



CHALMERS

Mixing cement with carbon dioxide – effect on early hydration

Bachelor of Science Thesis

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Abstract

It has been known since the 70s that carbon curing of cement can be beneficial to early strength development. A novel approach has been to add liquid carbon dioxide to industrial batches of concrete, promising increased early strength and disposal of unwanted CO₂. In this work, the effect on the first 24 hours of hydration of adding solid carbon dioxide to Portland cement during mixing was investigated. Lab scale batches of cement (w/c = 0.5) were mixed with solid carbon dioxide in doses ranging from 1 % to ~50 % by weight of cement and monitored with isothermal calorimetry, in-situ FTIR and thermogravimetric analysis.

Results from isothermal calorimetry show that doses of 2.5 to 10 % CO₂ increased the heat of hydration during the first 15 hours, while the highest doses show less effect. Calorimetry suggests that the increased heat is mainly from an acceleration of aluminate hydration.

In-situ FTIR shows little effect of CO₂-addition on the composition of cement hydrated for 24 hours, and no significant impact on silicate hydration. The most obvious effect shown by FTIR investigation is a large shift in the sulfate region and a crystallization of gypsum during the first 30 minutes of hydration.

TGA analysis suggest that the absorption of CO₂ added during mixing with cement is small and that calcium hydroxide is mostly unaffected after 24 hours of hydration. Cement samples showed similar mass loss over the temperature intervals assigned to Ca(OH)₂ (370-470 °C) and CO₂ (530-875 °C), regardless of CO₂-addition, suggesting that the cement may be saturated at less than 1 % by weight of cement, at the time of mixing.

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1 Introduction

Concrete is a composite material composed of an aggregate, usually sand or stone, and cement, that when reacted with water, produces an adhesive that hardens and bonds the material together. Concrete is the most commonly used building material in the world. The annual worldwide production of cement was estimated to 4100 million metric tons in 2015, with water being the only substance produced in greater quantities [1].

Cement, in some form or other, has been known to man since at least around 7000 BC, and was used in the ancient Rome to construct magnificent buildings such as Pantheon and the Colosseum. After the fall of the Roman Empire, cement was almost abandoned as a construction material, with only a few notable exceptions, until it was rediscovered in the 19th century. Many people had a hand in the development of modern cement, though one of several cement patents, granted to the Leeds builder Joseph Aspdin in 1824, is especially prominent. His patent described the cement as “Portland cement”, a name chosen to remind of the high quality stone from the isle of Portland, a description that served to give this type of cement its name. Cement produced since generally consists of Portland cement, or variants thereof, though some alternative cements exist, like geopolymer cement and calcium aluminate cement [2] [3].

Cement production, considering the giant quantities involved, is also an important contributor to global warming. The manufacture of one ton of Portland clinker leads to an emission of about the same amount of CO₂ and cement production is estimated to be responsible for 7 % of the world’s CO₂ emissions [4]. One suggested way to mitigate this is to add CO₂ to the concrete during early hydration, possibly also increasing the setting strength of cement.

1.1 Cement Chemistry notation

As certain compounds are ubiquitous in cement chemistry, a special shorthand notation where formulas are written in terms of oxides is often used, though this is not meant to imply that these oxides necessarily constitute a unit within larger compounds. Table 1 below present the most common abbreviations used in this work:

Table 1. Cement chemistry notation

CaO	C	Alite, 3CaO·SiO ₂	C ₃ S
SiO ₂	S	Belite, 2CaO·SiO ₂	C ₂ S
Al ₂ O ₃	A	Aluminate, 3CaO·Al ₂ O ₃	C ₃ A
Fe ₂ O ₃	F	Ferrite, 4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	C ₄ AF
MgO	M	Gypsum, CaSO ₄ ·2H ₂ O	CŜH ₂
SO ₃	Ŝ	Ettringite, (CaO) ₆ (Al ₂ O ₃)(SO ₃) ₆ ·32H ₂ O	C ₆ AŜ ₃ H ₃₂
H ₂ O	H	AFm, (Al ₂ O ₃ -Fe ₂ O ₃ -mono)	C ₃ (A,F)·CaX·xH

2 Aim

The aim of this work is to examine how early hydration of ordinary Portland cement is affected by addition of carbon dioxide during mixing. The experimental techniques used are isothermal calorimetry, Fourier transform infrared spectroscopy and thermogravimetric analysis.

3 Theory

3.1 Portland cement

Portland cement, commonly abbreviated OPC for ordinary Portland cement, is a form of hydraulic cement, meaning that it hardens through hydration with water and remains strong in a wet environment. Portland cement is regulated as CEM I in the European standard (EN 197-1) and as Portland cement Type I-V in the American standard (ASTM), where the type indicates the properties and area use of the cement. Before hydration, Portland cement clinker consists of four main components:

Alite ($3\text{CaO}\cdot\text{SiO}_2$)	50–70 weight-%
Belite ($2\text{CaO}\cdot\text{SiO}_2$)	15–30 weight-%
Aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$)	5–10 weight-%
Ferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$)	5–15 weight-%

The common names are often used for these phases, as they are not present in cement in pure form. Under the high temperatures of cement burning, other substances, such as magnesium, sodium, potassium and sulfur are incorporated to the clinker phases, potentially altering crystal structure and other properties in a significant way.

In order to produce Portland cement, the raw materials, consisting of calcium carbonate containing materials (e.g. limestone) is crushed together with a source of silica (such as clay), grinded and blended. Alumina (Al_2O_3) and iron oxide (Fe_2O_3) are often present as impurities in clay, but are sometimes also intentionally added to the mix.

The mix is heated in a kiln to a maximum temperature of around $1450\text{ }^\circ\text{C}$, where it is transformed to a solid material referred to as clinker. Below $1300\text{ }^\circ\text{C}$, clay minerals are decomposed and calcite dissociates to lime (CaO) and carbon dioxide. The lime then reacts with quartz and clay decomposition products to form belite, aluminate and ferrite. Little liquid is formed at this stage and it is thought that belite, ferrite and aluminate are formed mainly through reactions in the solid state. This part of the process is responsible for a major impact on the environment when carbon dioxide is released from calcium carbonate:



At higher temperatures, above around $1300\text{ }^\circ\text{C}$, melt is formed, mainly by ferrite and aluminate, which facilitates the formation of alite from belite and CaO at the highest

temperatures. After cooling, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), or some other source of sulfate, is added to the clinker, in order to make the aluminate less reactive during hydration, and the mix is ground to a fine powder [2] [5].

3.2 Cement hydration

Hydration is the process in which water reacts with the different species in cement and forms new compounds. It is a long-term process as cement continuous to hydrate over its lifetime, though, for practical reasons, early hydration is of particular interest. Several aspects of early hydration are important: the paste must retain its workability for some time in order to be cast, on the other hand, as a building material cement needs a quick development of strength after casting. Also, the heat evolution of hydration must not be too high, or in case of colder climates, must be high enough, in order for the cement to hydrate properly.

Hydration of calcium silicates is the most important part of OPC hydration. The hydration of alite and belite produces calcium silicate hydrate, or C-S-H in cement notation, and calcium hydroxide (in cement notation):



Since C-S-H is the main adhesive phase in Portland cement, the calcium silicates that produce it are the most abundant clinker phases in OPC by design. The dashes in the abbreviation are meant to indicate that it is not a well-defined phase, but have varying stoichiometry. The composition and structure of C-S-H varies depending on starting materials and hydration conditions and its Ca/Si ratio may vary from about 1.2-2.3, though normally it is around 1.75. The exact structure of C-S-H is not well known, despite much study, but is often described as a solid gel [2] [6].

Alite ($3\text{CaO} \cdot \text{SiO}_2$, C_3S) hydrates much faster than belite ($2\text{CaO} \cdot \text{SiO}_2$, C_2S), and is responsible for most of the early strength of cement, it is therefore of greatest concern here. Within a few hours, alite has begun to hydrate and form C-S-H. After 28 days of hydration, around 70 % of alite has been hydrated, and almost all after a year [5].

Almost all belite in cement is of the β -polymorph, which is not stable at room temperature, but is preserved in the production because of the rapid cooling of the cement melt. The γ -polymorph, though stable at ambient temperatures, is unwanted, because of its slow hydration. While belite reacts far more slowly than alite, it will overtake alite as a source of strength in the long run. After a year, pure belite and alite with the same w/c (water to cement) ratio, will be about equally strong, though almost all of the alite and only about 70 % of the belite has been hydrated. Belite hydration results in a higher C-S-H to calcium hydroxide ratio, a fact that is associated with its ultimately higher strength.

While aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$, C_3A) is needed in the production of cement, it reacts very quickly with water, producing AFm phases ($\text{C}_3(\text{A},\text{F}) \cdot \text{CaX} \cdot x\text{H}$, $\text{Ca}_4(\text{Al},\text{Fe})_2(\text{OH})_{12} \cdot \text{X} \cdot y\text{H}_2\text{O}$, where X denotes half an anion with double charge, or one anion with single charge). This may cause a so-called flash set, which will give the concrete poor final strength. To remedy this,

sulfate, usually in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is added to cement to retard the aluminate hydration through initial formation of trisulfate phases (AFt), most prominently ettringite ($(\text{CaO})_6(\text{Al}_2\text{O}_3)(\text{SO}_3)_6 \cdot 32\text{H}_2\text{O}$, $\text{C}_6\text{A}\hat{\text{S}}_3\text{H}_{32}$). When sulfate in solution has been depleted, aluminate reacts with ettringite and calcium hydroxide to produce AFm [5]:



Where C_4AH_{13} forms a solid solution with monosulfate ($3\text{C}_4\text{A}\hat{\text{S}}\text{H}_{12}$). Ferrite hydrates in a manner similar to aluminate, though at a slower rate, and is thus of less relevance to early hydration [5].

Cement hydration generally proceeds in four stages: the initial phase, the induction phase, the accelerating phase and the decelerating phase. Initially C_3S dissolves very fast after water is added, but dissolution is quickly decelerated long before equilibrium is achieved for reasons that are not well known. There is a strong evolution of heat for a few minutes, probably due to C_3S hydration and dissolution of C_3A and sulfates. The induction phase, characterized by a very slow rate of reaction, lasts for a couple of hours after initial mixing before hydration begin to accelerate. The mechanisms responsible for the slowdown are disputed. It has been suggested that a metastable layer of C-S-H forms on C_3S grains and acts as a barrier to solution. More recently, the slow dissolution of C_3S at this stage has been suggested as the retarding mechanism [7].

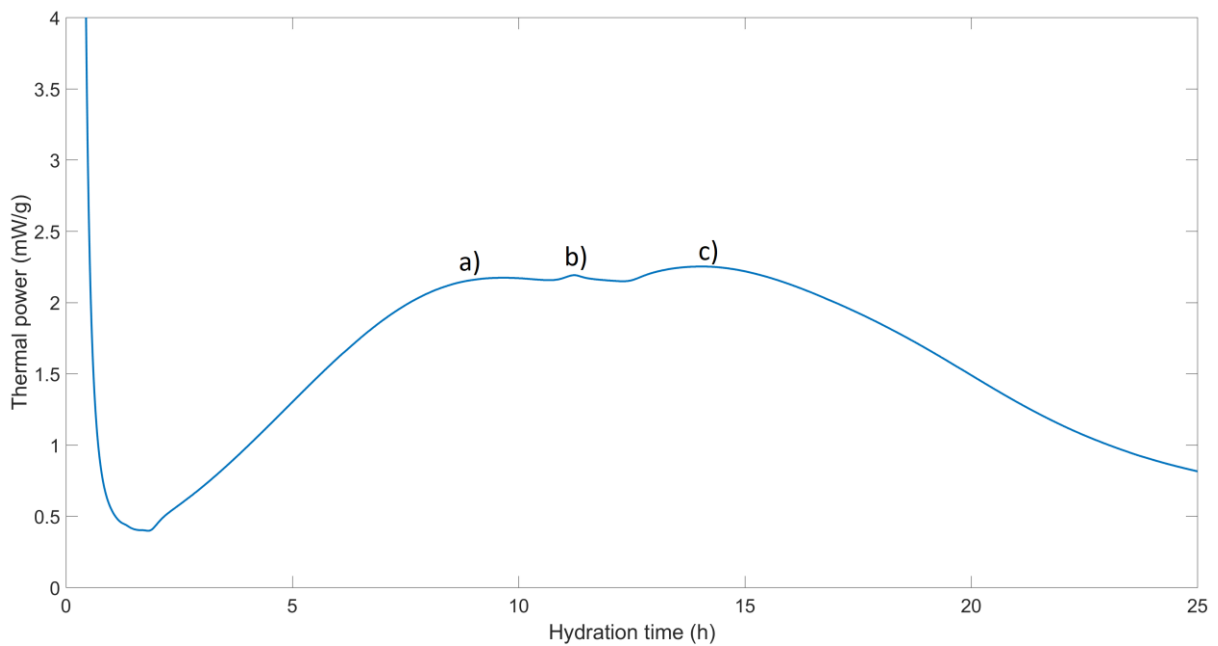


Figure 1. Thermogram showing heat output from the cement used in this work during the first 24 hours of hydration.

