous materials like limestone/ chalk and clay/ shale [Taylor, 1997]. Gypsum is a material which controls these hydration reactions by decelerating the induction period [Coumes *et al.*, 2011].

The main properties of cementitious materials are inextricably connected with the type of cement used. Five main types of cements occur with several subcategorizations for each type depending on the percentage of the additive (Table 2.2). Additives like silica fume, fly ash, granulated blast furnace slag or burnt shale lead to the distinction of the cement types. The most widely known and simple in composition cement is the ordinary Portland cement with the gypsum as the only component.

 Table 2.2 The main types of cementitious materials according to EN 197-1:2000

(†: Hewlett	(1998);	*: Neville	(2011))
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Main constituents of cement						
Alite		Belite	Aluminate	Ferrite		
Several components in cementitious materials						
Cementitious	Additive-component		Applications†	Cementitious nature of		
material				additive*		
Туре І	—		General purpose	Fully cementitious-		
			No sulphates	hydraulic		
	01		x 1 1 1'			
Type II	Slag		Large hydraulic			
	(6-20 % ar	nd 21-35 %)	structures-dams,			
			bridge piers-***			
	Silica fume		High degree of	Latent hydraulic		
	(6-10 %)		impermeability,	(physical in action)		
			High strength			
			Concrete**			
	Pozzolana	(6-35%)		Latent hydraulic with		
	Fly ash	Siliceous		Portland cement		
	(6-35 %)	High-lime		Latent hydraulic with		
				Portland cement but		
				slight hydraulic		
	Burnt shale (6-35 %) Limestone (6-35 %)					
				Physical in action,		
				Slight latent hydraulic		
				action with Portland		
				cement		
	Composite	cement				
Type III	e III (Ground granulated) blast furnace slag (36-95 %)		Moderately	Latent hydraulic		
			Aggressive	Occasionally hydraulic		
			Environment			
Type IV	Type IV Pozzolanic cement			Latent hydraulic with		
	(11-55 %)			Portland cement		
Type V	Composite	cement				
	(pozollana and silica fume, 18-50 %)					

: [Burg et al., 1994]; *: [Caldarone et al., 2005]

Neville (2011) (pages 62-65) cites a very controversial issue for the terminology of cement. He states clearly that a Portland cement is pure cement just after the outlet of the kiln. The "cement" that arises from the addition of gypsum or other grinding aids is called blended cement. Characteristically he states that: "The terms 'constituent' and 'component' run the risk of confusion with the chemical compounds in Portland cement...". The first term, 'constituent', is used to imply that a material is made of its main essentials and primary characteristics. The second term, 'component', means the coexistence of the main constituents with other secondary additives. It is of utmost importance to emphasize that Portland cement in its original form develops its robustness as a constructive material in normal conditions of pressure and temperature having only its main 'constituents'. Several other additives are used to convey to those particular characteristics in order to withstand the extreme conditions of other non-normal conditions. Thus, according to [Neville, 2011], the most appropriate term for all those cements who have at least one extra additive to their mixture must be called as cementitious materials. Table 2.2 summarises the main constituents and some of the components of cement together with the corresponding type of cement.

Described in the textbook literature [Neville, 2011] as core properties of cement are: (1) the heat of hydration, (2) fineness, (3) initial and final setting times, (4) the mechanical strength, (5) the permeability and finally (6) shrinkage/ creep. The quality of the cement or concrete application is described with the term durability which includes all the aforementioned properties as variables.

In brief, as hydration evolves, heat emission is observed as a result of the reformations of the clinker compounds and the rearrangements of the overall crystal structure (Figure 2.9). The environment of hydration combined with the fineness of the cement particles play a leading role for the setting and hardening of the cement paste [Ahmad, 2002].

Although the cement paste is a continuously evolving body of minerals responding to the surrounding environmental changes of humidity, temperature and pressure, the definite stiffening of the paste is assumed to happen when the rate of heat generation of hydration approaches zero. The acquired strength of the cementitious materials can be described in terms of cohesion between the hydrated cement particles [Jönsson *et al.*, 2004]. The empty places of the cement paste that are occupied by the "bulk" or "free" water force the paste to be permeable while keeping its durable character. Nevertheless, if the stresses exceed a threshold corresponding to the Young's modulus or if the water-cement ratio is not the optimum one then the overall or partial cohesion between the hydrated cement particles is deteriorates leading to the failure of the cementitious application [Jurowski *et al.*, 2015; Oliveira *et al.*, 1996]. In the first case for induced failure by external stresses the proper term is creep while in the latter case of inner autogenous or chemical stresses the result is shrinkage [Shen *et al.*, 2016].

2.2.5 Summary

The issue of studying in depth the chemistry of cement is not trivial. The hydration reactions are those which control the way that the microcrystals of cement powder will dissolute and react. Several additives, like gypsum, aid the workability of cement pastes while other components lead to the numerous types of cement for any real application. At last the ways of predicting the actual composition of cement from the elemental composition of a given clinker may conceal important sources of errors for the final design of a cement or concrete structure.

2.3 Microstructure of cement

2.3.1 Introduction

The microstructure of cementitious materials acts as a coordinator between the observed micro- and macro- scale imperfections and the properties of those materials [Jennings, 2008]. From the imperfections of the **nanostructure** of the C-S-H, and therefore at the cement particles, to the variable densities of the inner and outer products of the hydrated cement particles, and consequently the irregular and randomly formed pore network, the ways of organization of the micro-particles need to be studied rigorously for the fundamental understanding of the behaviour of cement. All the forms of cement microstructure, for the majority of cements, can be assumed to be represented by the microstructure of the various models of C-S-H [Paine *et al.*, 2015].

Since 1999 when Ian Richardson observed TEM images of hardened cement paste, a remarkable progress is ongoing in the field of cement particles organization [Paine *et al.*, 2015]. Cement particles, when hydrated and hardened, form two areas of distinct densities, the inner product and the outer product [Richardson, 2004]. The first one, being denser than the outer product corresponds to the high packing of particles of the model proposed by Jennings (2008). The sparse formation of the outer product is represented by the low density phases of the Jennings' model and is the most candidate formation for the main contribution in the creation of the capillary pores in cementitious applications [Jennings, 2007].

2.3.2 Calcium silicate hydrate phases

The nature of the hydrated calcium silicates is not a resolved issue. From the two schools of thought the one of Henry le Chatelier's supports the crystalloid structure of C-S-H while the second one considers C-S-H to be a colloid [Jennings *et al.*, 2009; Jennings *et al.*, 2006]. Since the times of le Chatelier (1919) several descriptions and terms of the inner and

outer products have been proposed with each one of them to represent different aspects of the cement particles [Jennings *et al.*, 2002]. Each one of those descriptions depends strongly on the method used for deciphering the C-S-H microstructure either directly by means of visual observations [Richardson, 2004] or indirectly by means of the change in a specific property of another material e.g. N₂ physisorption [Jennings *et al.*, 2009].

2.3.2.1 Structural models

Leveraging the origins of the properties of cementitious structures one should take into account the interactions at a molecular scale of the cement particles. As a reference point several models of the C-S-H **structures** have been proposed with the tobermorite- jennite, T/J, to be the most dominant model from a molecular point of view [Richardson, 2004]. The atoms of Ca, Si, H₂ and O₂ are connected covalently as tetrahedra in a first level of organization [Durgun *et al.*, 2012]. At a second level the **structure** of silicate tetrahedra that are formed, containing interlayer atoms of calcium which modulate the Ca/Si ratio. The cohesion of the cement emanates from this level of organization, with the calcium-to-silicon ratio to determine the electrochemical stability of the cement particles [Nonat *et al.*, 2005]. However, the very particulate formations of C-S-H structures contain several defects, like missing tetrahedra and additional Ca²⁺, leading to deviations from the ideal T/J model as depicted in Figure 2.11.



Figure 2.11 The second level of organization of the C-S-H phases [Murray et al., 2000]

Despite all the possible defects, Richardson (2004) managed to parallel the composition of the actual calcium silicate hydrates and to give a general formula as shown below for the location and composition of the calcium silicate hydrates comparing to that of portlandite, CH. It is quite interesting that the presence of CH is required for the electrochemical equilibrium of the overall system of C-S-H.

$$\underbrace{\begin{bmatrix} Ca_{2n}H_wSi_{(3n-1)}O_{(9n-2)} \\ \hline tobermorite & -core \\ \hline C-S-H \end{bmatrix}}_{Ca(OH)_w+n(y-2)}\underbrace{Ca_{(\frac{n\cdot y}{2})}\cdot[mH_2O]}_{Ca(OH)_2}$$

The previous formula highlights the important role of water in the overall chemistry of C-S-H and CH. The amount of water molecules that exist in the space within the C-S-H nanostructures and in the space between the cement particles are the ones dictating the magnitude of van der Waals forces [Hou *et al.*, 2015]. A high amount of water molecules may have the same destructive results with the low amount of water since the C-S-H particles

require a specific number of water molecules which lead to the electroneutrality and chemical equilibrium of a representative volume of particles [Manzano *et al.*, 2011]. This is a strong evidence of the importance of the water-to-cement ratio.

2.3.2.2 Colloidal nature of cement paste

Brunauer (1962) describes the tobermorite gel as colloid as "it loses water from its structure continuously when equilibrated at lower vapour pressures of water". Forty six years after, Jennings has presented a second edition of his colloidal interpretation of cement paste. This second edition reflects mostly the behaviour of water inside and outside C-S-H grains (Figure 2.12). On the other hand the first part of his modelling reveals information more relevant to the structural point of view of this chapter.



Figure 2.12 The second colloid model for the microstructure of C-S-H [Chen *et al.*, 2012]

With reference to Taylor (1997), Nonat (2004) gives the following definition of gels according to Everett: "dispersions in which the attractive interactions between the elements of the disperse phase are so strong that the whole system develops a rigid network structure and under small stresses, behave elastically".

In fact the attempt to describe the behaviour of the hydrated cement particles falls into the area of assessment of the nature of water from the nano-scale to the macro-scale. Water state analysis, either as chemically bound to the C-S-H structures, or gel water embedded as nanocrystals of the silicate tetrahedra, is able to describe the "attractive interactions between the elements of the disperse phase" of the colloidal cement particles.

2.3.2.2.1 Various forms of water in cementitious materials

The three main forms of water as described by the Power's model are [Jensen *et al.*, 2001]:

Chemically bound water: This kind of water is strongly affected by the clinker composition of cements and the amount of cement powder reacted with water [Brouwers, 2005]. In their experiments Powers and Brownyard (1947) have conceived that both the colloidal calcium silicates and the microcrystalline aluminate phases lose some water of crystallization. The chemical bound water can be characterized as non-evaporable water since it cannot be removed by the P-drying method [Korpa *et al.*, 2006]. Aligizaki (2005) refers to chemically bound water as water of "constitution", since it is embedded in the crystal structures of some of the components of the cement paste. These components are hydroxide groups *e.g.* Ca(OH)₂, water held with strong covalent bonds with a constant identity *e.g.* MgCl₂ · $6H_2O$ and finally water bonding with hydrogen bonds *e.g.* CuSO₄ · $5H_2O$.

 \checkmark <u>Gel water</u>: The term "gel" emanates from the experiments of Powers and Brownyard in an attempt to describe water that is held below RH=45% and which happens to be

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proportional of the amount of the cement powder that has reacted. At higher RH the water enters to the capillary pores too, hence the term capillary water or free water. Aligizaki (2005) (p7) specifies more rigorously the types of gel water into the following classification:

- i. Zeolitic-like water (interlayer water of [Jennings, 2008]), which is found between the tobermorite-like layers of C-S-H.
- ii. Lattice water, is the crystallization water in the $(CaO)_x$ (SiO_2) $(H_2O)_y$ structure. This kind of water is not connected chemically with the main structure of the calcium silicates.
- iii. Adsorbed water is the water that is connected with the surface with van der Waals bonds.

Capillary or free water: The term free water is relevant to the amount of non-adsorbed water inside the pores and has some degrees of freedom in contrast to the water that is chemically bound H_2O or crystallized H_2O within the hydrates' structures. Capillary water is found at higher RH% than gel water.

2.3.2.3 Chemo-mechanical models

Cement or concrete should not be regarded merely as a material with the ability to withstand stresses at a scale visible to the human eye. The mechanical durability of cementitious materials is already accepted to occur in correlation with the chemical nature of the cement particles at scales equivalent to some μ m. This is the view held by Ulm *et al.*, (2007) by implementing the principles of nano indentation to distinguish four levels of organization, in terms of the maximum scale which is able to reveal any reliable and quantitative relation between the chemical structure and the mechanical strength.

2.4 **Porosity of cementitious grouts**

In general concrete/cement is a poromechanic material. In other words, the mechanical properties of a cement are inherently coupled with the pore structure. Similarly to the chemomechanical approach of the cement particles, increasing the volume of reference to the inclusion of pores together with the cement particles the mechanical properties are significantly different. The surface forces originated from the inter-particle spaces have a central role in properties like creep and shrinkage as they determine the pore structure characteristics and the way that the "empty" spaces are created through the development of cement particles (Figure 2.13) [Gmira *et al.*, 2004].



Figure 2.13 The tortuous network of cementitious materials [Galucci et al., 2007]

2.4.1 The origin of porosity in cementitious materials

The structural units of materials are molecules which are connected covalently to create the particular orientations of each unit. These orientations are stacked in different modes creating crystals, polymers, colloids and suspensions. As shown in Figure 2.14 several translocations of the C-S-H particles take place induced by thermodynamical and electrochemical reasons. These translocations create gaps with several orders of magnitude size and mean diameter which allow the flow of fluids to create a very complicated pore

network [Roussel, 2012]. Another explanation of the generation of porosity from first principles can be explained by the fractal growth of the elementary C-S-H particles (Figure 2.14) [Livingston, 2000].



Figure 2.14 The fractal dimension of the growth of C-S-H particles creates unavoidable pores [Jennings *et al.*, 2008]

2.4.2 The pore network in cementitious materials

Gel pores, capillary pores and hollow shell pores are the main types of pores in concrete. The first two are located in the cement matrix and the last ones to the delicate structure of ITZ [Aligizaki, 2005]. These pores are inherently created from processes like mixing and placement of the cementitious paste. They are important to the durability of the structures since owning to entrapment of atmospheric CO₂, degradation is a highly probable effect.

Aligizaki (2005) (p4) states that there is a significant difference between the pores that are created due to inherent properties of the constituent materials of a cement paste and the discontinuities that arise due to improper mixing and setting. The pores which can be found within a cement paste are the following: (1) cement paste matrix pores, (2) pores from aggregates, (3) interface pores, (4) water voids and (5) internal discontinuities [Aligizaki, 2005] (p4-13).

In the first category of pores which happen to exist in the main matrix of cement are included the gel pores, the capillary pores, hollow shell pores and air voids.

✓ *Gel pores*

The gel pores are those located within the C-S-H globules. Aligizaki (2005) (p5) refers to the gel pores by mentioning that, due to their smaller size comparing to the capillary pores they could have little effect in the overall permeability. However gel pores influence the rates of hydration since they happen to occur at the inner of the hydration products that are grown at the surface of the unhydrated cement grains. The role of gel pores during hydration was assumed to be coupled with the fineness of the cement grains. As the hydration proceeds and the capillary pores are filled with the hydration products, then the gel pores gradually increase and control the hydration of the unhydrated grains; finer cement grains can lead to higher hydration rates due to faster generation of gel pores.

✓ Capillary pores

The capillary pores are these which accommodate the free or capillary water which can be used indiscriminately as hydration water. It is calculated that C-S-H crystals occupy 60% more volume than the initial mass of the cement powder [Aligizaki, 2005] (p5). Capillary pores are essential for cement hydration as they create the vital space for the hydration products which tend to expand during the hydration process.

✓ *The hollow shell pores*

The hollow shell pores can be created in the interface of cement's bulk phase with the aggregates. Additionally in the course of the production of inner and outer products, more hydration products can be created from the surface of the original cement grains and to create a displacement gap which is the hollow-shell pore or otherwise a "Hadley grain".

The connections of the hollow shells are not well studied but they seem to have an "ink-bottle" character which makes their detection very hard with the conventional porosimetry instruments. The pores that are characterized as hollow shells may have larger

size than the capillary pores but during drying they start to lose their water only when the capillaries are empty [Aligizaki, 2005] (p10-11).

Processes like mixing and placement of cement are connected intrinsically with entrapment of air bubbles which may have contradictory results. One the one hand they may be useful for protection against freezing, while on the other hand carbonation from the atmospheric CO_2 is inherent. Thus there should be a very thorough analysis on the optimum air quantity which is embedded into the cement paste since fractures may develop causing failures to the cement application.

From the point of view of the colloidal model [Jennings, 2008], pores within the C-S-H particles, called Integlobular Gel Pores (IGP), small gel pores (SGP) or large gel pores (LGP) are employed for the description of the process of aging and strength. In Figure 2.14 two different approaches for the classification of pores can be observed. The IGP occur inside the cement particles (arrow I), the small gel pores between the cement particles (arrow II) and finally with the arrow III are denoted the large gel pores. This approach is followed according to the colloidal model while in the same figure (Figure 2.14) is obvious the spring of pores from the fractal growth of the cement particles. In the case of the third arrow the small shift of the cement particles of the basic fractal unit (II) can be justified from factors like mechanical stress, air entrainment and/or desiccation stresses.

2.4.2.1 Porosity and colloidal model

One of the major recent models is that of Jennings (2008). He proposed the plateletlike scheme of C-S-H (Figure 2.15), in which foils are packed within globules. This model corresponds mainly to the first level of the chemo-mechanical model of Constantinides (2002), but may explain the aging process of a random cement paste. The globules of Jennings, 2008 are shown in Figure 2.16 along with the impact of the process of aging and drying in the fate of C-S-H particles. The foil-like shape of C-S-H has been found recently, by

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means of TEM, to be a real representation of the C-S-H microstructure along with the fibrillike shape [Richardson *et al.*, 2015]. The colloidal model as presented by Jennings (2008) is not the absolute structure of C-S-H, but a model based on the accessibility of nitrogen to the pores and the adsorption-resorption of water in the various levels of C-S-H globule packing. In general, however, the proposed microstructure and the differentiation of the pores was proved to depend of the analytical method used, as different methods give different characteristics of the cement gel and not necessarily wrong descriptions.



Figure 2.15 The different states of C-S-H particles with variable degrees of hydration [Jennings, 2008]



Figure 2.16 Illustration of the impact of aging and drying on the orientation of the large gel pores (LGP) and small gel pores (SGP) [Jennings, 2008]

These C-S-H globules are the natal structures for the three types of porosity within the gel of cement materials according to Jennings, 2008 (Figure 2.15):

- i. Interglobular Gel Pores, IGP: The origin of these pores is attributed, from Jennings, 2008, to the tobermorite and jennite types of the C-S-H [Richardson, 2004], with the packing of imperfect layers of C-S-H to create tiny gel pores, the IGP. When water leaves the IGP of a globule, what is left behind is a more sparse structure. This removal of water from the IGP happens at RH<11 % which can justify the decreased density.
- ii. **Small Gel Pores, SGP**: This is the empty space that is created due to the packing of the globules. It can be differentiated by the LGP with the arbitrary number of 3 nm, in such a way that from 1-3 nm to correspond to the SGP. The small gel pores are said to be connected with the outer porosity of the larger pores according to the percolation theory of the pores [Bentz *et al.*, 1991;Ye, 2005].
iii. Large Gel Pores, LGP: These pores have diameter in the range of 3-12 nm and have thermodynamic similarities with the capillary pores. According to this kind of pores, a critical point is defined which is just below RH=40% and dictates that shrinkage within the mass of gel stops. Several factors influence the stability of the LGP: (1) drying, (2) loading, (3) heat and (4) the course of time.

It should be noted that the LGP consist a part of the low density phase and there is evidence of the LGP to be interconnected with the main large capillaries of the bulk mass of cement paste [Thomas *et al.*, 2008]. Furthermore, it is quite remarkable that LGP collapse at a greater extend, when the meniscus of the water is outside of a large gel pore and not inside of the pore. LGP can be used as tools to interpret the aging process of cement paste: the collapse of the LGP which exist among the several flocs with the subsequent decrease of the volume of LGP may be one of the main interpretations of the aging of cement.

2.4.2.2 Definition of tortuosity

In real applications of cement paste or concrete the target is the minimization of the penetration of air, moisture or even aggressive ions. The pores in the nano- and microstructure are connected at a particular degree with the surface pores so as to create, frequently, a permeable mass and thus affecting the durability of the application. The measurement of the depth of the inlet of several species was necessary to be reflected in the calculations of the quality of concrete structures. The ratio, effective average path of the fluid-to-plane of the shortest distance, or the square of this ratio has been proposed as a measure for the complicated transport ways in porous materials [Bullard *et al.* (2011)]. According to another definition tortuosity corresponds to the longest path of a porous medium which passes through the solid matrix [Promentilla *et al.*, 2009]. According to Promentilla *et al.* (2009) the tortuosity factor depends on various assumptions like the orientation of the diffusion and the diffusion through capillary or gel pores. If Le if the real distance of a molecule diffusing through the pore network from point A to B and L is the ideal linear distance between A and B then tortuosity is defined as: $\tau = Le/L$.

2.5 Carbonation of cementitious grouts

2.5.1 Introduction

The principal target underlying the geological CCS technologies is the storage of CO_2 in deep geological formations and its assimilation from those formations in the long term in the forms of stable products. Geological CCS systems embrace all those issues of cement chemistry, cement microstructure and transport properties of carbon dioxide through the tortuous pore network of the cement mass. The need for understanding the principles under the reactive behaviour of a cementitious grout for a variety of conditions (temperature, pressure and pH) is essential for predicting and securing the long-term sealing of geological CO_2 capture wells.

2.5.2 Chemical reactions during carbonation

Carbon dioxide at the concentrations of the atmosphere is a harmless gas for cement's consolidation on condition that it is not found in the form of ionic species in an aqueous solution [Short *et al.*, 2001]. However when CO_2 is dissolved into water it forms carbonic acid which makes the aqueous solutions very acidic as in the reaction follows [Kutchko *et al.*, 2007].

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq)$$
 (Carbon dioxide dissolution) Eq. 2.3

It is of utmost importance to clarify that the word "attack" of carbonic acid against the cementitious grout is not the proper term for describing the actual phenomenon of carbonation. The actual phenomenon can be entitled as "neutralization" of the fluid that exists inside the pore network by the acidic action of the carbonic acid [Zivica *et al.*, 2001].

Portlandite (CH) has been shown to exhibit greater affinity for the reaction with the carbonic acid than the C-S-H phases [Sulapha *et al.*, 2003]. Analytically, CH first dissolves into calcium cations and hydroxyl anions which react with the carbonates of the carbonic acid forming calcium carbonate [Papadakis *et al.*, 1989].

$$Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2OH^{-}(aq)$$
 (Portlandite dissolution) Eq. 2.4

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
 (CaCO₃ Precipitation) Eq. 2.5

Figure 2.17 is a synopsis of all the possible reactants and products during carbonation. In the case that several types of bacteria exist in the depths of a CO_2 capture well then carbonation reactions interact with the sulphation reactions and aggravate the degradation of cement [Zivica *et al.*, 2001]. The presence of sulphates in the underground waters is able to cause the creation of products [Renaudin *et al.*, 2007] detrimental for the consistency of the cementitious grout like ettringite and monosulfoaluminates (Figure 2.17) [Mehta, 1973].



Figure 2.17 A holistic scheme of the carbonation reactions and their potential connection with sulphur species [Zivica *et al.*, 2001]

2.5.3 Cement and CO₂

Figure 2.18 shows the phase diagram of CO_2 with the critical point to be at (31.6 °C, P=73 bars). For higher temperatures and pressures CO_2 is characterized as supercritical which means that it has density as high as liquids and viscosity as low as gases [Sauki *et al.*, 2010].



Figure 2.18 The phase diagram for CO₂ (source: Asia Industrial Gases Association)

The concentration of CO_2 and the solvent in which CO_2 is dissolved influence its coefficient of diffusion in such a way that the injected cement may exhibit different macroscopic characteristics such as different depth of differentiation (Figure 2.19) between the affected and the intact regions which is called carbonation depth [Sauki *et al.*, 2010].



Figure 2.19 Carbonation depth owning to (I) CO₂-saturated brine and (II) wet supercritical CO₂ at 140 bar and 40°C (after Sauki *et al.*, 2010)

The carbonation of cement not only depends on the relative humidity of the supercritical CO_2 , but also from the curing conditions (Figure 2.20) [Kutchko *et al.*, 2007]. The temperature, pressure and chemical composition of the surrounding fluids are all conditions that predetermine the microstructure of cement and thus influence the final transport properties.



Figure 2.20 Impact of two different temperatures (I, 22°C; II, 50°C) at 1 bar for the curing of class H Portland cement [Kutchko *et al.*, 2007]

2.5.3.1 Zonal analysis of carbonated cement

The carbonation reactions do not occur at random locations in a cementitious grout. Surface reactions take place firstly and then because of the existence of specific routes due to the pore network the reactions are spread at the inner of cement as in Figure 2.21 [Rimmelé *et al.*, 2008]. These routes seem to be selective and to proceed with a specific sequence (Figure 2.22). The generation of calcium carbonate and the dissolution of portlandite seem to create several paleofronts as relics in the carbonated regions [Barlet-Gouedard *et al.*, 2007].



Figure 2.21 The propagation of carbonation reactions from the carbonated zone towards the inner part of the samples. The differentiation of the carbonated regions is well delineated from the existence of the carbonation front [Rimmelé *et al.*, 2008].



Figure 2.22 Real and ideal display of the carbonation reactions. At the left is shown a cement steel sample carbonated at 30°C and 80 bar for 110 days, where (A) is the carbonated region, (B) is the carbonation front, (C) is the inner core and (D) is the cement steel interface [Rochelle *et al.*, 2012]. At the right is shown the propagation of the carbonation reaction in a front-like shape with distinct zones (1 to 3) at the carbonated region [Kutchko *et al.*, 2007])

2.5.4 Carbonation and the properties of cement

Generally, the carbonated regions appear to be less porous than the actual uncarbonated cement. It has been mentioned that the carbonated cement areas have higher compressive strength [Barlet-Gouédard *et al.*, 2007]. However, due to the high solubility of carbonates, their dissolution leads to the erosion of the carbonated regions and the exposure of new unhydrated cement to the action of carbonation.

The main principle of degradation of the cementitious grouts when they are brought in contact with CO_2 underground fluids is the attainment of new equilibrium states between the alkalinity of cement and the acidity of these fluids. Calcium hydroxide and calcium silicate hydrates (C-S-H) are the main products of hardened cementitious materials. Portlandite is first attacked by the dissociated species of CO_2 , and then dissolves into cations of calcium and anions of hydroxide leading to significant porosity and permeability increase. The subsequent

precipitation of calcium carbonates forms reaction products within the pore network which then constricts porosity and can reduce permeability. The dissolution of CH takes place due to the presence of water; the latter acts as a medium for CO₂ dissolution and ionization to carbonic acid and carbonate ions [Papadakis *et al.*, 1989]. Both portlandite and C-S-H are chemically connected [Richardson, 2004] and they contribute to the high alkalinity of the pore fluid with pH \approx 12. Thus when the concentration of CH reaches very low values then the C-S-H phases start to dissociate, thereby enhancing the buffering action of CH [Matteo *et al.*, 2012] with the end product to be amorphous silica gel [Kutchko *et al.*, 2007]. The major point of denaturation of the cement paste is the instability of the new carbonate phases that redissolve in acidic conditions causing cyclical fluctuations to the values of porosity and mechanical fatigue to the mass of the grout.

The newly formed CaCO₃ can be found either at the loci of CH and C-S-H dissolution or in the intact cement owing to the transport of species through the pore network [Duguid *et al.*, 2010]. The accumulation of CaCO₃ may form a 'reaction front' that hinders further CO₂ diffusion thereby protecting active sites (CH and C-S-H) within the unreacted regions of cement. While in that case CaCO₃ reduces the permeability of the cement [Takla *et al.*, 2011], other evidence reveals substantial degradation and deterioration of the grouts [Duguid *et al.*, 2010]. Experimental evidence has demonstrated that the shape of the fronts is highly influenced by the interactions of the cement paste with the contacting rocks and the steel (Figure 2.23). Therefore, a detailed study of the effect of porosity on the diffusion transport properties and on the chemical and mineralogical alterations of the grouts will lead to significant advances in the fundamental understanding of the spatial and temporal evolution of cement carbonation phenomena.



Figure 2.23 The propagation of the fronts of a grout in the CR interface [Samson *et al.*, 2007].

2.5.5 The importance of porosity in the carbonation reactions

The ability of the cement paste to maintain its integrity is defined by its interactions with the surrounding rocks and the steel injection pipe. On the one hand, the rocks adjacent to the grout are characterized by a porosity network which through the cement rock interface determines the surface area of carbonation reactions to the grout according to their chemical composition and transport properties. On the other hand, pre-existing defects on the steel tube can provide sealing of the CS interface owing to the reduction of the CO_2 flow through the CS interface due to mutual interaction, *i.e.* precipitation of calcite and siderite substances [Carey *et al.*, 2010]. In both cases there seems to be a coupling between the steel electrochemistry and the rock features with the reaction fronts induced to the grout by carbonation reactions in the big depths of injection [Matteo *et al.*, 2012].

Thus the porosity influences not only the profile of carbonation propagation fronts of the grouts but also exhibits particular reactive characteristics in the CS and CR interfaces; hence its time evolution is essential to better understand how well sealing capacity can be secured for long-term storage of CO_2 allowing the primary leakage risk of CCGS to be better managed.

2.6 Summary

In the present chapter, a brief overview of cement production and cement hydration was given in order to understand sufficiently the carbonation induced microstructural alterations of cement based grouts. Despite the various cement based grouts used for CO_2 geological storage purposes, the main reactions that govern carbonation were assumed to be the same for all the types of the grouts. Those reactions were proved to be the same for cement samples reacted in the laboratory under accelerated carbonation reactions and for real cement cores taken from operating CO_2 injection wells.

The need to investigate the changes of the pore network parameters for class G cementitious grouts emanated on the one hand from poor analysis in the past for the evolution of the overall pore network parameters during carbonation of laboratory cement samples. On the other hand the reaction pathways during carbonation and the intrinsic permeability of the grouts were better defined and analysed in the present thesis for an already applied and popular cement mixture that allowed not only for comparisons with other laboratory samples but also with real CO_2 injection wells. The overall strategy of the thesis was to use conventional analytical techniques for monitoring chemical and pore network alterations but with emphasis on the proper integration of their results for a novel interpretation of the critical pore pathways for carbonation.

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3.1 Introduction

3.2 Preparation of materials

Cement-based pastes were produced in line with the mixing protocol that was implemented for the grouts used to seal the annular ring between the CO_2 injection tube and the surrounding rock formations of the Sleipner field operating at the North Sea [Rochelle *et al.*, 2013]. All the materials of the mix design are given at Table 3.1. The quantities shown correspond to the preparation of approximately 3 kg of cement paste.

Material	Code	Quantity (g)	Sequence of adding
Water		693.00	1
De-foamer	FP-16LG	3.11	2
Dispersant	CD-34L	18.66	3
Retarder	R-10L	18.09	4
Microsilica suspension	BA-58L	492.00	5
Fluid loss control additive	FL-67LE	135.62	6
Cement	Class G	1882.5	7

Table 3.1 Materials used for the production of the cement samples [Rochelle et al., 2013]

The mixing was done using a Hobart A120 – 12-Quart All Purpose Mixer with a new stainless steel bowl having a flat beater as the mixing medium (Figure 3.1). Pure cement samples were generated using cylindrical moulds with diameter of 4.7 cm and height of 2 cm. The fresh cement samples were placed for 3 days until they were set inside an inert chamber filled with N_2 gas at 1 bar to avoid carbonation. Then the plastic moulds were carefully removed and all the samples were allowed to cure for 25 days inside a single plastic container filled with the curing solution. The setting time of 3 days was said to be sufficient for the onset of stiffening of the cement samples, while the rest 25 days was in line with the common

cement practices for 28 days of curing. The curing of the samples was done at 30°C and 1bar in a temperature controlled incubator with the temperature to vary ± 1 °C. The curing solution was Ca(OH)₂ saturated distilled water, which was produced in a continuously stirred beaker.



Figure 3.1 Forced action paddle mixer used in the preparation of the cement grouts

According to the specifications from the National Lime Association in order the curing solution to be saturated with calcium hydroxide at 30°C and 1 bar, at least 0.159 g of Ca(OH)₂ must be dissolved in 100 g of water. In the present study, 4 g of white powder of Ca(OH)₂ supplied by Sigma Aldrich with purity \geq 95% were dissolved at 2000 g of distilled water. The 4 g are above the saturation value for the 2 l of water which was calculated to be 3.18 g/ 2 l water. Amount greater than 4 g would have led to extensive precipitation of portlandite to the surface pores of the samples, fact that could have delayed the onset of the interactions with the surrounding brines once the samples were placed into the reactors.