Figure 1 shows a thermogram from isothermal calorimetry of the cement used in this work. The accelerating phase lasts until approximately ten hours after wetting. At the end of this period C_3S has reached a maximal rate of hydration, corresponding to peak (a) in the thermogram. At this time, about 30% of the cement has reacted. A second peak (c) is often seen, and sometimes (as in this case) a small third peak (b), caused by reactions in sulfate and aluminate phases. Though the specific reactions causing these maxima of heat evolution has been disputed, a common explanation is that depletion of available sulfate disrupts the mechanism retarding aluminate hydration, causing rapid aluminate dissolution and a renewed formation of ettringite. This causes ettringite to become unstable and gradually convert to AFm phases with lower sulfate content. The decelerating phase will continue almost indefinitely as long as there is accessible water [5] [7].

3.3 Carbonation of cement

Natural reactions with CO_2 from the atmosphere will affect concrete during its service and is considered a durability problem. Concrete is usually very alkaline, and reaction with atmospheric CO_2 will make it more acidic, inducing corrosion of steel reinforcements. Carbonation is also associated with decreased porosity and eventually cracking due to shrinkage [6].

It is usually thought that calcium hydroxide in solution is the main cement phase to react with CO_2 , forming calcium carbonate [6]:



But it has been shown that CO_2 reacts with all major cement phases. C-S-H has been shown to react at an increasingly quicker rate with CO_2 , as it becomes more carbonated. Carbonation removes calcium ions from C-S-H resulting in the formation of calcite and amorphous silica gel ($Si_2O_3 \cdot xH_2O$), a reaction that proceeds faster with decreasing Ca/Si ratio. It has also been shown that alite and belite may react with CO_2 to produce silica and calcite. Carbonation of ettringite and aluminate may also take place, producing gypsum and alumina gel ($Al_2O_3 \cdot xH_2O$) [6].

Though carbonation is usually considered harmful for the concrete, early exposure to CO_2 may be beneficial. It was uncovered in the 1970s by Klemm and Berger that curing (storage in an environment favorable to hydration) in an atmosphere of CO_2 can increase early strength development. Carbon curing often uses low w/c ratios (0.1-0.2) and atmospheric and high CO_2 -pressure, with subsequent water spraying [8] [6].

Finely crushed calcium carbonate ($CaCO_3$) is sometimes used as filler in cement, and has been shown to interact in hydration reactions. $CaCO_3$ has been shown to play a role in cement hydration somewhat similar to that of gypsum. Hydration of C_3A mixed $CaCO_3$ will result in the AFm phase calcium monocarboaluminate ($C_3A \cdot CaCO_3 \cdot 11H_2O$), or hemicarbonat ($2C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H_2O$) at lower CO_3^{2-} activities. In the presence of gypsum, such as with hydration of C_3A -rich cements, $CaCO_3$ is known to accelerate early formation of

ettringite [9] [10]. CO_3^{2-} in cement paste has also been reported to stabilize ettringite indefinitely, as hemi- and monocarbonate phases free up sulfate [11].

Very recently, experiments have been made where CO_2 is introduced at the mixing stage. Relatively small amounts of liquid CO_2 was introduced to industrial scale batches of concrete by Monkman et al. while mixing, at the same time that water was added. An early strength development of 10 % at 1 day and 14 % at 3 days, as well as a halving of the induction period according to calorimetric testing, was achieved with a 0.05 % bwc (by weight of cement) CO_2 dose. Larger doses offered a smaller increase in strength, suggesting a small optimized dose is preferable [12]. In an earlier trial, a higher 0.3 % bwc dose of CO_2 , introduced at the batching stage, offered a 26 % increase in strength at day 3, although the initial hydration was retarded compared to the reference in this case [13].

It is suggested that the increase in early strength from CO_2 addition is due to formation of colloidal nanoparticles of CaCO_3 in the pore solution of cement. Such extra particles placed between the clinker grains would serve as additional nucleation points where C-S-H can form. In addition, early consumption of Ca^{2+} might result in a C-S-H with lower Ca/Si ratio. Such a layer of C-S-H is less dense and, if formed at the surface of clinker grains, may provide lesser resistance to hydration [12].

3.4 Isothermal Calorimetry

An isothermal calorimeter is a device used to measure the total heat flux of a sample. In order to avoid temperature interference on reaction rates and heat transfer, the samples are kept in an isolated container at a constant temperature, in this case 20 °C. The custom-built calorimeter used in this case holds two samples with corresponding non-heat evolving references in separate containers. The heat flux from the references, consisting of a fixed amount of water with a similar heat capacity, is subtracted from that of the samples to compensate for temperature fluctuations in the calorimeter.

3.5 Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy gives information on the chemical bonds present in a sample. As quantum physics states that changes in energy are quantized, the transition of a molecular bond from one vibrational state to another is associated with the absorption of a specific amount of energy. This amount usually corresponds to the energy levels of electromagnetic radiation in the infrared region. The infrared spectrum of a sample is inferred by detecting the intensity of infrared radiation, at known frequencies, that has passed through a sample. If the frequency of the radiation matches the vibrational energy of bonds in the sample, absorption occurs.

The infrared radiation is produced by an interferometer, in which the beam from a radiation source is split to two mirrors by a beam splitter. As one mirror is moving, while the other is stationary, there will be a path difference as the beams are mirrored back and rejoined. This causes an interference pattern as a function mirror position. The intensity of the radiation is then plotted against mirror position in an interferogram. The interferogram is then decomposed into its constituent frequencies through Fourier transformation, hence the name.

In this work, FTIR was used with an attenuated total reflection mode (ATR) accessory. In ATR the infrared radiation does not pass through the sample, but only through and internal reflection element (IRE). The radiation interacts with the sample through a so called evanescent wave, an electric field extending from the IRE, directly proportional in strength to wavelength. To obtain the spectra similar to those of IR in transmission mode, the spectra is multiplied by wavelength. FTIR-ATR has the benefit of very simple sample preparation and continuous monitoring, and is suited for samples where close contact with the IRE can be achieved, such as cement pastes [14].

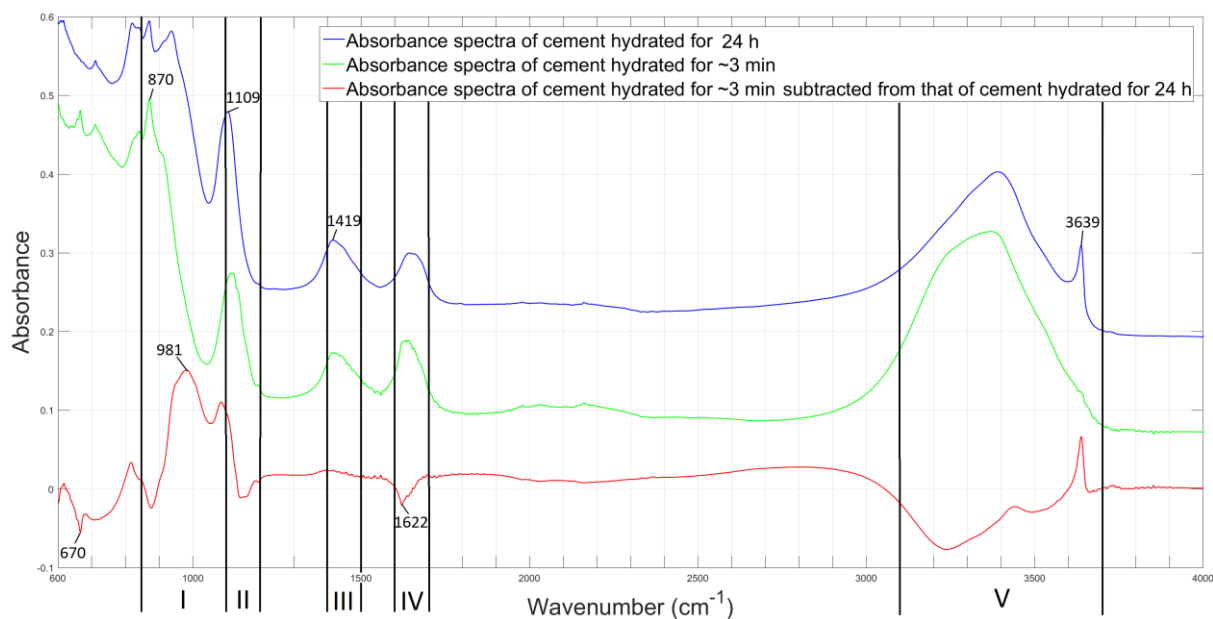


Figure 2. Demonstration of absorbance spectra of cement with some important regions and peaks marked out.

Figure 2 demonstrates FTIR-ATR spectra of the cement used in this work. It shows the absorbance spectra of cement hydrated for ~3 minutes, 24 hours and the difference spectrum acquired by subtracting that taken after ~3 minutes from that taken after 24 hours. By subtracting one spectrum from another, one might notice nuances that are not apparent in the unmodified spectra. Some regions and wavelengths are marked out. This is meant as a rough sketch open to debate and it does not take overlap into account. Region I is the silica-region, where the tricalcium silicate clinker phases and their main hydration product C-S-H appear. 981 cm^{-1} is the wavelength showing the greatest increase in this region. A shift from wavelengths $< 900\text{ cm}^{-1}$ to those closer to 1000 cm^{-1} is taken to represent the dissolution of alite and the growth of C-S-H. Region II is the sulfate-region where many different species of the sulfate-aluminate chemistry appear, making it difficult to interpret. 1109 cm^{-1} is typical of gypsum, but is also close to the main peak of ettringite. Region III is associated with the CO_3^{2-} ion, polymorphs of CaO_3 appears here. Region IV is associated with water; bulk water appears here, but also crystalline water. 1622 cm^{-1} is the more visible of two peaks (the other appearing around 1680 cm^{-1}) assigned to gypsum in this region. Region V is associated with the $-\text{OH}$ bond. It consists of many overlapping bands, but is dominated by water, and is difficult to resolve. The peak around 3639 cm^{-1} appears quite distinctly here and can be

assigned to $\text{Ca}(\text{OH})_2$. Many different species appears below $< 900 \text{ cm}^{-1}$, with crystalline CaCO_3 (870 cm^{-1}) and gypsum (670 cm^{-1}) being two peaks of interest [15] [16] [17] [18] [19] [20].

3.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is technique where a sample is heated while its weight is being monitored. As different compounds tend to leave within a specified temperature interval, TGA can be used to quantify the amounts of different phases in a sample. In cement, mass loss at up to about 600°C is mainly due to water lost from the system, while mass loss at higher temperatures is mostly from CO_2 leaving [21].

Differential thermogravimetry (DTG) is the study of the derivative of weight change with respect to temperature (or time). DTG is useful in order to show a higher resolution of weight change and to identify weight loss in individual species [21]. Figure 3 shows an example of a TGA and a DTG curve of the cement used in this work. The dashed lines illustrate the temperature intervals assigned to $\text{Ca}(\text{OH})_2$ ($370\text{--}470^\circ\text{C}$) and CO_2 ($530\text{--}875^\circ\text{C}$).