The curing of the samples was achieved in a single plastic container filled entirely with the curing solution with the negligible volume of air above the solution to prevent carbonation. After 28 days of total curing time, each sample was removed from the curing vessel, was cleaned with a piece of paper and then was placed immediately into the corresponding reactor.

3.2.1.1 Fluids composition

Below is shown the composition of the formation water that was used as the curing medium and the liquid phase of the reactors (see Table 3.2). It must be mentioned that the produced formation water had total salinity of 33,448 ppm (mg/l) and its composition is a simplified version of the formation water used by Rochelle *et al.* [2013] and the CO₂ GeoNet project. The brine can be said to be relatively diluted when compared to the fluids of real well formations (*e.g.* 21,500 to 159,000 mg/l [Duncan *et al.*, 2011]).

 Table 3.2 Quantities used for the preparation of 8 litres of simulated Utsira formation pore

 water [Rochelle *et al.*, 2013]

Component	Quantity (gr)
1. NaCl	207.00
2. KCl	3.20
$3. MgCl_2·6H_2O$	42.15
4. $CaCl_2 \cdot 6H_2O$	12.50
5. NaHCO ₃	1.73

3.3 Processing/ Carbonation process

The core experiments were conducted at a constant pressure 80 bar (8 MPa) in batch reactors at 60°C for 1 and 5 months and at 120°C for 1 and 3 months. The reactors were made of steel, had a polytetrafluoroethylene (PTFE) lining to inside (for preventing corrosion) and were continuously stirred by means of a magnetic stir bar. The liquid phase (formation water) placed in the reactors has been chosen to be four times the weight of each sample, *i.e.* solid: liquid mass ratio = 1: 4 with the samples to be fully immersed into the brine during each experiment. For the samples treated with the N₂ saturated brine, the hydration reactions were assumed to progress until full hydration of the remnant unhydrated particles. For the samples treated with the carbonated brine the full hydration was assumed to be completed for the inner parts of the samples, and took place simultaneously with the carbonation reactions.



Figure 3.2 The overall provision for the carbonation experiments [Rochelle et al., 2009]

Two tubes were connected to the reactors for all the period of the experiments; one was used for the injection of the gas (CO_2 or N_2) and the other for the sampling of the liquid phase (Figure 3.2). The sampling tube was used as a means of support to tie the samples and secure them from vibrations during the experiment, the depressurization and the transfer of the reactors inside and outside the ovens (Figure 3.3). In order not to disturb the two systems no sampling has taken place during the time period of 1, 3 and 5 months.



Figure 3.3 Photo of six reactors inside an oven with the magnetic stirrers and gas injection tubes and sampling tubes to be installed; for each reactor filled with CO_2 saturated brine a reactor filled with N_2 saturated brine was assigned.

At the end of each experiment, each reactor was kept inside the oven and the fluids were extracted though the sampling tube in clean syringes of 50ml each (Figure 3.4). The pressure was kept constant at 80 bar during the removal of the fluids in order to force the upwards fluid flow through the sampling tube and to prevent dissolution of the precipitated matter from the solid matrix due to depressurization. The samples after they have been removed from the reactors were placed individually in plastic containers with the air to have been replaced by N_2 gas to prevent carbonation of the N_2 treated samples and further carbonation of the CO_2 treated samples. With respect to the chemical analysis of the post reaction fluids, the pH was measured for unfiltered fluids the same day that each experiment was finished. The pH was measured for a 5 ml fluid sample after it has reached the room temperature (20°C) using a Thermo ScientificTM OrionTM Versa Star Meter. The pH meter was calibrated using calibration standards with pH₁ =4.01, pH₂ =7, pH₃ =10.01 and pH₄=12.46. Using the same instrument the relative conductivity of each solution was measured for filtered fluid samples. The conductivity electrode was firstly calibrated using the ZoBell's Solution with a relative conductivity at 20°C to be +228.5 mV ±5 mV. Finally, at least two vials with filtered and acidified fluid sample were sent for ICP-MS analysis for elemental analysis.



Figure 3.4 A reactor left on the bench of the hydrothermal laboratory at the British Geological Survey (BGS) for cooling. The reactor is empty of the liquid phase; the syringe is shown partially filled with the last part of the reactors' fluids and allowed for a smoother depressurization.

3.3.1 Sample coding and location of sub-samples

At the end of each experiment every sample was assigned to a specific code. The first part indicated the type of gas ('N' for N₂, and 'CO' for CO₂), the second part the temperature of the experiment ('60' for 60°C, and '120' for 120°C), and the third part denoted the duration. For example the 'N60/1' was used for the N₂ treated sample at 60°C for 1 month, and the "CO120/3" was used for the CO₂ treated sample at 120°C for 3 months.

The overall experimental approach for the analysis of a specific sample is shown at Figure 3.5 and the operator of each instrument along with the specifications of each sample in Table 3.3. Each sample, after having been transferred to the X-ray tomographer, was scanned without any pre-treatment and was placed back to its plastic container with gaseous N_2 to have replaced the atmospheric air. The use of N_2 as a storage gas to prevent interaction of the cement samples with the atmospheric CO_2 was a necessity in order to minimize any artifacts from products that were not created by the actual processing but due to treatment of the samples.

Once the 3D electron density mapping have been successfully recorded, then the samples were fragmented using a cold chisel in the way Figure 3.5 shows for compositional and pore structure analysis. Each sub-sample was carefully selected for each technique so as to minimize the pre-treatment and to prevent prolonged stresses until the analysis. For the powder XRD analysis different fragments were taken from random locations and were grounded into fine powder using a pestle and mortar. For samples treated with N₂ saturated brine the origin of the sub-samples was random due to the macroscopic homogeneity of the samples. For the samples treated with the CO₂ saturated brine, the powdered sub-samples were separated from two distinct areas, from the carbonation front towards the centre of the sample (termed 'inner' region) and from the carbonated area to the surface of the sample (termed 'outer' region).



Figure 3.5 Synoptic diagram of the analytical techniques used for the chemical and microstructural analysis of specific sub-samples for the samples treated with the N_2 -saturated brine

Table 3.3 Synoptic table of the analytical methods and techniques used in the present thesis for the examination of the solid and liquid samples; also shown are the operator of the corresponding provision and the basic characteristics of the sample

Technique used	Operator	State of the sample			
SOLID SAMPLES					
VRCT	Martin Corfield	Whole sample with no			
	Wartin Comera	pre-treatment			
SFM/SF	KG	Fresh fractured, Pt-coated rough			
SENI/SE	KO	area			
SEM/ BSE/ EDS	KG	Flat, polished, C-coated surface			
XRD	KG	Fine powder			
MIP	KG	Acetone treated, vacuum dried			
N ₂ sorption	Lee Stevens	fragments			
SAXS	Karen Edler	Powder			
LIQUID SAMPLES AFTER THE REACTION					
ICP-MS	Scott Voung	Filtered and acidified liquid at			
	Scott Toung	25°C			
pH, conductivity measure	ements KG	Unfiltered liquid at 25°C			
Bicarbonates	KG	Filtered liquid			

3.4 Analytical techniques

3.4.1 XRD

The mineralogy of the samples was investigated for powder specimens using a D500 model by Siemens for 2θ angles in the range 5° to 80° and scanning rate of the goniometer at 0.05° and a step time of 4 s. At least three different powders for each sample were examined for qualitative changes in the crystalline or semi-crystalline phases for the basic cement minerals (crystalline Ca(OH)₂, AFt and AFm phases, semicrystalline C-S-H) and for the various calcium carbonate polymorphs after the treatment with the CO₂ saturated fluids.

In the present study only the identification of the samples minerals was the target without their quantification. This target was fulfilled on the basis of the Bragg's law, which states that when the X-rays that have been diffracted within a crystalline lattice interfere constructively (Figure 3.6), they follow the relationship below [Fultz *et al.*, 2013]:

$n \lambda = 2 d sin(\theta)$

Equation 3.1

Where \boldsymbol{n} is integer, $\boldsymbol{\lambda}$ is the wavelength of the X-rays (for Cu K_{a1}, $\boldsymbol{\lambda} = 1.54$ Å), \boldsymbol{d} is the distance between the levels of atoms and $\boldsymbol{\theta}$ is the complementary angle of the incident beam. This constructive interference was delineated at the peaks of the diffractograms, *i.e.* the graphs of the intensity versus the 2 $\boldsymbol{\theta}$ angle.

For the particular case of approximating the size of the CaCO₃ crystallites the simple form of Scherrer's equation [Burton *et al.*, 2009]:

$$L = \frac{K\lambda}{\beta\cos\left(\theta\right)}$$
 Equation 3.2

Where *L* is the average size of the crystallite (nm), $\lambda = 1.54$ Å, β is equal to the width of the peak corresponding to the half maximum intensity of the peak (radians), *K* is a

constant depended on the crystallite shape and $\boldsymbol{\theta}$ is the angle corresponding to each $\boldsymbol{\beta}$. With the latter equation the target was the calculation of the size of the elementary crystal of the calcium carbonate polymorph and not the size of the ensemble of those repetitive elementary crystals. The size of the elementary crystal has been said not to exceed 100 nm [Monshi *et al.*, 2012].



Figure 3.6 An illustration of constructive interference of diffracted X-rays, *i.e.* a Bragg condition (L), and destructive interference (R)

3.4.2 SEM/BSE/EDS

3.4.2.1 Preparation

The preparation of polished and conductive surfaces was a necessity for the BSE imaging. In order to stabilize the specimens during the polishing stage and not to induce any artificial fracturing the cold mounting technique was implemented [Kjellsen *et al.*, 2003; Wong *et al.*, 2006]. The specimens after been impregnated using epoxy resin they were left for 24 hours to be hardened. The removal of the impregnated samples from the resin moulds was done by hitting gently the opposite side of the sample with a hammer and a small cylindrical steel piece.

The polishing stage included 6 steps using the model LaboPol-21 from Struers having two fittings of 20cm diameter each at a rotational speed of 250 rpm. The first four steps of grinding were done using 400, 600, 800 and 1200 grit SiC papers, while the rest two using soft discs of 6 μ m and 1 μ m diamond paste [Stutzman *et al.*, 1999].

During the coating procedure the polished surfaces were rendered conductive with approximately 15 nm of carbon using the Edwards 306 Vacuum Coater. In particular cases where the morphology of the calcium carbonates was the critical issue, the surfaces were platinum coated, directly as they were produced from the fracturing with the chisel using a SC7640 Auto/Manual High Resolution Sputter Coater (Quorum Technologies Ltd., Polaron).

3.4.2.2 Secondary electron imaging

At the start of each SEM analysis and before a suitable area for BSE to be selected, the entire surfaces were inspected under the secondary electron mode of the microscope. When the electron beam hits a specific point of the surface several elastic and inelastic phenomena occur. Electrons that are weakly bound to the surface atoms are detached from the atoms inelastically after interacting with the incident beam. Those electrons are called secondary electron have energies less than 50 eV and their production is coupled with energy loss. The secondary electron mode was used to reveal the topography of the carbonation products, namely calcium carbonates. Areas like pores, hollow regions, and obstructed areas will appear black in the SE mode since the emitted electrons are prevented to reach the detector. On the other hand, peaks and uninhibited areas will appear brighter since more secondary electrons will be characterized by intermediate shade of gray.

The Back-Scattered Electrons consist of a part of electrons emitted from greater depths of the examined surface and are elastically produced. The BSE imaging was attained primarily in flat and polished surfaces. The reason is that the backscattered electrons originate from interaction of the incident electrons with the nuclei of the atoms and thus are able to give compositional information for the sample, namely phase differentiation. In case that any surface defect existed, that would have created an artifact in the compositional fingerprint of the surface. BSE imaging coupled with the detection of the X-ray photons from the transition of an excited electron to the inner orbital, was used for simultaneous phase differentiation and elemental detection. The latter detection was feasible from the calculated energies of the emitted X-rays, which are characteristic for each element.

3.4.2.3 Backscattered electron imaging analysis

Backscatter electron (BSE) imaging was attained using the SEM XL30 model by Philips equipped with an energy dispersive analysis X-ray (EDAX) detector offering the opportunity for simultaneous phase differentiation and elemental mapping. The incident electron beam had an accelerating voltage of 20 kV while the working distance was kept at 10 mm. On the condition of flat and polished surfaces the backscattered electron imaging has been successfully implemented previously for phase identification in cement-based materials [Scrivener, 2004]. Since the backscattered electron current i_{BSE} is proportional to the average atomic number of the examined area \overline{Z} [Goldstein *et al.*], thus each phase is characterized by a specific backscattered electron coefficient [Stutzman, 2004].

In order to capture the Ca leaching and the distribution of the various carbonates, the spatial distributions of the various elements were recorded by means of elemental maps with the process time to be 5, the dwell time 50 μ s and the acquisition rate was set to a minimum of 3000 cps with a deadtime limit that did not exceed 40%. The differentiation of each element was attained through the detection of the characteristic X-rays emitted after the excitation of the electron(s) of each atom. The governing equation for differentiation of the various atoms is the Moseley's Law, $\mathbf{E} = \mathbf{C}_1 \cdot (\mathbf{Z} - \mathbf{C}_2)^2$, where C_1 and C_2 are constants with

different values for each series of X-rays (K, L, etc.) and E is the energy of each X-ray transition that depends monotonically on the atomic number Z of the atom [Goldstein, 2003].

For the quantification of each element a standardless analysis was achieved using the QuantMaps of the respective elemental maps from INCA software with the threshold level to be 0. The absence of standards, as controls for the detected quantities of elements, was resolved by converting the measured peak area and converting it into normalized % weight or % atomic mass after applying intensity corrections and peak deconvolution algorithms.

The normalized weights were extracted in the form of table which contained the weight for each element in a particular point along with the corresponding standard deviation for each point. The form of this table is shown in Figure 3.7 where each point of analysis is separated from another point by a distance of dx and dy. The table contains n series and k columns. The first column (from 11 to n1) is the surface of the sample which was directly exposed to the fluids. The latter column (from 1k to nk) corresponds to a depth (k*dx mm) from the surface of the sample towards the inner. This depth has been chosen so as to capture the elemental map over a region that showed particular compositional characteristics from its BSE micrograph. In the case of the samples treated with the CO₂-saturated brine then it was attempted to capture the entire carbonation depth and a small part of the inner and uncarbonated region.

Regarding the table shown in Figure 3.7, each point of the analysis represented the normalized weight of each element together with a standard deviation σ_{11}^{beam} . The value σ_{11}^{beam} reflected the deviation of the mean average of the number of pulses that were recorded by the EDS detector after the electronic transformation of the X-ray photons. It must be clear that the σ_{11}^{beam} emanates from merely one point in the elemental map (Figure 3.7).



Figure 3.7 Correspondence of the elemental mapping EDS analysis with a region (A) with a real sample (CO120/3); in fact the examined region was a flat, polished and C-coated area from a fragment of the sample as shown in Figure 3.5; the array with the *n* lines and *k* columns represents the spacings (dx, dy) in between the rastering pattern of the electron beam in each point of the elemental analysis.

mean average %wt.per column =
$$\frac{\sum_{i=n}^{j=1} \% wt_{k=constant}}{j}$$
 where $j = 1 \dots k$

Mean average
$$\sigma = \sqrt{(\sigma_{nk}^{point})^2 + (\sigma_{nk}^{k=constant})^2}$$

3.4.3 XRCT

For obtaining the non-destructive 3D volume imaging of the whole reacted and unreacted samples, X-Ray computed tomography (XRCT) was performed using an XRADIA VERSA XRM-500. The parameters for the instrument are shown in Figure 3.9. The reconstruction of the images was done automatically using the specific software provided by XRADIA.

XRCT is a valuable tool due to the requirement of no sample treatment before analysis, allowing either wet or dry samples to be examined. In the present study the samples (directly after their removal from the reactors) were transferred to the XRCT without drying or other preconditioning. The construction of the 3D images was done by the reformation of the 2D image stack acquired from each angle (θ) of sample's rotation by using tomographic computational mathematics (Figure 3.8). The 2D images constitute the remaining intensity ($I(x, z, \theta)$) after absorption of the incident X-rays ($I_0(x, z, \theta)$), *i.e.* absorption contrast imaging mode. Each pixel of a 2D projection represents the absorptivity to a specific point of the material, so as differences in the density and/or phase distribution and geometry (Figure 3.8).


Figure 3.8 The procedure of imprinting the 3D structure of a cement sample with XRCT [Landis et al., 2010].

XRCT is governed by the Lambert-Beer law given in Eq. 3.3-A [Han et al., 2013]. With (τ) is denoted the sum of the X-ray absorption in the direction dy of the X-ray and is given by the integration of the attenuation coefficient due to absorption $\mu(x, y, z, \theta)$ (or Radon transform). The minus sign of τ indicates the reduction of the emitted intensity by increasing the absorptivity of the sample. I_d is the noise of the detector due to its independent charge and which must be subtracted from the intensity of each beam [Landis et al., 2010].

Where

 $I(x, z, \theta) = I_0(x, z, \theta) \cdot exp(-\tau)$ **(A)** $\tau = -\int \mu(x, y, z, \theta) \cdot dy$ **(B) Equation 3.3** $\tau = \ln \frac{(I_0 - I_d)}{(I - I_d)}$ Or by solving (A) **(C)**

-				2 0.0	
maging Mode:	Tomogray	phy		Source Information	
Camera Binning:	1			Power:	9.91
Camera Temperature:	-59 C			Voltage:	159.91
File Data Type:	USHORT			Target Current:	61.96
lisplay Data Type:	FLOAT			Tube Current:	159.15
mage Size:	2048 x 20	048		Centering X:	199.18
File Size:	8000.000	0 MB		Centering Y:	237.11
Source Setting	160	KV 62	uA	Vacuum Level	1.61
Source-RA distance:	86.0002	2	mm	Focus Current:	2645.34
Detector-RA distance:	30.0006	5	mm	Hours on target:	20.85
Pixel size:	25.0338	5	um	Target turn #:	99
Optical Magnification:	0.3998	:"LFOV		Filament:	1.708
Exposure Time:	5.0000		sec		
Camera Readout: Heated Sample Temp:	Fast (2.5	MHz)			
Date and Time	10/22/13	10-42-42			

Figure 3.9 Parameters used for XRCT scanning of all samples

3.4.3.1 Image analysis (ImageJ)

The analysis of the reconstructed X-ray density images was attained by means of the commercially available image analysis software ImageJ (IJ 1.46r). The image processing started, by adjusting its brightness and contrast (B&C, Figure 3.10-A), in order to fit the histogram to the minimum and maximum pixel values. Every image had a resolution of 8bit and thus a maximum of 256 grey level pixels were generated. After the B&C correction, grey level equal to zero (black points-areas) represented pores and the brighter pixels (maximum grey level) denoted the highest density products. Secondly, in order to smooth the grey levels of the image a median filter was used with radius 2 pixels (Figure 3.10-B). Up to this point

only the images taken from XRCT were processed. For the BSE micrographs the smoothed image was made binary using the manual threshold as described by Padmanabhan *et al.* [2010].



Figure 3.10 (A) Original BSE micrograph for the unreacted grout sample; (B) Micrograph corrected for its brightness and contrast; (C) Binary image, where black stands for pores and white is the solid part

3.4.4 He Pycnometry

The AccuPyc 1330 model by Micromeritics was used for measuring the apparent porosity. The equilibration rate was set to 0.0050 psig/ min with the mean temperature during each test to be $19^{\circ}C \pm 1^{\circ}C$ and the filling pressure to be 19.5 psig. The number of purges was set to 60 while the number of runs to 30, similarly to Stange *et al.* [2013]. In fact the choice of the operation parameters was a matter of investigation from sample to sample due to the observed heterogeneities of the properties of the cement-based materials [Poyet *et al.*, 2013]. It is crucial to differentiate the calculated apparent porosity by He pycnometry and the effective porosity as the latter is used only for interconnected pores that are not dead-end pores and contribute substantially to the transport of chemical species [Stephens *et al.*, 1998].

3.4.4.1 Number of purges

The number of purges of the sample cell, before the actual measurement was taken, appeared to be the most critical factor in determining repeatability of skeletal density measurements, as found in other previous studies [Stange *et al.*, 2013]. The total mass of the fragments emplaced inside the sample cell varied from 2 g to 4 g, and gave a mean skeletal density of 2.22 ± 0.14 g/cm³ after 60 purges (N60/1). Three repeated measurements were made on the same sample during the course of 1 week, resulting in a variability of, *i.e.* ± 0.004 % in the skeletal density. The samples were stored in a constantly-operating vacuum desiccator at 20°C in between measurements. When the number of purges was set to 10, a significantly lower skeletal density of 1.88 ± 0.016 g/cm³ was observed. This suggested that the cleaning of the sample cell was insufficient leading to underestimation of the actual skeletal density due to the remnant moisture and other volatiles trapped inside the pores [Viana *at al.*, 2002].

3.4.4.2 Number of runs

In addition the duration of runs had insignificant influence (in contrary to the importance of the number of runs) to the He skeletal densities. For unreacted samples weighing \approx 3 g, 20 runs lasted up to 4 hours resulting in a density of 2.34 ±0.015 g/cm³, and 30 runs lasted 11 hours resulting in density 2.29 ±0.041 g/cm³. This showed that the duration of a pycnometric analysis did not necessary affect the repeatability error.

Interestingly, for 4 g sub-samples from the N60/1, 30 runs lasted for 9 hours indicating that the duration of the runs depended on the sample itself and perhaps more specifically on the connectivity of the pore network. Based on the hypothesis that the He flow rate inside the pores is controlled by the pore throats and the volume of He is dependent on the size of the larger pore cavities, a rough indication of the pore network connectivity can be the time needed to complete a specified number of runs, $t_{X runs}^{He}$. However, it must be pointed

out that the time $t_{X runs}^{He}$ is strongly dependent on the number of the various throats and cavities per gram and per sample as well as the relative sizes of each sample.

3.4.5 MIP

3.4.5.1 Pre-treatment of samples

Mercury intrusion porosimetry (MIP) was conducted using an AutoPore IV by Micromeritics. All the specimens before the analysis were placed in pure acetone (inside an Erlenmeyer flask) for approximately 7 days, gently stirred and dried in a vacuum desiccator for at least 48 hours. It must be pointed out that the small size of the samples used (\approx 1.5 g) certified that the moisture of pores down to 3 nm was removed before the MIP measurements. For each MIP analysis, one fragment was placed inside the penetrometer in order to avoid disturbances in the intrusion/extrusion from a possible failure of a piece due to fracturing. The fragments were prepared by natural fracturing with a cold chisel to avoid applying vibration from a core-drill or by abrasive sawing [Ma, 2014].

3.4.5.2 Operational parameters

The Hg contact angle was assumed to be 130° ; the Hg surface tension was set to 485 dynes/cm, and the Hg density to 13.5327 g/ml. The pressure was raised from 0.5 to 60,000 psia (0.03 to 4137 bar) obtaining 54 experimental points during intrusion and from 60,000 psia to 15 psia obtaining 30 experimental points during extrusion. The evacuation target was set at 50mm Hg (or 66.65 $\cdot 10^2$ Pa or 6.665 $\cdot 10^{-2}$ bar) and was kept steady for 30minutes. In all the analyses the stem volume of the 5cc solid penetrometer was at least 30% and no more than 50% as suggested by Ouellet *et al.* (2007).

3.4.5.3 Impact of sample mass and size on Hg intrusion

From all the operational parameters, the ones tested for any probable impact on the critical parameters from MIP were the mass of the sample, the total intruded/ extruded volumes and the equilibration time. On the one hand, a big sample has the potential of artefacts from micro-fractures induced due to drying shrinkage and on the other hand a small sample might not be representative of the actual characteristic pore network parameters [Moro *et al.*, 2002]. The equilibration time has such an impact on the attainment of the each pressure, in the sense that the inadequate time for Hg to equilibrate would result in transition of the cumulative curve towards larger pore access sizes [Ma, 2014]. Assuming cylindrical shape of pores, the application of the Washburn equation would have caused an overestimation of the pore sizes for lower pressures than the targeted ones:

$$d = \frac{-4 \gamma_m \cos (\theta)}{P}$$

Equation 3.4

Where, *d* is the diameter of the hypothetically cylindrical pore (μ m), *P* is the applied pressure of Hg (psia), γ_m is the surface tension between Hg and pore walls (dynes/cm) and θ is the contact angle of the intruded/extruded Hg with the pore walls (degrees) [Aligizaki, 2006].

The mass of all the sub-samples of the N_2 and CO_2 treated samples along with the corresponding intruded volume is shown at Table 3.4 and Table 3.5. Even though the maximum cumulative Hg pore volumes have been found to decrease with decreasing the sample mass [Hearn *et al.*, 1992], for each of the N_2 treated samples and the unreacted grout sample, those pore volumes were constant for fragments between 2 g and 1 g (Appendix 2). The variability of the pore volumes with respect to the mass of the fragments for each sample was reflected at the standard errors of the mean pore volumes.

Serial Number	System	Temperature (°C)	Duration (months)	Mass (g)	Intruded volume (cm ³ /g)	Mean intruded volumes (cm ³ /g)
1600	Unreacted	-	-	1.9246	0.1848	
				1.1816	0.1225	0.1615±0.0190
				1.1095	0.1773	
1628	N_2	60	5	1.2326	0.2001	
				1.1826	0.1874	0.1815 ± 0.0221
				1.2127*	0.3066*	0.1813-0.0221
				1.0908	0.1571	
1629	CO ₂ (inner)	60	5	0.2487	0.2008	
				0.5727**	0.3945**	0.2976 ± 0.0810
				0.5036***	0.0726***	
1629	CO ₂ (middle [#])	60	5	0.9059	0.1145	0.11715±0.0026
				0.9105	0.1198	
1629	CO ₂ (outer)	60	5	1.2411	0.1344	0.1392±0.0033
				1.3409	0.1440	
1630	CO ₂ (inner)	60	1	0.3090	0.1394	0.1557±0.0085
				2.6630	0.1590	
				1.2892	0.1686	
1630	CO ₂ (outer)			0.1283	0.0710	0.06071±0.0229
				0.2775	0.1271	
1631	N_2	60	1	1.5905	0.1788	
				1.1199	0.1768	0.1831±0.0053
				1.0392	0.1937	

Table 3.4 Repeatability of the MIP measurements of the N_2 and CO_2 treated samples at 80 bar and $60^{\circ}C$

Notes: (*), not taken into consideration due to large deviation from the mean cumulative/ incremental graph (Chapter 6); (**), fragments (not solid) placed in the penetrometer; (***), abnormal small intrusion due to shrinkage of the sample, not included in the mean average;([#]), corresponds to fragments taken from the reacted volume near the carbonation front.

Serial Number	System	Temperatu re (°C)	Duration (months)	Mass (g)	Intruded volume (cm ³ /g)	Mean intruded volumes (cm³/g)
1633	CO ₂ (inner)	120	3	0.7759	0.2956	0.3009±0.0042
				1.6331	0.3061	
1633	CO ₂ (outer)	120	3	0.2616	0.2267	0.2509±0.0197
				0.3220	0.2750	
1634	N_2	120	3	1.2836	0.2631	
				1.0907	0.2724	0.2699±0.0034
				1.9458	0.2743	
1635	CO ₂ (inner)	120	1	0.9098	0.2075	0 2133+0 0055
				0.5516	0.2243	0.2155±0.0055
				1.5794	0.2080	
1635	CO ₂ (outer)	120	1	0.2298	0.1373	0.1373
1636	N ₂	120	1	1.6054	0.2895	
				1.2199	0.3051	0.2881±0.0102
				1.0888	0.2696	-

Table 3.5 Repeatability of the MIP measurements of the N_2 and CO_2 treated samples at 80 bar and 120°C

3.4.5.4 Impact of equilibration time on the intrusion profile

Regarding the equilibration time of the present study no change was found for 10 s and 50 s (Figure 3.11), confirming the findings of Ma, 2014. In another study, a transition of the critical pore throat from 30 nm to 40 nm was found for 30 s instead of 10 s [Giesche, 2006]. In the latter study, the critical pore throat could correspond to material other that cement. It could be argued that the effect of the equilibration time on the intrusion curve is less pronounced for materials, like the cement grout samples of the present study, where the critical throat for most of the samples is not greater than 12 nm due to the lower time needed for Hg to stabilize towards nanopores in contrast to the higher time for the Hg to stabilize in mesopores or macropores.



Figure 3.11 Comparison of two different equilibration times in the cumulative intrusion/ extrusion of Hg for two different fragments of the unreacted grout sample; the squares and circles denote respectively the re-intrusion/ re-extrusion of Hg for the same sample without removal from the high pressure port

3.4.6 N₂ Physisorption

3.4.6.1 Comparison with MIP

 N_2 physisorption consists of the physical adsorption of N_2 (in the gaseous state) at the outside surface and inside the pores of a solid after application of a finite pressure [Aligizaki, 2006]. In contrast to mercury intrusion porosimetry, the adsorption process takes place without application of excessive forces that could alter or damage the pore network. N_2 physisorption was used to capture changes in the pore size distribution, the specific surface area and the micropore volume. Water can be also used as an adsorbate but its reaction with the cement minerals renders it inappropriate for use in the present thesis [Aligizaki, 2006].

3.4.6.2 Operation of the technique

The applied method of physisorption was the volumetric method, where the amount to physically adsorbed/ desorbed N₂ was calculated by applying gas laws. The physisorption instrumentation consisted primarily of a vacuum pump, a Dewar vessel filled with liquid nitrogen and a nitrogen cylinder. The vacuum target was set to 13.3Pa (10^{-4} bar) and the temperature of the adsorbed nitrogen equal to 77.3K (-195.7°C). The temperature was kept constant for the entire duration of the experiment as the sample glass bulb was immersed inside it. After the evacuation of the samples to remove any existing atmospheric gases, the sample tube was calibrated using helium of a known volume. Then helium was removed and the incremental adsorption of N₂ took place until the saturation pressure (P/Po≈1). A mass of 1.5 gr crushed cement powder was used in order to have a correspondence with the MIP mass.

3.4.6.3 Pore size and Kelvin equation

The applied pressure was translated into pore radius using the Kelvin equation assuming cylindrical pore shape, incompressibility of the condensed liquid and much greater molar volume for the gas in comparison to the liquid. If r_K is the pore radius where condensation takes place (nm), V_m is the molar volume of condensate (m³/mol), θ is the contact angle between the cement pore wall and the liquid, γ is the surface tension of the liquid adsorbate (N/m) and R=8.314 J/(K·mol) is the global gas constant, then Kelvin equation is as follows:

$$r_{K} = \frac{-2 \cdot \gamma \cdot V_{m} \cdot \cos(\theta)}{R \cdot T \cdot \ln(\frac{P}{P_{0}})} \xrightarrow{nitrogen} r_{K} = \frac{-41.5}{\ln(\frac{P}{P_{0}})} [nm]$$
 Equation 3.5

3.4.6.4 Pore size distribution (BJH method)

The pore size distribution was calculated based on the Barrett-Joyner-Halenda method (BJH) method. As in the Kelvin equation, the pores were assumed to be cylindrical in shape, but with the addition that the actual pore size is the sum of the Kelvin radius plus the thickness t of the adsorbed film on the pore walls, *i.e.* $r_p = r_K + t$. The BJH assumes that the thickness of the adsorbed film inside the pores is the same to the thickness of the same adsorbed film on a flat surface. According to the BJH method the pores were divided into groups with average size r_p .

For the adsorbed film t onto the surface the Harkins and Jura equation was used, which assumes hexagonal close packing for the nitrogen molecules resulting in 0.354 nm approximately according to their proposed equation (Eq. 3.6):

$$t = \sqrt{\frac{13.99}{0.034 - \log \left| \frac{P}{P_0} \right|}}$$

Equation 3.6

3.4.6.5 BET specific surface area

The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) theory which assumes: (1) that all the sites available for adsorption are energetically identical, (2) that no adsorbate-adsorbate interactions exist, and (3) on the ideal condition of the complete filling of the monolayer, then the subsequent layers have the same properties, *i.e.* the same heat of liquefaction.

The specific surface area was calculated from Eq. 3.7 after calculating via the BET equation (Eq. 3.8) the volume V_m of the adsorbed gas corresponding to the coverage of the entire surface from a monomolecular layer:

$$S = n_m A_m N_A = \frac{V_m N_A A_m}{V_M} \quad [m^2/g]$$
 Equation 3.7

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1) P}{V_m C P_0} \qquad \text{(linear form of BET equation)} \qquad \text{Equation 3.8}$$

In the previous equations: n_m is the amount of the gas adsorbed in the entire monolayer, A_m is the average area of one molecule of the adsorbate when the entire monolayer is completed (m²/molecule), N_A is the Avogadro number equal to 6.023×10^{-23} (molecules/ mol) and *C* is the BET constant which is a function of the net heat of adsorption (q₁-q_L). With q₁ is denoted the heat of adsorption of the first layer and with q_L is the heat of liquefaction of the liquid adsorbate.