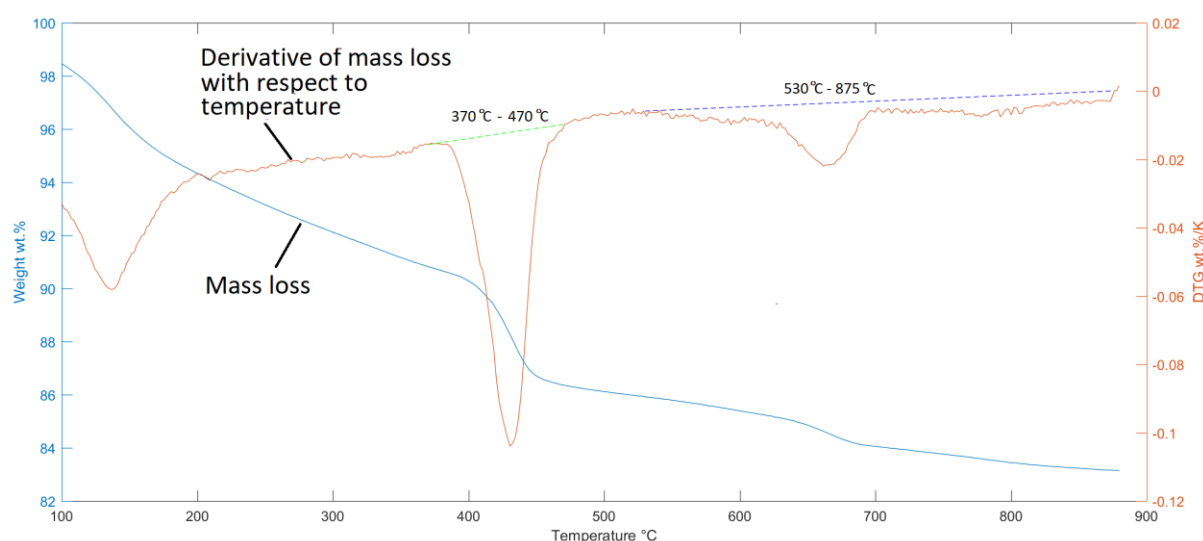


Figure 3. TGA and DTG curves of the cement used in this work. The dashed lines illustrate the temperature intervals used to quantify $\text{Ca}(\text{OH})_2$ and bound CO_2 .

4 Experimental

4.1 Sample preparation

Cement pastes were made from 20 g Portland cement (CEM I 52.5R, Snabbhårdnande cement (rapid hardening cement) Cementa AB) and 10 g deionized water ($w/c = 0.5$). Water and cement was weighed in advance and mixed for 90 s by hand. Carbonated water was made by Sodastream from fridge-cold deionized water. The amount of CO_2 in the water was not quantified.

The addition of solid carbon dioxide to samples proved difficult to quantify at lab scale as the rate of sublimation is quite rapid. An amount of about twice that intended for mixing was first put on a scale and then mixed with cement and water after enough CO_2 had sublimated to reach the intended weight. It was not possible to measure the amount of CO_2 absorbed by weighing the sample before and after mixing. In fact, the scale showed a slight decrease in mass after CO_2 was mixed in, possibly due to water evaporating with CO_2 gas and/or cold affecting the calibration of the scale. Attempts were also made to mix in a “very large” dose of solid CO_2 by consecutive mixing, possibly saturating the cement with respect to carbon dioxide. To achieve this 5 times $\sim 1\text{--}2$ g of solid CO_2 was mixed with the cement and stirred until no visible trace was left over a period of about 5 minutes, equaling a possible maximum dose of up to 50 % bwc.

Sodium bicarbonate was mixed with water and left to dissolve for about one hour, stirred occasionally, before mixing with cement. With a dose of 5 % bwc NaHCO_3 , not all NaHCO_3 was dissolved at the time of mixing with cement. Stiffening of the cement occurred within minutes when mixed with larger doses of NaHCO_3 .

4.2 Isothermal calorimetry

In the isothermal calorimetry measurements, samples of ~ 5 g cement paste were kept in plastic 20 mL ampules and kept in isolated containers for ~ 24 hours at a constant temperature of 20°C . The containers are in contact with a heat-flow sensor, mounted on a heat sink. The temperature inside was kept at a constant with a thermostat which were controlled by a thermoelectric air-air heater cooler (AA-100-24-22, SuperCool, Gothenburg, Sweden).

4.3 In situ FTIR-ATR

The FTIR-measurements were made with a Nicolet 6700 and diamond IRE at a resolution of 2 cm^{-1} between 550 and 4000 cm^{-1} . Hydrating cement paste were placed on the IRE about 2 minutes after mixing, rapidly covered with plastic film and kept in place by a clamp. A piece of wet paper was placed next to the sample under the film and the film was taped to the sample holder, in order to keep the sample at 100 % relative humidity. Hydration was monitored for 25 hours with measurements made every 10 minutes. The room held a temperature of about 20°C .

4.4 Thermogravimetric analysis

After an initial hydration period in the isothermal calorimeter of about 24 hours, some of the samples used in calorimetry were used for thermogravimetric analysis. The cement were removed from the ampules and ground to a powder under nitrogen gas flow, in order to minimize CO₂ uptake. Samples were subsequently stored and dehydrated in a container with constant nitrogen flow.

For the thermogravimetric analysis, about 15-20 mg of ground mortar was heated at a rate of 20 °C/min to 900 °C, in an alumina crucible. The instrument used was a TGA-Q 500 from TA Instruments. Nitrogen with a flow of 90 mL/s was used as purging gas during measurements.

5 Results

5.1 Isothermal calorimetry

Calorimetric results of carbonated water are very similar to those of cement mixed with uncarbonated water (Figure 4). The most notable difference is that the small peak between the shoulders of the thermogram has advanced in time. This peak may represent a renewed formation of ettringite after depletion of available gypsum [7]. The maximum height of the thermogram may vary somewhat from sample to sample, but there seems to be a slight acceleration the first ~8 hours and some deceleration after ~14-16 hours. The second shoulder is also somewhat more pronounced compared to the first.

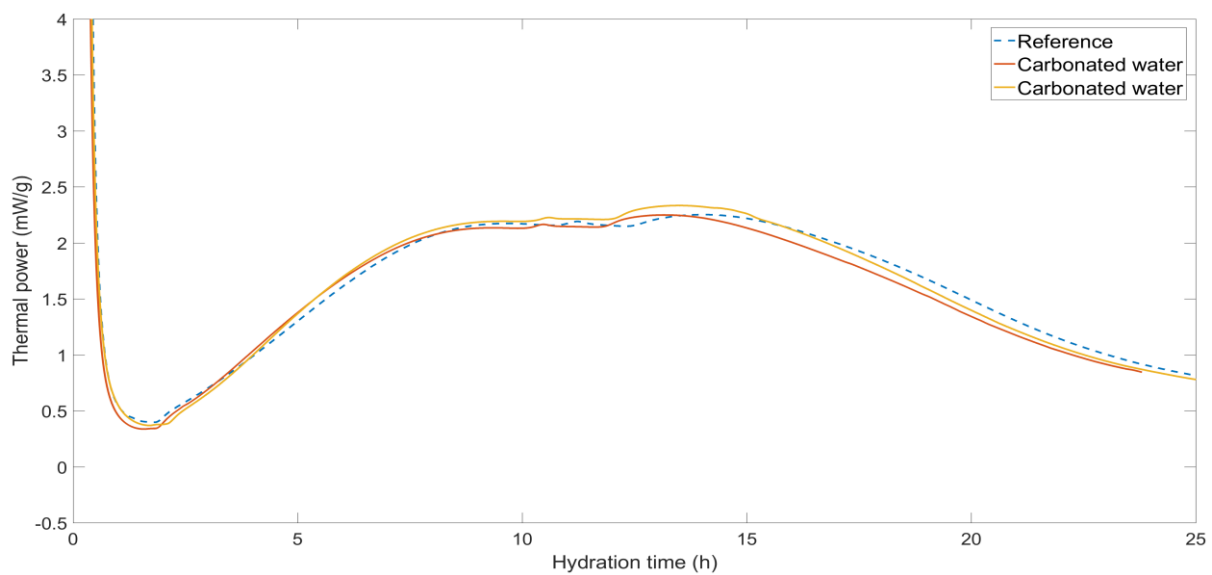


Figure 4 Thermogram of cement mixed with carbonated water showing the heat output during the first 24 hours of hydration.

Figure 5 shows thermograms of cement mixed with solid CO_2 in doses of 5-10 % bwc. Considering the difficulties duplicating the process of mixing cement with solid CO_2 , a certain variation in the result may be expected, though the result seems to be quite reproducible. A dose of 5-10% CO_2 bwc will accelerate early hydration up until about 15 hours, though after this time, hydration has lower heat profile compared to that of reference. CO_2 in these doses will also give a higher maximum heat of hydration, and the second shoulder is increased in comparison to the first. This seems to indicate that CO_2 primarily reacts with sulfate and aluminate, as modern cements are designed to let reactions involving these phases reach a maximum rate after C_3S does. This is in contradiction to the results of Monkman et al. [12] that showed a greater increase in the first, C_3S -associated, peak, something that might be explained by the use of different kinds of cement or differences in concentration of CO_2 . Like in the case with carbonated water, the small peak between the shoulders is advanced in time.

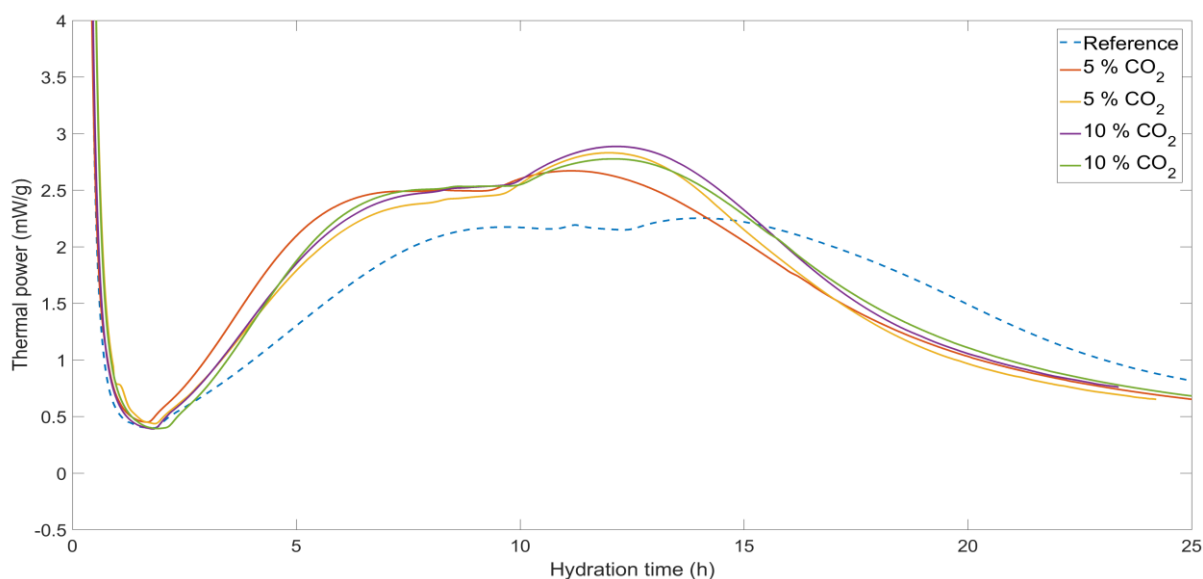


Figure 5. Thermogram of cement mixed with 5-10 % bwc solid carbon dioxide showing the heat output during the first 24 hours of hydration.

A “very large” dose of solid CO_2 does not seem to accelerate early hydration to the same degree as doses of 5-10 % CO_2 (Figure 6). It seems to prolong the induction period, something that may be in part due to initial cooling of the sample, although temperatures should be equalized after some time in the calorimeter. In addition, it does not show the same increase of the maxima in the thermogram as lower doses, nor a similar increase in the second shoulder. This result is in accordance with those of Monkman et al. [12] in showing an upper limit for acceleration of hydration at higher doses of CO_2 . Cement mixed with 1 % carbon dioxide does not differ noticeably from reference, as this was probably too small a dose for significant amounts of CO_2 to be absorbed during mixing. The thermogram of cement mixed with 2.5 % CO_2 is especially interesting however. The 2.5 % dose seem to accelerate very early hydration more than any other, and, unlike other samples, show an increase in the first shoulder of the thermogram compared to second. It should be noted that this 2.5 % sample is not the same 2.5 % sample shown in the FTIR section. No IR analysis was made of this sample.