3.4.6.6 Micropore volume (Dubinin Astakov equation)

The Dubinin Astakov equation (Eq. 3.9) was implemented for the calculation of the micropore volume from the maximum micropore adsorption capacity V [Gil *et al.*, 1996]. This equation was created as an attempt to correlate mathematically the adsorption potential A with the relative adsorption θ , which is defined as the ratio V/V_0 . E is the characteristic energy for a given adsorbate-adsorbent system, and the exponent n was attributed to the degree of heterogeneity of the micropore system. The use of Dubinin Astakov instead of other equations [Burevski, 1982] was justified due to the successful linearization of the adsorption isotherms over a wide pressure range according to the transformation of Eq.3.9 to its linear form (Eq. 3.10).

$\boldsymbol{\theta} = \frac{V}{V_0} = \boldsymbol{exp}[-\left(\frac{A^n}{E}\right)]$	(Dubinin Astakov)	Equation 3.9
$\log V = \log V_0 - D \cdot (\log \frac{P_0}{P})^n$	(Dubinin Astakov - linear)	Equation 3.10

3.5 Intrinsic permeability

3.5.1 Simulated values (PoreXpert)

The commercially available software PoreXpert was used for the 3D representation of the cumulative Hg intrusion curves in simulated pore network models. The adjustment of the cumulative curves to a 3D model was attained automatically by several algorithms [Matthews *et al.*, 2013; Matthews *et al.*, 2014]. Based on those models the permeability for the various throat size distributions was calculated. The use of N_2 as the simulated gas was necessary in order to compare the simulated permeabilities with the experimental values as measured by the same gas (3.5.3).

3.5.2 Calculated values (Katz-Thompson)

The estimated permeabilities for the cement samples from the MIP cumulative intrusion curves were calculated according to equations proposed by Katz and Thompson (1986). Although their theory was created based on mercury intrusion experiments in rocks [Katz *et al.*, 1987], the application of the Katz- Thompson equation to cements was proven to be reliable [Nokken *et al.*, 2006]. The original equation proposed by Katz- Thompson is Eq. 3.11, with d_c the critical throat diameter (m), σ the bulk conductivity of the sample (S/m) and σ_0 the conductivity of the pore solution (S/m).

$k = \frac{1}{226} d_c^2 \frac{\sigma}{\sigma_0}$ Equation 3.11 $\frac{\sigma}{\sigma_0} = \frac{d_{max}^e}{d_c} \eta S(d_{max}^e)$ Equation 3.12

The constant 1/226 has been found to depend on the assumptions for the pore network [Halamickova *et al.*, 1995]. In other words the value of the constant depends on the correlation of the permeability with the ratio σ/σ_0 . This correlation was not measured experimentally for each sample but Eq. 3.12 was implemented, which was found to correlate well the ratio σ/σ_0 with parameters taken directly from the Hg intrusion cumulative curves [Nokken *et al.*, 2006].

3.5.3 Experimental permeability (micro-permeametry)

In an attempt to measure experimentally the gas permeability (k in mD) of the samples treated with carbonated brine, a Temco MP-402 micropermeameter was used as shown in Figure 3.12. The cement surface in contact with the measuring tip of the fitting was set to be as flat and steady as possible in order to avoid leaks of the N₂ flow (Figure 3.13). In order to regulate the N₂ pressure the control valves were constantly used until a stable volumetric flow rate Q_b was achieved. The overall concept of the provision was to maintain a steady flow of N₂ and to monitor the decline ΔP of the downstream pressure P_2 which was detected (due to pressure loss) from the expected upstream pressure P_2 if there was not a pressure loss. The flow rate and the pressure were recorded from a computer that was calculating automatically the permeability using Eq. 3.11:

$$k_a = \frac{2 \mu Q_b P_b T_{act}}{a G_0 (P_1 - P_2) T_{ref}}$$
 Equation 3.13

Where: μ = viscosity (cp); Q_b = volumetric flow rate (cm³/s); P_b = reference pressure (atm); T_{act} = actual temperature (°C); T_{ref} = reference temperature (°C); G₀ = dimensionless geometric shape factor; a = internal radius of the tip of the permeameter (cm). It should be noted that the permeability was close to the lower limit of measurement for the capability of this technique due to the inherent limitations of the pressure transducer to measure pressure differences for flow rates less than 0.5cm³/s.



Figure 3.12 The overall provision for measuring permeability located at the Centre for Ecology & Hydrology in Wallingford, Oxfordshire



Figure 3.13 The measuring Swagelok fitting in contact with different cement samples

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4.1 Introduction

The current chapter describes the impact of temperature and time on the elemental composition and spatial distribution of elements in class G cement grouts and the corresponding mineralogical changes. The objectives of this chapter are to give a sufficient description of the solid phases before and after a realistic scenario of CO_2 storage in a reservoir.

Table 4.1summarizes the analytical techniques used in order to fulfil the previous objectives. The table shows the technique, the location and state of the sample and the information taken. For the samples treated with N_2 saturated brine the SEM/ BSE/ EDS analysis was sufficient at areas close to the surface. Areas in the centre of the sample appeared to be the same with the unreacted sample but not to have a distinct line of differentiation from the outer regions. The XRD graphs were taken for powder samples from several fragments of the entire sample.

For the samples treated with the CO₂ saturated brine, the SEM/ BSE/ EDS analysis was conducted not only near to the surface but also around the carbonation front and across the entire carbonated regions. Where necessary, the samples were examined under SE mode for non polished and flat surfaces. The target was to reveal the morphology of several microstructural characteristics visible under BSE but with not clear orientation and structure when BSE imaging was used. Finally, XRD for the carbonated samples was conducted for powder samples, by selecting fragments from a region with the same elemental profile. Attention was given so as not to mix powders taken from the carbonated region with the inner region and vice versa.

Analytical technique	Location of the sample	State of the sample	Information from each technique
SEM/ SE/ BSE	Near to the surface/ Carbonation front	Solid	BSE micrographs
SEM/ EDS	Near to the surface/ Carbonation front	Solid	Elemental analysis (%wt. maps)
XRD	Areas with similar elemental profile	Powder	Mineralogy

Table 4.1 Analytical techniques used for the compositional analysis of the samples

4.2 Hydration of class G cements

4.2.1 Distribution of elements and hydration degree of the hardened cement

Calcium, silicon, iron and aluminium were the main elements (wt.% >2) detected at the hydrated cured cement grouts and were distributed evenly from the outer part of the grouts towards the inner part (Figure 4.1). Magnesium, sulphur and sodium were present in the EDS graph but in negligible quantities *i.e.* less than 2 %wt (Table 4.2). Ca rich areas (Figure 4.1-B) from which elements like Si, Fe and Al were absent (Figure 4.1), denoted mainly Ca(OH)₂ and potentially unhydrated (residual) cement grains as previously observed in hardened cement pastes [Diamond, 2004].

In the particular surface examined in Figure 4.1-A, the information for the actual hydration degree from BSE images could be inadequate. This is true since backscattered electrons are being emitted from lower penetration depths (0.1-1 μ m) than the X-rays (0.2-2 μ m), and thus are unable to give a representative compositional profile from deeper penetrations [Scrivener, 2004]. The position of a cementitious grout located across a well could vary depending on depth and humidity of the rock formation in contact. As a result, the usage of electron microscopy for evaluation of the actual degree of hydration or local water to cement ratio should be used with caution in real cases, despite its good results in the laboratory scale [Thaulow *et al.*, 2004; Wong *et al.*, 2009].



Figure 4.1(A) BSE micrograph of the hydrated (untreated) class G cement grout; (**B-E**) 2D elemental maps of the spatial (wt.%) profiles of (**B**) Ca, (**C**) Si, (**D**) Fe and (**E**) Al; (**F**) 1D distribution of Ca and Si from the surface (x=0 mm) towards inner regions (x=1.6 mm) for parallel zones to the surface for differential distances dx=12.3 μ m; (**G**) The overall EDS spectrum of the BSE surface of (**A**).

Table 4.2 Mean weights (%) of the detected elements for the unreacted sample grout; each value was calculated as the mean average from EDXA analysis of at least three BSE micrographs for every sample (*e.g.* Figure 4.1-A); for the correction of the Smart X-ray Maps the QuantMap option from INCA (suite version 5.03) was implemented with resolution 256 x 256, and sigma value of 1.

		Ca	Si	Fe	Cl	Al	Mg	Na
				wt. 9	6			
Unreacted sample	-	39.46	16.02	2.43	0.10	1.44	0.47	0.16

The presence of unhydrated cement grains was also identified in the corresponding XRD graphs (Section 4.2.3, Figure 4.8). This was consistent with previous studies in which alite and belite grains were found to be present in class G cement grouts cured in brine after 1 month and absent after 1 year [Saoût *et al.*, 2006]. Thus, regarding the time span of operation of existing and newly formed CO_2 injection wells (a few decades) full hydration of the grouts is likely to occur if proper cementing practices have been applied and without loss of the necessary hydration water.

The assumption of the full hydration in the long-term for the class G oilwell cementitious grout of the current study held only for the particular curing conditions *i.e.* 30°C, 1atm, 28days and specific group of additives. For curing conditions other than the above, the use of specific standards must be followed like the ones proposed by the American Society for Testing and Materials (ASTM) and the American Petroleum Institute (API), *e.g.* API Spec.10B. However, the use of a particular grout should be accompanied by a site-specific investigation satisfying its proper curing and thus ensuring zonal isolation; some factors that could influence the curing of the grout are: (1) potential contamination from oils [Nicot, 2009] or salts [Zhou *et al.*, 1996] and (2) the conditions of the reservoir [Kutchko *et al.*, 2007; Taha *et al.*, 2012] and the chemistry of the surrounding formations [Carey *et al.*, 2010]. These two factors could influence the water to cement ratio from one depth to another and therefore could lead to local deviations from the essential water for the proper formation of C-S-H phases [Gallucci *et al.*, 2013].

4.2.2 Ca/Si ratio

The mean value of the molar Ca/Si ratio of the BSE image, shown in Figure 4.1, was found to be 1.74 ± 0.67 from the respective elemental maps (Figure 4.1, B, C) using the procedure presented in Chapter 3, Section 3.4.2.2 (see Figure 4.2). At first sight the mean value of 1.74, along with the deviation of the Ca/Si from 2.41 to 1.07, seemed to conform to

the compositional requirements for the C-S-H phases as summarised from Richardson (2004). However, the Ca/Si of the C-S-H must be distinguished from the bulk Ca/ Si of the BSE micrograph which was calculated in the present thesis for every sample (see Figure 4.1, A). Regarding the C-S-H phases the variation in the Ca/ Si is mainly due to spatial changes in the chemistry of the C-S-H particles, as far as the degree of polymerization of the silicate structures, the various defects of the chains and the degree of substitution by other elements are concerned.



Figure 4.2 Spatial distribution of the bulk molar ratio Ca /Si from the surface (x=0mm) towards the inner for the unreacted grout (the area of reference is Figure 4.1, A).

On the other hand, the bulk Ca/ Si contains the Ca from the calcium hydroxide, calcium aluminate, calcium aluminoferrite phases and the Si from the microsilica. Thus the bulk Ca/ Si is not the real ratio for the C-S-H phases but only an approximation of the mean ratio for all the cement hydrates and additives. In order to subtract the contributions from the other hydrates to the Ca /Si ratio of the C-S-H phases, the plot shown in Figure 4.3 was used,

in a procedure already used by Kocaba [2009]. The ratios Al/ Ca and Si/Ca were calculated for each BSE micrograph (Figure 4.1, A) from the corresponding wt.% elemental maps (Figure 4.1, B, C, E) as described in Chapter 3, Section 3.4.2.2. The procedure revealed a Ca/ Si=1.6 for the inner C-S-H neglecting all the other phases like outer C-S-H and aluminoferrite phases. The same value for the Ca/ Si ratio was calculated from the Fe/ Ca versus Si/ Ca plot, showing that the coordinates did not have any impact on the final value of the Ca/ Si ratio.



Figure 4.3 Procedure for finding the exact Ca /Si ratio of the inner C-S-H phase using a plot of the molar ratios Al/ Ca versus Si/ Ca as described by Kocaba [2009].

The detailed calculation of Ca/ Si ratio in the present study was not a primary objective, but rather the approximation of an average value for a specific area in which no alteration of the mean Ca/ Si was observed (Figure 4.2). The mean average of the Ca/ Si ratio based solely on EDXA data was further confirmed by the composition of the main CSH phase as identified by XRD (4.2.3). With the first technique Ca/Si=1.7, while with the second Ca/Si=1.5. The good agreement between the two techniques was found also by Escalante-

Garcia *et al.* (1999). However, it was assumed that, due to the majority of the C-S-H phases being amorphous [Zeng *et al.*, 2014], the Ca/Si ratio as taken from the XRD composition of CSH (Table 4.4) could not have been the actual mean average ratio for the entire cement gel.

In Figure 4.1-A no signs of discrete microsilica particles were observed. Three hypotheses could have led to the lack of microsilica particles in the BSE micrographs examined: (1) The size of the particles was below the magnification of the SEM, (2) The particles were big enough to be delineated but they were not distinct from the cement phases and (3) The microsilica has reacted with portlandite to produce secondary C-S-H phases. From the above hypotheses the second is the overarching one due to the similar backscattered electron coefficients between the C-S-H and the unreacted microsilica particles [Stutzman, 2004]. This similarity between the BSE coefficients was proved from the overlapping of the gray levels as generated from a BSE micrograph (see Figure 4.4). In Figure 4.4, the examined area of the BSE micrograph is shown in the yellow rectangle and the corresponding gray level histogram appears to have two peaks A and B. Peak A corresponds to the unhydrated cement grains and the Al-, Fe-rich phases. Peak B contains the main cement phases, namely C-S-H and CH (see Figure 4.5). The bimodal histogram appeared not to have a separate, third, peak that could allow the delineation of microsilica particles.



Figure 4.4 A BSE micrograph with the corresponding gray value histogram for the unreacted sample grout. The separation of the two peaks A and B is shown in Figure 4.5.



Figure 4.5 The separation of the cement hydrated phases based on the gray value histogram shown in Figure 4.4. Area 'A' shows the unhydrated cement grains and the cement phases rich in Al and Fe. Area 'B' shows primarily the hydrated cement phases (C-S-H) with the white areas to be the area 'A' after adjusting the brightness (maximum gray value 125 approximately).

Points (1) and (3) are also real phenomena that explain the lack of microscopic observation of the microsilica particles. In the present thesis, it was assumed that the particles of the microsilica suspension followed a distribution with a mean average value 0.24 μ m. Thus a group of the particles would have been smaller than 0.24 μ m and thus would be consumed faster by portlandite to form secondary C-S-H phases following hypothesis (3). On the other hand, large silica particles were hypothesized to exist in the microsilica suspension which would have delayed pozzolanic reactivity in comparison to the finer particles. The latter phenomenon will be seen to be real in sample CO60/ 1 (see Figure 4.24) after the Ca leaching has revealed the borders of the microsilica particles.



Figure 4.6 Accessibility of nano- and micro-silica at the inner and outer C-S-H phases; the C-S-H shown as black lines are not the real structure of the C-S-H but here they are employed to show the different levels of filling depending on the particle size of silica

The inclusion of microsilica (or silica fume) in cement pastes is already known to reduce the Ca/Si ratio of the C-S-H phases, either by modifying the existing C-S-H phases or producing additional C-S-H through the pozzolanic reaction of $Ca(OH)_2$ with SiO_2 [Gaitero *et al.*, 2008]. The final content of the C-S-H phases with the incorporation of microsilica has been found to increase the compressive strength of cement [Qing *et al.*, 2005]. Furthermore,

properties like yield stress, setting time and strength have been found [Senff *et al.*, 2009] to improve considerably with the addition of nano-silica instead of microsilica. The latter suggests that the packing of the silica particles is different depending on the mean particle size and that a different mechanism of pozzolanic reactions could exist depending on the access of the silica to the outer or inner product of the C-S-H phases (see Figure 4.6).

4.2.3 C-S-H and other phases

Three main phases were identified in the unhydrated class G cement powder (Figure 4.7 and Table 4.3). The overall Ca/ Si ratio of these phases was calculated to be 2.37 and specifically for the calcium silicate oxide equal to 3.



Figure 4.7 XRD diffractogram of unhydrated class G cement; 'CS' calcium silicate oxide; 'CAF' calcium silicate aluminoferrite

Table 4.3 Crys	stalline composition	n of the class	G cement clinker	from XRD*
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Components of initial cement	Name	Typical cement	
powder*		notation	
$Ca_3(SiO_4)O$	Calcium silicate oxide	CS	
$(c_1, c_2)(a_1, c_2)(s_1, c_3)$	Calcium silicate	CAE	
$(a_{2,5}Fe_{0,5})(AI_{1,7}Fe_{0,2})(SIO_4)_3$	aluminoferrite	C ₃ AI ⁺	
	Iron aluminium calcium	CAE	
$\operatorname{Fe}_2 \operatorname{O}_3 \operatorname{H}_2 \operatorname{O}_3 (\operatorname{CaO})_4$	oxide	C4AI*	

Notes: *, from the database of the diffractometer Siemens D500

After 28 days of curing in saturated $Ca(OH)_2$ deionised water at 1 bar and 30°C portlandite, calcium silicate hydrate, ettringite, and brownmillerite were found to be the main crystalline hydrated products (Figure 4.8 and Table 4.4).



Figure 4.8 XRD diffractogram of two powder samples for the hardened unreacted grout; 'E' stands for ettringite, 'B' for brownmillerite, 'P' for portlandite, and 'CSH' denotes the detected C-S-H phase with the composition shown in Table 4.4; 'A' is alite and 'Be' is belite

As all the oxides dissociated in the presence of water, and liberate Ca^{2+} that along with the $(AlO_4)^-$ (Table 4.3, components 2,3) and $(SO_4)^{2-}$, from gypsum (as evident from the sulphur detected in Figure 4.1-G) constructed ettringite. Gypsum is well known to be a constitute of class G cements according to API specification 10A [2009]. Furthermore, brownmillerite (Figure 4.8) was the product of hydration where most of the Fe³⁺have been consumed after reaction with aluminium and calcium cations. The chemistry of the overarching crystalline C-S-H phase is shown in Eq.4.1.

 $2Ca_3(SiO_4)O(s) + (2x+6)H_2O(l) \leftrightarrow 2(CaO)_{1,5}(SiO_2) \cdot xH_2O(s) + 3Ca(OH)_2(s)$ Eq.4.1

Table 4.4 Crystalline products of the class G hydrated paste *

Chemical formula of hydrate	Name
$Ca(OH)_2$	Calcium Hydroxide (Portlandite)
$(Ca0)_{1.5}(Si0_{3.5}) \cdot xH_20 / (Ca0)_{1.5}(Si0_2) \cdot xH_20$	Calcium Silicate Hydrate
$Ca_2(Al_{0.7}^{3+}Fe_{0.3}^{3+})O_5$	Brownmillerite
$Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12} \cdot 26H_{2}O$	Ettringite

Notes: *, from the database of D500

4.3 Impact of brines on class G cements

4.3.1 Ca/Si and phase analysis for N60

No macroscopic change in the distributions of the various elements occurred in the N_2 treated samples as indicated by their corresponding weight (%) maps (see Appendix 1). Likewise with the unreacted grout all the elements were found to have generally even spatial distribution (see Appendix 1). The even distribution will be further understood in the samples treated with CO₂ saturated brine where a clearly delineated line, namely the carbonation front, separated the elemental maps into two well defined regions.

At 60°C after 1 month no change in the bulk mean Ca/ Si ratio was observed (Ca/Si = 1.75) and only after 5 months a decrease to 1.52 was evident (Figure 4.9). The almost steady mean values of Ca/Si, for every duration, contradicted the 94% increase in Ca concentration level that was detected in the reactor fluids after 1 month. The rate of increase of the leaching Ca from 1 month to 5 months was found to decrease to 41% and then it was assumed to decline even further leading to no leaching in the long term.

It was suggested that initially, after 1 month, Ca leached rapidly from surface layers (without a clearly defined depth of leaching) to the adjacent fluids but was quickly replaced by Ca^{2+} from the inner regions. The Ca from the inner regions did not seem to precipitate to the outer parts of the samples but to enrich the brine with a decreasing rate until a chemical equilibrium was achieved, *i.e.* the concentrations of Ca in the solid and fluid to be the same.

This chemical equilibrium could be potentially disturbed in aquifers with flowing brines [Birkholzer *et al*, 2008; Pruess *et al.*, 2002] or if the ratio (%wt.) of the brines to the cementitious grout exceeds the 4:1 ratio of the present study. Similar observations for the deceleration of the Ca leaching in time were made in a previous study by Tognazzi *et al.* (2000).



Figure 4.9 Bulk Ca/ Si ratio of N60 (continuous line) correlated with the Ca concentration, *i.e.* [Ca], in the brine (segmented line)

The increase in total deviation of Ca/ Si after 1 month, in comparison to the unreacted samples, was attributed to the redistribution of Ca and Si due to the calcium loss. As cement components close to the surface dissociate, silicon rich structures are left temporarily with a net negative charge attracting Ca^{2+} from the inside of the sample to obtain neutrality [Richardson, 2004; Jonsson *et al*, 2004]. This reorganization of the calcium (that were diffused from inner regions of the sample) in the C-S-H structures near the surface delayed to lead to stable structures; thus the standard deviation of the average mean Ca/ Si ratio after one month represented a snapshot of the local structural heterogeneities whose spatial variation is reduced after 4 months (Figure 4.9). These stable structures finally obtained a lower Ca/Si

ratio (*i.e.* due to further calcium leaching) consisting of widely distributed sub-unities; these sub-unities must have been C-S-H particles with almost the same degree of substitution of their silicate structures but with higher distance within those structures due to the Ca further leaching from 1 to 5 months (Thomas *et al.*, 2004).

The decalcification of the C-S-H particles for the N60 was evident from the methodology proposed by Kocaba [2009]. For the inner C-S-H it was found that the Ca/Si ratio declined from 1.60 (for the unreacted sample grout) to 1.34 (for the N60/1) and then to 1.36 (for the N60/5). It must be mentioned that the use of the molar Ca/Si ratio from the inner C-S-H is not representative of the extent of the Ca leaching process. Ca diffuses not only from the inner C-S-H product but also from the outer C-S-H, the Aft, AFm and C-A-H. Thus it is rather the Ca diffusion from the bulk volume of the cement that specifies its chemical degradation after the Ca leaching, so taking into account the Ca/Si ratio only from the inner C-S-H neglects the contribution of the rest of the hydrates and also percolation effects that will be associated in Chapter 6.

It seemed that the decrease of the Ca/ Si ratio happened due to slower diffusion of calcium from the inner areas and that the remnant structures were more homogeneous (deviation = ± 13 %) having C-S-H phases with smaller mean values of their Ca/Si ratio. The calcium loss, being a definite sign of chemical destabilization of the C-S-H phases, reduced the residual stiffness of the outer C-S-H and simultaneously that of the inner C-S-H phases [Ulm, 2003]. Likewise in the study of Ulm, [2003], it can be suggested for the present study that the loss of stiffness between the C-S-H particles could generate fractures in the scale of a few nanometres, owing to geomechanical stresses or from over-pressurization due to CO₂ injection. This can dramatically decrease the overall hardness of the oilwell grout [Ulm, 2003] and perhaps create CO₂ migration pathways.

Qualitative XRD analysis of N60 showed the composition of the solid phases to be comparatively stable but with ettringite having disappeared after 5 months treatment (Figure 4.10). The presence of portlandite, even after 5 months, was suggested from the high pH (12.14) of the post reaction brines. The stability and presence of portlandite at this pH was also found by Calvo *et al.* (2010). The high pH was due to the OH⁻ present in the pore fluids; the OH⁻ has been found previously to leach at a higher rate than calcium [Planel *et al.*, 2006], verifying that the interlayer Ca²⁺ will remain among the C-S-H structures and thus preserving the calcium hydroxides required for the neutrality of the C-S-H particles [Richardson, 2004].



Figure 4.10 XRD diffractograms of the N60/1 and N60/5; it is observed the overlapping between the graphs of the unreacted sample grout and the N60/1.

At a pH \approx 12, the main forces that retain the C-S-H particles together are strong attractive ionic, despite the reduction in Ca/Si ratio over time [Jonsson *et al*, 2004]. The presence of Ca(OH)₂ acts as a barrier to the further calcium loss, certifying that these forces will be preserved and hence reducing the risk of chemical and further mechanical degradation of the oilwell grout. However, the C-S-H particles seemed to have obtained a smaller crystal size from the small swift of their peaks (regarding the 2θ axis), and to have become more homogeneous (acquisition crystalline orderliness) as evident from the less broad peaks (Figure 4.11) [Marinoni *et al.*, 2008]. The homogeneity of the C-S-H particles has also been
found in the case of small deviation of the Ca/Si ratio while the small crystal size could be a consequence of the less available Ca^{2+} to prevent the collapse of the silicate structures.



Figure 4.11 Detail of Figure 4.10 showing the change in the width of the peaks of the C-S-H phases

The reduction in size of the "crystalline" C-S-H particles over time could create more favourable paths in grouts neighbouring with brines and that are destined for CO_2 injection, increasing the potential for chemical degradation of the grout from an early age of operation of the CO_2 injection well. However, this reduction could have caused reorganization of the C-S-H particles in a more dense structure, and thus blocking the open porosity and decreasing permeability. The shrinkage of the overall cement structure immersed in brine has not been addressed in this study, but whether a Ca leached cement paste is subjected to shrinkage in a real oil or gas well due to decalcification it would be a crucial topic of research to avoid the generation of possible CO_2 migration pathways.

4.3.2 Ca/Si and phase analysis for N120

Regarding N120, the bulk mean average Ca/Si remained stable after 1 month at 1.74, with an increase after 3 months to 1.80 (Figure 4.12). The leached Ca (from cement) increased by 160% after 1 month and by 30% after 2 months. At this temperature Ca diffusion from the inner seemed to take place without inhibition. The calcium origin from the inner of the cement was definite from the continuously increasing leaching of Ca and the increasing Ca/Si (after 3 months) as well.



Figure 4.12 Bulk Ca/ Si of N120 (continuous line) correlated with the Ca concentration, *i.e.* [Ca], in the brine (segmented line)

The deviations of the Ca/Si values in Figure 4.12 were almost constant showing that the C-S-H phases near the surface of the grout have preserved their initial structure, but with higher degree of substitution of the OH- from Ca²⁺ after 3 months. The pH of the post reaction brines confirmed the presence of significant OH- with only a slight decrease from 11.98 to 11.82. The substitution of OH by Ca²⁺ after 3 months was justified on the basis of the ratio w/n *i.e.* the degree of protonation of the silanol groups w of the silicate sheets (Richardson, 2004); as the degree of protonation is being reduced, then the Ca/Si ratio increases. The previous observation for the degree of protonation and the Ca/Si ratio suggested that a certain mechanism governs the liberation of a Ca^{2+} for its substitution with OH⁻; thus it would have required further investigation for the preservation of Ca in the cement in order to maintain its chemical and mechanical purposes for long term durability. A specific grout in an oil or gas well that has experienced expensive Ca leaching would have less Ca available to restrain a CO_2 attack.

Table 4.5 Mean weights (%) of the detected elements for the N60 and N120 samples; each value was calculated as the mean average from EDXA analysis of at least three BSE micrographs for every sample (*e.g.* Figure 4.1-A); for the correction of the Smart X-ray Maps the QuantMap option from INCA (suite version 5.03) was implemented with resolution 256 x 256, and sigma value of 1.

	Duration (months)	Ca	Si	Fe	Cl	Al	Mg	Na
		wt. %						
N60	1	37.73	15.54	2.44	1.01	1.41	2.21	0.56
	5	35.97	16.77	2.26	0.46	1.45	1.95	2.20
N120	1	39.53	15.74	2.38	1.07	1.36	0.54	0.47
	3	39.25	15.73	2.16	1.68	1.23	0.75	0.66

Despite the preservation of the Ca/Si ratio, and regardless the time period, portlandite at 120°C appeared to be unstable (Figure 4.13) while the crystalline structure of the C-S-H seemed to be the same (Figure 4.14). In contrast, the amorphous C-S-H phases appeared to have constant Ca/ Si at the inner C-S-H after 1 month (Ca/Si of N120/1 = 1.66) which declined in the N120/ 3 sample to 1.49. The Ca/ Si = 1.49 was in opposition to the increase in the bulk Ca/ Si = 1.80 from EDXA. That implied the decalcification of the inner C-S-H was higher than the bulk volume of cement hydrates that appeared to have gained Ca, mainly in the outer C-S-H in order to obtain higher bulk Ca/ Si.



Figure 4.13 Loss of the main portlandite peak of the N120; the chosen scale aimed at a clearer representation of the portlandite loss at 120°C; the diffractogram for portlandite was taken from the RRUFFTM Project database.



Figure 4.14 XRD diffractograms of the N120/1 and N120/3; the diffractogram for portlandite was taken from the RRUFFTM Project database.

4.3.3 Impact of temperature

In static conditions and at a weight ratio brine-to-solid equal to 4-to-1, Ca leaching at 80 bar increases with temperature and duration (Figure 4.15). It seemed that 120°C caused the accumulation of Ca towards the outer parts of the grouts to happen faster than the calcium loss from the grouts. The dependence of calcium loss on temperature showed that leaching is a thermally dependent process. In fact the thermal dependence of Ca leaching was not attributed to the solubility of either of the cement phases, since portlandite is less soluble when increasing temperature [Dolejš *et al.*, 2010; Seewald *et al.*, 1991] and C-S-H phases follow the same pattern of decreasing solubility with increasing temperature [Gisby *et al.*, 2007; Clodic *et al.*, 1997].

Assuming that an Arrhenius type equation can be applied to the concentration of the Ca in the brine the following relationship can be applied for calculating the amount of energy E_A^C (Joule) that is required for the leaching of 1 mole of Ca from the cement paste [Larrard *et al.*, 2010]. The following procedure for calculating the activation energies at different temperatures is coupled with several assumptions. Firstly, the dissociation of Ca is a first order 'reaction', *i.e.* the rate of Ca releasement from the cement particles is proportional to the concentration of Ca. Secondly, the electrostatic forces from the pore walls do not influence the diffusion of a calcium cation from the dissociation path, *i.e.* the tortuosity is assumed to be 1. Of course those assumptions, were said to be valid only in pores larger than that of the cement gel (>12 nm) and for the initial stages of leaching from regions close to the surface of cement. In fact [Ca] was found to be proportional to the square root of time (Figure 4.15), indicating that Ca leaching was inhibited in the course of time possibly due to modifications in the pore structure.

Setting T_0 to be the reference temperature equal to 298.15 K, R = 8.314 Joule/ (mole \cdot K) and T to be the temperature corresponding to the brine, the Arrhenius equation is as follows:

$$C = C_0 \cdot \exp\left(-\frac{E_A^C}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

Using the previous equation, the activation energy of the grouts corresponding to the N_2 treated samples was determined at 30°C, 60°C and 120°C after 30, 90 and 150 days for each temperature of the leaching process (Figure 4.16). The values of E_A^C are listed in Table 4.6 and demonstrated that in the long term, after 150 days, the class G cement grouts when immersed in pure brines are better stabilized independently of the temperature (highest E_A^C) in comparison to the 90 days that exhibited the most unstable systems (lowest E_A^C). The stabilization referred solely to the Ca loss from the grouts under static or semi-static conditions, with a linear relationship between the calcium concentration of the brine with time. From the above it can be deduced that even though the temperature influences the quantity of the leached calcium, and the energy required for calcium loss from the grouts, time plays a major role in the stabilization of the cement particles so as they could be more resistant to attack from the injected CO₂.



Figure 4.15 Calcium concentration in the brine versus $\sqrt{\text{(time)}}$ for N60/1, N60/5, N120/1 and N120/3; the calcium leached for N30 was taken after Rochelle *et al.*, 2009; the extrapolated values in the Y-axis depend on the initial [Ca] in the brine and the order of dissociation.



Figure 4.16 Plot illustrating the calculation of the $(-E_A^C/R)$ for the individual time spans of the N₂ treated samples

Time (days)	Activation energy (J/ mole)
30	8,321
90	7,536
150	9,615

Table 4.6 Time evolution of the activation energy for the Ca leaching for N60, N120

4.3.4 Influence of the Ca/Si ratio

Surface analysis using EDXA revealed a small decrease in the bulk Ca/ Si ratio at 60°C while at 120 °C the surface components could be more chemically resistant to further Ca loss than at 60°C. The higher bulk Ca/Si ratio of areas near the surface at 120 °C led to higher substitution of the silicate structures and in particular the OH- (effective ionic radius = 110 nm) by calcium (atomic radius = 194 nm). Therefore, under static conditions at 120 °C the surface C-S-H phases were likely to be more stable since they occupy more pore space. The chemical stability of the C-S-H phases was also confirmed by the Ca /Si of the inner C-S-H, which was found to be greater in the CO120 samples (1.66 and 1.49) than the CO60 samples (1.34 and 1.36).

However, it must be pointed out that the calcium enrichment of C-S-H phases could not only neutralize the negative charge of the SiO but potentially to generate a positive overcharge without necessarily bonding covalently to the silicate structures [Jonsson *et al.*, 2004] but rather being as interparticle cations [Al-Ostaz *et al.*, 2010]. To conclude, the higher Ca/Si ratio of the C-S-H phases near the surface could provide less pore space in the case of a forthcoming CO₂ injection generating products that could seal better the outer part of the grouts for further CO₂ ingress.

Finally an important distinction of the different mechanisms was made for N60 and N120. These mechanisms are illustrated in Figure 4.17. With deep grey is the portlandite of the unreacted grout that due to leaching leaves the space in between the silicate structures empty. The proposed mechanisms are based on the model proposed by Richardson (2004) and

earlier by Feldman *et al.* (1968) and can be said to take place gradually from the outer product of C-S-H towards the inner and denser structure C-S-H for each temperature.



Figure 4.17 Proposed mechanisms for the behaviour of silicate **structures** for the N60 (**A**, **B**, **C**) and N120 (**A**, **D**, **E**); the black arrows represent repulsive forces from the decalcified Si-O chains; "ms" denotes the microsilica particles

In the case of N120 the assumption, that the pozzolanic reactions had happened already in less than a month, justified the absence of microsilica particles from D and E. This assumption along with the calculated activation energy for Ca leaching at 120°C, led to the hypothesis that the fast electrochemical transport of Ca^{2+} maintained the size of inter-gel space. The Ca/ Si of the inner C-S-H confirmed that hypothesis showing a chemical degradation of the cement gel to a lesser extent than at 60°C. With respect to N60, the retarded diffusion of Ca^{2+} led to the repulsive forces between the negative and decalcified structures to dominate. In the case of 60°C the pozzolanic reactions led to the longer stability of microsilica particles among the C-S-H. In this case the microsilica particles acted as barriers to the extensive expansion of silicate structures leading to local confinements and

expansions (Figure 4.17, B, C). This hypothesis was further tested with the analysis of the pore network parameters (Chapter 6).

In Figure 4.17, the C-S-H particles are illustrated as structures. These structures are the silicate skeleton where the Ca is been attached. In reality the C-S-H particles are organized in the three dimensions as a silicate matrix that folds randomly to create the amorphous cement gel, and the term 'structures' is used to denote the cross section of that matrix. In reality, the microsilica particles in Figure 4.17 have become partially or fully secondary C-S-H which along with the remaining microsilica particles will inhibit the expansion of the negatively charged silicate structures due to decalcification at 60°C. On the other hand at 120°C, the almost complete disappearance of microsilica would have led to densification of the C-S-H that would ultimately have led to the generation of inner C-S-H with higher Ca/Si than at 60°C. Chapter 6 will decipher if the associated changes in Ca/Si and CH depletion are validated from the pore network alterations.

4.4.1 CO60/1



Figure 4.18 (**A**) BSE micrograph of the CO60/1 along with the 2D elemental maps of the spatial (wt.%) profiles of (**B**) Ca, (**C**) Cl, (**D**) Si, (**E**) Fe; (**F**) 1D distribution of Ca and Si from the surface (x=0 mm) towards inner regions (x=2.1 mm) for parallel zones to the surface for differential distances dx=12.3 μ m.

4.4.1.1 Drop of Ca/Si ratio due to Ca leaching

In comparison to the reference case of the N60/1, the CO60/1 was characterized by a clearly defined Ca leached area from the surface up to a specific depth ($x \approx 0.33$ mm) from both the Ca Quant Map (Figure 4.18-A) and the plotted values of the Ca and Ca/Si (Figure 4.19). The drop of the Ca/Si ratio is represented in an ordered way in Figure 4.20.



Figure 4.19 Spatial profile of the BSE image illustrated in Figure 4.18 for the Ca/Si for CO60/ 1

As observed in Figure 4.20, not all the parts of the grout had a mean average Ca/Si less than 1.79 and only an outer layer was calcium depleted with a mean Ca/Si = 1.28 ± 0.48 . Whether the Ca has actually leached or deposited as part of the carbonation zone was unclear. The total absence of portlandite from the outer part (x < 1 mm, Figure 4.20 and Figure 4.25) suggested that this part has fully reacted with the effluent carbonate ions (HCO₃⁻ and CO₃²⁻), but that the depth at which portlandite became absent did not coincide with the calcium loss depth. The lower values of Ca/Si ratio (down to 0.8) in the leached area, most likely denotes complete decalcification of the C-S-H phases. The decalcification of the C-S-H phases seemed to have taken place gradually as evidenced by the zone with steady Ca wt.% (Figure 4.20). This region is located between the carbonation front and the Ca leached area,

confirming the lesser vulnerability of the C-S-H particles to leaching with respect to portlandite [Duguid *et al.*, 2010]. The complete decalcification of the C-S-H phases was not an ubiquitous fact for the leached zone due to the inclusion of the pores at the weight elemental maps during the surface scanning of the electron beam. The decalcification was assumed to be complete from the Ca saturated interlayer pores and from bigger capillary pores. However, regarding the intralayer Ca these were suggested to have reacted with the effluent bicarbonates and to have precipitated within the silicate structures in the form of amorphous calcium carbonates.



Figure 4.20 Zonal analysis of the Ca/Si based on Figure 4.19; the distinction of the three different samples (unreacted, N60/1 and CO60/1) can be clearly seen.

Based on the existence of the carbonation front (Figure 4.18-A), the Ca appeared to be transported by a diffusion-controlled mechanism through the matrix towards the fluid phase. The inner part of CO60/1 appeared to be similar to the unreacted grout and the corresponding CO60/1 (Figure 4.20). Despite the decreased value $[Ca]_{CO60/1} = 196.52 \ mg/l$ in the post examined fluid of CO60/1 ($[Ca]_0 = 410 \ mg/l$), it was whether the Ca had been deposited in

the grout. Some of the calcium was observed to have precipitated onto the surface of the samples (see Figure 4.21-B) in the form of calcite (Figure 4.22).

This implied that the growth of calcite (Figure 4.22) emerged from surface reactions between the dissolved Ca^{2+} (from both brine and cement) and the HCO_3^- (from the carbonated brine). The hypothesis behind the external calcite growth was the inhibition of calcite precipitation at the inside of the sample due to restrictions of the pore network. In the corresponding N60/1 (Figure 4.21-A) the white precipitates (more homogeneously distributed) were formed from the rapid carbonation of portlandite from the atmospheric CO_2 .



Figure 4.21 Snapshots of the N60/1 (I), and CO60/1 (II) immediately after their reaction



Figure 4.22 Secondary electron micrograph illustrating the morphology of the calcite precipitated at the surface of CO60/1

Two mechanisms of Ca leaching were identified: the first one denoting C-S-H decalcification (Figure 4.23), and the second showing local inhibition of the Ca leaching (Figure 4.24). On the one hand, the Ca loss from C-S-H particles left clearly delineated silicate structures likewise in the example in the Figure 4.24. It should be stated that the term 'structure' is not a vague description of the silicate assemblages. In fact those assemblages are stacked in a matrix-like structure, with the silicate matrix to intersect each other. However the term 'structure' refers to the elementary unit of the 'matrix'. In this case the C-S-H particles were suggested to be inflated from the dissociation of Ca (Figure 4.24), leaving the silicate structure negatively charged. This finally led to the development of repelling forces between the structures increasing the distance between them.



Figure 4.23 (**A**) BSE micrograph from a part, vertically orientated, to the surface for the carbonated region of CO60/1; (**B**) EDS atomic wt.% map illustrating the calcium loss, through (**C**) agglomerated particles of microsilica. (**D**) EDS atomic wt. % map for Fe.



Figure 4.24 (A) BSE micrograph from a part, near to the surface at the carbonated region of CO60/1; (A1) Detail of (A); (B) decalcified silicate gel and (C) residual agglomerates of Sirich particles are well defined, surrounded by (D) calcium-aluminate-ferrite phases; the scale bar equals 40 μ m.

Both Figure 4.23 and Figure 4.24 showed apparent inhibition of the Ca leaching primarily from the silicate structures and to a lesser degree from immobilized aluminoferrite phases. Decalcified hydrated cement particles like the two illustrated in Figure 4.23 had the same morphology with leached structures at the surface of samples taken from a class G cemented well, indicating an affinity of the current experiments with real bottom hole conditions (88°C, 162 bar) [Scherer *et al.*, 2011].

4.4.1.2 Ca precipitation/ Calcium carbonates

A mixture of calcium carbonates was found in the carbonated part (Figure 4.24), while the inner area (as expected from its Ca/Si ratio) had no major alteration of its mineralogical content with portlandite still present (Figure 4.25). This suggests that all interactions between the cement and carbonated brine occurred in the outer part (x < 1 mm). These interactions had a border the zone at the carbonation front (Figure 4.20), where the Ca/Si reached its maximum limit equal to 2.55.



Figure 4.25 XRD diffractogram for the inner region of the CO60/1; 'E' stands for ettringite, 'B' for brownmillerite, 'P' for portlandite, and 'CSH' denotes C-S-H phase

Figure 4.27 and Figure 4.28 illustrate the morphology and chemistry for two of the calcium carbonate polymorphs found in Figure 4.26. Rhombohedral calcite was found not only at the outer surface but also at an inner void of the carbonated part a few microns away from the carbonation front. At the same void (Figure 4.28) orthorhombic crystals of aragonite were also found. The gradual appearance of calcite at the outer and less unstable calcium carbonates (*e.g.* vaterite) towards the inner parts of the grouts that was seen in Figure 4.28 has

been also found after carbonation of class G cement after reaction at 120°C and 500 bar after 2 months [Jacquemet *et al.*, 2007].



Figure 4.26 XRD diffractogram of the outer (carbonated) part of the CO60/1; the diffractograms for calcite and aragonite were taken from the RRUFFTM Project database.



Figure 4.27 Calcite crystals inside a surface cavity in the carbonated region of CO60/1; scale bar equals 40 μ m.



Figure 4.28 (A) Secondary electron image inside the carbonated part of CO60/1 (B) illustrating a void partially filled with calcite (c) and aragonite (a)

4.4.1.3 Chloride ingress

In the current study no CI⁻ bearing phases were detected in both inner and carbonated regions for the CO60/1 (Figure 4.25 and Figure 4.26). However, based on the elemental distribution of CI⁻ (Figure 4.29), it was concluded that chlorine anions were attached in amorphous phases rather than crystalline or semi-crystalline, *i.e.* those detectable by XRD. From Figure 4.29, chlorides seemed to be almost absent from the carbonated part (less than 2 wt.%), whereas their concentration increased from the carbonation front towards the inner (approximately 3.5% - 4 wt.%). The negative error bars in the range (0 – 1 mm) in Figure 4.29 indicated greater heterogeneities in the spatial distribution of chlorides in the carbonated region owning to the absence of chlorides or from the noise of the sum of spectra for the chlorides (in the carbonated region).



Figure 4.29 Wt.% profile of Cl⁻ (for the BSE micrograph in Figure 4.18) of the CO60/1

Since any chlorides present in the pore fluids could have leached out from the base and polished surfaces, only structural chlorides were anticipated in the solids. These chlorides comprise those that have been incorporated in the structural units of cement, even though the final content of solid chlorides in the cement paste has been described to be lower than the chlorides in the pore fluids [Taylor, 1997]. For detection of chlorides, ion chromatography could have been used [Page *et al.*, 2002] (after dissolving chlorides in an appropriate solvent). However, the low content of the class G cement in Ca3Al₂O₆ suggested that the binding of chlorides was less than that of older cementitious grouts based on ordinary Portland cement [Lambert *et al.*, 1985].

Additionally, the lack of chlorides at the carbonated region was attributed to the alteration of the surface charge of the C-S-H phases [Saillio *et al.*, 2014], as the decalcification of the C-S-H particles reduced the positive charge of the particles that could make chlorides to be adsorbed physically or as a complex with the calcified silanol groups, \equiv SiOCaCl [Elakneswaran *et al.*, 2010]. The negligible physical or chemical adsorption of chlorides to the carbonated region was proved in this thesis also by the pH of the post reaction fluids which was around 6. Since the pH was lower than 11.1, which was found elsewhere to be the iso-electric point for the attachment of Ca²⁺ to the C-S-H particles [Elakneswaran *et al.*, 2010], it was implied a very weak positive change at the surface of the particles and thus the chlorides binding to be inhibited. This inhibition was not only due to charge effects but also the enhanced polymerization of the silicate **structures** and the inability of the diffused Ca to attach to the negatively charged silanol groups.

The previous values for the content of chlorides were thought to be important only in oil or gas wells with the injection tube to be made of susceptible metal (commonly duplex stainless steel) [Azuma *et al.*, 2013; Sánchez *et al.*, 2008]. Chloride concentrations, as the ones found in the current study, from 0.5 to 2.0wt.% were previously proposed to be the threshold values for depassivation of typical concrete repairs for ordinary Portland cement with various additives [Raupach *et al.*, 1996]. These values however are only indicative and a specific system of cement and casing should be tested individually satisfying for: (1) proper bonding and compactness, and (2) non-extensive cement carbonation that would weaken these

bonds. Even in the case of aggravated carbonation (sub-chapter 4.4.2) the cement microstructure should not allow the contact of chlorides with the casing. This applies only for old tubing with no or little tolerance to chloride-induced corrosion. However even in modern tubing systems with liners or coatings [Nygaard *et al.*, 2010] probable scratches, induced by the surrounding rocks, must not allow for propagation of the corrosion.

4.4.1.4 Proposed mechanism of Cl ingress and carbonation reactions

In contrast to N60/1, the CO60/1 appeared to have experienced greater chloride ingress. This was clearly shown in Figure 4.29 and Figure 4.45 for the CO60 and CO120 samples (chlorides' wt.% approximately 4%) and for the N60 and N120 samples in Table 4.5 (chlorides' wt.% less than 1.7%). This behaviour was explained due to the presence of $HCO_3^$ in the case of CO60/1 (Eq. 4.2). The reaction of HCO_3^- with the Ca^{2+} from portlandite (Eq. 4.3) and from C-S-H (Eq. 4.4) was leaving an instant net positive charge in the solution due to the remaining H^+ . The lowering of pH due to increased $[H^+]$ led to the dissolution of the carbonation products into secondary Ca_{sec}^{2+} and $HCO_{3(sec)}^-$ [Morse *et al.*, 2007].

- Dissolution of
$$CO_2$$
: $CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3(aq)$ Eq. 4.2

- Portlandite carbonation:

$$Ca(OH)_{2}(s) + HCO_{3}^{-} \leftrightarrow \{Ca^{2+}CO_{3}^{2-}(aq) + 2OH^{-} + H^{+}\} \stackrel{\circ}{\Leftrightarrow} Eq. 4.3$$
$$\stackrel{*}{\Leftrightarrow} CaCO_{3}(s) + H_{2}O + OH^{-}(pore\ fluids)$$

- C-S-H carbonation:

$$2(CaO)_{1.5}(SiO_2) \cdot xH_2O(s) + 2HCO_3^- \rightarrow 2CaCO_3 + SiO_2 \cdot xH_2O(s)$$
 Eq. 4.4

At this stage it was logical to assume the formation of $CaCl_2$ simultaneously with the formation of $CaCO_3$. In other words the formation of $CaCO_3$ either from portlandite (Eq. 4.3) or from C-S-H (Eq. 4.4) was accompanied by the precipitation of chloride based phases. These chloride based phases happened *via* the exchange of the Cl^- from the brine with the OH of portlandite [Justnes, 1998]

The lack of detection of crystalline chloride bearing phases like $CaCl_2$ or even $MgCl_2$ was justified from the rapid reaction of Ca^{2+} (from $CaOH_2$) to form $CaCO_3$ and the attachment of the effluent Cl^- as part of the amorphous silicate structures. Chlorides could be attached either to structural branches of the structures like Si-O- Ca^{2+} or directly in the silicate structure in the position of a leached OH⁻. However, due to the greater vulnerability of $CaOH_2$ and its faster dissolution than C-S-H, the attachment of Cl⁻ could have happened as part of silicate structures with poor crystalline shape.

Some of the Ca_{sec}^{2+} ('sec.' means the secondary-free- calcium after the dissolution of a precipitated phase) may have leached into the fluid, whilst some may have diffused towards the inner region. At the same time the $HCO_{3(sec)}^{-}$ would have move towards the inner, and so would be able to react with the inner Ca^{2+} and precipitate as $CaCO_3$. This transport of Ca_{sec}^{2+} and inner Ca^{2+} could have led the attraction of Cl^{-} and the temporary attachment to decalcified C-S-H structures. Hence (after several steps of formation and dissolution of $CaCO_3$) the Cl^- moves into the inner region at a greater concentration and each time attaches more easily to the continuously-decalcified silicate structures.

The proposed hypothesis of chloride attachment to the decalcified C-S-H requires further investigation since they have been previously observed [Barberon *et al.*, 2005] to attach only to Al-bearing phases and not to C-S-H. However, chlorides have been found to promote the hydration of the remnant unhydrated cement grains. In the present study the mode of transport of chlorides was deduced to be diffusion from the outer towards the inner. In general, the formation of chloride-bearing phases (*e.g.* hydrocalumite; Friedel's salt) would have required higher chloride concentrations than those of the current study (>2 mM) Yauri *et al.* [1998] found that these chloride-bearing phases are less soluble at high pH, which confirms the hypothesis of this work, where during the movement of carbonation front towards the inner the drop in pH leads to their disappearance from the carbonated region.

4.4.2 CO60/5

4.4.2.1 Ca leaching/ transport

Regarding CO60/5, Ca leaching was clearly evident from the calcium concentration in the post reaction fluids containing 2437 mg/L, which is a 500% increase from the initial brine (410 mg/L). According to the Ca in the fluid, the mean Ca/Si ratio in the outer part of the grout was calculated to be reduced to 1.66 ± 0.77 in contrast to the unreacted grout with a Ca/Si ratio of 1.74 ± 0.67 . The lower limit of the Ca/Si ratio (0.89) corresponded to the absolute decalcification of the C-S-H particles [Richardson, 2004]. The fate of the calcium from these particles seemed to be, on the one hand towards the surrounding fluids and on the other hand into previously internal air voids. This supports the observed upper limit of Ca/Si ratio, which was 2.4 (See section 4.4.4.2, Figure 4.32).

In the case of the CO60/5, a simple separation of the various zones with particular chemical characteristics was not observed likewise in Figure 4.20 (see Figure 4.30). In general, a decalcified silicate structure with Ca/Si ratio of 0.89 was the overarching microstructure of the carbonated region, with small calcite and vaterite crystals within the silicate structures and big aragonite crystals in large air voids. This overall structure did not appear to have diversifiable areas in the direction of CO_2 diffusion; only a clearly defined Ca leached zone was noticed from the surface up to 0.4 mm (Figure 4.31). This Ca-leached surface zone was assumed to be preserved from 1 month up to 5 months. In a possible scenario that this zone could not be healed (either with Ca from the inner of the grout or with Ca from the brine or

the surrounding rocks), then it would have generated a micro-annulus, weakening the bond with the casing and creating pathways favourable for CO_2 migration.



Figure 4.30 (A) BSE micrograph for the carbonated region near the surface of CO60/5 along with the corresponding (A1) Ca and (A2) Si EDS wt.% maps; (B) the adjacent to (A) BSE micrograph from the same surface together with (B1) Ca and (B2) Si EDS wt.% maps.



Figure 4.31 The distribution of Ca and Si (wt.%) from the surface towards the inner of the CO60/5 sample. The data of the graphs emanate from the elemental maps of Ca and Si illustrated in Figure 4.30. The carbonated region does not encompass the entire carbonated part but a representative graph of the weights.



Figure 4.32 Ca/Si (molar scale) of the consecutive BSE areas (Figure 4.31) as calculated from the EDXA data taken from Figure 4.31.

In comparison to the carbonated region, portlandite was absent even from the inner part of the grout (Figure 4.33). Even though the Ca/Si ratio was preserved equal to the unreacted grout, *i.e.* 1.76 ± 0.58 , the actual Ca/Si was anticipated to be lower from the growth of ettringite crystals (Figure 4.31) that have consumed Ca from both the dissociation of portlandite and the onset of Ca loss from the C-S-H particles. The interactions of the carbonated brine with the cement matrix have taken place not from the surface up to the carbonation front but also to the inner part. In the case of the CO60/ 5, areas similar to Figure 4.20 could not be outlined in a definite way in the direction of CO₂ diffusion. Three areas were observed to exist: the inner part which was not unaltered from the carbonated brine (Figure 4.34) and the outer part that was mainly composed of amorphous silicate **gel** and discontinuous air voids filled with calcium carbonates. The third "area" was said to be the carbonation front, which was still present (Figure 4.34) but thinner than the carbonation front of CO60/1.



Figure 4.33 XRD diffractogram of the inner part of CO60/ 5; "*" indicates ettringite



Figure 4.34 (**A**) BSE micrograph for the inner region of CO60/5; (**B**) Ca, (**C**) Si, (**D**) Cl EDS wt.% maps.

4.4.2.2 Calcium carbonates

Regarding the outer part of CO60/ 5, the same carbonates have been identified with the CO60/1 (Figure 4.35). These carbonates were again rhombohedral calcite, orthorhombic aragonite and hexagonal vaterite. The 4 months difference between CO60/1 and CO60/5 seemed to have preserved all the calcium carbonates providing environments in the pores that were in favour of the less stable forms like vaterite and aragonite. From all the calcium carbonates only aragonite was observed macroscopically (SEM images, Figure 4.36), with the other polymorphs to be distributed within the silicate structures; not in big assemblages, but in small crystals.



Figure 4.35 XRD diffractograms of the outer parts of the CO60/ 5; the two different diagrams for calcite and aragonite were used for clarity reasons; the diffractograms for calcite and aragonite were taken from the RRUFFTM Project database.

The size of calcite, aragonite and vaterite was calculated by means of the Scherrer equation [Burton *et al.*, 2009] and found to be 26.1 ± 2.2 nm, 43.8 ± 9.8 nm and 25.9 ± 2.0 nm, respectively. For comparison the carbonated region of CO60/1 was characterized by sizes, 26.1 ± 5.4 nm for calcite, 39.8 ± 2.5 nm for aragonite and 26.8 ± 3.9 nm for vaterite. For both CO60/1 and CO60/5 the stability in the size of calcite and vaterite was remarkable and only a small increase in the average mean size of aragonite was observed.

Aragonite crystals appeared to have filled the air voids of the outer part fully in a shell morphology where the growth of the crystals started from a single point and extended axially (Figure 4.36). Voids near the carbonation front (Figure 4.37) were not filled completely with

large and well oriented crystals but with small needles that had diverse orientations (Figure 4.38). These voids in both the unreacted and N60/5 were unfilled and unmineralised. The size of the crystals in Figure 4.36 should not be confused with the size calculated using the Scherrer equation. In other words, the size of the aragonite crystals filling the voids was the repetition of the elementary unit that resulted in the coherent X-ray scattering giving the diffraction pattern of aragonite in Figure 4.35B. This separation of basic and repetitive crystal unit was stated by Burton *et al.*, 2008.



Figure 4.36 Aragonite crystals growth inside an air void at a distance 3mm from the outer surface of the carbonated region of CO60/ 5

The localized presence of aragonite crystals inside air voids of both CO60/1 and CO60/5 was not in line with the "zonal" profile of calcite, aragonite and vaterite in class G cement grouts cured at 90°C/ 210 bar and immersed into carbonated water at 90°C and 300 bar [Corvisier *et al.*, 2010]. Morphological and chemical analyses of the carbonated volume of the CO60/ 5 have demonstrated the occurrence/ stability of aragonite, from air

voids near the surface (Figure 4.36) to air voids near the carbonation front (Figure 4.37, Figure 4.38). The higher curing temperature and pressure used by Corvisier *et al.* (2010), in comparison to the 30° C/ 1 bar used in this study, could have caused the entrained air voids to be absent in the hardened grouts.



Figure 4.37 The interface in secondary electron mode (carbonation front) separating the carbonated region (upper right) and the inner region (lower left) for the CO60/ 5. Air filled voids are also shown; frames with continuous lines, near carbonation front; frames with dotted lines, inner region.

The lack of observation of large calcite crystals was hypothesized to be due to the high pH of the pore fluids. Despite the low pH (6.23) of the reaction fluid after 5 months, it was reasonable to anticipate a gradual increase of the pH from the outer surface towards the inner core. As pH increased, the attachment of HCO_3^- to the Ca^{2+} passed through the instantaneous formation of amorphous calcium carbonates [Cölfen *at al.*, 2008] with the final form to be dependent on the one hand to the pH [Ruiz-Agudo *et al.*, 2011] and on other hand to the

available space for nucleation [Meldrum *et al.*, 2014]. Since basic environments (pH>9) decreased the growth rate of calcite [Ruiz-Agudo *et al.*, 2011] and confined spaces (*i.e.* smaller than 0.2 μ m) this inhibited the vaterite transformation into aragonite or calcite. Hence in the passage of the carbonation front both calcite and aragonite was suggested to fill the space inside and within the silicate **gel** in the form of small crystals. Aragonite was also found to be nucleated in the presence of air voids and in conditions favourable for the experimental pressure and temperature (80 bar, 60°C).



Figure 4.38 Air voids filled with aragonite crystals from Figure 4.37 (a) Newly formed aragonite crystals growing inside air voids at the boundary of the carbonation front, (b) Aragonite crystals at a metastable state at the inner region and (c) Stable crystals of aragonite.

4.4.3 Time evolution of solid phases for CO60 and importance of Ca/Si

The previous analysis for the carbonation of class G cements at 60°C revealed that the reactions were pH driven due to the inequality in the concentration of H⁺ of the brine with the cement pore fluids. The brines after treatment of the cement samples with nitrogen had higher pH \approx 12 due to the OH⁻ leaching from cement and substitution of the negatively charged end-groups of the decalcified C-S-H, *i.e.* SiO⁻, by H⁺/Na⁺. On the other hand, brines after treatment of the cement samples with carbonated brine had lower pH \approx 6, due to the dissolution of CO₂ and the consumption of the formed HCO₃⁻ in the form of calcium carbonates, having as a consequence the increase in the concentration of H⁺.

This acid-base character of the reactions between fluids with pH <12 with cement has been identified as the principle of chemical attack neutralizing the alkaline pore fluids of cement-based grouts [Zivica *et al.*, 2001]. In general, the reactions of dissolved CO₂ with the cement started with the dissociation of portlandite to Ca^{2+} and OH and then followed the controlled decalcification of the C-S-H phases, as evident from the stable Ca^{2+} zone in the carbonated region after 1 month (Figure 4.18).

Near the surface of CO60 where pH was less alkaline, the proposed mechanism of carbonation was through amorphous calcium carbonates that were transformed rapidly into calcite. This hypothesis was confirmed by Rodriguez-Blanco *et al.* (2012). Calcite as the most stable form amongst the various calcium carbonates was present in the high ionic environments generated locally from the Ca(OH)₂ dissociation. This transformation of portlandite directly to calcite in those high local charges was supported by Sekkal *et al.* (2013) and has been observed also to exist in surface cavities of cement in real CO₂ injection wells (Carey *at al.*, 2007).

As the carbonation progressed towards the inner parts of the grout where pH is higher, *i.e.*11.5, the transformation of the amorphous calcium carbonate to calcite occurred via the formation of vaterite (Rodriguez-Blanco *et al.*, 2012). The process of transformation is

governed by the confinement sites that control the reorganization of vaterite to calcite. Vaterite due its high solubility dissociated and re-organized into aragonite crystals. This reorganization occurred gradually by the calcium of vaterite and partially by diffused Ca from other areas. After 1 month, the air void shown in Figure 4.28, demonstrated the partial filling due to precipitation of aragonite and calcite. After 5 months the complete filling of the air voids that were away from the carbonation front, by aragonite, along with the highly ordered shape of the crystals (Figure 4.36), required the existence of proper pH conditions and the supersaturation of Ca²⁺ and HCO₃⁻ (Perdikouri *et al.*, 2011).

From the latter we can conclude the decisive significance of the pore space that controls the Ca dissolution and transport from the C-S-H particles as well with the importance of air voids as calcium storage spaces for buffering the effluent bicarbonates. The air voids have been trapped due to mixing of the cement with water in the laboratory or from the pumping of the cement slurry to the annulus. Presumably, the lack of air voids could not have led to extensive leaching after 5 months as the newly formed calcium carbonates (vaterite and aragonite) could have blocked the capillary pores more effectively. This would have generated a denser carbonation front, which under supersaturation conditions with respect to calcium and bicarbonates would be more chemically stable.

In downhole conditions where the injected CO_2 is continuously mixing near the cement, the aragonite (which is more favourably formed at high pressures) has been claimed to transform into calcite after a few thousand years [Budd, 1988]. Calcite is anticipated as the final product of aragonite from a controlled mineral transformation due to the gradual undersaturation of the bottomhole fluids in CO_2 , owing to its mineralization from the reservoir's rocks. With reference to the mixing of the injected CO_2 with the adjacent fluids to the injection well, this depends on the well design. For example, in a simple vertical well the continuous mixing would be valid close to the well, but for other wells where the injected CO_2 -plume migrates away from the well (*e.g.* Sleipner), the interactions of supercritical CO_2

bubbles was found (experimentally) to create calcite rendering the grout more resistant to further chemical degradation [Hidalgo *et al.*, 2008; Garcia-Gonzalez *et al.*, 2008].

Additionally, previous studies (*e.g.* Regnault *et al.* [2009], Galan *et al.* [2015]) showed a protective calcium carbonate layer that sealed and protected the portlandite crystals during carbonation for dry scCO₂, and relatively wet mixtures of scCO₂ and H₂O. This protective layer, as proven for cements in contact with brines (*e.g.* CO60), experiences fast dissolution and re-precipitation cycles until calcite is the final polymorph of calcium carbonates [Gomez-Villalba *et al.*, 2012]. The ultimate dominance of calcite during cement carbonation was found by Gomez-Villalba *et al.* (2012) to be dependent on the lattice defects of aragonite and vaterite, and was hypothesized to be dependent on the pore network parameters that control the diffusion of additional HCO_3^- and give the available space for renucleation of an existing *CaCO*₃ crystal.

4.4.4 CO120/1

4.4.4.1 Ca transport/ leaching

Regarding CO120/1 the transport of Ca was found to be less clear than CO60/1.Based on the Ca concentration in the post reaction fluids no conclusion for actual Ca leaching was suggested from the cement matrix for the CO120/ 1 (Figure 4.39). This was despite its reduction from $[Ca]_0 = 410 \ mg/l$ to $[Ca]_{CO120/1} = 56.67 \ mg/l$. As in the case of the CO60/ 1 the concentration of Ca in brine was not representative of the leached Ca due to carbonate precipitation at the surface of the samples. In order for the leaching to be captured, this would have required sampling of the fluids in the interim reaction period. However, the sampling would have introduced disturbances to the reactors in the sense of destabilizing the carbonation reactions.


Figure 4.39 BSE micrograph of CO120/1 and 2D EDS wt. % maps for Ca, Si along with the 1D spatial distribution of the Ca and Si; ' t_c ' denotes the thickness of the carbonation front.

The average Ca/Si of the inner region of CO120/1 was approximated to be 1.71 ± 0.81 (Figure 4.41), which was almost constant with the unreacted grout (Figure 4.2) and the corresponding N120/ 1 sample (Figure 4.12). The minor decrease of the mean Ca/Si ratio could be justified from the absence of portlandite and subsequently the Ca loss from the C-S-H phases (Figure 4.42).

The case of CO120/1 was the first time when portlandite was found to be absent, most likely due to its thermal instability at 120°C in contrast to 60°C. This instability was evident disregarding the presence of N₂ or CO₂ in the reactors and thus irrespective of the acidity/ alkalinity of the brines. Firstly, the presence of $Ca(OH)_2$ at N60 and not at N120 would have meant that the accelerated Ca leaching at 120°C was perhaps being the cause of $Ca(OH)_2$ dissociation due to concentration gradients (faster diffusion) and not temperature. Secondly, at CO60 the gradual disappearance of portlandite occurred due to the presence of HCO_3^- in the surrounding fluids and not due to temperature. Therefore, the disappearance of $Ca(OH)_2$ from the inner region of CO120/1 was not a consequence of the carbonated brine but due to the supply of additional energy at 120°C such that $Ca(OH)_2$ could overcome the dissociation energy barrier.