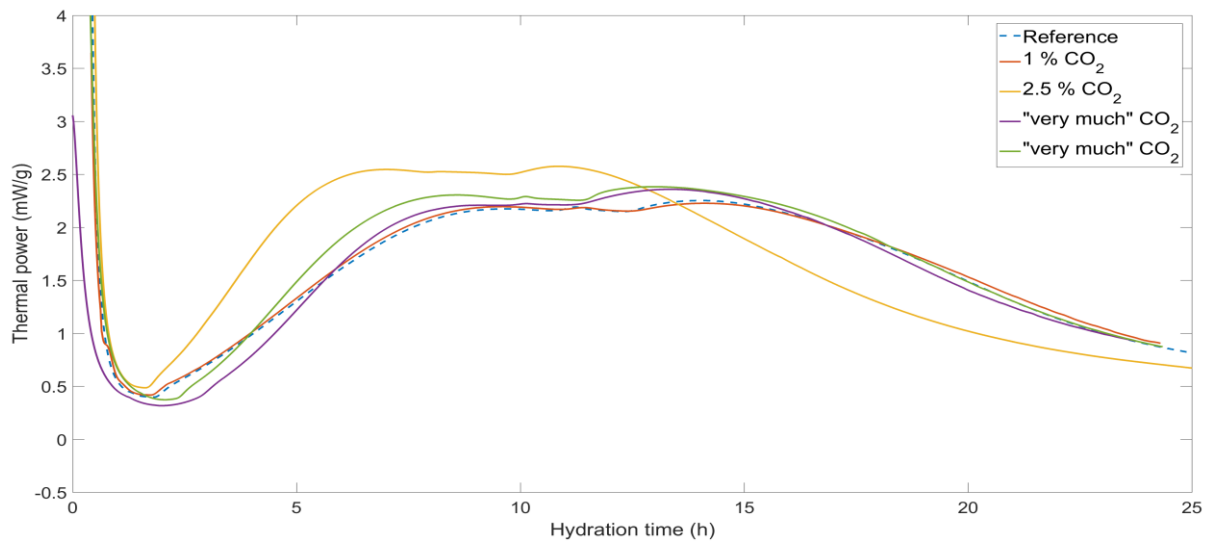


Figure 6. Thermogram of cement mixed with 1 %, 2.5 % and “very much” solid carbon dioxide showing the heat output during the first 24 hours of hydration.

Attempts was also made with sodium bicarbonate (NaHCO_3) to, possibly, emulate the effect of mixing in CO_2 (Figure 7). Sodium bicarbonate in higher doses acts as an accelerator of early cement hydration. Cement with 5 % NaHCO_3 will reach a maximum heat of hydration after only ~5 hours of hydration and then quickly decelerate, with only a single peak on the thermogram. A dose of 0.5 % NaHCO_3 bear a reasonable resemblance to that of a 5-10 % dose of solid CO_2 , with an early acceleration and a pronounced second shoulder. Intermediate doses seem to retard hydration at the early stage, instead accelerating hydration after ~12 hours, with a large increase in the second shoulder on the thermogram.

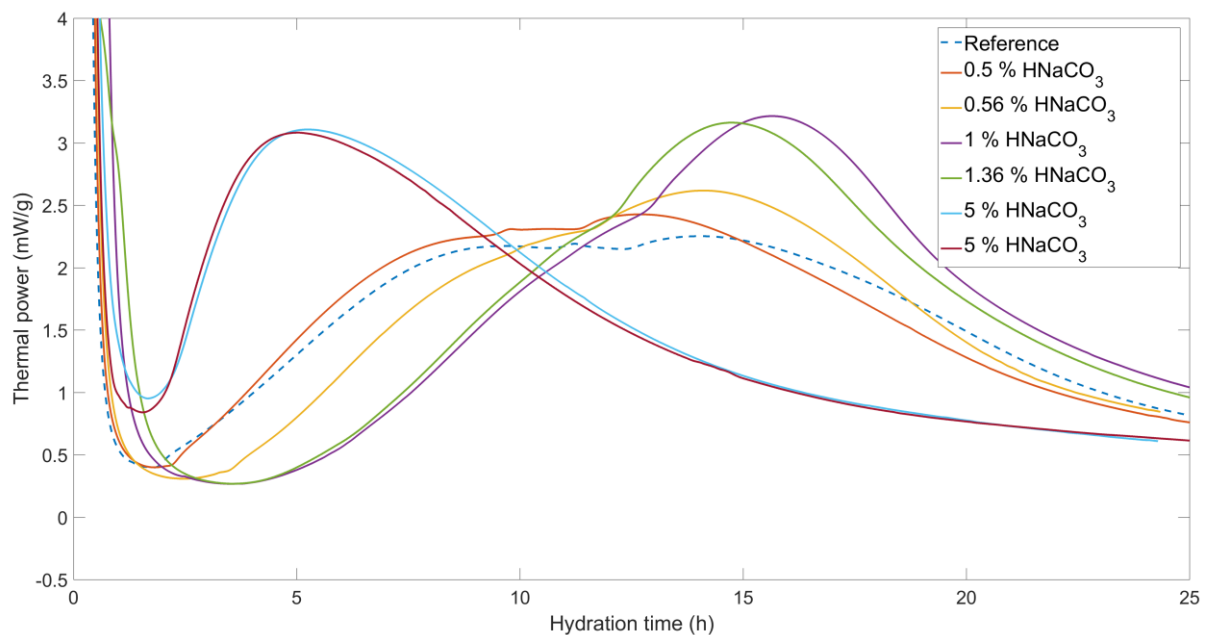


Figure 7. Thermogram of cement mixed with sodium bicarbonate showing the heat output during the first 24 hours of hydration.

5.2 In situ FTIR-ATR

Figure 8 shows the initial FTIR spectra of cement hydration (taken approximately 3 minutes after mixing), as well as that taken after 20 hours. Usually, contrasts in such unmodified spectra are too subtle to notice, and it is more useful to subtract one spectrum from another to see where they differ. With pure substances it is far easier to identify specific peaks, but cement is a heterogeneous mix of many different phases and with many overlapping peaks. Most peaks seen in cement spectra are actually the combined result of more than one closely spaced peaks. By subtracting one spectrum from another, it is possible to notice minor contrasts, making it possible to resolve individual peaks in greater detail and see where the spectra differ. Thus, the following section will be concerned mostly with differences between spectra.

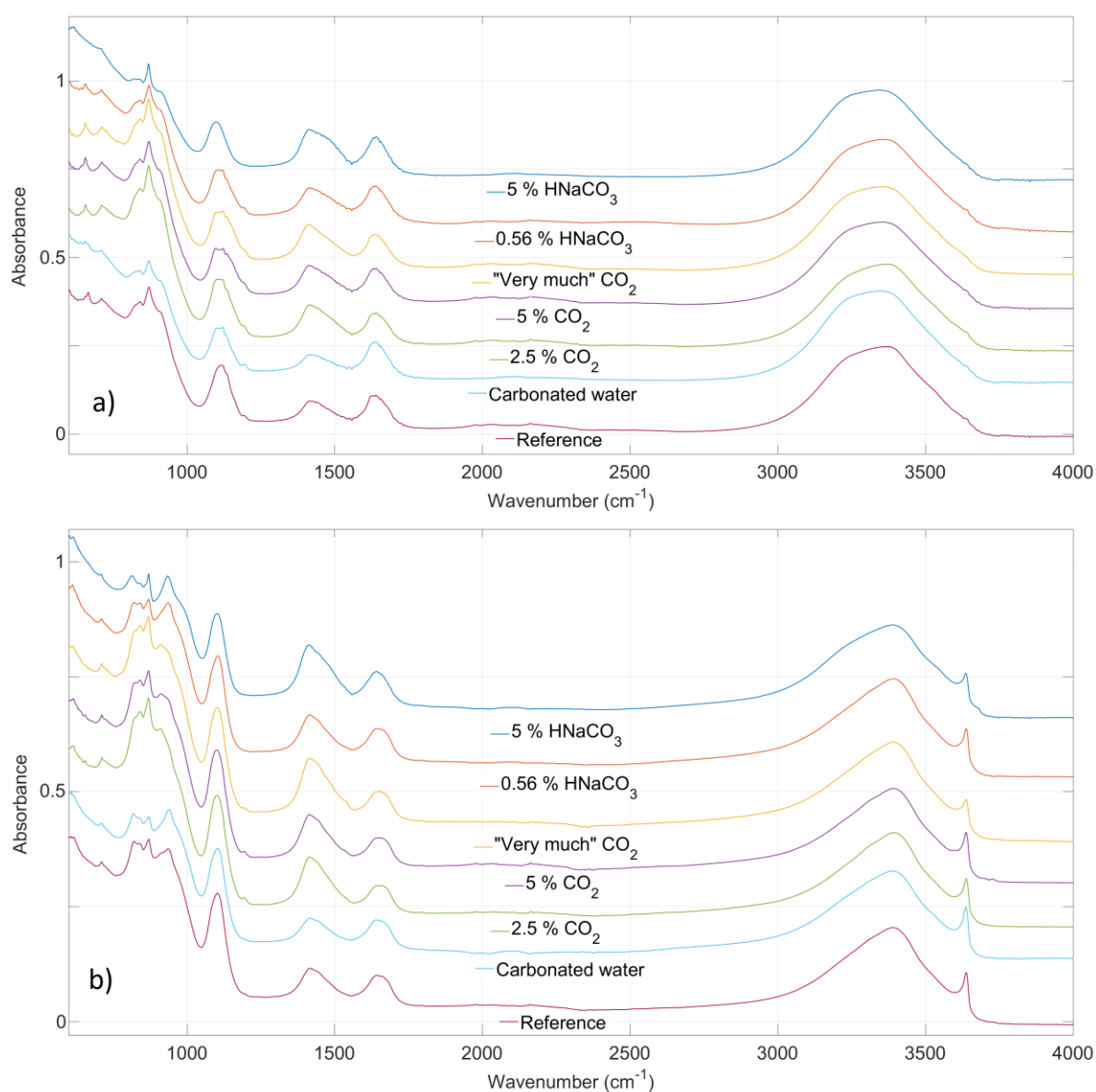


Figure 8. FTIR spectra of cement with various degrees of carbonation, taken after a. ~3 minutes and b. 20 hours of hydration. The spectra are shown offset for clarity.

In the initial spectra, taken ~3 minutes after mixing, differences can be seen in carbonated samples compared to reference (Figure 8). The peak at 667 cm^{-1} in reference, associated with gypsum, seems to appear at 656 cm^{-1} in carbonated samples, a wavenumber more consistent with anhydrite or hemihydrate [22] [16]. Carbonated cement, even cement mixed with carbonated water containing very little CO_2 , seem to have more complexity in the sulfate range at $\sim 1100\text{-}1200\text{ cm}^{-1}$. Small peaks can be noticed at 1099, 1111, 1122 and 1136 cm^{-1} . There is a broad peak at $\sim 1400\text{-}1500\text{ cm}^{-1}$ in all spectra, indicating carbonate ions are originally present in the cement, regardless of CO_2 -addition. This band is difficult to resolve, as all polymorphs of CaCO_3 as well as monocarbonate appear here [23]. Calcite is the most probable species though, being more stable than other forms of CaCO_3 . A sharp peak at 870 cm^{-1} can also be seen, indicating a crystalline form of carbonate, likely calcite [18]. Water appears in the spectra at $\sim 1600\text{-}1700\text{ cm}^{-1}$, and in the O-H stretching region at $\sim 3000\text{-}3700\text{ cm}^{-1}$, where also a distinct peak around 3640 cm^{-1} , associated with Ca(OH)_2 , may be found. The calcium silicate clinker phases, as well as their hydration product, calcium silicate hydrate, appear in the silica region, stretching from ~ 900 to $\sim 1100\text{ cm}^{-1}$. A shift from lower ($\sim 875\text{-}930\text{ cm}^{-1}$) to higher ($970\text{-}1080\text{ cm}^{-1}$) wavenumbers is indicative of a dissolution of C_3S and the formation of C-S-H, eventually overlapping with, and obscuring the sulfate region [19] [17].

Subtracting the initial spectra of CO_2 -mixed samples from that of reference (Figure 9), one can notice a higher peak at 870 cm^{-1} , with an increase in the entire $\sim 800\text{-}950\text{ cm}^{-1}$ range, as well as in the shoulder peaks at 1410 and $\sim 1485\text{ cm}^{-1}$, all signs of higher carbonate concentration. The area around $\sim 1100\text{-}1150\text{ cm}^{-1}$ is initially below that of the reference with dips centered around 1117 and 1128 cm^{-1} . Around this area, two peaks centered at 1092 and 1182 cm^{-1} also appears in carbonated cement. The two dips at 1620 and 1684 cm^{-1} are associated with water in sulfates and may indicate a lower amount of gypsum in carbonated samples than in reference [22].