In comparison to the carbonation front of CO60/ 1, where Ca/Si = 1.97 ±0.42, the carbonation front of CO120/1 exhibited greater mean average Ca/Si ratio, at 2.03 ±0.81 (Figure 4.41). Although the difference of the two mean averages was negligible, in fact the maximum ratio at $Ca/Si_{CO120/1} = 2.84$ suggested a higher density of calcium carbonate crystals at 120°C than at 60°C.

The leached zone was characterized by the same ratio at Ca/Si = 1.71 ± 1.32 for the inner region, but with wider spatial heterogeneities as discussed by Giannoukos *et al.* (2014). At 120°C (similar to 60°C) in the leached depth calcium did not leach rapidly from the carbonation front towards the outer surface, but in a controlled mechanism. This mechanism resided in the various carbonate fronts that were within the leached zone, almost in parallel to

the outer boundary of the surface. Their existence seemed to be independent of the diffusion of bicarbonate through the leached zone for the formation of the main carbonation front.



Figure 4.40 Spatial graph of the Ca /Si of the BSE area shown in Figure 4.39; the artefact at 0.05mm is omitted from the discussion of Ca leaching as a non-genuine experimental artefact



Figure 4.41 Zonal summary of the Ca/Si ratio of the CO120/1 from Figure 4.40



Figure 4.42 XRD diffractogram for the inner region of CO120/1; the diffuse 2θ angle in the range 28° - 36° corresponds to the C-S-H phase; 'B' stands for brownmillerite

4.4.4.2 Ca precipitation

Calcite, aragonite and vaterite with the same polymorphism as CO60 (sub-chapter 4.4.2.2) were found exclusively in the carbonated region of CO120/1 (Figure 4.43). Calcite appeared to be the major calcium carbonate to fill the air voids almost ubiquitously (Figure 4.44-I), in contrast to the coexistence of calcite and aragonite in the carbonated region of CO60/ 1 and the exclusive presence of aragonite in the voids of the reacted part of the CO60/ 5 (Figure 4.36). However, aragonite crystals have been also found from crushed fragments of the reacted region of CO120/1 showing that after 1 month and 120°C aragonite was still stable.



Figure 4.43 XRD diffractograms of the carbonated parts for CO120/1; the diffractograms for calcite and aragonite were taken from the RRUFFTM Project database.



Figure 4.44 Calcium carbonates at the carbonated parts of the CO120/1; (A) Calcite crystals growth inside an air void; (B) aragonite crystals of a crushed sample; (C) vaterite in a cauliflower shape as a precursor for the aragonite growth in the direction of the arrows $\mathbf{a} \rightarrow \mathbf{b}$

The higher stability of calcite crystals inside the air voids at 120°C was justified based on the fact that by increasing temperature the solubility of CO₂ decreases [Mehrotra *et al.*, 1989]. Thus the concentration of HCO_3^- should have been reduced in comparison to the CO60, with less available quantity of HCO_3^- to diffuse in the cement pore fluids. The lack of supersaturation conditions should have given the necessary space for the aragonite and vaterite crystals to transform into calcite. Despite the lack of a strong ionic environment due to the lower concentrations of HCO_3^- at 120°C, calcite would not be formed as less activation sites were available for the essential dissolution and re-precipitation. Nevertheless, due to lower solubility of calcium carbonates with increasing temperature [Coto *et al.*, 2012], the various *CaCO*₃ polymorphs were assumed to have the required stability.

According to the Scherrer equation, the diameters of calcite, aragonite and vaterite crystals were calculated as 27.8 ± 14.0 nm, 56.4 ± 2.9 nm and 35.6 ± 2.1 nm, respectively. The mean average size of calcite seemed to be the same as at CO60/1 (26.1 nm), suggesting that the growth of the elementary calcite crystal was governed by the available space for nucleation, despite the different chemical potentials for crystallization at 120° C compared to 60° C. This space was assumed to depend on nucleation site (Ca(OH)₂, inner or outer C-S-H) and the pore space available for the growth. The higher variation in the size of calcite for the CO120/1 may indicate shrinkage and expansion of the crystallite. However, whether this change in crystallography is actually significant for controlling the permeability of the carbonated region is a matter of future research.

Vaterite was not detected macroscopically by means of secondary electron imaging as a separate assemblage, but rather as part of a dynamic system of continuously transforming calcium carbonates (Figure 4.44-B). It seemed like the process of cement carbonation at 120°C after 1 month was a dynamic phenomenon consisting of precipitation and dissolution cycles of the calcium carbonates. In contrast to the rhombohedral calcite having filled compactly the air void in Figure 4.44-A, the aragonite crystals from the crushed solid Figure 4.44-C showed the presence of cruciferous vaterite. Firstly, the direction of the arrows $a \rightarrow b$ showed that the fragments of aragonite crystals consisted of the same overall structure and has probably been separated during sample preparation caused by the pressure applied to the carbon tab for the stabilization of the fragments. Secondly, the vaterite in Figure 4.44-C was found to be an integral part of the aragonite crystals from Figure 4.44-B.

4.4.4.3 Chloride ingress

The spatial distribution of chlorine is given in Figure 4.45. Chlorides detected near the surface that show mass greater than 4% emanate from the resin used for the cold mounting of the sample and more specifically the epichlorohydrin, C₃H₅ClO [Struers ©]. The chlorides seemed to exhibit greater values from the carbonation front towards the inner region denoting lower affinity to the chemical structures of the carbonated part of the grout to chlorides. This observation of chloride absence from the carbonated region of CO120/1 agreed with the CO60/1 indicating either (i) the lack of chemical binding of chlorides to carbonates and the decalcified silicate structure, or (ii) the widening of the pore network. Similarly to the mechanism for Cl⁻ ingress proposed at section 4.4.1.4 at 60°C, the higher solubility of Cl-bearing phases at 120°C in the carbonated part due to the low pH (reflected in Figure 4.45 for x < 0.75 mm) appears to lead to continuous dissolution and precipitation of those phases as the carbonation front moves further inside the sample.

The profiles of chloride ingress between CO60/1 (Figure 4.29) and CO120/1 (Figure 4.45) showed the apparently strong impact of temperature on the diffusion of Cl^- . At 120°C the diffusion was so fast that the profile of chlorides was steeper at the carbonation front than that at 60°C. The reason for this observation was attributed to the carbonation front at 120°C being a more effective barrier to diffusion from the inner towards the outer. The higher corrosion rate of steel reinforcement in cements (induced by chlorides) as temperature

increases has been identified in previous studies, due to lowering the threshold value above which cement is not resistant to the chemical binding of chlorides [Hussain *et al.*, 1995].



Figure 4.45 Distribution for chlorides of CO120/1 for the BSE image in Figure 4.39

4.4.5.1 Ca leaching/ Silicates polymerization

After the passage of 2 months for CO120/1, significant Ca loss appeared to have occurred for CO120/3 due to portlandite loss at the inner region of the grout (Figure 4.47), along with the extensive decalcification of the C-S-H; the latter being evident from the Ca/Si ratio of the inner region (Figure 4.50). Due to the precipitation of the Ca-bearing phases (mostly calcite) from the fluids to the surface of the CO120/3 (Figure 4.46), the value of $[Ca]_{C0120/3} = 84.56 \text{ mg/l}$ in the fluid after the reaction was not representative of the actual leached Ca. The existence of those precipitates at the outer surface, and not only the inner region of the cement, suggested that the inner precipitation is diffusion-limited due to the pore network interconnectivity and geometry.



Figure 4.46 The CO120/3 sample; calcite crystals have covered the entire surface of the sample; the outer ring with a pale tint of orange was found to be rich in Fe. The distance of 2.35 cm corresponds to the radius of the cyclic projection of the sample (diameter=4.7 cm)

The carbonation front, as well as the Ca-leached front (Figure 4.50), had significantly lower values for the CO120/3 in comparison to CO120/1 (Figure 4.41). The calcium loss, as shown by the Si elemental map in Figure 4.48-C, left a silicon-rich zone in this area. The Sirich remnants, originating from the silicate **gel** of the decalcified C-S-H, have been found in previous studies [Fernandez Bertos *et al.*, 2004] to polymerize into a silicate microstructure (gel) due to the bonding of the free branches of SiO⁻. The silicate polymerization at 120°C has not been observed at 60°C, showing the promotion of gel polymerization at the highest temperature. This is also serves as an analogy with the exponentially increasing rate of silicate polymerization as temperature increases [Hamouda *et al*, 2014]. Furthermore, the continuous flow of Ca²⁺ from the inner region not only accelerated the creation of silica gel but also the final silicate structures appeared to be more insoluble in various pH conditions.



Figure 4.47 XRD diffractogram for the inner region of the CO120/3; 'B' stands for brownmillerite



Figure 4.48 (A) BSE micrograph for CO120/3 where t_c denotes the thickness of the carbonation front; (B) Ca, (C) Si, (D) Cl EDS wt.% maps; (E) 1D spatial distribution of the Ca and Si from **B** and **C**.



Figure 4.49 Spatial graph of the Ca /Si of the BSE area shown in Figure 4.48; the artefact at 0.3 mm is omitted from the discussion of Ca leaching as denotes the calcite precipitated to the surface of the sample



Figure 4.50 Zonal summary of the Ca/Si (Figure 4.49) for the BSE surface illustrated in Figure 4.48-A

4.4.5.2 Ca precipitation

The morphology of the Ca-rich phases in Figure 4.51, gave evidence of the existence of calcite and aragonite. The mineral surfaces of the crystals in the bottom half in Figure 4.51-I, are either stepped crystal faces or etching along cleavages following a rhombohedral pattern. Calcite has this rhombohedral cleavage and can exhibit rhombohedral faces [Bisschop *et al.*, 2006; Vavouraki *et al.*, 2010], whereas aragonite is orthorhombic with cleavages at 90° [Godelitsas *et al.*, 2003].

The sizes of the elementary crystallites (determined using the Scherrer equation) of calcite, aragonite and vaterite were 30.7 ± 4.1 nm, 53.7 ± 10.9 nm and 35.5 ± 2.1 nm, respectively. The size of calcite appeared to increase in comparison to CO120/1 (27.8 nm), which is evident from Figure 4.51-I. Vaterite had the same size for both CO120/1 and CO120/3 equal to 35.5 ± 2.1 nm.



Figure 4.51 Calcium carbonates at the carbonated parts of the CO120/ 3; (A) Calcite crystals growth inside an air void; (B) aragonite crystals of a crushed sample



Figure 4.52 XRD diffractograms of the carbonated part for CO120/3; the diffractograms for calcite and aragonite were taken from the RRUFF[™] Project database.

4.5 Summary

In the present chapter it became apparent that the chemistry and microstructure of class G cementitious grouts depended on the stage of CO_2 injection to the batch reactor. The first case was the assessment of grouts that were in contact with brine before the CO_2 injection. Calcium leaching from class G cementitious grouts was found to be a thermally-dependent process. A necessary implication of the Ca leaching is related to the rise in temperature due to the enthalpy associated with injecting supercritical CO_2 . Temperatures higher than 60°C lead to the full conversion of portlandite to other forms, which caused chemical instabilities of the grouts. In general, the lack of the calcium provided by portlandite that could buffer the dissolved CO_2 species tend to make C-S-H more prone to dissociation.

However, increasing the temperature from 30°C to 120°C seemed to facilitate the calcium transport towards the surface generating more stable C-S-H phases near the surface. As temperature rises near the annular cement, from the injection of supercritical CO_2 , the diffusion of calcium towards the carbonated zones become more immediate and could generate more robust barriers to CO_2 diffusion (Figure 4.53).



Figure 4.53 Implications of temperature and time on the chemical resistance of the class G cements to inhibit the carbonation after Ca leaching

The second case was the investigation of cementitious grouts after CO_2 injection has already been initiated. The chemical degradation of class G cement grouts immersed in CO_2 saturated brines was found to decrease by increasing temperature. The shape and size of the calcium carbonates found in a grout appears to be directly related to the temperature history. At 80 bar and 120°C, the calcite-filled voids indicated faster attainment of equilibrium in contrary to the aragonite-rich voids observed after treatment at 60°C. As predicted (for N120), the stimulation of the outer cement particles by additional Ca^{2+} led to faster supersaturation conditions for vaterite and aragonite, which at higher temperatures re-precipitated faster to calcite. The higher resistance to degradation at 120°C was consistent with a silicate polymerized "skeleton" being generated (in decalcified C-S-H) near the surface. This appeared to control the Ca diffusion rate and subsequent precipitation as calcium carbonates better than at 60°C.



Figure 4.54 Overall compositional changes during carbonation of class G cements at 80 bar and 60°C, 120°C.

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5.1 Introduction

Having given the chemical identities of the structural units of cement before and after treatment with N_2 and CO_2 saturated fluids, this chapter aimed at the prediction of the time needed for full carbonation of the examined samples. The time for full carbonation has been calculated based on extrapolations of the power law equation. It was found that the rate of change of the carbonation depth depends on the chemical alterations of grouts immersed in CO_2 rich fluids.

The location of the carbonation front, *i.e.* carbonation depth, as an indicator of the degradation of the grouts exhibited significant local heterogeneities at the scale of a few μ m or even mm. These local heterogeneities have been found not to be of major importance, in order to allow for a good approximation of an average mean depth. In the present chapter the carbonation depth (being the denser continuous part of an ongoing carbonated cementitious grout) was analysed in order to determine the correlation between its clear delineation in the X-ray projection images (XRCT) and its compositional features as captured by SEM-BSE.

Table 5.1 summarizes the analytical techniques used for the study of the rate of change of the main carbonation front. The use of SEM was the same as in Chapter 4, but in the present chapter the changes in chemistry were regarded from the point of view of the rate of change in time. The evolution of the main carbonation front that was detected by means of X-ray reconstructed images was used to assess if the chemical changes occurred randomly or concealed information about the diffusion mechanism.

Before any analysis of the XRCT density images to take place, it was recognized that the diffusion regime in cement based materials will depend in many variables that are not only related with the final hardened cements. Variables like T and P change both carbonated and inner regions of the cement in time, and thus diffusion will be constantly changing from place to place for the same material. The decision in the present thesis was to choose the 'rate of change of the carbonation front' and not the continuous evolution in time. In order for a continuity to express the diffusion, a model needs to incorporate the alterations of the diffusion 'constant' for each time. Those alterations happen not only for different cement mixture but also for the same mixture under various T, P conditions. Thus the diffusion regime(s) must be examined individually during carbonation of the various classes of cements. The present chapter, however, presents a global method for detecting the carbonation front that could be applied in any CO_2 injection well and highlights the importance of coupling the diffusion regime with the chemical alterations.

Analytical technique	Location of the sample	State of the sample	Information from each technique
SEM/ SE/ BSE	Near to the surface/ Carbonation front	Solid	BSE micrographs
XRCT	Entire sample	Solid	X-ray density images

Table 5.1 Analytical techniques used to study the evolution of the carbonation front

5.2 Eligibility of the carbonation depth measurements

5.2.1 Initial conditions

The example of CO60/5 is given here for reasons of defining the mean position of the carbonation front (Figure 5.1 and Figure 5.2). The corresponding N60/5 did not have a carbonation front (Figure 5.3 and Figure 5.4) and therefore it was used as the reference point (0 days, 0 mm) in the equations for the time evolution of the carbonation front. For all the other CO₂ treated samples the same process of measurement was followed for their final values of their carbonation front.



Figure 5.1 X-ray tomographic volume section of the CO60/ 5; the white spots within the carbonated region denote aragonite crystals.

carbonated volume	main carbonation front x=0cm	CO ₂ diffusion
	(inner cement	2.35 cm

Figure 5.2 A ZY projection of a central slice from Figure 5.1. The direction of CO_2 diffusion is shown with black filled arrows. The change of the point of reference (x=0 mm) from the surface (Figure 5.1) to the centre of sample is explained at section 5.2.4. The distance 2.35 cm corresponds to the radius of the sample as the entire sample was 4.7 cm.



Figure 5.3 X-ray tomographic volume section of the N60/ 5; in contrast to the carbonated region for CO60/ 5 (Figure 5.1) no white spots where detected; the black dots indicate air voids with no connectivity at the spatial resolution of the XRCT (25 μ m).



Figure 5.4 A ZY projection of a central slice from Figure 5.3; the corresponding gray value histogram is superimposed for emphasizing the curing effects (A-B) described at section 5.2.2

5.2.2 Curing effects on the gray values histograms

The calculation of the location of the carbonation front was done by plotting the gray values across line segments that were extended from the centre of the sample up to the surface of the samples (Figure 5.5). This technique of identification of the carbonation front from X-ray tomographic images has already been applied to the problem of cement carbonation in previous studies [Han *et al.*, 2013]. However, the abovementioned plots were not used in isolation from the visual inspection of the corresponding X-ray reconstructed image (Figure 5.4).

The first reason is described in section 5.2.3 and was related to the similar densities of dispersed carbonates with the carbonation front. The other reason was related to the intensity of the grey values across a sample due to the attenuation caused by the sample size [Cnudde *et al.*, 2013] and the curing effects. In Figure 5.4, a ZY projection is illustrated from sample N60/5, where in the segment A-B the gray values showed a decrease in their intensity in comparison to the grey values of the rest of the sample. This decrease in intensity at the centre of the sample was attributed to the higher density of the products from the inner towards the outer of the sample. This was either due to material precipitation from the brine (*e.g.* chlorides), or to more effective curing of the outer layers and generation of dense hydration products.

The shape of the gray value histogram in Figure 5.4 was found to be similar for noncarbonated samples with a water/cement ratio ranging from 0.35 to 0.23 [Han *et al.*, 2012]. This shape was evidence that the curing of the samples in the present study has been accomplished in the proper way since the water/cement ratio used (0.37) led to the outer regions obtaining a higher density. The less dense microstructure of the inner region (segment A-B), compared to that of the outside of A-B, implied that the curing generated more pore volume, perhaps due to improper, *i.e.* higher, water to cement ratio.



Figure 5.5 The location of the carbonation front as measured for CO60/5 from an XY plane as taken from Figure 5.2; the reference point (x = 0 mm) is shown at position (0) while the numbers 1-8 denote the directions for the measurement of the gray value plots.

5.2.3 Impact of the geometry of the samples on the grey value histogram

Firstly, it is important to state that for cylindrical samples the measurement of the carbonation depth must be done across lines that are perpendicular to the tangent of the surfaces in order to avoid overestimations of the depth from sloping lines. Secondly, the choice of the centre as the point of reference ensured that the same procedure was followed for all CO_2 treated samples in terms of capturing any probable asymmetry of the main

carbonation front due to local heterogeneities of the samples during CO_2 diffusion. Thirdly, several surfaces appeared to have very low adsorption coefficients (most likely due to Ca leaching) making choice of reference from the periphery of the projections difficult.

5.2.4 Carbonation depth measurement

The first step in the measurement of the carbonation depth was to find the exact location of the centre of the sample. This was measured as the cross section of the diagonals (*i.e.* 1-5, 3-7) that were created by connecting the two edges of a square that had sides tangential to the surface (Figure 5.5). Having the centre as the point of reference (0), the straight line of measurement from ImageJ was rotated anticlockwise in the eight directions shown in Figure 5.5 with an angle 45° (*e.g.* 0-1 up to 0-8). From each straight line a lineal plot of grey values was acquired. Finally, the mean values of the eight measurements were used to graphically calculate the carbonation front position (Figure 5.6).



Figure 5.6 Graph of mean grey values for segments from Figure 5.5; a part of the XY plane as defined in Figure 5.1 is given for more accurate detection of the carbonation front

In the particular example of CO60/5 there were no visible signs of the carbonation front from the histogram (Figure 5.6). The air voids of the carbonated volume that were filled with dense aragonite crystals (see Section 4.4.2.2) appeared to have higher X-ray adsorption coefficients, μ , in terms of the Lambert-Beer law [Chotard *et al.*, 2003], so they appeared brighter than the carbonates of the main carbonation front. This made it difficult to detect the main front without observing the corresponding reconstructed projected image. Black dots in Figure 5.5 and in Figure 5.6 denote entrapped air voids that exhibited no X-ray adsorption, and thus $\mathbf{I} = \mathbf{I}_0$. The higher adsorption coefficients of X-rays from aragonite and the lowest from the pore space were given by Mason *et al.*, (2014) verifying the previous assumptions.

After the calculation of the mean location of the carbonation front, the final step was to incorporate the heterogeneities in the shape of the asymmetric front. For this reason, for each one of the segments (*e.g.* 0 - 1 *etc.*; Figure 5.5) the value of the carbonation depth, X_C , was found individually by subtracting the distance corresponding to zero grey value from the distance corresponding to the carbonation front as in Eq.1 (Figure 5.7).

$$x_{C} = x_{zero grey} - x_{carbonation front}$$
 Eq. 1

The standard deviation of the eight values was considered as the measure of the heterogeneous diffusion of bicarbonates through the cement matrix, and the lack of symmetry of the main carbonation front from the periphery of the samples. The zero grey value $X_{zero grey}$, corresponds to the outer surface of the sample. The choice of the reference point as the centre of the sample gave almost constant values across the line segments of Figure 5.5 as seen in Figure 5.7, fact that proves the lack of symmetry of the carbonation front.



Figure 5.7 The deviation of the carbonation depth as measured from the centre of the sample; the zero gray distance represents the distance from the centre of sample where the gray value is zero, *i.e.* the surface; the eight segments correspond to those depicted in Figure 5.5.

The previous methodology, which is illustrated in Figure 5.5 and Figure 5.7, has important implications in the monitoring of ongoing carbonated cements in real CO₂ injection wells. The asymmetry of the carbonation front in poorly consolidated and sealed wells (*e.g.* Choi *et al.*, 2013) could be crucial when the casing is not centralized to the well. The lack of centralization [Albawi, 2013], if the real width of cement is unknown, can lead to underestimation of the carbonation depth (in the thinner side) and thus to potentially misleading conclusions for the extent of carbonation.

5.2.5 Lateral and Edge carbonation front

The values for the carbonation front at 60°C and 120°C were taken exclusively from the XY projections that correspond to the middle of the puck samples. However, as seen in Figure 5.2, the carbonation front with reference to the lateral cylindrical surface is not a parallel line but a curve. In fact, the carbonation front measurements in Figure 5.5 were taken on images at a cross-sectional depth (in the XY plane) corresponding to the maximum width 188 of the unreacted core, Figure 5.2. The downside of the sample in Figure 5.2 that shows no CO_2 diffusion was attributed to the fluid sampling pipe, while the upper side had a delay in its reactivity due to the small distance (~2 cm) from the Teflon liner; a period at least 1 month for cases of both 60°C and 120°C.

5.3 Equations governing the carbonation front movement at 60°C and 120°C

After the proper detection of the main carbonation front from the X-ray reconstructed images described in section 5.2.4, the time-evolution of the calculated carbonation depths was investigated in order to reveal the diffusion mechanism of the carbonated brine into the cement. This time evolution was not a detailed study for the movement of the carbonation front from multiple samples for each temperature that could allow the statistical accuracy of the $(x_c - t)$ graphs. In fact, from the number of samples used in this study the main objective was to capture the rate of change of the carbonation front and the prediction of the diffusion regime from the fitting of the carbonation depths to the square root law of time.

This law results from the Fick's first (Eq. 2) and second (Eq.3) laws for diffusion:

$$j = -D_i \frac{dc_A}{dy}$$
 (Fick's first law) Eq. 2
 $\frac{\partial c_A}{\partial t} = D_i \nabla^2 c_A$ (Fick' second law) Eq.3

where *j* is the molar mass flux of HCO_3^- , D_i is the intrinsic diffusion coefficient, dc_A is the change of the concentration of HCO_3^- from c_{A0} (surface) to 0 (main carbonation front) and $\nabla^2 c_A$ is the gradient of the concentration profile in space at a specific time. Although both laws have been used to derive different forms of the square root law [Tsao *et al.*, 2015], in fact only the first form was proved to have a realistic background for cements [Papadakis *et al.*, 1989]. Fick in 1855 has published the laws for diffusion in correspondence to the heat conduction equations, but with no experimental data, fact that allows for great deviations when applied in diffusion through heterogeneous materials like cements. Even though the diffusion though cements could be described by more accurate equations, in fact the applicability of the square root law of time is sufficiently accurate for many types of cements and any comparisons in real applications can be easily achieved using a carbonation coefficient [Marcos da Silva Lopes Simas, 2007].

Table 5.2 shows the choice of the carbonation depth measurement from a sample inside the reactor, the values of the carbonation depths and two important rates for the diffusion. The first is the rate of carbonation in $\frac{mm}{day}$ and the second is the rate of carbonation according to the square root law of time in $\frac{mm}{\sqrt{day}}$. From those rates (Table 5.2) the carbonation at 60°C the carbonation seems to delay up to 30 days and then the carbonation reactions to take place faster increasing the carbonation rate. At 120°C the behaviour is different to 60°C, where the carbonation rate seemed to decrease from 1 month up to 3months.

This behaviour can be clearly seen at the $(x_c - \sqrt{t})$ graphs in Figure 5.8 for each temperature. Those graphs as mentioned earlier in this section 5.3 could have been statistically correct if more samples have been used. However, for the current thesis the information for the revelation of the diffusion regime was sufficient from three samples for each temperature. In Figure 5.8 the slope of the line at 60°C is entirely deviant from the slope at 120°C and with a much lower R² value. In other words, the diffusion reactions at 120°C appeared to have followed the square root law of the time, showing that the assumptions made for the derivation of this law were better fulfilled at 120°C that at 60°C.



Table 5.2 Synopsis of the carbonation depths for each sample and rates of change of the depths based on the linear evolution of the depths in time and the square root law of time

In order the Fick's first law to be satisfied a system must be characterised by a steady state flux and have a uniform concentration gradient. The shape of the carbonation front in the samples of the present thesis showed microscopically a front that is not clearly in parallel to the outer surface. This is an important characteristic that shows not only the heterogeneously distributed Ca, but also that the diffusion though the pores does not have a single value of gradient. In other words, the diffusion of the carbonate anions depends on the gradient of concentration which appeared to be different in the 3D coordinates, presumably due to pore restrictions.



Figure 5.8 Evolution of the carbonation depths versus \sqrt{time} at 60°C (black segmented trend line) and at 120°C (gray segmented trend line).

In a porous material like cement with spatial heterogeneities and a pore network that has random 3D hierarchy the application of the Fick's laws is not ideal. As these laws have been derived for diffusion of gases in open spaces [Webb *et al.*, 2003], their application in solids must be treated with caution. In fact, no actual flux of species can be assigned through the pores of cement but rather a continuous precipitation-dissolution sequence of reactions. Based on the values of the rate of change in $\frac{mm}{\sqrt{day}}$, the square root law of time shows a better applicability at 120°C which is translated into the inhibition of carbonation front advancement towards the inner parts of cement in the course of time.

At 60°C the accelerated reactions from 1 month to 5 months support the fact that the diffusion in terms of Fick's first law could not describe the actual process of carbonation. In this section the applicability of the Fick's first law was considered to be not the proper mathematical expression. In Section 5.3.1 this is explained on the basis of the power law and in Section 5.4.1 the exact mechanism of front propagation is discussed at 60°C.
Appendix 3 shows the exact calculation of the diffusion equations assuming that no change in the trend occurs in between the points. The equations however do not represent the actual trend of the carbonation depth versus time since several steps of increasing and decreasing rate should be attributed to the overall carbonation process.

5.3.1 Discussion: Power law and CO₂ diffusion

The times for full carbonation in Appendix 3 were calculated based on the dependence of the carbonation depth on the square root of time. The validity of this relationship, between x_c with \sqrt{t} , depends inherently on the validity of the assumptions from which this relationship was calculated [Liang et al., 2002]. These assumptions are known to be: (1) isotropic behaviour in homogeneous material without cracks, (2) the applicability of Fick's laws. The first assumption was initially said to be invalid as cements are heterogeneous materials and their properties depend on the sample surface location, e.g. relative to the curing position [Poyet et al., 2013] and contact environment. However, the shape in which the carbonation reactions proceeded, *i.e.* as a front, indicated the synchronization of the reactions across the same boundary, despite the microscopic heterogeneities. In other words, the carbonation did not happen across a specific route (tortuous pore pathway) from the surface to the centre of the sample, but rather from simultaneous carbonation of the cement particles across this boundary. Regarding the first assumption, a hypothesis was made in the present study that the Knudsen diffusion in a continuously carbonated region was, (1) the contributing factor for the shape of the front and (2) the reason of applicability of the power law in cement carbonation [Fedotov et al., 2007].

The second assumption is a typical condition for $\mathbf{x}_{\mathbf{C}} = \mathbf{A} \cdot \mathbf{t}^{0.5}$, according to which the diffusion of CO₂ through a cement matrix is due to concentration gradients [Milligen *et al.*, 2005]. The power law, where ⁿ = 0.5 [Papadakis *et al.*, 1989] or 0.4 [Sisomphon *et al.*, 2007], has been used to describe the evolution of the carbonation depth for cements with various R² 193 values. The determination of the index requires sufficient experimental points for various durations and a parametric analysis. This power as discussed by Sisomphon *et al.* [2007] could be related to the pore network parameters and not merely on the chemistry of cement.

From the graphs presented in Figure 5.8, the value of the power that was equal to 0.5 should be treated with attention. Equation $\mathbf{x}_{c} = \mathbf{A} \cdot \mathbf{t}^{a}$ states that the carbonation depth reaches a plateau for $\alpha < 1$ and increases monotonically for $\alpha > 1$. Hence, the evolution of the carbonation depth at 60°C could be a consequence not of real carbonation after 5 months but rather a sequence of an initial carbonation ($\alpha < 1$), and then dissolution of calcium carbonates ($\alpha > 1$). More experiments could have taken place from 1 to 5 months and beyond; in fact Figure 5.8 illustrated correctly this carbonation/ dissolution sequence. The variability of the power α was stated to be not only an experimental fact [Sisomphon *et al.*, 2007], but also a mathematical solution to the theoretical evolution of the carbonation depth [Aiki *et al.*, 2011].

The diffusion according to Equations 2a and 3a (Appendix 3) implied that the proportionality constants remained constant in the course of time. These constants, however, were assumed to be identical and independent from temperature, since the same cement grout mix was used and thus the products of hydration were assumed to be identical for all the samples before reaction. These products along with the constant concentration of CO_2 in the fluids were said to be the proportionality constants after the equation proposed by Papadakis *et al.* (1989). In Equations 2a and 3a, however, the proportionality constants were not equal suggesting that the temperature has altered the effective diffusivity of $CO_2(D_{e,CO_2})$.

5.4 Carbonation front evolution at 60°C and 120°C

5.4.1 Deviations from the diffusion-controlled mechanism at 60°C

As seen at Equation 2a (Appendix 3) the fitting of the experimental carbonation depths at 0, 1 and 5 months could not be assigned to the classical diffusion-controlled mechanism of carbonation. This would have been evidenced by linear dependence of the carbonation depth on the square root of elapsed time. During cement carbonation at 60°C the diffusion mechanism can be clearly revealed by the shape of the carbonation front and the polymorph type of the calcium carbonate.

At 60°C after 5 months the carbonation reactions seemed to take place in a controlled way leaving clearly delineated but non-continuous lines of previous carbonation fronts (Figure 5.9). Even though only the main carbonation front at 1 month was detected unambiguously, it was strongly suggested that the fronts generated from the 1D lateral diffusion after 2 months were superimposed to the fronts that were generated due to diffusion from the two circular sides (Figure 5.9). Furthermore, the diffusion after 3 and 4 months would have been caused from the superposition of the fronts generated from the lateral and circular sides. The use of samples without coating in the two circular sides, although used in other studies for cement carbonation [Han *et al.*, 2012], prevented any artefact from precipitation of the coating material in the pores. In the case that coating was used and assuming axial diffusion from the outer towards the inner, the ideal case for the carbonation fronts to follow the square root law would have led to: (i) front 'ab', which due to diffusion from the two sides led to (ii) front 'cd', and finally (after 5 months) to (iii) front 'gh' (Figure 5.9).

If the square root law of time could be applied in the case of the 60°C carbonated samples then, ideally, the evolution of the carbonation depth in the course of the square root of time would have led to a smaller carbonation coefficient at 60°C than that at 120°C (see Appendix 3, Figure Ap. 3.3). This is explained on the basis of the kinetic theory of gases

which states that by increasing temperature, the kinetic energy increases as well and thus the diffusion coefficient leads to higher carbonation coefficients.

Appendix 3 shows not only the ideal case for the evolution of the carbonation depth at 60°C, but also a rational approach in the determination of old paleofronts with distinct relics rich in calcium carbonates. In this approach the carbonation fronts were approached to be ellipses and were detected visually but with attention to include the major relics from old fronts.



Figure 5.9 Graphical illustration of the time evolution of the carbonation fronts based on the relics of CO60/5

The generation and preservation of old carbonation fronts is explained from Figure 5.10 to Figure 5.13. Those relics were not visible in SEM/ BSE, due to the small area of examination, even in the lowest magnification, but useful information was extracted on the mechanism that the old fronts are created from compositional features. In these figures the carbonation front moves, once generated onto the surface of the cement (Figure 5.10), in a precipitation dissolution mechanism towards the inner regions of cement. Both Ca^{2+} and HCO_3^- must diffuse in opposite directions in order the chemical potential in both solid and carbonated brine to equilibrate. Their diffusion is not influenced by the temperature up to 1 month as the rates at 60°C and 120°C are the same (see Table 5.2).



Figure 5.10 Calcite (A) inside an air void a few μ m near to the surface of sample CO60/1; this the initial carbonation front created a few hours after the dissolution of CO₂ into the brine; the pore filling refers to the onset of the calcium carbonate precipitation in pores towards the inner of the sample. The characterization of the **CaCO₃** as calcite took place at section 4.4.1.2

Figure 5.10 shows that calcite has partially filled an air void, while the CaCO₃ precipitation continues in a pore filling mechanism following random carbonation pathways (Figure 5.11). The pore filling at sample CO60/1 appeared to be diffusion controlled from the presence of both aragonite and calcite crystals (see Figure 5.12). The presence of both forms indicated that diffusion is governed by the local pore characteristics that led to the supersaturation in Ca^{2+} and HCO_3^- from the one side of the air void and the controlled formation of calcite to the other side. From the partial filling of the air void at Figure 5.10 and the empty pathway towards the outer surface at Figure 5.11 it is evident the basic mechanism of dissolution of the fronts, the diffusion of the dissolved CaCO₃ in any direction and the inner for the generation of a new carbonation front.

At a point in time, where the dissociation of the main carbonation front happened either at 1 month (for CO60/1) or a few days after the one month, the main differentiation line appeared for the two temperatures with respect to the diffusion regime. At 60°C the pore filling continued without inhibition of the carbonation reactions due to CaCO₃ precipitation (see Figure 5.13).



Figure 5.11 The precipitation and dissolution of calcium carbonates take place across random pathways governed by the pore structure



Figure 5.12 Calcite and aragonite in voids (B) close to the main carbonation front where the pores are entirely filled; secondary carbonation fronts are signs of partial dissolution of the main front and its advancement towards the inner.

The detection of the relics of the old carbonation fronts was done for carbonation fronts that were partially dissolved but they maintained their distinct shape and density that was easily detected by means of XRCT (see Figure 5.6). The mechanism of creation of those paleofronts is shown simplified in Figure 5.13. The pore filling, shown in Figure 5.6, refers to the aragonite crystallization. The formation and dominance of aragonite in previously empty air voids could not be regarded as a separate fact from the rate of carbonation at 60°C and its deviation from the square root law of time.



Figure 5.13 Modelling of the carbonation front evolution for sample CO60/5; the outer surface is exposed to continuous cycles of precipitation/ dissolution of $CaCO_3$; towards the inner the carbonated part is characterized by paleofronts of carbonation that due to partial dissolution create pathways for further diffusion of HCO_3^- until a new carbonation front to be formed.

The diffusion could not only be regarded as Fickian but a mixture of Knudsen (molecule-pore walls interactions), Fickian (molecule-molecule interactions) and advective flow. The latter was attributed to the presence of well crystallized aragonite assemblages with perfect symmetry in a shell like shape (see Figure 5.14). The main nucleation site and the orientation of the aragonite crystals denote higher reactions rates for calcite growth and at the same time advective flow that could allow for the supersaturation of the air void with respect to the effluent HCO_3^- . Both calcite and vaterite were excluded from their nucleation in the air voids due to reasons stated in section 4.4.2.2.

The proposed model for the advective flow of the effluent HCO_3^- is justified from the size of the air void close to 100 µm that excludes any interactions with pore walls and other ions. The advection mechanism explains one the one hand the growth of aragonite from a single point and on the other hand the shell-like shape of the aragonite crystals. In Figure 5.15 the onset of aragonite precipitation close to the entrance is justified from the rapid

precipitation of $CaCO_3$ due to reaction of the newly arrived HCO_3^- with the Ca^{2+} of the pore fluid.



Figure 5.14 Aragonite filled air voids with a single nucleation point and growth in a shell shape



Figure 5.15 The advective flow of HCO_3^- leads to supersaturation conditions with respect to HCO_3^- and Ca^{2+} at the inside of air voids; the nucleation of aragonite to take place in the shell like shape that transforms the advective flow to pure diffusion.

5.4.2 Correlations between composition and evolution of the carbonation front

At 60°C the diffusion seemed to take place at a higher rate in comparison to the 120°C. The diffusion was described on the one hand in terms of actual diffusion of bicarbonates from the carbonated brine through the pores and on the other hand to the outward diffusion of Ca^{2+} towards the brine. The fast diffusion and leaching of Ca^{2+} leads to retardation of the carbonation reactions as, from the Le Chatelier principle [Hillert *et al.*, 1996], the drop in the concentration of calcium in the reaction allowed less $CaCO_3$ to be formed and for the previously-formed $CaCO_3$ to dissolve:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$

This leads the equilibrium towards the dissociation of $CaCO_3$. This dissociation leads to the release of CO_3^{2-} that diffuses further inside the grout and generates new carbonation fronts through reaction with the inner Ca^{2+} (Figure 5.16).

At 60°C the gradual shrinkage of the carbonation front (Figure 5.16) denoted that diffusion became gradually less important and that the available active sites of C-S-H (for acceptance of CO_3^{2-}) controlled the evolution of the carbonation front, *i.e.* the pore area and not the pore size. On the other hand at 120°C, the diffusion controlling mechanism, as shown by equation 3a, implied that the reactant species did not have more degrees of freedom due to the higher temperature leading to equal probabilities for a reactant to move towards the solid or towards the fluid [Berg, 1993]. This behaviour at 120°C could be justified from the peculiar structure of the polymerized silicate structure (Figure 5.16) that was assumed to control the movement of Ca^{2+} and CO_3^{2-} allowing for a more thermodynamically stable environment for growth of thick crystals of calcite.



Figure 5.16 Conceptual models for the time evolution of the various chemical zones at 60°C (left) and 120°C (right) along with the spatial profile of the Ca/Si ratio; 'c' is calcite and 'a' is aragonite

5.5 Implications of temperature on real CO₂ storage wells

5.5.1 Imprinting of the microstructure and pore structure to the power law

The previous analysis indicated the importance of temperature on the diffusion mechanism of carbonated brine to class G cement grout with a specified composition. The change in temperature appeared to vary the diffusion rate of CO_2 by altering the composition and microstructure of cement. The application of the square root law reflected those alterations, and was therefore indirectly connected to the polymorph type of calcium carbonate. It was assumed that in order for the power law to apply (with the power less than 1), the polymorph should have been in the most stable form like calcite. This assumption is valid since the more stable the form is, the slower the rate of dissociation and thus the rate of carbonation reactions will also decline.

As the microstructure changed with temperature, it was made clear that the pore structure would also change. Since the pores allow access of the external species (N2, CO2) the pore structure is likely to determine the power law and thus the diffusion regime (Knudsen or Fickian). In other words the equation that governs the evolution and shape of the carbonation front is a representation of both the microstructure of cement and the available space for diffusion.

5.5.2 Diffusion in real wells and time for carbonation

In general the lower carbonation depths of CO120 were attributed to the decreasing rate of carbonation owing to the decreasing solubility of CO₂ in water as temperature increases [Bertos *et al*, 2004]. In fact temperature has been documented to play a greater role for the carbonation of cement than the pH of the fluids [Duguid *et al*, 2010]. From the perspective of the current study, the evolution of the carbonation depth and the CO₂ diffusion regime (Knudsen) is most likely to depend solely on any modification that occurs in the cement structure due to temperature. Despite the acidity/ alkalinity of the surrounding fluids, the cement will experience such carbonation depths and diffusion regimes as the pore structure enables.

Changes in temperature did not only influence the fluid composition, but also the microstructure of cement for the given set of curing conditions (T, P, and curing solution - see Chapter 3). The curing conditions (T, P) were found to change this microstructure and to affect the shape of the carbonation front. For example for low curing T, P conditions the subsequent carbonation front was ill defined [Kutchko *et al*, 2007], as in the case of CO60/1. This was thought to be the reason of the deviation from the widely applied \sqrt{t} -law (See: Section 4.4.1). The definitive observation of the carbonation front is quite important for bottom-hole cements since: (1) it represents fast response of the grouts to carbonation and (2) a decreasing rate of carbonation according to the \sqrt{t} -law.

The characterization of the carbonation front at CO60/1 and CO60/5 as ill defined was attributed at the surrounding brine and the diffusion mechanism within the pore structure. The saturated conditions with respect to the carbonated brine seemed to delay the carbonation of the C-S-H, since the carbonated species had to diffuse firstly through the water layer around the C-S-H particles. Regarding the diffusion mechanism at 60°C, the existence of the aragonite crystals ahead of the main carbonation front followed the pattern in Figure 5.13; the flow in air voids is advective leads to aragonite precipitation (see Figure 4.37) while in the cement gel the flow is governed by pure diffusion. This diffusion will be feasible only if substantial part of the main carbonation front is dissolved and new C-S-H phases are revealed for carbonation leading primarily to calcite and secondarily to aragonite and vaterite within the cement gel.

The low proportionality constant at high pressure observed by Kutchko *et al.*, (2007) was justified by the high pressure (303 bar) at 50°C. Increasing pressure of course leads to increase in the solubility of a gas in a liquid [Carvalho *et al.*, 2015; Pistone 2011]. This case referred previously to unsaturated conditions for the environment of the cement, *i.e.* relative humidities (RH) less than 100% [Fardis *et al.*, 1992]. In the present study the cement was surrounded constantly by brine and thus the relative humidity was said to be 100%. Even though in the present study pressure was constant at 80 bar, the increase in pressure was assumed to saturate the surface of the sample with CO_2 and thus to generate a shielding effect from the CO_2 in the bulk solution [Nam *et al.*, 2003].

Assuming that the carbonation reactions took place only through the cement matrix, as observed in previous studies of a similar nature (Kutchko *et al*, 2008), then the crucial parameter for guaranteeing the long term stability of the injected CO_2 is the time needed for full carbonation of a specified length of cement (see Appendix 3). The calculated estimates should be coupled with the mechanism of the physical trapping (hydrodynamic or stratigraphic) in order to predict if the storage security is low or high [IPCC, 2005]. Assuming

lateral migration of the CO₂ plume into the host rocks of the reservoir then the previous time scales $(10^3 - 10^5 \text{ years})$ might allow for primarily ionic and subsequent mineral trapping. Those times in fact will depend on several assumptions like Fickian diffusion and that no fracture will occur at the cement during the operation of the CO₂ injection well. In fact merely the deviation from the first assumption could introduce significant errors in the times for full carbonation. Due to fact that the cementitious grout will experience continuous interactions with the subterranean fluids, streams that would decalcify parts of cement above the main carbonation front (Figure 5.17), would ultimately lead to low buffering capacity of the effluent HCO₃.



Figure 5.17 (A) CO₂ leakage pathways after Gasda *et al.* [2004] and area of interest showing the profiles of the carbonated regions for wells at: (B) 60°C and (C) 120°C.

The times for full carbonation for given lengths of cement presented in Table Ap. 3.1 were found to be temperature-dependent. These times were related to the evolution of the carbonation front and the specific mode of diffusion, which was represented by the history of the carbonation reaction in the carbonated region. Two examples in Figure 5.17depicted the

correlation of the history of the carbonation reactions with the evolution of the carbonation depth over time.

On the one hand, the longer time of a class G cement grout at 120°C to be fully carbonated up to 1m (Figure 5.17-C) could perhaps be controlled (at 120°C) by the enhanced silicate polymerization of the carbonated region leading to slower diffusion rates. On the other hand, at 60°C the faster reactions showed a deviation from the Fickian behaviour indicating other types of diffusion that leave behind relics of old carbonation fronts. The analysis of the pore network parameters (Chapter 6) was imperative for understanding the actual mechanism of carbonation through deciphering the tortuous pathways that are critical for the carbonation reactions.

5.6 Summary

In Chapter 5 the main target was the analysis of spatial and temporal evolution of the carbonation front for class G oilwell cement grouts at 60°C and 120°C at a constant pressure 80 bar. The spatial profile of the carbonation front seemed to be independent from the local compositional heterogeneities of the grout. The samples examined by XRCT showed two clearly defined areas (inner core and carbonated region) for any duration, that were separated by a sharp carbonation front.

A clear definition of the carbonation depth was given based on the detection of the carbonation front from grey value histograms as calculated from X-ray reconstructed images. A reliable technique for detecting the asymmetry of the carbonation depth from the geometry of the samples was generated. This technique was extended to real CO_2 injection wells with the asymmetry of the carbonation depth to be a crucial issue for undermining the consolidation of the well. The time evolution of the carbonation depth was found to follow a power law equation that reflected the rate of diffusion for each temperature. The power law

(with power >1) showed higher rate of diffusion at 60°C, which was reflected by faster local supersaturation conditions in the pores (with respect to Ca^{2+} and HCO_3^{-}) justifying the growth of aragonite crystals. On the other hand, at 120°C the slower rate of diffusion (power < 1) was reflected by the growth of calcite.

Finally, the rate and type of diffusion (at 60°C and 120°C) was found to determine the time needed for full carbonation of a specific length of grout, with increasing temperature to allow for longer times for carbonation. This is perhaps due to an increase in Fickian diffusion (as opposed to Knudsen) as the pore volume and mean diameter increase. Based on the dependence of the carbonation depth on the square root of time, the calculated times for full carbonation were found to allow for efficient CO_2 storage.

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6 Time-evolution of the pore network parameters of class G cement grouts and the effect of temperature

6.1 Introduction

The scope of this chapter is to study the alterations of the pore structure of class G oil well cement grouts after exposure to various elevated temperature and pressure conditions, and in the presence of N_2 or CO_2 gases. Changes in the effective porosity and the critical parameters of the pore network were reflected by the compositional profiles of the grouts and thus it was necessary to identify the critical pore pathways for CO_2 diffusion. This gave the two different trends for the carbonation depth versus time previously observed and described at Chapter 5. These pathways had specific geometries (slit, cylindrical) and connectivities (throats, cavities) that appeared to control the permeability of the grouts to carbonated fluids.

Table 6.1 gives all the analytical tools used for the characterization of the pore structure. He pycnometry was attained for the same fragments as in the case of MIP but with larger size in comparison to the N_2 sorption. The first technique was used to calculate the apparent- open porosity and not the effective and closed porosity. The lack of any deformation pressures during the pycnometric analysis made this technique the best method for the extraction of the real open porosity. MIP was deduced to be not representative for the open porosity, but a valuable tool for finding the critical entrances in the different levels of organization of cement hydrates. The MIP results were not taken to be the absolute representation of the Hg behaviour, particularly during the extrusion, and thus a correction method was used to correct for hysteresis phenomena.

Regarding N_2 sorption, the acquired information was the isotherms of adsorption and desorption of N_2 . From the processing of those isotherms the pore size distribution, the specific surface area and the micropore volumes were extracted. This method was used in integration with the throats taken from MIP so as to find the critical pathways for decalcification and carbonation.

Analytical technique	Location of the sample	State of the sample	Information from each technique
He pycnometry		Solid	Apparent porosity
MIP	 Random position (N60/ N120) Carbonated/ Inner regions 	Solid Pore throats Ink-bottle pores	
N ₂ sorption	(CO60/ CO120)	Fragments	Pore size distribution Surface area Cavitation
SAXS	Carbonated/ Inner regions (CO120)	Powder	Intensity profiles versus scattering vector

Table 6.1 Analytical techniques used for deciphering the pore network parameters

Regarding permeability three different methods were applied both experimentally and theoretically from the intrusion volumes of Hg and the critical throats (Table 6.2). The first method, namely micropermeametry was implemented using a portable permeameter for a fast tracking of intrinsic permeability. This method which has been already used in field permeability measurements in rocks proved the suitability of the tested samples for sealing CO₂ geological wells setting an upper limit for class G cements. The simulated method using PoreXpert, was proved useful for differentiation of the various permeability areas of cement showing that the cement gel and the capillary space could be organized separately in ordered networks allowing specific types of diffusion between them. Finally the method proposed by Katz and Thompson, although initially applied for rocks based on conductivity measurements, in fact under specific realistic assumption was able to give a rational range of permeabilities based solely on an interconnected pathway with size close to the critical throat.

Method for permeability measurement	State of the sample	Type of technique	
Micropermeametry	Solid	Experimental	
PoreXpert	Fragments	Simulation	
Katz- Thompson	Fragments	Modelling	

 Table 6.2 Summary of the methods used for the calculation of permeability

6.2 Impact of temperature and time (CO₂ free brine)

6.2.1 Apparent porosity and Ca leaching

The skeletal density and apparent porosity of the N₂ treated samples, as measured by He pycnometry and Hg porosimetry, are shown in Table 6.3. In general, for each sample the skeletal density as measured by He pycnometry was higher than that measured by Hg porosimetry. This is due to the accessibility of He into pores less than 3nm, which is the minimum size accessible to Hg at 60,000psia when θ =130° and γ = 0.485 N/m (25°C). However, Hg porosimetry not only underestimates the true skeletal density, but also can lead to overestimates due to the probable compression of the pore walls [Olson *et al.*, 1997] or revelation of closed pores from the high compressive pressures of the high pressures from Hg intrusion (N₂ treated sample, 60°C, 5 months). For this reason, the skeletal density and apparent porosity in the current chapter will be referred to those measured by He pycnometry unless stated otherwise.

Nevertheless, these fractures appeared to be only on the surface and not throughout the whole mass of the sub-sample, as this would have caused splitting of the sample which was not observed. The presence of those fractures was proved to have no impact on the intrusion curves and thus not to induce changes on the critical pore network parameters (*e.g.* critical throats, Section 6.2.2). The reason of fracturing at 60°C and not at 120°C could have been the thinner pore walls at 60°C did not sustain the high pressures and have been partially collapsed. The localized thinning of the pore walls was confirmed later in this chapter from

the isotherm analysis and besides it was testified as one of the major causes for damage of the cement's microstructure [Willis *et al.*, 1998].

	Bulk densities* (g/cm ³)	Skeletal (apparent) densities		He porosity	MIP porosity	Porosity undetected		
		(g/cm ³)		(%)	(%)	by MIP(%)		
	MIP	He	MIP					
<u>N60**</u>								
Unreacted	1.53±0.06	2.31±0.29	2.04±0.18	33.9±0.9	24.7±3.1	+2.9/ +15.5		
1 month	$1.54{\pm}0.02$	2.22±0.14	2.14±0.06	31.0±2.5	28.1±0.9	+1.4/ +4.43		
5 months	1.53±0.004	2.15±0.30	2.41±0.39	28.8±2.0	28.1±1.7	-2.2/+3.6		
N120**								
1 month	1.36 ± 0.03	2.44±0.16	2.33±0.06	44.1±1.0	40.1±0.86	+3.1/+4.9		
3 months	1.40 ± 0.02	2.38±0.05	2.26±0.05	41.1±0.7	37.9±0.95	+2.3/+4.2		

Table 6.3 Bulk and skeletal densities, and, porosity measured He pycnometry and Hg porosimetry for the N_2 treated samples

{Notes: (1)*,at 0.55 psia; (2)**, see Chapter 3.3.1, (3) the uncertainties of the values were reflected to the standard errors}

Regarding the compressibility of the sub-samples by Hg intrusion up to 60,000 psia, it was noteworthy the generation of fractures in the NS60 and not at NS120 (Figure 6.1).



Figure 6.1 (**A**) Fracturing of a NS60/5 due to the Hg intrusion; (**B**) Resistance to fracturing due to Hg intrusion of NS120/1

In the present study no measurements for the compression of the sub-samples were done. However, it was assumed that the compressibility of the sub-samples to be less than the compressibility of the Hg [Cebeci, 1977], and thus no changes to the bulk-envelope volumes were concluded to have happened due to the high pressures of Hg (NS60, Table 6.3). The decreased values of bulk densities for the NS120 were justified owning to the increase in apparent porosity due to Ca leaching.

Another indication of the durability of the sub-samples at the high pressures was reflected to the porosity which was not detected by MIP but was accessed by He (Table 6.3). If the pore network of the pieces had experienced extensive degradation by the high pressures of Hg, then most of the values of the undetected porosity would have had a negative sign, *i.e.* $\Delta(porosity_{He} - porosity_{MIP}) < 0$; however this applies only for N60/5. Each value of the undetected porosity was calculated by subtracting the lowest value of $porosity_{MIP}$ from the maximum value of $porosity_{He}$ (maximum Δ) and the maximum value of $porosity_{MIP}$ from the minimum value of $porosity_{He}$ (minimum Δ).

Recalling the continuous Ca loss (Chapter 4) from the NS60 and NS120, the samples at both temperatures would be expected to become more porous in time. This is validated, only for the NS120, where the apparent porosity increased from 33.9% (before treatment) to 41.1% (NS120/3), with a maximum apparent porosity for the NS120/1 equal to 44.1% (Table 6.3). The correlations of the alterations of the apparent porosity with the microstructural causes at 120°C are shown at Table 6.4. The increasing/decreasing trends of the apparent porosity for the NS120/1 and NS120/3 have been assigned due to the statistical independence of the values of apparent porosities at Table 6.3.

Evolution of the apparent porosity and microstructural causes for N120							
Period (months)	Apparent porosity		Causes				
0→1	Increases	1.	Portlandite depletion (widening of				
			capillary pores, <i>i.e.</i> 10 nm- 50 nm)				
		2.	Generation of gel porosity from C-S-H				
			decalcification				
		3.	Chemical shrinkage of C-S-H				
1-3	Decreases	1.	Chemical expansion of the silicate gel				
			(expansion smaller than the shrinkage)				
		2.	Precipitation in throats and cavities				

Table 6.4 Correlations between the evolution of the apparent porosity and the microstructural alterations for the N120

It must be mentioned that the generation of gel porosity due to C-S-H decalcification (described in point 2 in the period $0 \rightarrow 1$ month, Table 6.4) could have been a real fact although less probable than points 1 and 3. The main cause for the gel porosity generation was assumed to be the defects of the silicate sheets that inhibited the sheets to obtain a denser packing after their decalcification (Figure 6.2).

The case of C-S-H decalcification for the N120 samples should not be confused with the carbonation of the C-S-H. During decalcification the silicate matrix is free from the bonding of interlayer or intralayer Ca and thus has more degrees of freedom so as to adjust to the space restrictions. On the other hand the carbonated silica gel must be denser than the decalcified gel due to the precipitation of calcium carbonate within the C-S-H structure. This hypothesis was confirmed by the BJH pore size distributions of N120 (Figure 6.8) and CO120 (Figure 6.24). For CO120 it will be seen that gel pores were blocked in the carbonated regions, whereas for N120 the gel pores increased their number.



Figure 6.2 Upper: Ideal collapse of the interlayer space due to decalcification of the cement gel (the silicate tetrahedra are omitted from the collapsed interlayer). Lower: the basic mechanism proposed for the generation of gel pores due to the inability of the paired tetrahedra to bond each other

As opposed to the increase in the apparent porosity induced by the Ca leaching, the NS60 appeared to become less porous during time (Table 6.3). At 60°C, taking into consideration that portlandite is still present after 5 months, and assuming that part of the leached Ca originates from the decalcified C-S-H particles, the main causes of the decrease of the apparent porosity would therefore be: (1) increased dissolution in cavities followed by throat blocking (generation of closed pores) or (2) preservation of the throats with irreversible expansion of the decalcified silicate **gel** (increase in cement gel porosity).

It is important to state that, within their error limits, the values of the apparent porosities of N60 appeared to overlap partially from 1 month (27.5%-33.5%) to 5 months (26.8%-30.8). Thus the blocking of the open porosity seemed to have happened in particular regions in the examined sub-samples, with other regions to possess the same apparent

porosity in the course of time. The current notice did not negate the microstructural causes for the N60, but suggested higher degree of microstructural heterogeneities for the N60 than at N120.

Furthermore, it is crucial to state that the conclusions for the N60 would have been changed if the Hg porosity was taken into consideration (Table 6.3). In that case the blocking of the open porosity would have erroneously been replaced by the continuous widening of the open pore space (statistical independence of the MIP porosities for N60 and unreacted grout sample). This example demonstrated that the type of method of measurement of the apparent porosity could lead to false observations if only a part of the porosity is measured, *i.e.* greater than 3 nm

It is noteworthy that at 60°C and 120°C, the leached Ca increased within the same order of magnitude (+132%, +206%) with blocking and widening of the apparent pore volume correspondingly. Since portlandite has been fully dissociated at 120°C, while at 60°C it is still present, it is logical to assume that the pores, that control the flow rate of pore fluids carrying dissolved Ca from the C-S-H gel, have been widened or increased their pore volume at 120°C and not at 60°C.

6.2.2 Analysis of Hg intrusion/ extrusion curves

The intrusion - extrusion curves for the N60 and N120 are shown at Figure 6.3. The curves were found to be reproducible with a maximum standard error of 2% for the total Hg intruded /retained volumes (Table 6.5) and identical critical throats (Appendix 2). Furthermore, the entire cumulative intrusion/ extrusion curves for each sample were found to coincide from piece to piece (*e.g.* N120/3, Figure 6.4) validating the uniformity of the pore network across the mass of the whole sample.



Figure 6.3 Hg porosimetry intrusion and extrusion curves vs. pore access diameter for the N60 and N120; The points and lines are both experimental data, with the points to have been used for reasons of clarity.



Figure 6.4 Example of the reproducibility of the MIP analysis for three different sub-samples for N120/3; (A) Intrusion/ extrusion curves, (B) Throat size distributions

It must be stated that the intrusion-extrusion curves in Figure 6.3 are transformations of the original intrusion-extrusion curves for each sample (Appendix 2), and take into consideration the variation of the product $\gamma_m \cos \theta$ with respect to the pore access diameter after applying the Kloubek correction for contact angle hysteresis (Chapter 3.4.7.3). The intrusion curves appeared to be the same irrespectively of the Kloubek correction (Section 3.4.7.3). This can be explained from the analysis of the intrusion of Hg for each intrusion step; the flow of Hg depends merely on the size of the throats of the solid and thus the product $\gamma_m \cos \theta$ can be assumed to be constant from fragment to fragment for the same N₂ treated sample.

Since each intrusion curve for each sample was identical before and after the Kloubek corrections, the threshold and critical throats were also found to be unchanged. Even though several definitions of the threshold diameter have been given [Cahyadi *et al*, 2003], in the present study the pore access size from which the intruded volume of Hg starts to increase monotonically with the applied pressure is defined as the threshold diameter [Beazi-Katsioti *et al.*, 2009]. In most cases it was found that this point corresponds to Hg intrusion not more than 2% of the apparent porosity and approximately around 5% of the total intruded volume.

	Total Volume	Total Hg	Relative	Total Hg	Retention			
	of Adsorbed	Volume	difference in	Volume	Factor,			
	\mathbf{N}_2	Intrusion	volumes*	Not retracted	R **			
	(cm ³ /g)***	(cm^3/g)	(%)	(cm^3/g)				
<u>N60</u>								
Unreacted	0.103	0.181±0.034	+75.5	0.104 ± 0.011	0.573			
1 month	0.118	0.186±0.007	+58.2	0.117 ± 0.004	0.627			
5 months	0.177	0.182±0.022	+2.8	0.152 ± 0.030	0.837			
<u>N120</u>								
1 month	0.202	0.288±0.018	+42.64	0.127 ± 0.008	0.440			
3 months	0.181	0.270±0.006	+48.81	0.106	0.393			
$\{*, \frac{\Delta(V_{Hg}^{TOTAL} - V_{N_2}^{TOTAL})}{V_{Hg}^{TOTAL}}; **, \mathbf{R} = \frac{V_{extrusion}}{V_{intrusion}}; ***, \text{ at } \mathbf{P}/\mathbf{P}^{\circ} \approx 1\}$								

Table 6.5 Hg retention factor for the N60 and N120; the volumes of adsorbed N_2 are also compared to the intruded volumes of Hg.

For the N120 the threshold throat was found to remain the same as the unreacted grout sample at approximately 40 nm (Figure 6.3), while for the N60 the threshold throat was found to decrease to 16 nm irrespective of time. This was a first indication that throat blocking might have occurred at 60°C, since the impact of equilibration time has been shown to be negligible in the samples of the current study (Section 3.4.6). The throat blocking was assigned primarily to the precipitation of Ca-bearing phases (*e.g.* re-calcified C-S-H); the contribution of other elements like Cl⁻ or Na⁺ from the brine was assumed to be negligible as their concentration in the solid was less than 2% (Chapter 4).

This throat blocking for N60 was further validated from the existence of cavitation phenomenon observed at the BJH desorption pore size distributions for N60 and not N120 (Section 6.2.3, Figure 6.8 B). In contrast to the threshold diameter, the critical throat was found to be widened from the unreacted grout sample (4 nm) to the N60 (8 nm-4 nm) and finally to the N120 (12 nm; Figure 6.5). Since the critical throat has been assigned to control the permeability of cement pastes, it was anticipated that the N120 to allow for faster diffusion of Ca than the N60, without inhibition by the smaller throats of N60 (Section 6.2.4).

Within the errors of the high pressure part, the previous values of the critical throats were found to be statistically dependent between the N60 and N120. Taking into consideration that the error is ± 2 nm (quoted by the manufacturer of the pressure transducer) for each value, then the critical throat of N60/5 could resemble to those of N120/1 and N120/3. Despite this closeness of the critical throats for the two temperatures, the critical throats at 120°C were deduced to be in reality distinct than those at 60°C. This conclusion was based on the evidence of decreased Hg retention factors for N120 (Table 6.5) and furthermore on the lack of a pore size where cavitation has occurred (Section 6.2.3).



Figure 6.5 Throat size distributions from MIP for the N60 and N120; The points and lines are both experimental data, with the points to have been used for reasons of clarity.

The extrusion, being ideally –without hysteresis- the reversible process from intrusion, requires the retraction of Hg not only from cavities and capillary pores (>10 nm), but also from the Hg attached at the pore walls. The attachment of Hg, could be either due to structural traps like ink-bottle pores or cavities across the pore walls, and thus depends on the inherent structure of the pore walls like chemistry and roughness [Rigby *et al.*, 2009] and it requires additional energy (lower pressures) to be removed.

This additional energy can be assigned to the tension applied to the receding meniscus due to the attached Hg to the pore walls. In fact, the "attachment" refers to the high pore potential of the intruded Hg due to high interfacial energy in confined spaces [Shields *et al.*, 1982]. The tension at the interface of Hg, pore wall and empty pore space was not accounted by Washburn but was addressed after the corrections of Kloubek (1981) using "controlled pore" diameters as measured by means of electron microscopy and Hg porosimetry and correlating each of these diameters to the corresponding changes to γ_m and $\cos \theta$. The pore network for N120 appeared to be controlled by throats of critical size around 12 nm for both 1 and 3 month(s) (Figure 6.5). This size, according to the colloidal model proposed by Jennings (2009), corresponds to the upper limit of large gel pores (3 nm-12 nm), and thus for N120, the Ca leaching was said to be controlled by the percolation pathways among the C-S-H particles. This upper limit resembles to the concept of the threshold value from the percolation theory (not to be confused with the threshold diameter) [Bentz *at al.*, 1992], where the throats of N120 appeared to have created a continuous network where all the C-S-H particles to have access to the external fluids through the critical throat of 12 nm.

Furthermore, with reference again to the N120 sample, below 12 nm and above 3 nm no shielding of larger pores by small throats can be inferred at 120°C, after having proved that Hg extrusion is reversible in between 3-12 nm following the same path as the intrusion (Figure 6.3). Therefore, the Ca dissociation from the C-S-H sheets takes place progressively, with a decreasing throat size as Hg intrudes into the cement gel. The deviation of the extrusion curve from the intrusion path was assigned to reasons other than ink-bottle phenomena for the N120. Those reasons have been identified also by Moro *et al.*, 2002 and in this study are highly proposed the pore wall defects, dead-end pores and leftover Hg across the pores due to gradual breakage of the menisci of the fully Hg-saturated sub-sample.

For the N60 sample, as depicted at Figure 6.3, the Hg extrusion curve did not match the intrusion curve for any of the throat sizes. That mismatch suggested a pore network where the entrapment of Hg was due to real structural heterogeneities, *i.e.* bigger cavities and smaller throats.