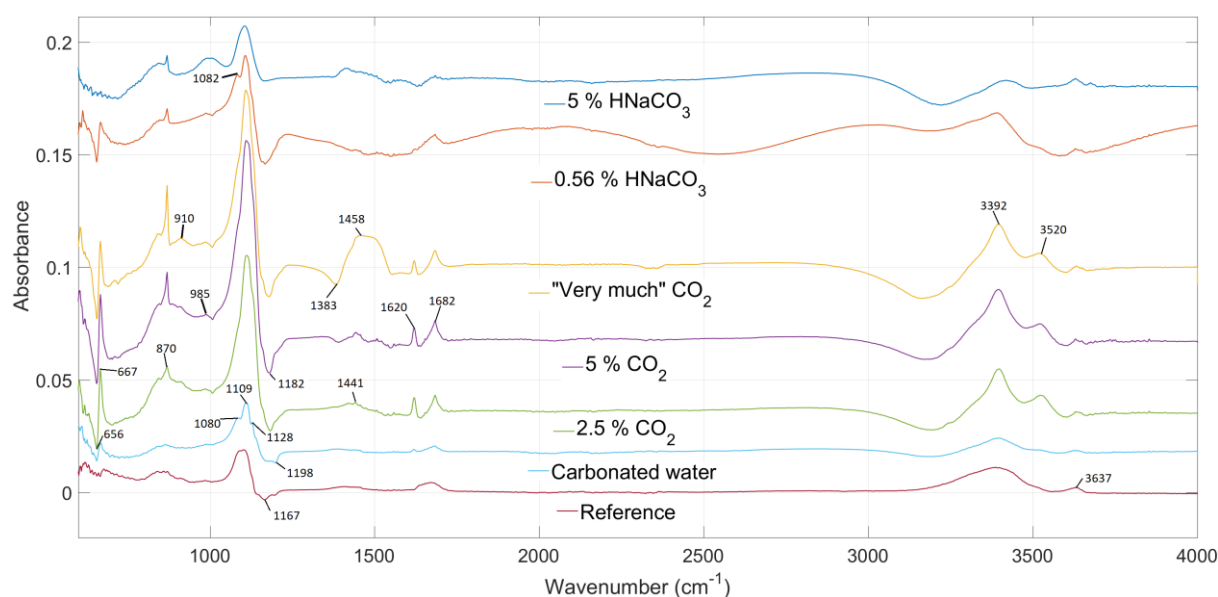


Figure 9. FTIR spectra of hydrated cement where the spectrum taken after 30 minutes for each sample has been subtracted from the initial spectra (~ 3 minutes after mixing). The spectra are shown offset for clarity.

After 30 minutes of hydration it seems evident that gypsum content has increased in the carbonated samples, indicated by the increase in peaks at 1620, 1682, 3392 and 3520 cm^{-1} (Figure 9). There is a sharp dip and peak at 656 and 667 cm^{-1} in CO_2 -mixed samples, possibly representing a hydration of anhydrate or hemihydrate to gypsum [22] [16]. Two minor peaks also seem to appear at 912 and 987 cm^{-1} . In addition, there is a large increase in the area 1080-1160 cm^{-1} , consisting of three (or more) overlapping peaks at 1109, 1122 and 1134 cm^{-1} . The dip around 1176 cm^{-1} is also larger. This hump-dip in the sulfate region indicates a greater shift in sulfate phases early on in carbonated samples. These bands are very difficult to resolve as many different compounds might appear here, including AFm, AFt, calcium sulfates, syngenite ($\text{K}_2\text{Ca}(\text{SO}_4) \cdot \text{H}_2\text{O}$) and amorphous sulfates [19]. The peak at 1109 cm^{-1} is consistent with the absorption spectra of gypsum, a fact that fits in well the observation of other gypsum-associated peaks [20]. A shift towards lower wavelengths in the sulfate region has also been taken as indicative of ettringite formation, something that may contribute to the spectra [5] [17]. Cement with a 0.56 % dose of sodium bicarbonate behaves much in the same manner as that mixed with solid CO_2 , though shifts in the sulfate area and signs of gypsum increase are smaller. A larger dose of 5% NaHCO_3 does not differ much from reference in the sulfate area, but seem to already show a shift to higher wavelengths in the silica region, with a dip around 900 cm^{-1} , and a peak centered at 1000 cm^{-1} , associated with dissolution of alite and formation of C-S-H [19]. Cement with carbonated water is almost indistinguishable from reference, except from a small peak-dip at 656-667 cm^{-1} and a peak at 1109 cm^{-1} .

An increase in the sharp peak at 870 cm^{-1} over a broader band at $\sim 800\text{-}900 \text{ cm}^{-1}$, associated with out of plane vibration of CO_3^{2-} , can be seen in all carbonated samples, except for that with carbonated water. There is also an increase in two peaks in the area around $\sim 1400\text{-}1530 \text{ cm}^{-1}$, associated with asymmetric stretching of CO_3^{2-} , in carbonated cement [18]. A dip at around $\sim 1383 \text{ cm}^{-1}$ is especially prominent in samples with a “very large” dose of CO_2 , but also seem to appear in the spectra of 5 % CO_2 and 0.56 % NaHCO_3 . How to assign this wavenumber is difficult to know, but monocarbonate or hemicarbonate seems reasonable [15] [23].

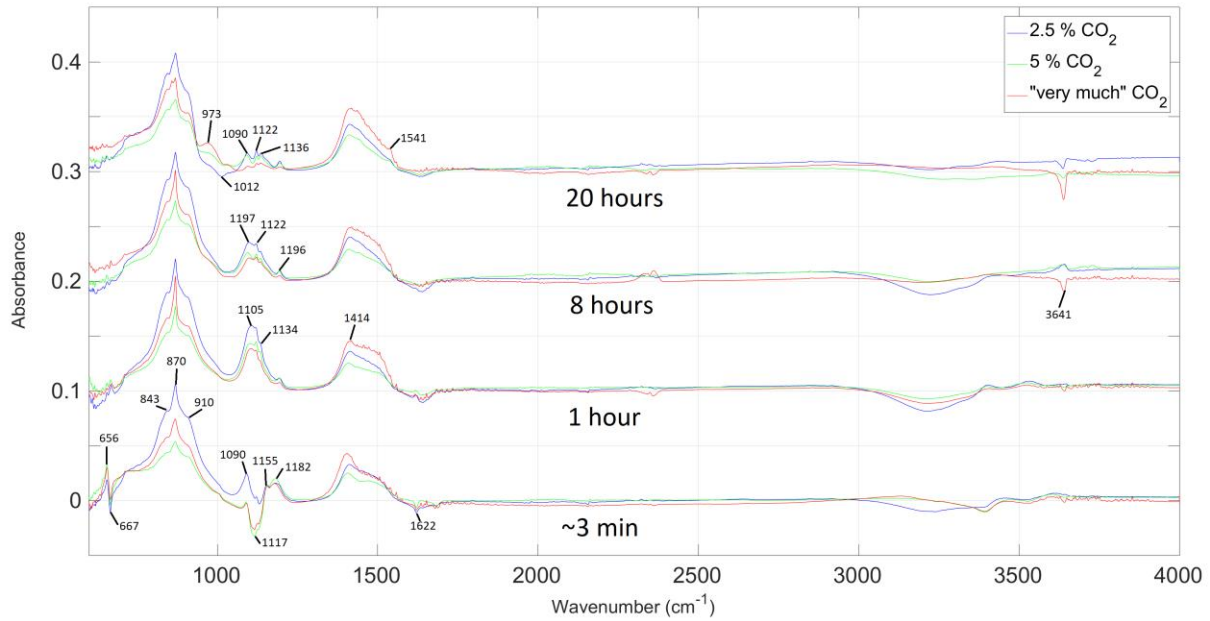


Figure 10. FTIR spectra of a reference sample subtracted from the spectra of samples mixed with 2.5 %, 5 % and “very much” CO₂ at different times of hydration. The spectra are shown offset for clarity.

After the first 30 minutes of hydration it becomes more difficult to detect any influence from carbonation in the spectra, and sample to sample variation (especially among reference samples) seem to contribute much to the variation. As can be seen in Figure 10, throughout the first 24 hours of hydration the difference between reference and CO₂-mixed samples follows a pattern. It seems like different doses of CO₂ have a similar effect on the spectra, showing peaks and dips compared to reference at much the same wavenumbers. There is a sharp peak at 870 cm⁻¹ and the broad band around it is heightened, as well as dual peaks around ~1410 and ~1500 cm⁻¹, all signs of increased carbonate content. There is also a heightening of the ~1100-1200 cm⁻¹ region with consistent peaks at 1122, 1134 and 1196 cm⁻¹ in carbonated samples, and a peak at 1092-1101 cm⁻¹, shifting to lower wavenumbers as hydration progresses and flattening with time. The region around ~1624 cm⁻¹ associated with water in sulfates also seems somewhat lower in CO₂-samples. Although not always the case, the calcium hydroxide peak around 3640 cm⁻¹ is sometimes decreased in carbonated samples compared to reference. This could be due to a retardation of silicate hydration, but there are no signs of a corresponding lowering of the C-S-H associated band around ~980 cm⁻¹.

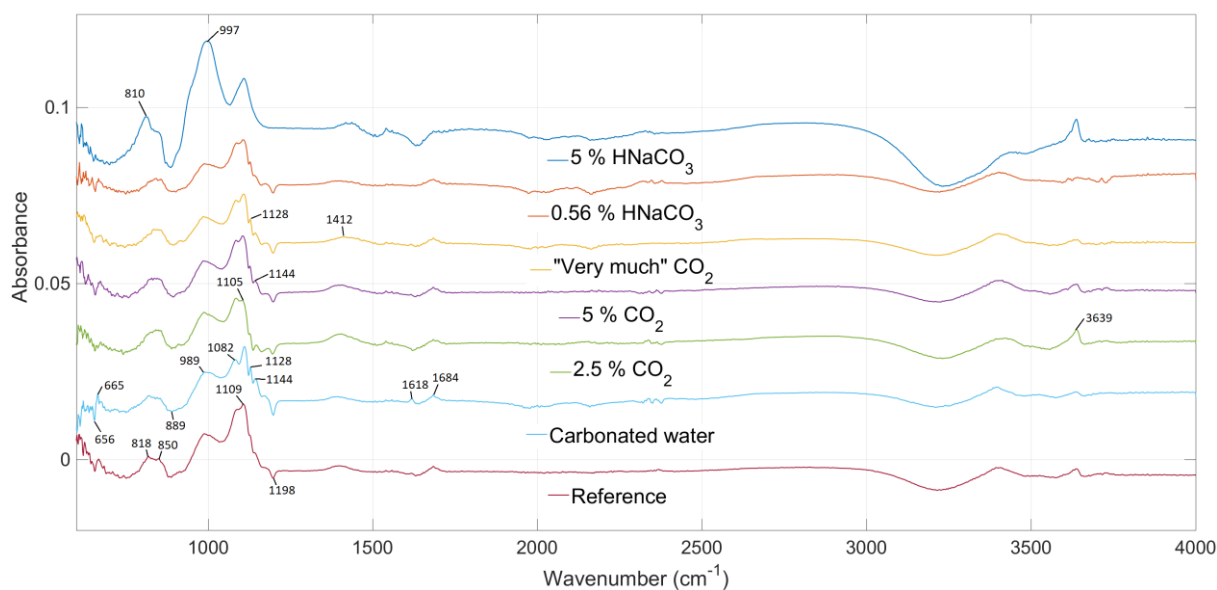


Figure 11. FTIR spectra of hydrated cement where the spectrum taken after 30 minutes for each sample has been subtracted from that taken after 3 hours. The spectra are shown offset for clarity.

The IR spectra of hydration between 30 minutes and about 3 hours (Figure 11) show little variation between samples. The only major differences are seen in samples with 5 % NaHCO_3 , with a large hump-dip around 887 cm^{-1} and 995 cm^{-1} . Considering the calorimetric results, showing a greatly increased early hydration, this might be expected. A prominent peak at 816 cm^{-1} and a lack of the 1198 cm^{-1} dip also separates this sample from the rest. From around two hours of hydration the 1620 cm^{-1} peak has begun to decrease while there's still an increase at 1684 cm^{-1} in all samples. This might indicate that the concentration of gypsum has begun to decrease, but also that free water has begun to deplete, as can be seen in water associated bands around $\sim 1650\text{ cm}^{-1}$ and $3000\text{--}3700\text{ cm}^{-1}$.

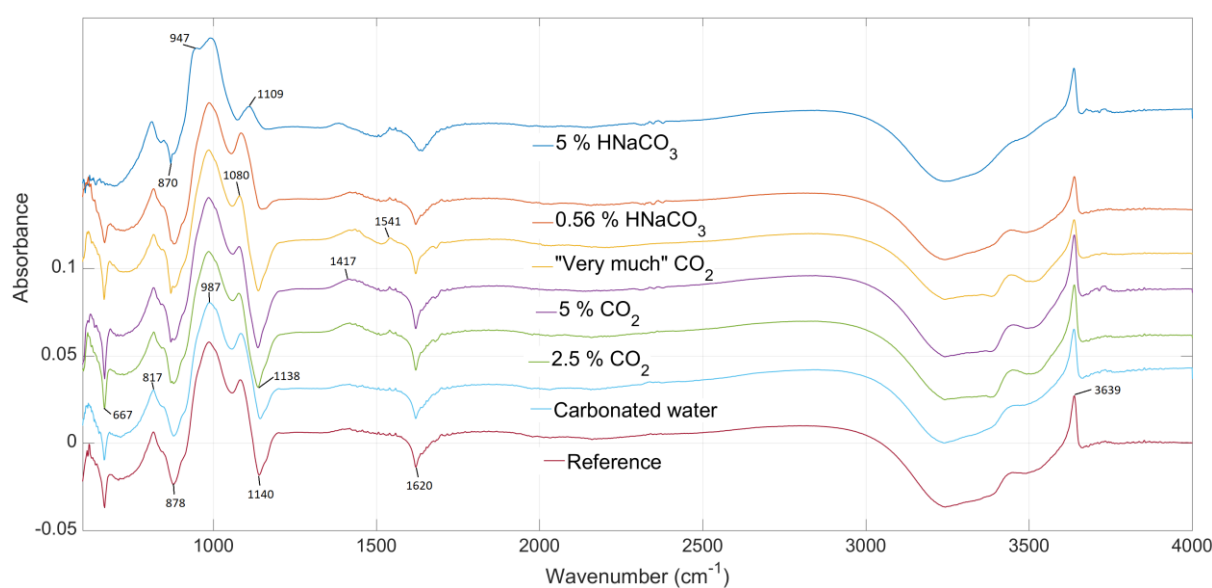


Figure 12. FTIR spectra of hydrated cement where the spectrum taken after 3 hours for each sample has been subtracted from that taken after 8 hours. The spectra are shown offset for clarity.

Looking at the changes between 3 and 8 hours of hydration (Figure 12), the shift to higher wavenumbers seen in the ~ 850 to ~ 1000 cm^{-1} range is an indication that silicate production has begun to accelerate. The dip around 877 cm^{-1} is associated with the dissolution of C_3S , while the peaks centered at ~ 985 cm^{-1} and ~ 1080 cm^{-1} represent a growth of C-S-H. Only minor differences in samples mixed with CO_2 can be noted. There is an additional dip at 870 cm^{-1} , associated with calcite, in spectra of cement mixed with CO_2 , as well in that of 5 % NaHCO_3 . Despite this, the two CO_3 associated peaks at ~ 1420 cm^{-1} and ~ 1540 cm^{-1} seem to increase carbonated in all samples, while the spectra of reference and carbonated water show a minor peak at ~ 1412 cm^{-1} . Also, the dip at 1142 cm^{-1} in reference appears at 1136 cm^{-1} in samples mixed with CO_2 . The main silica related peaks are of similar size in all samples, with a high dose of sodium bicarbonate as the only exception, already showing a decreased rate of hydration and a different peak shape. This deceleration may be caused by the presence of Na^+ , as the addition of NaOH to cement shows a similar effect [24]. Sharp dips at 670 cm^{-1} in all spectra, except that of 5 % NaHCO_3 , indicates a lowered concentration of gypsum.

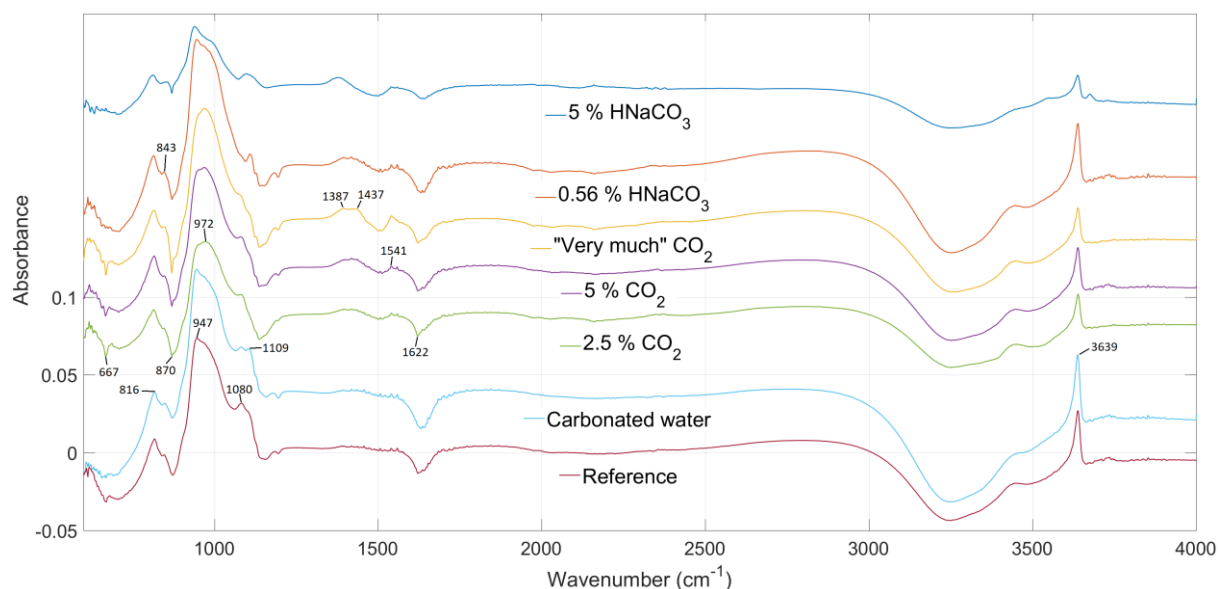


Figure 13. FTIR spectra of hydrated cement where the spectrum taken after 8 hours for each sample has been subtracted from that taken after 20 hours. The spectra are shown offset for clarity.

In the difference between the spectra taken after 8 hours of hydration subtracted from those taken after 20 hours of hydration (Figure 13), there are again only minor contrasts. There seem to be a slight lowering in the region $\sim 1050\text{--}1150\text{ cm}^{-1}$, with a peak at $\sim 1082\text{ cm}^{-1}$ disappearing faster in samples with CO_2 . A dip at 870 cm^{-1} , and two peaks around $\sim 1420\text{ cm}^{-1}$ and $\sim 1540\text{ cm}^{-1}$, can be noticed in the spectra of carbonated cement. In addition, there seem to be another peak at $\sim 1387\text{ cm}^{-1}$ in these samples. This might be a sign of monocarbonate or hemicarbonate (or both), as they display peaks reasonably close to both 1387 and 1420 cm^{-1} (monocarbonate show peaks at 1367 and 1416 cm^{-1} in diffuse reflection FTIR) [23]. It can be noted that the shape of the main Si-O peak, centered around $\sim 950\text{--}1000\text{ cm}^{-1}$ will develop differently after about 10 hours, though the effect is quite subtle. In all difference spectra, this peak tends to be more shifted towards lower wavenumbers as hydration progresses, a process that is delayed with cement containing CO_2 (Figure 14). What this means is difficult to tell, as a peak with a more rounded shape may be a sign of C-S-H with a higher Ca/Si ratio, while a peak shifted towards lower wavelengths may be indicative of C-S-H with a lower Ca/Si ratio [15]. Though, as calcium carbonate, hemicarbonate and monocarbonate all incorporate Ca^{2+} , the second option seems more probable.

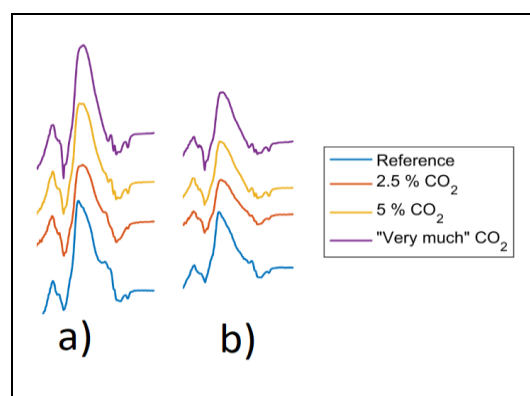


Figure 14. An illustration of the shape of the main silicate peak at a. 16-12 hours and b. 24-16 hours.

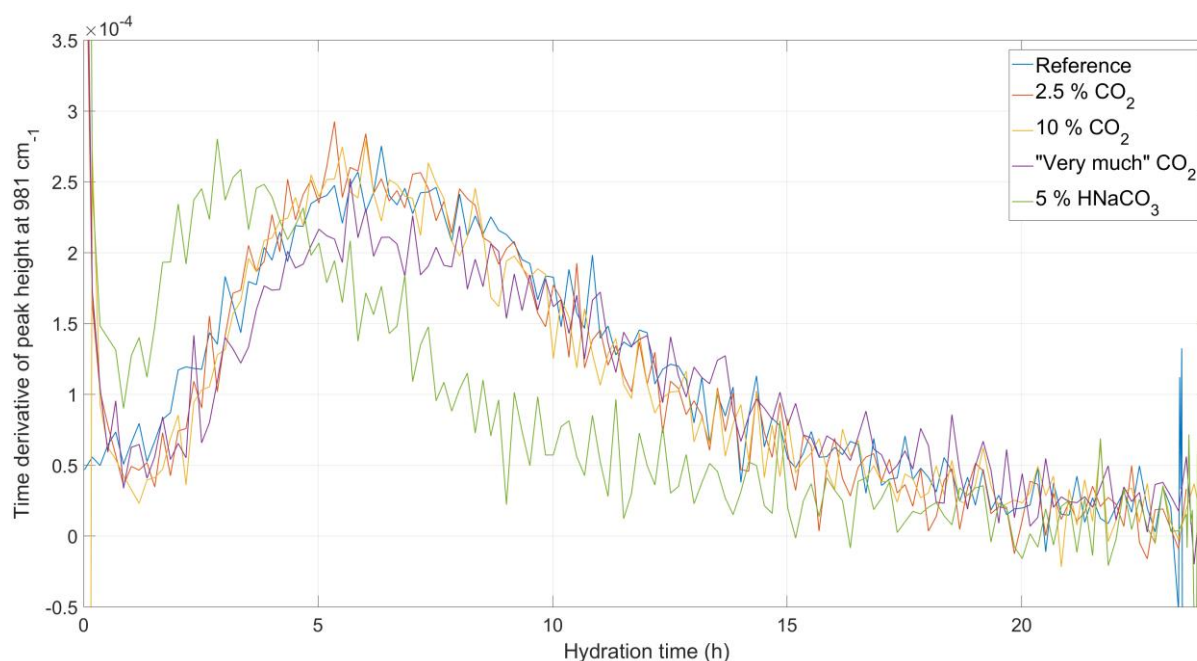


Figure 15. Derivative of peak height at 981 cm^{-1} , the wavenumber with the largest increase in absorbance after 20 hours of hydration, with respect to time.

Taking the peak height at 981 cm^{-1} to represent the growth of C-S-H, as this is the wavenumber in the silicate region showing the greatest increase in absorbance after 20 hours of hydration. Additionally, this peak has the advantage of a stable absorbance, making it

possible to assess it without the complicating factor of establishing a baseline. The derivative of the peak heights at 981 cm^{-1} with respect to time suggests that there is no obvious beneficial influence on the growth of C-S-H from the addition of CO_2 (Figure 15). Though the effect is very small, the retarding effect of a “very large” dose of CO_2 is corroborated by a similar effect in isothermal calorimetry. Only a large dose of sodium bicarbonate will significantly accelerate the growth of this peak.

5.3 Thermogravimetric analysis

Quantification of CO_2 in cement by TGA is difficult for several reasons. There are different opinions in the literature on the appropriate temperature interval to use to determine mass loss [25]. Usually, most of the decrease in mass below $600\text{ }^\circ\text{C}$ in cement is due to loss of water, while mass lost above $600\text{ }^\circ\text{C}$ is mainly from dissociated CO_2 . The dip between $600\text{--}700\text{ }^\circ\text{C}$, seen in the derivative of mass loss in Figure 16, likely represents a loss of CO_2 . Calcite (CaCO_3) usually decomposes to CaO and CO_2 at higher temperatures and this temperature interval may be more representative for decarbonation of carboaluminates and poorly crystalline CaCO_3 . Carbon may also be present in more loosely bound forms however, and amorphous calcium carbonate may decompose to CaO and calcite at temperatures as low as $400\text{ }^\circ\text{C}$, making it difficult to determine the appropriate temperature interval for decarbonation [21]. The fact that, as can be seen in the IR-spectra, the cement used in this work already contains a substantial amount of carbonates also provides a problem, as carbonation content might vary from sample to sample. Cement is a heterogeneous mix of different clinker phases, and one sample might differ considerably in its composition to another.