6.2.3 Nitrogen sorption isotherm analysis

All of the N₂ treated samples exhibited a type IV isotherm, indicative of a pore network consisting primarily of mesopores (2-50 nm) (Figure 6.6 and Figure 6.7). In brief, during adsorption, the initial formation of a monolayer, $P/P^{\circ} \in (0, 0.04)$, was followed by multilayer adsorption, $P/P^{\circ} \in (0.04, 0.4)$, and then capillary condensation occurred for $P/P^{\circ} \in (0.4, 1)$ [Aligizaki, 2006]. During desorption, the observed hysteresis with reference to the increased adsorbed N₂ volume for each P/P° , from $P/P^{\circ} \approx 1$ to $P/P^{\circ} \approx 0.5$, exhibited a steep drop from $P/P^{\circ} \approx 0.5$ to $P/P^{\circ} \approx 0.45$ and then followed the same path with adsorption below $P/P^{\circ} \approx 0.45$. The total N₂ adsorbed volumes for the N120 were found to be increased in contrast to the same volumes of the N60°C (Figure 6.6); a fact which was consistent to the greater Ca leaching at 120°C. The values of final P/P^{\circ} for N60 and N120 are given at Table 6.6.

Table 6.6 Relative pressures at the saturation point for N₂ adsorption of N60 and N120

Sample	Unreacted	N60/1	N60/5	N120/1	N120/3
P/P°	0.9970	0.9919	0.9869	0.9947	0.9938



Figure 6.6 N_2 sorption isotherms for N60/1 and N60/5 ("ads." stands for adsorption and "des." stands for desorption)



Figure 6.7 N_2 sorption isotherms for N120/1 and N120/3 ("ads." stands for adsorption and "des." stands for desorption)

The isotherm of N60/1 was almost similar to the unreacted sample grout (Figure 6.6) with a partial blocking of the initial cement gel pores (<12 nm) and the onset of dissolution mainly from the cavities with critical size around 50 nm (Figure 6.8). The N60/5 was characterized by increased volumes of both gel pores (3-12 nm) and medium capillaries (12-50 nm) (Figure 6.8 A), with the modal cavity to have been preserved at 50 nm (Figure 6.6). The hypothesis of throat blocking with dissolution in cavities stated in section 6.2.1 is verified, but with the critical throat to widen in time from 3 nm to 7 nm.

The above analysis for the N60 seemed to lead to continuous degradation of the grout after 5 months, increasing the volume of the modal cavities, generating new gel pores and widen the critical throat. On the other hand, even though the apparent porosity increased with time at 120°C, the size of the modal cavity after 1 month and 3 months decreased to approximately 20 nm with partial blocking of the capillary pores up to 50 nm (Figure 6.8 A). The size of 20 nm resembles the critical throat at 1 and 3 month(s) around 12 nm (Figure 6.5) and could potentially justify the decrease of the retention factor of Hg from approximately 0.6 to 0.4 (Table 6.5).



Figure 6.8 BJH pore size distributions for the adsorption (A) and desorption (B) isotherms regarding N60 and N120
Both N60 and N120 showed an increase in specific surface area after 5 and 3 months relatively to the unreacted grout sample (Table 6.7). The main reason of this increase is most likely the mass loss due to decalcification of the cement particles (mainly C-S-H phases) and Ca leaching to the surrounding brine.

Table 6.7 Specific (BET) surface areas and micropore volumes with the equivalent areas for

 N60 and N120

	SSA _{BET}	C _{BET}	Micropore	Micropore SSA*
			Volume	
	(m^2/g)		(cm^3/g)	(m^2/g)
		<u>N60</u>	<u>)</u>	
Unreacted	44.0±0.09	78.0	0.017175±0.000029	34.8
1 month	38.4±0.02	78.0	0.015006 ± 0.000048	28.2
5 months	73.7±0.04	79.1	0.028452±0.000018	60.0
		<u>N12</u>	<u>0</u>	
1 month	73.9±0.03	86.0	0.031665±0.000057	65.0
3 months	66.1±0.04	66.5	0.034348±0.000049	65.5

Notes: *, Specific Surface Area for micropores from Dubinin-Astakhov

Regarding N60/1, the blocking of gel pores and reduction of the overall apparent porosity seemed to have caused the reduction in SSA_{BET} by 12% relatively to the unreacted grout sample (Table 6.7). The increase of the specific surface area for N60/5 by 67.5% with further decrease of the apparent porosity by 7% (Table 6.3) implies either the creation of new pores smaller than the pores of the initial grout sample or the increase in the roughness of the pore walls. The first observation is, in fact, validated after the increased volume of N₂ adsorbed for every P/P^o for the N₂ treated sample after 5 months (Figure 6.6). Regarding the pore walls, these seem to have retained their initial roughness, having surface fractal dimension $D_f = 2.04 \pm 0.02$.

The N120 appeared to have increased surface area when the apparent porosity increases, after 1 month, and to be characterized by reduced surface area when the apparent porosity decreases after 3 months (Table 6.7). In fact the N₂ treated samples at 120°C appeared to have obtained surface fractal dimensions $D_f = 2.16 \pm 0.05$, implying that the decalcification of cement gel resulted in pore walls with increased number of defects, in contrast to the N60, which is consistent with the increased micropore volumes (Table 6.7).

6.2.4 Permeability and pore connectivity

The permeability values as measured experimentally, and as calculated from the Katz-Thompson model and PoreXpert are listed at Table 6.8. In general, the values of the table differ by three orders of magnitude, from 10^{-2} to 10^{-5} mD. Irrespective of the calculation method, the N120 were more permeable than N60. The permeability for the N₂ treated samples refers primarily to the transport of Ca²⁺ and less to the transport of other species like OH⁻, Na⁺, Cl⁻, and thus Table 6.8 gives the permeability of the cement pastes as far as the Ca leaching is concerned.

	k _{exp}		$k_{Katz-Thompson}$		k _{PoreXpert}	
			(mD)			
		C=1/89	C=1/226	3-11 nm	11-40 nm	
		<u>N₂ system</u>	<u>s, 60°C</u>			
Unreacted	$(7.1\pm0.5) \times 10^{-2}$	2.4×10^{-4}	9.56E-05	3.52E-03	0.0137	
1 month	$(7.2\pm0.5)\times10^{-2}$	1.4×10^{-4}	1.53E-05	5.64E-03	0.0054	
5 months	$(7.6\pm0.7)\times10^{-2}$	8.7×10^{-5}	3.44E-05	6.49E-03	0.0017	
		<u>N₂ systems</u>	s <u>, 120°C</u>			
1 month	$(7.6\pm0.7)\times10^{-2}$	3.1×10^{-4}	1.21E-04	3.74E-03	0.0141	
3 months	$(7.9\pm0.7) \times 10^{-2}$	2.9×10^{-4}	1.14e-04	4.63E-03	0.0138	

Table 6.8 Experimental, calculated and simulated intrinsic permeabilities for N60, N120

The experimental permeabilities were always greater than the calculated ones, owing to the limitation of the pressure transducer to measure pressures at flow rates lower than $0.5 \text{ cm}^3/\text{min}$. According to the values of k_{exp} (Table 6.8), the N60 appeared to become more permeable over time (despite the blocking of the apparent porosity and the reduction of the critical diameter) but less permeable than N120. However, due to the abovementioned limitation for pressure measurement, the previous trends should be treated with caution and only with comparisons with other experimental or simulated techniques.

The N₂ treated samples at 60°C were less permeable than at 120°C when the permeabilities were calculated by means of the Katz-Thompson model. The calculated permeabilities are shown in Table 6.8; the only parameter that has changed was the constant c of the Katz-Thompson equation. The constant c, expresses the ratio $\left(\frac{\sigma}{\sigma_0}\right) / \left(\frac{k}{d_c^2}\right)$ *i.e.* the ratio of the electrical conductivity of the cement normalized with respect to the electrical conductivity of the fluid, versus the intrinsic permeability k of a pore network with critical throat d_c . In fact the constant c, would have required the independent measurement of the σ/σ_0 and k. Nevertheless an indirect calculation of permeability was done based on data acquired by mercury intrusion porosimetry. The conclusion of decreasing permeability at 60°C in time, in contrast to the 120°C, was independent of the value of the constant c (Table 6.8); the increased permeabilities after increasing the c value, can be justified due to the inclusion of the calculated permeabilities of other factors of the pore network e.g. the more elongated and open pore network at low c values.

Regarding the permeabilities calculated from PoreXpert the cement pastes were more permeable at 120°C in the course of time with decreasing permeability at 60°C. Due to inherent limitations of the software to represent accurately the throat distributions from mercury intrusion porosimetry the intrusion data used as the input to the software were divided from the threshold diameter to approximately 11 nm and then from 11 nm to 3 nm (Table 6.8). An example (which similarly applies to all the N_2 treated samples) for the justification of the choice of the simulated permeabilities (Table 6.8) is presented below from the analysis of the throat-pore size distributions (Figure 6.9 and Figure 6.10). Before acquiring the values of permeabilities the throat and pore size distributions were tested if they matched with the experimental data from MIP and N_2 sorption. The simulated and experimental distributions of pore throats (Figure 6.9) appeared to have the same shape and within the errors included in the distributions from the pressure measurement of the porosimeter (± 2 nm) the experimental distribution.

The corresponding pore size distributions for each throat distribution were for all the samples similar in shape to the BJH pore size distributions (Figure 6.10). The modal size of the simulated cavities was equal to the modal size from the BJH adsorption pore size distribution when the pores were fully open at both ends (F=1). This equality was assigned to the lack of functionality within PoreXpert to represent dead-end pores and thus to the continuous (fully opened at both ends) simulated pore network. Here F is defined as the fraction of the total connected pores through which a particle can enter from one side and exit from another different site without it's inhibition from a dead end pore.



Figure 6.9 Comparison of the experimental (MIP) and simulated (PoreXpert) throat size distributions for the unreacted grout sample the corresponding models for each increment for the simulated distributions are given in Figure 6.11



Figure 6.10 Comparison of the experimental (N_2 adsorption) and simulated (PoreXpert) pore size distributions for the unreacted grout sample; the corresponding models for each increment for the simulated distributions are given in Figure 6.11

Based on the good correspondence of the simulated and experimental distributions (Figure 6.9 and Figure 6.10), the simulated values of permeability were concluded to be realistic and representative of the actual pore network. For each sample two pore network models have been generated based on the large centre zone model of PoreXpert. All the other options of models were found to give distributions entirely deviant from the experimental ones. In general the pore networks above 11 nm had greater permeabilities than the networks below 11 nm. Since at 120°C the big pores are not shielded by the smallest and at 60°C the cavitation phenomenon is dominant the pore network models presented at Figure 6.11 were proposed.



Figure 6.11 Proposed arrangement of the simulated pore networks for N60 and N120

For the sake of calculating the overall simulated permeabilities the electrical analogue was implemented using the Ohm's law, where the difference in pressure was assigned to the voltage gradient ($\Delta p \rightarrow \Delta V$), the flow through the cement was represented by the current (q = i) and finally the reciprocal of resistance of cement to Ca diffusion, namely k, was assigned to the electrical resistance (1/k = R). In other words 1/k represents the resistance of the solid cement, and not the ease of diffusion through the pore space expressed by k.

Two major modes of Ca leaching have been suggested based on the structure of Figure 6.11 that are illustrated at Figure 6.12. The case I refers to the Ca leaching mainly from a cement sample in the laboratory scale when it is surrounded by the brine (Figure 6.12). In this case the permeabilities are added as follows $R_{TOTAL} = R_1 + R_2 = 1/k_1 + 1/k_2$. The case II corresponds to the case in which the cement is confined from the casing and the surrounding rocks, and the Ca diffuses mainly through Area 2 from the upper cement layers towards the brine. In case II the permeabilities are added as follows $R_{TOTAL} = 1/R_1 + 1/R_2 = 1/R_1 + 1/R_1 + 1/R_2 = 1/R_1$

The N60/5 appeared to have greater resistance to further Ca leaching than N120/ 3. From Figure 6.11 the appropriate mechanism for Ca leaching at 60°C is case I (Figure 6.12), and at 120°C is case II (Figure 6.12). The implications of the two different regimes of Ca leaching are not depended merely on temperature but also on the time that mediates until the CO_2 injection takes place. It seemed that at 60°C the grout can better seal the outer area at longer times than at 120°C, before the CO_2 operation to initiate, and thus to prevent the generation of pathways in the cement-casing and cement-rock interfaces.

On the other hand at 120°C, class G cement grouts were found to be less resistant at the outer area to Ca leaching, and thus it is essential for the CO_2 injection not to be delayed so as the Ca loss from the grout not to allow extensive de-bonding from the casing and thus to create continuous paths for CO_2 leakage.



Figure 6.12 Scenarios of Ca leaching for N60 and N120 based on the models proposed in Figure 6.11

6.2.5 Conclusions: Pore network effects on the Ca diffusion/leaching

The N₂ treated samples were found to be more permeable regarding the transport of Ca at 120°C than at 60°C. This transport was found to be controlled not only by the activation energy of the Ca leaching process but also by the hierarchy of pore network at the two temperatures. On the one hand, the activation energies ($E_A^{120^{\circ}C} = 12 \ kJ$, $E_A^{60^{\circ}C} = 17 \ kJ$) indicated the ease of Ca to be dissociated from the cement particles at 120°C rather at 60°C. On the other hand, from the previous analysis, it was found that these two energies led to two distinct leaching mechanisms (Figure 6.12).

These mechanisms appeared to emanate from the packing of the cement gel particles and to control differently the diffusion of the dissociated Ca; either the particles blocked the throats among them leading to the mechanism at 60°C, or they enlarged the size of the throats leading to the mechanism at 120°C (Figure 6.13). At 60°C the diffusion of Ca was found to be controlled by the critical throats (~4 nm) and at 120°C the movement of Ca appeared to be governed by the interparticle gel pores and the defects of the pore walls that become less pronounced in pores larger than 12 nm (Figure 6.13).



Figure 6.13 Schematic summary of the connections of the macroscopic (CO_2 injection well), mesoscopic (width of annular cement) and microscopic (throat/ cavity) perspective of the Ca leaching before the CO_2 injection to commence.

6.3 Impact of carbonated brine on the pore structure

6.3.1 Apparent porosity

In general, the C120/3 appeared to be more porous (+6%), Figure 6.15) than the initial sample grout and the CO60, with the latter samples to obtain lower (-5%) or equal apparent porosities to the unreacted sample grout after 1 and 5 month(s) respectively (Figure 6.14).

The carbonated regions, of the CO60, appeared to have lower apparent porosities (-6% and -11%) than the inner regions of the same samples after 1 and 5 month(s) respectively (Figure 6.14). This blocking of the apparent porosity can be assigned to the precipitation of

aragonite and calcite due to the reaction of Ca^{2+} with the effluent HCO₃⁻ (subchapter 4.4.1.2). In comparison to the N60, the carbonated brine at CO60 seemed initially (\approx 1 month) to seal the inner region (through the creation of the denser outer –carbonated- region) preserving its microstructure as evident from the presence of portlandite after 1 month irrespectively of the N₂ or CO₂ saturated brine. The higher apparent porosity of the inner region of the CO60/5 than N60/5 was attributed not only to the complete dissociation of portlandite, but also to the greater decalcification of the C-S-H phases due to the carbonated brine which in contrast to the N60/5 could have led to greater increase in the gel porosity (<12 nm) for the case of CO₂.

With respect to the CO120 the apparent porosity of the inner region after 1 month was preserved equal to the unreacted grout sample (33.2%), but obtained higher values after 3 months (\approx 40.4%, Table 6.9). As with treatment at 60°C, at 120°C after 1 month the carbonated region was denser (from 33.9% of the unreacted sample grout to 24.2%), but appeared to become significantly porous after 3 months (46.2%) (Table 6.10).

	Bulk densities* (g/cm ³)	Skeletal (apparent) densities (g/cm ³)		He porosity (%)	MIP porosity (%)	Porosity undetected by MIP (%)	
	MIP	He	MIP				
<u>CO60 (inner parts)</u>							
Unreacted	1.53±0.06	2.17±0.16	2.04±0.10	33.9±0.5	24.7±3.1	+2.9/ +15.5	
1 month	$1.60{\pm}0.04$	2.25±0.12	2.15±0.08	28.1±0.7	25.1±0.9	+0.3/ +5.7	
5 months	1.47 ± 0.01	2.20±0.01	2.09±0.06	33.3±0.1	29.5±1.9	+0.2/+7.4	
		<u>CO120</u>	(inner parts)			
1 month	1.51±0.04	2.26±0.01	2.23±0.03	33.2±1.0	32.2±0.4	-1.5/+3.5	
3 months	1.35±0.01	2.27±0.04	2.26±0.03	40.4±1.8	40.8±0.8	-4.95/+4.2	

Table 6.9 Bulk and skeletal densities, and, porosity measured He pycnometry and Hgporosimetry for the inner parts of CO60 and CO120

{*,at 0.55 psia; the error bars indicate standard errors}

	Bulk densities* (g/cm ³)	Skeletal (apparent) densities (g/cm ³)		He porosity (%)	MIP porosity (%)	Porosity undetected by MIP (%)	
	MIP	He	MIP				
CO60 (carbonated parts)							
Unreacted	1.53 ± 0.06	2.17±0.16	2.04±0.10	33.9±0.5	24.7±3.1	+2.9/ +15.5	
1 month	1.70 ± 0.008	2.16±0.01	2.04±0.10	21.7±0.1	21.6±0.7	-1.6/ +1.4	
5 months	1.76±0.03	2.25±0.01	2.29±0.04	28.8±2.0	22.7±1.3	+0.3/+11.9	
CO120 (carbonated parts)							
1 month	1.53±0.05	2.01±0.02	1.93±0.03	24.2±1.0	21.0±0.5	+0.54/+5.86	
3 months	1.28±0.02	2.36±0.01	1.90±0.09	46.2±0.7	32.2±0.5	+11.85/+16.15	

Table 6.10 Bulk and skeletal densities, and, porosity measured He pycnometry and Hg

 porosimetry for the carbonated parts of CO60 and CO120

{*,at 0.55 psia; the error bars indicate standard errors }



Figure 6.14 Time evolution of the apparent porosity of CO60 (the N60 were overlaid for reasons of comparison)

For CO120/1, portlandite was absent for both the inner region and the corresponding N120/1, but the apparent porosity was reduced by -11% for CO120/1 in comparison to the N120/1. Thus the volume of gel porosity was said to be decreased for the CO120/1 than the N120/1, since less C-S-H phases would have needed to be dissolved for CO120/1. However, the inner region of CO120/3, obtained the same apparent porosity as the corresponding N120/3 (Figure 6.15). That was indicative that a possible mechanism should govern the evolution of the cement gel pores in both CO120/3 and N120/3, in contrast to the higher apparent porosity of the inner region of CO60/5 which leads to greater degradation of the sample in comparison to the respective N60/5 (Figure 6.14).



Figure 6.15 Time evolution of the apparent porosity of CO120 (the N120 were overlaid for reasons of comparison)

In the case of the CO₂ treated samples, the increase/ decrease of the apparent porosity was not related to the Ca concentration of the fluids after reaction, but rather to the decrease of Ca/Si ratio as discussed in Chapter 4. In both CO120/1 and N120/1 the Ca/Si ratio remained the same to the unreacted grout sample (\approx 1.74) verifying the sealing behaviour of the carbonated region. The CO120/3 had significantly lower Ca/Si ratio (\approx 1.59) than the 240 corresponding N120/3 (\approx 1.80) which is inconsistent with the steady values of their apparent porosities. Similarly, the inner region of CO60/1 had the same Ca/Si as the respective N60/1 (\approx 1.74), while after 5 months the Ca/Si ratio in both cases was found to be reduced.

Thus, in order to explain the inconsistency of the decline of Ca/Si ratio with the reduction of the apparent porosity, the pore network parameters have been examined below. The overall correlations regarding the Ca: Si ratio and the apparent porosities, for each pair of N_2 / CO_2 system at a particular time are given in Figure 6.16.



Figure 6.16 Correlation of the apparent porosity to the Ca/ Si ratio for the CO60 and CO120

6.3.2 Analysis of Hg intrusion/ extrusion curves

The cumulative intrusion curves of Hg for the CO60 are shown in Figure 6.17 and for CO120 in Figure 6.18. The total intruded volumes of Hg (Table 6.11) appeared to be consistent with the evolution of apparent porosity discussed in section 6.3.1.

Regarding the CO60/ 1 the critical throat of the inner region was found to be approximately 13 nm with a secondary peak at 5 nm. In comparison to the unreacted grout sample, where the critical throat was around 4 nm and the secondary peak around 20 nm, it seemed that the partial dissociation of portlandite led to the throats among the C-S-H particles to be the critical ones [Jennings, 2008].

With respect to the CO60/5, the entire disappearance of portlandite from the inner region, induced the generation of new throats from 40 nm to 20 nm, but with the critical ones to be at 3 nm, 5 nm, 10 nm within the cement gel. From the latter fact it was implied that the decalcification of the C-S-H particles was not a random phenomenon but potentially followed a hierarchical order for the Ca dissociation and transport at 60°C. The initial widening of the critical throats after 1 month and shrinkage after 5 months is reflected to the decrease and increase of the retention factor respectively (Table 6.11).

On the other hand the carbonated parts of CO60 appeared to have an almost constant critical throat, in the range 3nm to 5nm (Figure 6.17 B). These throats were created probably among the decalcified silicate **gel** and the pores that have been blocked from the calcium carbonates. Just after 1 month, new throats have been noticed in the range of 20 nm – 40 nm, which after 5 months appeared to have been blocked. It could be that the Ca loss, primarily from portlandite, caused these new throats to be created after 1 month, and after 5 months they have been entirely filled by calcium carbonates (see Chapter 4).

Regarding the carbonated parts of CO60 and CO120 it remained unclear whether the detected critical throats are mainly among the crystals of $CaCO_3$ or in between decalcified silicate **gel**. This distinction could be crucial for the determination of the state of the carbonated cement, *i.e.* whether it is in the stage of carbonation and so the throats would correspond to those among the CaCO₃ and shrink in time or in the stage of dissolution and thus the throats would be principally within the silicate **gel** and widen in time.

With respect to the CO120, their inner parts appeared to have widened critical throats after 1 month (~20 nm), which were partially blocked after 3 months (~7 nm) (Figure 6.18 B). The outer parts of CO120/1 and CO120/3 months had critical throats at 7nm and 13nm, respectively. The shrinkage of the critical throat at the outer region was in line with the

significant decrease of porosity after 1 month (Figure 6.14), indicating that the critical throats of the unreacted sample at 4 nm have been fully blocked and greater capillaries have been partially blocked with calcium carbonate crystals.



Figure 6.17 (**A**) Cumulative intrusion curves and (**B**) inset throat size distributions from MIP, for the CO60/1 and CO60/ 5



Figure 6.18 (**A**) Cumulative intrusion curves and (**B**) inset throat size distributions, for the for the CO120/1 and CO120/3

	Part	Total Hg Volume	Total Hg Volume	Retention			
		Intrusion (cm ³ /g)	Extrusion (cm ³ /g)	Factor, R			
	CO60						
Unreacted		0.181±0.034	0.104±0.010	0.573			
1 month	Inner	0.154±0.009	0.055 ± 0.011	0.357			
	Outer	0.127 ± 0.026	0.031±0.010	0.244			
5 months	Inner	0.201±0.079	0.107±0.015	0.532			
	Outer	0.128 ± 0.006	0.047 ± 0.005	0.367			
			CO120				
1 month	Inner	0.213±0.005	0.078 ± 0.005	0.366			
	Outer	0.137±0.014	0.023±0.009	0.168			
3 months	Inner	0.301±0.004	0.115 ± 0.004	0.382			
	Outer	0.227±0.024	0.061±0.025	0.269			

Table 6.11 Entrapment of Hg in the inner and carbonated regions of CO60 and CO120

Note: the error bars represent standard errors

6.3.3 Nitrogen sorption isotherm analysis

The N₂ sorption isotherms for the inner and carbonated regions of CO60 are shown in Figure 6.19 and Figure 6.20, respectively. At 60°C the total volumes of adsorbed N₂ were found to be greater for the carbonated regions (Figure 6.20) than the inner regions (Figure 6.19) indicating increased volumes of medium capillary pores (12 nm-50 nm) and/or gel pores (less than 12 nm). The relative saturation pressures, at which the total volumes of adsorbed N₂ were adsorbed N₂ were recorded, are shown in Table 6.12.

Table 6.12 Relative pressures at the saturation point for N_2 adsorption for the inner and carbonated regions of CO60 and CO120

Sample	Region	CO60/1	CO60/5	CO120/1	CO120/3
P/P°	Inner	0.9848	0.9913	0.9960	0.9964
	Carbonated	0.9939	0.9967	0.9962	0.9952



Figure 6.19 Nitrogen sorption isotherms for the inner regions of CO60



Figure 6.20 Nitrogen sorption isotherms for the carbonated -outer- regions of CO60

From Figure 6.19 it was noticed that for the inner region of the CO60/1, the blocking of the apparent porosity (Figure 6.14) occurred primarily due to blocking of gel pores (below 13 nm), but maintaining the same modal size as in the case of the unreacted sample grout ($\approx 60 \text{ nm}$) (Figure 6.21 A). This blocking of gel pores was followed by halving of the SSA_{BET} with respect to the unreacted sample grout (Table 6.13). Although, the reduction of the SSA_{BET} with pore blocking would have been anticipated, nevertheless the increase in the fractal dimension of the pore walls from 2.01 to 2.21 would have acted in the direction of increasing the SSA_{BET}. A possible explanation was proposed to be that the blocking of the cement gel pores to cause greater decrease in the SSA_{BET} than the remaining capillary pores and pore wall defects.

The increase in pore wall roughness for the inner region of CO60/1 should be treated with care [Rigby *et al.*, 2005]. It could have been that the lost porosity could have been with smoother pore walls (less defects) and thus to have led to smaller mean value for the fractal dimension. Thus the value of 2.21 for the fractal dimension could be hypothesized as the mean value for the remaining capillary porosity for the inner region of CO60/1 that had roughness similar to the unreacted grout sample.

On the one hand, the preservation of the pore wall roughness after 1 month of carbonation would have been a plausible scenario. This was logically justified, since the smaller a pore is, the less defects was anticipated to have than a larger pore (like the medium capillaries, *i.e.* \leq 50 nm). As the pores became larger there must be a transition limit where the roughness is not detectable by N₂ sorption, due to restrictions in the size of pore where capillary condensation occurs. Since the gel pores of CO60/1 (inner region) have been blocked the remnant capillary pores could have led to an increase of the detectable roughness by N₂ sorption.



Figure 6.21 BJH pore size distributions for the CO60 with respect to the adsorption (A) and desorption (B) isotherms from Figure 6.19

		SSA _{BET}	C _{BET}	Micropore	Micropore
				Volume	SSA*
		(m^{2}/g)		(cm^{3}/g)	(m^2/g)
			<u>C(</u>	060	
Unreacted		44.0±0.09	78.0	0.017175±0.000029	34.8
1 month	Inner	17.0±0.07	72.6	0.007511 ± 0.000010	14.8
	Outer	59.7±0.03	80.8	0.030989 ± 0.000030	59.2
5 months	Inner	94.0±0.08	76.2	0.044248 ± 0.000090	86.9
	Outer	86.8±0.04	99.8	0.043701±0.000122	86.7
			<u>CC</u>	0120	
1 month	Inner	61.4±0.03	83.6	0.030422±0.000092	37.8
	Outer	44.0±0.03	85.9	0.018359 ± 0.000021	37.8
3 months	Inner	82.0±0.05	101.4	0.039272 ± 0.000087	78.2
	Outer	48.8±0.02	76.2	0.018071±0.000071	37.9

Table 6.13 Specific surface area, micropore volume and micropore surface area for the CO₂ treated samples at 60°C and 120°C

Notes: *, Specific Surface Area of the micropores from Dubinin-Astakhov

The inner region of CO60/5 appeared to have a modal cavity size around 167 nm and a secondary peak at 9 nm with the cavities around 60 nm of CO60/1 (inner region) to be blocked (Figure 6.21 A). The presence of ink-bottle pores is similar to the inner region of CO60/1 (Figure 6.21 B), with the maximum cavity to throat ratio to be around 55 (calculated from 167nm/3nm) and the lowest around 3 (9 nm/3 nm). The three times greater cavity size after 5 months than after 1 month, was followed by a five times increase in the SSA_{BET}, an increase that was assessed to be rational since the total volume of nitrogen adsorbed increased twofold, from 0.10 cm³/g (1 month) to 0.20 cm³/g (5 months). After 5 months no increase of the fractal dimension was observed (2.26) and thus the increase of the SSA_{BET} was claimed to be exclusively due to the enlargement of the pre-existing cavities.

With respect to the carbonated part of the CO60/1, the modal cavity size was found to be close to 9 nm (Figure 6.21 A), which was attributed either to the porosity within the decalcified silicate **gel** or the pores due to the packing of the calcium carbonate crystals. The corresponding surface area increased threefold in comparison to the inner region (Table 6.13), even though the apparent porosity of the carbonated region decreased even further than the inner (see Figure 6.14). That fact was suggested to happen owning to the increase of the surface roughness due to precipitation of calcium carbonates which was confirmed by the increase of the fractal dimension (from $D_f^{unreacted} = 2.01$ to $D_f^{CO60,1 (outer)} = 2.13$). In this case of the carbonated region, ink-bottle pores appeared to be dominant as well as at the inner region (Figure 6.21 B), but to have even smaller cavity to throat ratio (9 nm/4 nm \approx 2).

After 5 months, the carbonated region of the CO60, appeared to be similar to that after 1 month in the sense of preservation of the modal cavity around 9 nm (Figure 6.21 A) and with the critical throat to be 5 nm (see Figure 6.17). These two sizes suggested that the dominant throats and cavities were close enough, suggesting that the pore network resembled the shape of elongated 'tubes', that have pore walls of size from 5 nm to 9 nm. However, the ink-bottle characterization also applies to the carbonated region at 60°C after 5 months as seen from the cavitation at 3.3 nm (Figure 6.21 B), which is verified from the secondary peak of the throat size distribution at around 4 nm (Figure 6.17 B).

The N_2 sorption isotherms for the inner and carbonated regions of CO120 are shown in Figure 6.22 and Figure 6.23, respectively. The inner regions of CO120 had greater volumes of total adsorbed N_2 than the outer regions, due to increased skeletal densities of the inner regions (Table 6.9 and Table 6.10). The fact that for the inner regions of the CO120 the skeletal densities from MIP and He pycnometry were the same for each time period, was reflected to the almost similar volume of pores smaller than 12 nm of CO120 with the unreacted grout sample (Figure 6.22 and Figure 6.23).



Figure 6.22 Nitrogen sorption isotherms for the inner regions of CO120



Figure 6.23 Nitrogen sorption isotherms for the carbonated -outer- regions of CO120



Figure 6.24 BJH pore size distributions for the CO120 with respect to the adsorption branches of the isotherms from Figure 6.22 and Figure 6.23



Figure 6.25 BJH pore size distributions for the CO120 with respect to the desorption branches of the isotherms from Figure 6.22 and Figure 6.23

The inner regions of the CO120/1 and CO120/3 were characterized by cavities with modal size around 12 nm with only the pore volume corresponding to this size to increase with time; the outer parts of the same samples had cavities with modal size around 20 nm (Figure 6.24). Irrespectively of time, for both inner and carbonated (outer) regions, no inkbottle pores were assumed, as seen from the elimination of the steep hysteresis loop in all the isotherms of the CO₂ treated samples (Figure 6.22 and Figure 6.23) which was translated into the absence of cavitation phenomenon during the N₂ desorption (Figure 6.25).

After 1 month for the CO120, the stability of the apparent porosity of the inner region (Figure 6.15) appeared to happen simultaneously to the blocking of the capillary pores around 60 nm (Figure 6.24); this blocking led to throats around 20 nm to be the critical ones, instead of the critical throats of the unreacted sample grout which were around 4nm (see Figure 6.5). The generation of pores due to the decalcification of the cement gel could be one of the causes of the increase of the SSA_{BET} by 38% (with respect to the unreacted sample grout) after 1 month, which occurred in the inner region after treatment at 120°C (Table 6.13). The increase of the SSA_{BET} can be also assigned to the increase in the roughness of the pore walls (from 2.01 to 2.14).

After 3 months for the CO120, at the inner region, the increase of the apparent porosity (Figure 6.15) could be justified from the increase of the cavities with size around 12 nm (Figure 6.24). The increase of the SSA_{BET} can thus be attributed to the increase in the pore volume of those cavities (Table 6.13). The lack of cavitation is justified from the size of the critical throat (7 nm, Figure 6.25), with the pore network to be characterized by almost similar throats and cavities. Overall, despite the generation of more porous grouts at 120°C (Figure 6.15), after treatment with CO₂-saturated brine, it appeared that up to 3 months the entire pore network was refined; this refinement resided to the generation of cavities and throats of similar sizes, and not to the intensification of the ink-bottle phenomenon of CO60/5 where 44times greater modal cavity (Figure 6.21 A).