The amount of CO_2 was quantified by reading the difference in mass between 530 and $875\text{ }^\circ\text{C}$ (the so called stepwise method). These temperatures were chosen as the DTG-curve exhibits a drop around $\sim 530\text{ }^\circ\text{C}$, connected to the large CO_2 -associated mass drop between $\sim 600\text{--}700\text{ }^\circ\text{C}$ (Figure 16), indicating that CO_2 has begun to dissociate, and because $875\text{ }^\circ\text{C}$ is around the highest temperature before readings are distorted from the switch from heating to cooling. $530\text{ }^\circ\text{C}$ also coincides with the lowest temperature for release of CO_2 from cement suggested by [25]. The mass was rescaled to 100% at $300\text{ }^\circ\text{C}$ in order to compensate for differences in the amounts of loosely bound water between samples. The results are shown in Table 2 below:

Table 2. Thermogravimetric quantification of CaCO_3 in cement, measured as the mass loss between 530 and $875\text{ }^\circ\text{C}$.

	Mass lost, wt. %
Dry cement	1.9291
Reference cement 1	2.9783
Reference cement 2	2.6642
Cement with 1 % CO_2	2.9017
Cement with 2.5 % CO_2	2.7520
Cement with 5 % CO_2	3.0611
Cement with 10 % CO_2	3.0068
Cement with “very much” CO_2	3.3725

The results of Table 2 are probably not accurate enough to tell the exact amount of CO₂ absorbed by cement. Despite this, it can be noted that two of the CO₂-mixed cement samples show less weight loss than a reference sample, and that the sample mixed with a “very large” dose of CO₂ only exhibits a mass loss of about 0.4 to 0.7 % more than reference. These results make it reasonable to assume that the absorption of CO₂ during mixing is small, and that the cement, at the time of mixing, might be saturated with respect to carbon dioxide at less than 1 % bwc. Dry cement are about 1 wt.% lower in mass loss than other samples. This indicates that CO₂ uptake during storage may be an important factor. In addition, if CO₂ is bound in other phases than CaCO₃, such as carboaluminates, it is possible that it dissociates outside the chosen interval.

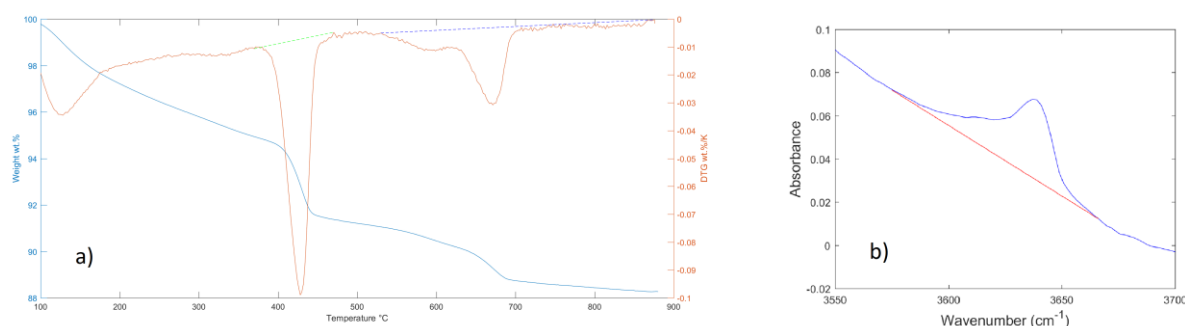


Figure 16. An illustration of TGA and DTG curves for cement mixed with 5 % CO₂ and integration of the FTIR spectrum of cement mixed with 5 % CO₂ over a baseline from 3575 and 3666 cm⁻¹ after 8 hours of hydration. The complete set of figures can be found in the appendix.

Calcium hydroxide (Ca(OH)₂) is often considered the main component of cement to be carbonated, and it seems reasonable to expect less calcium hydroxide in cement mixed with CO₂. Even if carbonate doesn't react with calcium hydroxide directly it is likely to form compounds containing Ca²⁺ (such as calcite and carboaluminates), resulting in a lower ratio of Ca²⁺ to OH⁻. As calcium hydroxide appears quite distinctly in DTG of cement (Figure 16), an attempt at quantification was made by reading the mass loss between 370 and 470 °C. The result, shown in Table 3 below, indicates that there is no obvious impact on calcium hydroxide from mixing with CO₂. Dry cement is excluded.

Table 3. Thermogravimetric quantification of Ca(OH)₂ in cement, measured as the mass loss between 370 and 470 °C.

	Mass lost, wt. %
Reference cement 1	4.7875
Reference cement 2	3.6818
Cement with 1 % CO ₂	3.6541
Cement with 2.5 % CO ₂	3.6590
Cement with 5 % CO ₂	3.7441
Cement with 10 % CO ₂	4.6768
Cement with “very much” CO ₂	3.5194

As a compliment to thermogravimetric analysis, the peak around 3639 cm^{-1} in FTIR spectra of cement, associated with calcium hydroxide, was integrated. Because of much overlap in the OH-bending region, this peak is quite difficult to resolve. Integration over a baseline between 3575 and 3666 cm^{-1} was chosen, as it seems to incorporate the peak in all cases. An illustration of this is shown in Figure 16, while the complete set of figures can be found in the appendix. The results of the integration, presented in Table 4 below, agree with those from TGA, as the peak areas from cement mixed with CO_2 are quite similar to those of reference cement.

Table 4. Integration of FTIR-spectra over a baseline from 3575 and 3666 cm^{-1} after 8 and 24 h of hydration.

	8 h	20 h
Reference cement 1	0.6355	1.1444
Reference cement 3	0.6068	1.1738
Cement with 2.5 % CO_2	0.7527	1.1035
Cement with 5 % CO_2	0.5851	0.9528
Cement with 10 % CO_2	0.6552	1.0051
Cement with “very much” CO_2	0.7082	1.0419

6 Discussion

The purpose of this work was to investigate the effect on early hydration of carbon dioxide addition to ordinary Portland cement during mixing. Previous work by Monkman et al. raised expectations of an increase in early strength development and an accelerated silicate hydration [13] [12]. These experiments were made at an industrial scale however, while the experiments in this work were all made in the lab. Lab scale mixing of carbon dioxide with cement presented an initial problem. Solid carbon dioxide sublimates very quickly at ambient temperature and pressure, and it was initially unknown if it would react quickly enough with cement to have a noticeable impact on hydration. When subsequent calorimetric and IR testing made it clear that this was the case, the question of how much CO₂ was absorbed became pertinent. As it was expected that, when mixing sublimating solid CO₂ in an open container with small amounts of cement, most would escape as gas, relatively high doses of 5-10 % by weight of cement was initially tried. As cement mixed with these doses did show an increased heat of hydration it seems possible that the amount of CO₂ absorbed corresponds to those of Monkman et al., even though much smaller amounts of CO₂, less than 1 % bwc, was used in their industrial scale experiments.

Thermogravimetric analysis was used in an attempt to quantify the amount of CO₂ absorbed during mixing. As can be seen in Table 2, differences in mass loss between reference and samples mixed with various amounts of carbon dioxide are small. The maximum difference between samples was about 0.6 wt.%, with a “very large” dose only 0.375 wt.% above a reference sample. As the “very large” dose of CO₂ may be as high as 50 % bwc, little of the CO₂ must have been absorbed in this case. These observations make it seem reasonable to assume that the amount of CO₂ absorbed during mixing was small, not more than 1 % bwc. Calorimetric results with sodium bicarbonate, where doses of more than 0.5 % bwc shows a retardation of hydration, at least up to a point, can be used as comparison. Assuming a similar effect on early hydration by CO₂ and NaHCO₃, would, after adjustment for differing molar masses, indicate that the absorption of CO₂ for a 5-10 % dose would be around 0.25 % bwc. The fact that IR-spectra of cement show a similar pattern, whether mixed with 2.5 % solid carbon dioxide or a more than 10 times larger dose, also supports the conclusion that the cement was saturated somewhere far below the highest dose.

There are caveats to this conclusion though. The temperature interval, between 530 and 875 °C, was chosen because CO₂ is expected to dissociate from calcite in this range. If CO₂ is bound to other phases, such as monocarbonate or amorphous CaCO₃, mass loss due to CO₂ might occur outside this interval. Uptake of CO₂ during storage is another concern, and though the samples were stored under a constant flow of nitrogen gas, some uptake of CO₂ is inevitable. The samples were stored for different amounts of time, something that might have an impact on CO₂ content. It is also possible that samples mixed with CO₂ was less receptive to subsequent carbonation, and that CO₂ content was evened out during storage.

Neither did TGA show any obvious impact from CO₂-mixing on the calcium hydroxide content. As seen in Table 3, there is some spread in the results, with one reference sample and 10 % CO₂ showing about 1 % higher mass loss than other samples. There is however no sign that CO₂-mixed samples would generally have a lower amount of Ca(OH)₂. Table 4 shows an attempt to complement the TGA with an integration of the Ca(OH)₂ associated peak from FTIR spectra. The results are fairly even, and there is no apparent difference between CO₂-

mixed samples and reference. Nor do the two samples with higher mass loss in the TGA measurement show a higher peak area. The spread in the result make them less certain, and is likely explained by different hydration times, as the exact time before the samples were crushed and dehydrated was not recorded. This is of less consequence to CO₂ quantification as the hydrating samples were kept in closed containers, but Ca(OH)₂ is a product of tricalcium silicate hydration, and a longer hydration time will result in more Ca(OH)₂. This would also explain why there is no correlation between FTIR and TGA in this case, as FTIR spectra show the samples at an earlier stage of hydration.

The expectation that Ca(OH)₂ will be consumed when cement reacts with CO₂ comes from experience with carbonation of hydrated cement, and may not apply when CO₂ is added during mixing. That CO₂ reacts with Ca²⁺ to produce CaCO₃ can be seen quite clearly in the FTIR spectra (Figure 9 and Figure 10), where carbonated cement shows higher peaks at the CaCO₃ associated wavenumbers 870 and 1400-1500 cm⁻¹. With less Ca²⁺ available, a lower production of Ca(OH)₂ may be expected. It is also possible that much of the calcium is taken from C-S-H production, resulting in C-S-H with higher Ca/Si ratio. The difference in peak shape between CO₂-mixed and reference cement, shown in Figure 14, may be interpreted this way, though this is conjecture. Even if it is the case that CO₂-mixing leaves Ca(OH)₂ mostly unaffected after 24 hours of hydration, it does not necessarily mean that this holds true over longer periods of time. It is possible that carbonate ions bound in other cement phases will react with calcium hydroxide later on.

The most unambiguous effect of CO₂-mixing is seen in the results from isothermal calorimetry. As can be seen in Figure 5 and Figure 6, doses of 2.5 % to 10 % CO₂ show an increased heat of hydration for the first 15 hours or so, indicating an acceleration of early hydration. The result is also quite reproducible, despite the difficulties of mixing in exact amounts of solid CO₂ with the cement. A “very large” dose of CO₂ did not provide the same acceleration, a result that is in accordance with those of Monkman et al. [12] in showing an upper limit to the amounts of CO₂ providing accelerated hydration. The analogy is not perfect, as on the industrial scale, cooling of the cement from mixing with carbon dioxide must be quite negligible. It is possible that initial cooling of the sample may delay subsequent hydration and that a loss of water during mixing, due to the sublimation of CO₂ has a retarding effect as well. Carbonated water shows only a very slight effect in isothermal calorimetry and a 1 % dose was probably too small for any significant amounts of CO₂ to be absorbed by the cement.

With only one exception, the second and third maxima in the thermogram are more notably affected by CO₂-addition than the first. The second shoulder of the thermogram is pronounced and the small peak between the shoulders appears ahead in time, compared to reference. As modern Portland cement is designed to let alite hydration reach a maximum before aluminate hydration, this is an indication that aluminate hydration is more affected by the addition of CO₂ than silicate hydration. Judging from the shape of the calorimetric curves, most of the extra heat evolution is due to an acceleration of the aluminate-sulfate system. Only one 2.5 % sample showed the same behavior reported by Monkman et al. [12], with an increase in the first shoulder of the thermogram, suggesting the possibility that the concentrations of CO₂ investigated in this work were too high to achieve optimal results. Isothermal calorimetry is a technique that only measures the total heat of hydration however. It is not possible to individuate specific reactions from calorimetry only.