The carbonated region after 1 month at 120°C, which appeared to be denser than the respective inner region (Figure 6.15), showed similar SSA_{BET} to the unreacted, but with reduced in size modal cavity due to carbonates precipitation. The increased surface area was reflected in the increased roughness of the pore walls, where fractal dimension $D_f = 2.17$. In the case of the carbonated region, after 1 month treatment at 120°C, the ink-bottle pores did not seem to have a great impact on the pore network, which had a critical throat of around 7 nm (Figure 6.18 B) due to the absence of the cavitation phenomenon from the respective N₂ desorption pore size distribution (Figure 6.25). Despite the presence of the throat at 4 nm (Figure 6.18 B) the lack of the shielding effect from 3 nm to 40 nm denoted that the cavities detected by N₂ sorption at 20 nm are before the throats detected in this particular range.

Finally, after 3 months the carbonated part at 120°C, was found to have the same modal cavity as after 1 month (20 nm, Figure 6.24), but again with the same value of SSA_{BET} as in the case of the unreacted sample grout (Table 6.13). The stability of the surface area is justified from the blocking of gel porosity (below 13 nm) (Figure 6.24) and the generation of new throats (from 20 nm to 200 nm, Figure 6.18).

For the CO_2 treated samples at 120°C, further analysis using small angle X-ray scattering was needed in order to verify the fractal dimensions calculated from the N₂ sorption data and the actual differentiation of the calcium carbonate crystals within the silicate gel due to the elevated temperature.

The Porod plots of the log(I) versus log(Q) for the inner and carbonated (outer) parts of the CO₂ treated samples (at 120°C) are shown at Figure 6.26 and Figure 6.27, respectively. No change in the Porod plots was noticed for the inner parts from 1 month to 3 months and with the surface fractal dimension to be D_f =6-3.49=2.51. The underestimation of the fractal dimension from the N₂ sorption was assigned to be the inability of the fractal BET theory to incorporate the exact monolayer, not only on the surface area, but also around defects. The fractal dimensions of the carbonated parts were not distinct from the inner parts (after 1 month $D_f = 2.57$; after 3 months $D_f = 2.41$) indicating that the elementary particles had the same microstructure and possibly with similar degrees of hydroxylation.

The second objective of differentiating the final products of carbonation for the CO120 was clearly deciphered by SAXS. Figure 6.28 shows a clear kink of the Porod plot for the carbonated part after 3 months in comparison to the similar plot after 1 month. This kink took place around 20 nm and differentiated on the one hand the polymerized silicate structure (sizes greater than 20 nm) and on the other hand the calcium carbonates (sizes less than 20 nm).

It is remarkable that even after 3 months the modal cavity has been preserved and only the volume of the same cavities was increased. That suggests the re-dissolution of the carbonates occurred under the control of the pore network parameters of the silicate matrix like the critical throat. On the one hand, dissolution of throats and on the other hand the strength of the silicate matrix could prevent the modal cavity to be changed. This translated to similar permeabilities of the carbonated parts at 120°C regardless of the elapsed time.



Figure 6.26 Porod plots for the inner regions of CO120



Figure 6.27 Porod plots for the carbonated regions of CO120; the continuous curve with the "+" denotes the CO120/1 and the curve with "♦" stands for the CO120/3; the trend-lines of three basic differentiating regions are also delineated.



Figure 6.28 Overlapping of the pore size distributions from N₂ adsorption curves and SAXS curve

The previous value for the maximum size of carbonates at 20 nm seems to be contradictory to the calculated values for samples CO120 using the Scherrer equation (sections 4.4.4.2 and 4.4.5.2). When using the latter equation several assumptions were made regarding the shape of the elementary crystallite for each carbonate, the choice of the lattice planes for the calculation of the full width at half maximum (FWHM), the definition of the specimen broadening as FWHM and the presence of broadening from the instrument and several strains. These factors could have led to the decrease in the size of the crystallite size of the calculation arbonates, due to changes in the values of the K constant and β (section 3.4.1), that would ultimately have led to crystallite sizes less than 20nm.

Despite those assumptions underpinning the Scherrer equation, its application was useful for relating the size of the carbonate with the T, P conditions and pore restrictions. However, the SAXS experiment, particularly at 120°C (Figure 6.28), demonstrated the segregation of the carbonated region in two distinct structures. The one structure was attributed to the overarching silicate matrix (20-50 nm) and the other was said to be the calcium carbonates (<20 nm). Those carbonates were hypothesised to partially dissolve from 1 month to 3 months so as to increase the roughness of the surface area of the silicate matrix (higher inclination of the Log(I)-pore size for CO120/3 below 10 nm).

The separation of the carbonates as calculated from the kink in the LogI - LogQ graph, shows that that those carbonates were not part of the silicate matrix, but possessed a different structure which was inherently attached to the matrix. This is an important observation since at 120°C the matrix of enhanced polymerized silicate **gel** appeared to be the controlling microstructure for the controlled precipitation of calcite. At 60°C the ubiquitous presence of aragonite did not seem to have followed a controlled mechanism due to the supersaturated conditions leading to less stable calcium carbonate polymorph.

6.3.4 Permeability and pore connectivity

Similar to the N₂ treated samples, the CO₂ treated samples appeared to be more permeable after treatment at 120°C and less so after 60°C. The permeability in the case of CO₂ treated samples refers to the transport of: (1) Ca²⁺ towards the outer of the samples, (2) HCO₃⁻ from the carbonated brine towards the inner and (3) the dissociation and re-dissolution of calcium carbonates which refers only for the carbonated regions.

The experimental, calculated (Katz-Thompson model) and simulated (PoreXpert) permeabilities for the inner and carbonated regions are shown at Table 6.14 and Table 6.15, respectively. No matching was observed among the values for the same part and duration and thus the signs of each value were recorded in order to correlate the timely evolution of permeability with the alteration of throats and cavities (Table 6.14).

	k_{exp}	k_{Ka}	atz–Thompson	k _{PoreXpert}					
		(mD)							
		C=1/89	C=1/226	3-11nm	11-40nm				
		<u>CO60</u>							
Unreacted	$(7.1 \pm 0.5) \times 10^{-2}$	2.43E-04	9.56E-05	3.52E-03	0.0137				
1 month	$(7.2 \pm 0.6) \times 10^{-2}$	1.00E-04	3.96E-05	3.15E-03	0.0105				
5 months	$(8.3 \pm 0.8) \times 10^{-2}$	4.02E-05	1.58E-05	2.66E-03	4.21E-03				
		<u>CO120</u>							
1 month	$(7.3 \pm 0.5) \times 10^{-2}$	3.92E-04	1.54E-04	3.74E-03	0.0141				
3 months	$(8.8\pm0.6)\times10^{-2}$	6.96E-05	2.74E-05	5.08E-03	0.0138				

Table 6.14 Experimental, calculated and simulated intrinsic permeabilities for the inner parts

 of CO60 and CO120

	k_{exp}	k_{K}	atz–Thompson	$k_{PoreXpert}$				
		(mD)						
		C=1/89	C=1/226	3-11 nm	11-40 nm			
		<u>CO60</u>						
Unreacted	$(7.1\pm0.5) \times 10^{-2}$	2.43E-04	9.56E-05	3.52E-03	0.0137			
1 month	$(7.8\pm0.7) \times 10^{-2}$	9.57E-06	3.77E-06	4.04E-03	0.0121			
5 months	$(7.4 \pm 0.3) \times 10^{-2}$	5.18E-05	1.33E-05	1.77E-03	2.16E-03			
		<u>CO120</u>						
1 month	$(6.1 \pm 0.7) \times 10^{-2}$	3.32E-04	1.31E-04	2.35E-03	4.17E-03			
3 months	$(1.2\pm0.8)\times10^{-2}$	3.63E-02	1.43E-02	4.44E-03	0.0159			

Table 6.15 Experimental, calculated and simulated intrinsic permeabilities for the carbonated

 parts of CO60 and CO120

Based on the models presented at Figure 6.11, at 60°C the CO_2 treated samples are a sequence of high permeability zones inside lower permeability zones for both inner and carbonated regions. On the other hand, at 120°C the CO_2 treated samples are a sequence of low permeability zones inside high permeability zones. At 60°C the more permeable inner zones (high k) justify the clear delineation of aragonite crystals, while at 120°C the less permeable inner zones justify the existence of calcite crystals. In the first case the supersaturation of the cavities with Ca^{2+} and HCO_3^- was said to be faster and in the latter case the limited transport of those species to the inner allow the various calcium carbonate forms to rearrange and generate the most stable form of calcite. These conclusions are in accordance to the secondary electron images at the carbonated regions of the CO_2 treated samples and provide the kinetic explanation of carbonate crystals from the arrangement of the pore network.

In general the calculated and the simulated permeabilities appeared to have almost the same sign for each column, whereas the experimental values were found to be greater than the initial unreacted sample grout.

Based on the models presented at Figure 6.11, at 60°C the CO2 treated samples are a sequence of high permeability zones inside lower permeability zones for both inner and carbonated regions. On the other hand, at 120°C the CO2 treated samples are a sequence of low permeability zones inside high permeability zones. At 60°C the more permeable inner zones (high k) justify the clear delineation of aragonite crystals, while at 120°C the less permeable inner zones justify the existence of calcite crystals. In the first case the supersaturation of the cavities with Ca2+ and HC O_3^- was said to be faster and in the latter case the limited transport of those species to the inner allow the various calcium carbonate forms to rearrange and generate the most stable form of calcite. These conclusions are in accordance to the secondary electron images at the carbonated regions of the CO2 treated samples and provide the kinetic explanation of carbonate crystals from the arrangement of the samples, which are the resistances of the grouts to decalcification of the inner parts and the carbonation/ re-dissolution of the outer parts for the two different mechanisms of diffusion presented at Figure 6.12.

Permeability	CO60				CO120			
	Inner	Carb.	Inner	Carb.	Inner	Carb.	Inner	Carb.
	1 m	onth	5 m	onths	1 n	onth	3 m	onths
Experimental	Ø	+	+	-	Ø	-	+	+
Calculated	-	-	-	+	+	Ø	-	-
11nm-3nm	-	+	-	+	+	Ø	+	+
40nm-11nm	-	-	-	-	Ø	-	Ø	+
R1 + R2	+	Ø	+	+	Ø	+	-	-
1/R1+1/R2	+	Ø	+	+	Ø	+	-	-

Table 6.16 Qualitative evolution of permeability of the inner and carbonated regions for the

 CO60 and CO120

With respect to the CO60 the simulated positive resistances match the negative signs of the calculated permeabilities. The main cause of the increased resistance of the inner parts and the outer parts (after 5 months) was attributed to the decrease in porosity over time. The blocking of porosity was said to be an aftermath mainly from the complete and partial blocking of the critical throats despite the widening of the modal cavity from 60 nm to 167 nm. Thus at 60°C the resistance of the grouts to the carbonation and decalcification happened mainly due to throat blocking, that in the course of time led to decreased connectivity of the interconnected pore pathways.

After treatment at 120°C in CO_2 , the samples appeared to be resistant to diffusion only in the case of the carbonated region after 1 month, which was confirmed also by the experimental permeability. In this case, the decreased permeability of the outer region after 1 month was identified to happen due to the decrease of the apparent porosity. This was a consequence of the shrinkage of the modal cavity from 60 nm to 20 nm and not a cause of the widened critical throat. The increased resistance to diffusion of the outer part after 1 month led to the preservation of the permeability of the inner part after 1 month, despite the increase of the critical throat and the decrease of the modal cavity. Finally, after 3 months, the CO_2 treated samples appeared to have negative resistance to further diffusion, owning to the increased volume of the modal cavities around 12 nm at the inner of the sample, and, the onset of throat widening of the carbonated part.

Based on the models presented at Figure 6.11, at 60°C the CO₂ treated samples are a sequence of high permeability zones inside lower permeability zones for both inner and carbonated regions. On the other hand, at 120°C the CO₂ treated samples are a sequence of low permeability zones inside high permeability zones. At 60°C the more permeable inner zones (high k) justify the clear delineation of aragonite crystals, while at 120°C the less permeable inner zones justify the existence of calcite crystals. In the first case the supersaturation of the cavities with Ca²⁺ and HCO₃⁻ was said to be faster and in the latter case

the limited transport of those species to the inner allow the various calcium carbonate forms to rearrange and generate the most stable form of calcite. These conclusions are in accordance to the secondary electron images at the carbonated regions of the CO_2 treated samples and provide the kinetic explanation of carbonate crystals from the arrangement of the pore network.

6.3.5 Conclusions: Pore network effects on the carbonation reactions

The permeability-pore structure relationship during carbonation of class G oilwell cementitious grouts was studied for cement samples immersed inside CO₂-saturated brine at 80 bar/ 60°C and 80 bar/ 120°C up to 5 and 3 months respectively. At 60°C and 120°C, both inner and carbonated parts exhibited a sealing stage (up to 1 month) and a dissolution stage (up to 5 and 3 months). The terms "sealing" and "dissolution" referred only for changes in the apparent porosity but in reality these changes were found to reflect the changes of the critical cavity to throat ratio due to different temperature and time. At 60°C the permeability was proved to be controlled by the critical throats (big values of the ratio) and at 120°C by the size of the critical cavity (small throat to cavity ratio).

At 60°C the great values of the cavity to throat ratio resulted into the ink-bottle phenomenon which was said to control the transport of the various species. At the inner part of CO60/5 the presence of modal cavities with size three times greater than the initial grout sample implied thinner pore walls than after treatment at 120°C up to 3 months. At 120°C the pore network had throats and cavities with almost similar size, *i.e.* around 12 nm which despite the increase in porosity led to thicker pore walls. As a consequence at 120°C the fracturing at the inner-uncarbonated- parts was assumed to be less probable, than at 60°C, since the silicate **gel** was proved to keep the critical throat and cavity at the level of packing of the C-S-H particles cement particles according to the colloidal model. In other words, at

120°C the silicate **gel** was prevented from extensive de-bonding that would result a big loss of C-S-H particles to generate big cavities.

The critical size of the pores/throats at 120°C close to 12 nm, supported the unrestricted diffusion of calcium towards the outer and hence the faster buffering of the effluent bicarbonates. At 120°C, the buffering was found to take place at the surface sites of the C-S-H particles and thus from structural Ca²⁺. At 60°C the restricted transport of species due to the small critical throats (~4 nm) resulted in the big cavities which were the loci of aragonite crystallization from the free Ca²⁺. This distinction of "diffusion" at 120°C and "restricted transport" at 60°C, was the key point for the better fitting of the time evolution of the carbonation front to the $x_C = A \cdot t^{1/2}$ for the CO120 (Chapter 5).

6.4 Summary

In the current chapter the pore network parameters were examined for class G cementitious grouts treated with N_2/CO_2 saturated brine at 80 bar and 60°C/ 120°C. From other studies it was identified that any comparison should take into account not only the process variables but also the type and conditions of each analysis.

A first example is the comparison between the changes of the real open porosity and the microstructural cause(s). With reference to the Ca leaching cement samples (N₂ treated samples), the two porosities (helium, mercury) led to contradicting results at 60°C (Table 6.3), showing that usage of mercury porosity could indeed alter the comparisons of the accessible porosity with the compositional changes. Studies of Ca leaching for ordinary Portland cement pastes that have demonstrated the decalcification resulted to continuously increasing mercury porosity should be treated with attention since the final conclusion could be altered if He pycnometry was implemented to measure the real accessible porosity [Haga *et al.*, 2005]. However the study of Haga *et al.* [2005] demonstrated correctly that in general the portlandite dissolution lead to increased porosity [Carde *et al.*, 1997; Burlion *et al.*, 2006]. In the present

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study the increase or decrease of apparent porosities cannot be assigned to the portlandite dissolution due to its pozzolanic reactions with the microsilica particles for the production of additional C-S-H phases [Gaitero *et al.*, 2008]. Thus in the long term, for cementitious grouts containing microsilica or other appropriate additive [Kutchko *et al.*, 2008] it is anticipated for portlandite to be absent on the one hand due to possible pozzolanic reactions [Lin *et al.*, 2013] and on the other hand from its dissociation due to Ca leaching.

Even though in old oil wells portlandite was found to be present [Carey *et al.*, 2007], in fact in new wells designated for CO_2 injection (*e.g.* Sleipner, North Sea), the interactions of cement initially the additives and the brine and subsequently with the bicarbonates will exclude the presence of portlandite and they will depend on the physical and chemical features of the C-S-H phases. These features define not only the pore wall chemistry and roughness, but also the connectivity of the C-S-H structures and thus their permeability/ durability during leaching and carbonation. The parameters that influence these features are not only the curing conditions [Kutchko *et al.*, 2007] and the type of cement/additives but also the environment of reservoir (temperature, pressure, reservoir's rock pore fluid).

From the previous it is logic to assume that the behaviour of C-S-H phases to control the final performance of class G cements with microsilica suspension as additive. Thus the pore network properties of these phases can be said to control ultimately the transport properties. The initial sealing and subsequent dissolution for the samples of the current study has been also found from similar experiments for class G cement grout samples carbonated at 90°C and 280 bars up to 6 months [Rimmelé *et al.*, 2008]. The latter researchers showed that the critical throat shrinks as a result of calcium carbonate precipitation due to reaction of the Ca^{2+} from portlandite and C-S-H with the dissolved CO₂. While the sealing/ dissolution phenomena of the carbonated regions referred to the precipitation/ dissociation of the calcium carbonates, in fact the C-S-H structures of the inner parts of the CO₂ treated samples behaved on the one hand at 60°C like particles [Jennings, 2008] and on the other hand at 120°C like tobermorite chains [Richardson, 2004].

At the inner parts of the CO₂ treated samples at 120°C, in order the throats and cavities to resemble in size the silicate **gel** must have experienced simultaneously localized expansion (decreasing the cavity size) [Heukamp *et al.*, 2003] and shrinkage (throat enlargement) [Chen et al., 2006]. At 60°C the preservation of the threshold diameter, the intensified ink-bottle phenomenon (Figure 6.29) and same critical throats close to 3 nm, could have been caused due to: (1) the retarded pozzolanic reactions at 60°C that would have caused the throats to be mechanically stable due to the microsilica particles [Cahyadi *et al.*, 2003], and, (2) the small activation energy for the C-S-H particles to re-organize their structures and to align them leading to silicate condensation and polymerization [Heukamp *et al.*, 2003].

The previous analysis demonstrated the importance of C-S-H structures in controlling permeability of a given cementitious grout (Figure 6.30). Despite the recent advances of new types of cements [Nasvi *et al.*, 2013; Nasvi *et al.*, 2014], the plethora of existing oilwells sealed with ordinary Portland cements globally, dictates that the permeability of the entire well to CO₂ fluids will rely on the diffusion among the pores of the previous structures. The schematics at Figure 6.29 and Figure 6.30 connect the different length scales from the nanometer to the actual width of annular cement. The changes of the pore structure at the nano- and micron- meter scale, defined the diffusion regime namely Knudsen/ Fickian at 120°C and advective diffusion at 60°C. Despite the increase of the apparent porosity at 120°C and the blocking at 60°C, it was observed that the rate of advection at 60°C was higher than the diffusion at 120°C. The permeability of the examined G cement was dependent on both temperature and time that cumulatively contributed to each diffusion regime. Increased temperatures gave higher activation energies for C-S-H decalcification, preservation of the lower k areas (cement gel) inside higher k areas (capillaries) and slower kinetics for carbonation due to the finer pore network. Unlike 120°C, at 60°C the pore throat blocking
seemed to have been caused by the faster kinetics due to advection, although the C-S-H phases delayed, due to the lower activation energy for decalcification, until they become the lower k areas.



Figure 6.29 Schematic overview of the ink-bottle phenomenon during carbonation of class G cement at 60°C and correlation of the pore structure with the permeability. 'C.f'= carbonation front, 'A'=aragonite



Figure 6.30 Schematic overview of the refined pore structure during carbonation of class G cement at 120° C and correlation of the pore structure with the permeability. 'C.f' = carbonation front, 'C'=calcite.

The resistance of the cements to chemical and mechanical degradation was previously found to depend on the relationship of permeability and porosity for the carbonated region [Fabbri *et al.*, 2012]. Even though the decrease in permeability due to decrease in porosity is the optimum scenario for the carbonated region of cement, in fact the present study has identified as crucial the pore structure of the inner region as well, along with other pore network parameters like critical throat and modal cavity. Overall the permeabilities of the current study (from 70 μ D to 0.1 μ D) not only conform to the value of 200 μ D given by the API recommendations [Kutchko *et al.*, 2008], but also to a real CO₂ injection well operating for 30 years (100 μ D) [Carey *et al.*, 2007]. Since the latter has sustained for a few decades with permeabilities higher than those of the present study then it was deduced that the class G cement grouts will be able to provide proper sealing for more decades on the condition of good cementing practices.

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7.1 Conclusions

The purpose of this project was to gain a fundamental understanding of the carbonation-induced alterations in borehole grouts. This was approached by determining the relationship between the chemical denaturation of the minerals in the evolving pore network and its associated transport properties. These changes resulted from material processing under a range of simulated underground temperatures, pressures and pH. The pore network geometry and transport properties were examined as a function of the degree of structural and mineral alteration. These alterations were then macroscopically related to the depth evolution of the carbonation fronts under elevated temperature and pressure conditions.

Despite the numerous laboratory investigations for the carbonation of grouts used in borehole sealing of CO_2 geological wells [Zhang *et al.*, 2011; Huet *et al.*, 2011], several examples of real cement sampling (SACROC [Carey *et al.*, 2007], Teapot Dome Oil Field [Scherer *et al.*, 2011], Secarb Cranfield [Hovorka, 2013]) dictate that more demonstration *in situ* is required. The existing sampling procedures (*e.g.* core drilling, well log) do not seem to cover the entire monitoring of a cementitious grout as far as the chemistry, carbonation front evolution and pore structure are concerned. The current thesis revealed that the microstructure, pore network and permeability are not independent from each other but should be examined as an ensemble in both laboratory scale and in field as well, if the CO_2 geological storage is wished to be a crucial part of the portfolio for tackling climate change and prevent human casualties.

Although other variables could influence the progress of the carbonation reactions (*e.g.* pressure, brine salinity, chemistry of adjacent rocks), temperature was the most sensitive variable to control the rate of alteration in both the microstructure and the pore network.

Calcium leaching from class G cementitious grouts was found to be a thermally dependent process. At temperatures higher than 60°C full conversion of portlandite to other forms was observed and appeared to cause chemical instabilities within the grouts. The higher activation energy for Ca diffusion in higher temperature wells (\approx 120°C) appeared to result in: (1) faster inhibition of the effluent bicarbonates, (2) more efficient healing of fractures, and (3) more stable calcium carbonates that were less susceptible to dissolution, *i.e.* calcite. The faster diffusion of bicarbonates translated (at the macroscale) into smaller carbonation depths, which suggests that the probability of de-bonding between the grout and the steel casing would most likely be reduced. The stimulation of the outer cement particles (caused by elevated Ca²⁺ concentration diffusing from the inner region) led to faster supersaturation conditions for vaterite and aragonite. At higher temperature this resulted in transformation to calcite. The higher resistance to degradation at 120°C may result from a silicate polymerized 'skeleton' being generated near the surface. This would more greatly reduce the rate of Ca diffusion (and precipitation as calcium carbonates) than at 60°C.

The permeability values from this study (ranging from 70 μ D to 0.1 μ D) are below the upper limit of 200 μ D stated in API recommendations [Kutchko *et al.*, 2009], and those of samples taken from a CO₂ injection well operating after 30 years operation (100 μ D) [Carey *et al.*, 2007]. The interactions of cement (initially additives and brine; subsequently bicarbonates) will exclude the presence of portlandite and depend upon the physical and chemical features of the C-S-H gel. These features defined the pore wall chemistry and geometry, and the associated alteration to the C-S-H structures and permeability.

The major significance of the present thesis was that it provided a better understanding of the relationship between the cement microstructure with its pore network parameters, a relationship that ultimately determined the permeability and extent of carbonation in the long term. In other words the aim of the thesis was fulfilled giving a more comprehensive image during carbonation of a class G oil well cement grout in a realistic scenario of geological storage of CO₂, with temperature and time to be the only variables. The implications of the studied temperatures (60°C and 120°C) and durations (1, 3 and 5 months) in real CO₂ injection wells, could provide better assessment of legacy injection wells (containing aged cement grouts) and more efficient design of new CO₂ injection wells. The presence (or absence) of portlandite, the type of calcium carbonate polymorph, the evolution of the carbonation depth profile, and the critical pore network parameters (throat/cavity ratio), are essential data to inform quality control of grouts for old and new wells. Ideally, the operator of the injection well must have the entire set of those data, in order to secure the long term stability of the CO₂ injection well.

7.2 Recommendations for future research

Despite the outcomes of the thesis, many other questions emerged that would lead to even better understanding of cement carbonation from first principles to macroscopic observations. These questions are:

- Understanding of the mechanism of Ca dissociation and re-attachment from the various C-S-H phases from an atomistic point of view. Although the silicate **gel** is characterized by various defects [Richardson, 2004], in fact the decalcification of the CO₂ treated samples was shown to happen in synchronization across the same border *i.e.* carbonation front.
- Design of new group of additives that could potentially control the decalcification of cement pastes from the abovementioned elementary level of atoms.
- Analysis of the connectivity of the decalcified silicate **gel** implementing TEM or FTIR. It is important to understand the bonding of the silicate **matrix** and the variability of this bonding with temperature, in order to reveal any possible control over the carbonation reactions.

• Understanding of the chemistry of the pore throats and cavities. This will aim to decipher where exactly the precipitation reactions take place and how they behave in the long term using natural analogues.

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Appendix 1: Cement composition

<u>N60/1</u>











<u>N120/1</u>



<u>N120/3</u>



Appendix 2: Mercury intrusion porosimetry data



<u>N60/1</u>





<u>N60/ 5</u>





<u>N120/1</u>





<u>N120/3</u>









Kloubek corrections











Appendix 3: Diffusion equations for the evolution of the carbonation front

<u>Note</u>: The current appendix presents the best fitting of the experimental carbonation depths to the square root law of time. Although more research is required for the exact mathematical formulation of diffusion during cement carbonation, the application of this type of equation for the diffusion allowed for comparisons of the carbonation coefficient with the literature.

> Diffusion equations during carbonation of class G cement at 60°C and 120°C

The location of the carbonation front at both temperatures of CO60 and CO120 was expressed using the following generalized equation:

$$\mathbf{x}_{\mathsf{C}} = \mathbf{A}_1 \cdot \mathbf{t}^2 + \mathbf{B}_1 \cdot \mathbf{t}$$
 Equation 1

Where $[\mathbf{x}_{\mathbf{C}}] = \text{carbonation depth in mm}$ and $[\mathbf{t}] = \text{time in days.}$ It is crucial to mention that $\mathbf{x}_{\mathbf{C}} = 0 \text{ mm}$ for $\mathbf{t} = 0$ days which was justified after the absence of carbonates in the unreacted grout sample at the beginning of the carbonation reactions (Section 5.2.1). More specifically for each temperature the previous equation had the specific forms:

$$\begin{aligned} x_{\text{C}, \ 60} &= 0.0007 \cdot t^2 + 0.0103 \cdot t \quad (60^\circ\text{C}) & \text{Equation 2} \\ x_{\text{C}, \ 120} &= -0.0001 \cdot t^2 + 0.0339 \cdot t \ (120^\circ\text{C}) & \text{Equation 3} \end{aligned}$$

The previous equations correspond to Figure Ap. 3.1 and Figure Ap. 3.2 and were based purely on the experimentally-measured carbonation depths at 60°C. In the same figures, the standard deviation error bars are given as well incorporating the local variabilities in diffusion due to chemical heterogeneities of the grouts. In the context of the square root time law [Papadakis *et al.*, 1989] the previous equations are transformed into Equation 2a and Equation 3a. The proportionality constants in those equations are the carbonation coefficients.

$$x_{c=60} = 1.1014 \cdot \sqrt{t}$$
, $R \approx 0.80$

Equation 2a

$$\mathbf{x}_{\mathsf{C}, 120} = \mathbf{0}.\,\mathbf{1853}\cdot\sqrt{\mathsf{t}}\,\mathsf{, R} \approx \mathbf{0}.\,\mathbf{98}$$
 Equation 3a

Based on equations 2a and 3a the time for complete carbonation of the samples used in this study was calculated by substituting $\mathbf{x}_{c} = \frac{(47 \text{ mm})}{2} = 23.5 \text{ mm}$, where 47mm is the diameter of the samples:

 $t_{60} = 455 \text{ days} \approx 1.3 \text{ years}$

$$t_{120} = 16,084 \text{ days} \approx 44 \text{ years}$$



Figure Ap. 3.1 (**A**) Time evolution of the carbonation depth at 60°C, 80 bar; (**B**) fitting of the mean average values of the carbonation depths ($y=0.0007 \cdot x^2 + 0.0103 \cdot x$) from (**A**) to the square root law of time



Figure Ap. 3.2 (**A**) Time evolution of the carbonation depth at 120°C, 80 bar; (**B**) fitting of the mean average values of the carbonation depths ($y=-0.0001 \cdot x^2 + 0.0339 \cdot x$) from (**A**) to the square root law of time

> Approximate detection of the carbonation paleofronts using sample CO60/5

The positions of the carbonation depth for 2, 3 and 4 months for sample CO60/5 are shown in Figure Ap. 3.3 -B and -C. The mechanism of creation of these fronts is described in section 5.4.1. The new equation 4 is similar to equation 2 where the R denotes the inclusion of the relics.

$$x_{C, 60}^R = 0.0004 \cdot t^2 + 0.0497 \cdot t$$
 (60°C)Equation 4OR $x_{C, 60}^R = 0.9989 \cdot \sqrt{t}$, R ≈ 0.7747 Equation 4a

If the carbonation fronts were to follow the square root law then the idealized curve of Figure -D would have emerged. This curve was based on the calculation of the proportionality constant (*A*) and was based solely on the carbonation depth at 1 month, with the assumption of the power equal to 0.5:

$$A = \frac{x_C}{\sqrt{t}} = \frac{0.85}{\sqrt{30}} = 0.155 \ mm / days^{0.5}$$

The idealized curve at 60°C was characterized by the following equations (Figure Ap. 3.4 and Figure Ap. 3.5):

$$x_{C, 60}^{I} = -8 \cdot 10^{-5} \cdot t^{2} + 0.0248 \cdot t$$
 Equation 5
 $x_{C, 60}^{I} = 0.1548 \cdot \sqrt{t}$, R ≈ 1 Equation 5a



Figure Ap. 3.3 (A) Approximation of the relic carbonation fronts for CO60/5 with ellipsoid fronts from 1 to 5 months; Independent measurements of the carbonation depth where taken for the (B) left and (C) right parts of the overall X-ray image at (A); (D) Interpolation of the fronts from (B) and (C) to the experimental data of **Figure Ap. 3.1** for the CO60.



Figure Ap. 3.4 Assessment of the applicability of the square root law of time for the various interpolated carbonation depths for CO60/5



Figure Ap. 3.5 Fitting of the ideal carbonation depths of CO60 to the square root time law and comparison with the CO120

> Times for full carbonation of a specified length of cement

Examples at 30°C, 60°C and 120°C of the time needed for complete carbonation of a cement column with lengths 23.5 mm, 1 m and 10 m are given in Table . The calculated years for full carbonation included only the case where the cement has been carbonated without accounting any further dissolution of the carbonates in the long term. The calculated times for the three lengths were plotted in Figure Ap. 3.6 and showed faster carbonation for 30°C and 60°C. The time when the carbonation depths had started to increase significantly (threshold time) was from 2,000 to 4,000 years, respectively. For 120°C and for the ideally moving front at 60°C the threshold time was 80,000 to 200,000 years, respectively.



Figure Ap. 3.6 Time evolution for complete carbonation of a cement column up to 10 m assuming square root law dependence of the carbonation depth; the graphs for 60°C and 120°C are extrapolations from the real depths of the current study; the idealized graph at 60°C is from interpolated data (**Figure Ap. 3.5**) and at 30°C from data taken from Rochelle *et al.* [2013]

Table Ap. 3.1 Time for full carbonation of class G cementitious grouts for 1 m and 10 m of acement column at 30°C, 60°C and 120°C.

		Time for full carbonation of x_c in years		
Temperature	А	23.5 mm	1 m	10 m
(°C)	mm/ \sqrt{days}	(samples of this study)		
30	0.7847	2	4,449	444,938
60	1.1014	1	2,258	225,848
60, ideal case	0.115	114	207,162	20,716,264
120	0.1853	44	79,791	7,979,143