In general, the absorbance spectra of cement mixed with CO₂ show little difference to those of reference. The most obvious effect is seen at the carbonate associated wavenumbers 870 and 1400-1500 cm⁻¹. The absorbance at 870 cm⁻¹ increases during the first 30 minutes (Figure 9), but then begins decrease after about 3 hours (Figure 12 and Figure 13). This peak is associated with calcite, and its formation soon after mixing cement with CO₂ is no surprise. The AFm phases hemicarboxylate and monocarboxylate are more thermodynamically stable and have a lower solubility than calcite however [10], so the most likely explanation is that calcite dissolves and CO₃²⁻ reacts with ettringite to form carboxylates instead. The dip at 870 cm⁻¹ also seems to be accompanied by a peak around ~1387 cm⁻¹ that may belong to monocarboxylate or hemicarboxylate, suggesting that carbonate ions from calcite is incorporated in phases of AFm.

FTIR does not show any signs of an increase in silicate hydration. The peak height of the main silicate peak is comparable to that of reference at all times. Taking the absorbance at 981 cm⁻¹, the wavenumber in the Si-O region with the largest increase in absorbance after 24 hours of hydration, as a measure of C-S-H growth, there seem to be virtually no impact on the rate of C-S-H from CO₂-addition. Figure 15 shows the derivative of the absorbance at 981 cm⁻¹ with respect to time, and as can be seen, cement mixed with CO₂ displays a curve almost identical to reference. This result fits well with the shape of the calorimetric curves for CO₂-mixed cement, showing an increased heat output that seem to stem from an accelerated aluminate hydration.

This is by no means conclusive proof that CO₂-mixing does not interfere with silicate hydration. The choice of a single wavenumber as measurement of C-S-H formation seems less valid if the hydration products differ between samples. C-S-H is not a well-defined phase and may have a different composition in cement mixed with CO₂, thus it is conceivable that it could absorb radiation at different wavelengths. Nonetheless, FTIR suggest that silicate hydration proceeds much in the same manner during the first 24 hours, whether cement is mixed with CO₂ or not. The only difference that was noted in the spectra was a delay in the shift towards lower wavelengths in the growth (as seen when a spectrum from an earlier time is subtracted from a later one) of the main silicate peak after about 10 hours. This effect is slight, but it suggests that the type of C-S-H growing in CO₂-mixed cement between about 10 and 20 hours corresponds to C-S-H formed in the reference cement some hours earlier, possibly with a lower Ca/Si ratio.

It is quite certain from the FTIR results that CO₂-mixing affects the sulfate chemistry very early on. This happens from the time of mixing, as evident from the first FTIR spectra after about 3 minutes after mixing (Figure 9). At this time, there already seem to be more variation in the sulfate region of carbonated cement. This may indicate that CO₃²⁻ is quickly incorporated together with SO₄²⁻ in reactions with C₃A, as AFm and AFt of different compositions are known to form solid solutions. As CO₃²⁻ is already in solution, it can be expected to react quite rapidly from the moment of mixing and to possess an advantage in competition with SO₄²⁻ dissolved from calcium sulfates. Rehydration of gypsum after wetting also seem slowed by addition of CO₂, as it is quite clear from the first FTIR difference spectra that carbonated cement shows an increase in many peaks associated with gypsum, combined with a sharp dip that probably represents hemihydrate or anhydrate. It seems likely that anhydrite or hemihydrate (or both) are dissolved and then recrystallizes as gypsum. An increased ionic activity in pore solution might cause a decrease in the solubility of gypsum.

As gypsum causes a delay in the dissolution of C_3A it seems reasonable to expect that this early interference from CO_3^{2-} with sulfate chemistry would affect the mechanism retarding aluminate hydration. As the results from calorimetry also suggest that mainly aluminate is affected by CO_2 -addition, with thermograms showing a pronounced second shoulder, early interaction between CO_3^{2-} and C_3A may provide an acceleration of the sulfate-aluminate chemistry. This interpretation would be in accordance with the observation that $CaCO_3$ -blended cements show a similar effect on early hydration [9] [10], and can be explained as follows: CO_3^{2-} initially form carboaluminates at the surface of C_3A grains, creating a more permeable surface layer than a compact layer of ettringite (or adsorbed sulfate), thus increasing aluminate dissolution and consumption of gypsum. This is corroborated by the fact that IR spectra seem to show a somewhat higher consumption of gypsum in CO_2 -mixed samples (Figure 10), indicating an increased rate of reaction. One might speculate that perhaps if CO_2 was mixed in a bit later, after the sulfates have been given some time to dissolve and react with the aluminate phase, that carbonate would form more $CaCO_3$ and have a greater impact on initial silicate chemistry.

During the first 30 minutes of hydration, carbonated cement shows a greater shift of absorbance towards lower wavenumbers in the sulfate range of the IR spectrum. Part of the large increase in the peak close 1100 cm^{-1} is most likely due to the crystallization of gypsum, but a shift towards lower wavenumbers is also a sign of ettringite formation. Ettringite displays a peak very close to that of gypsum and much overlap can be expected. It also seems that the gypsum associated peak at 1624 cm^{-1} is somewhat weaker in carbonated cement throughout the first 24 hours, though it is obscured by the overlapping bulk water band. As an increased rate of aluminate reaction would be accompanied by an increased consumption of gypsum, this fits well. As seen in Figure 10, after the initial shift, the absorbance in the sulfate region is higher in cement mixed with CO_2 , though the difference evens out with time. This range is difficult to resolve, but the fact that there is a clear difference here suggests an impact on sulfate chemistry during the first 24 hours.

From the results of this work, it is difficult to see the benefit of using cement as a deposit for unwanted CO_2 . Of course, the relative absorption of CO_2 is likely much higher on the industrial scale. Still, it seems little CO_2 may be bound to cement at the time of mixing, and the process of compressing and transporting the carbon dioxide comes with an environmental cost of its own. In addition, one might question if not the same amount of carbon dioxide would end up in the cement after some time in any case, as cement inevitably reacts with CO_2 during its lifetime.

From an environmental perspective, a strength gain would probably be the main benefit of adding carbon dioxide to cement during mixing. With increased strength, a lower ratio of cement to aggregate can be used, something that would have a real impact on the environmental cost. It is not possible to tell the impact on strength from the results of this work however, though some things are worth considering. If it is correct that CO_2 mainly interferes with aluminate, there will be an increase in AFm and AFt while less Ca^{2+} is available to form $Ca(OH)_2$ and C-S-H, something that might be detrimental to the final strength of cement. On the other hand, CO_2 -mixing does seem to increase the rate of hydration, and it is possible that this will help to meet demands of early strength.

7. Conclusion

- Isothermal calorimetry shows that cement mixed with 2.5 % to 10 % solid CO₂ by weight of cement will display an increased heat of hydration for about 15 hours. Mixing cement with a very large dose of CO₂ (up to 50 % bwc) will not result in the same increase.
- Isothermal calorimetry indicates that aluminate and sulfate chemistry is accelerated by addition of CO₂, with the second shoulder of the thermogram being especially pronounced.
- Thermogravimetric measurements of the mass loss between 530 and 875 °C suggest that the amount of CO₂ bound in cement at the time of mixing is small. The fact that cement mixed with very large doses of CO₂ display a mass loss close to that of reference indicates that cement is saturated somewhere below 1 % bwc.
- FTIR investigation of cement hydration shows no sign of increased silicate hydration during the first 24 hours. The growth of C-S-H seems to be almost identical to reference.
- FTIR indicates that calcium carbonate is formed initially, but begins to dissolve after about 3 hours.
- FTIR shows a recrystallization of sulfate to gypsum and a larger shift towards lower wavenumbers in the sulfate region during the first 30 minutes of hydration in cement mixed with CO₂, indicating an early effect on sulfate chemistry.
- CO₂-mixed cement displays a higher IR absorbance in the sulfate region after the first minutes of hydration, compared to reference.

8. Future Research

Further investigation includes a closer determination of the amount of CO₂ absorbed during mixing, perhaps through thermogravimetric analysis conducted after only a few minutes of hydration as well as after longer periods of time.

A deeper study on the reaction mechanism and hydration products of cement mixed with carbon dioxide and how it relates to cement composition and dosing would be interesting, in order to test the hypothesis that CO₂ reacts mainly with the aluminate phase and if this holds true in the more general case. This might include x-ray diffraction to determine crystalline phases and investigation of the morphology of C-S-H through electron microscopy as well as pore solution analysis.

Strength testing and durability studies of CO₂-mixed cement, including service carbonation, resistivity and shrinkage, are also needed before CO₂-mixed cement are used in practical applications.

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Appendix

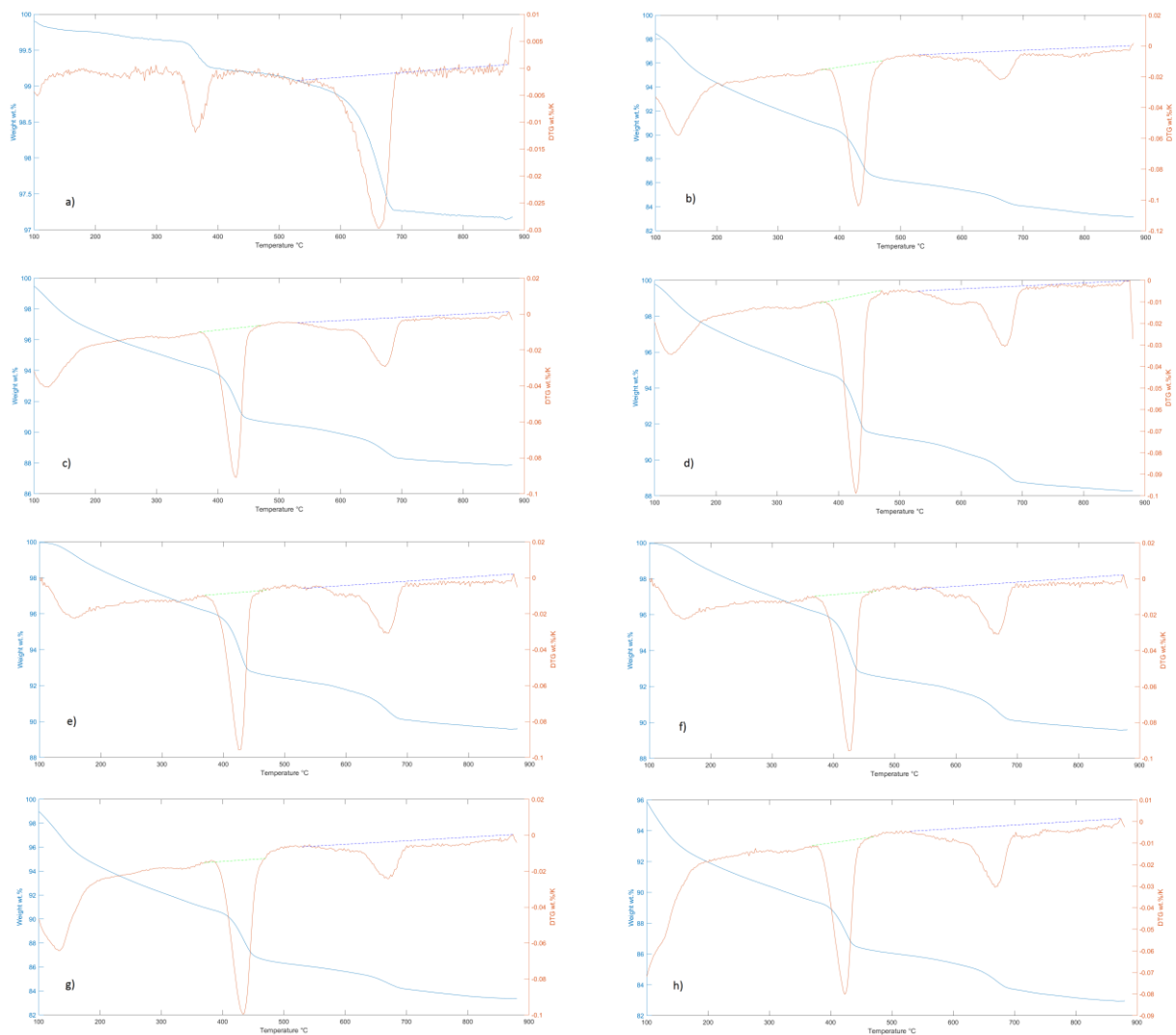


Figure 17. TGA and DTG of cement. (a) Dry cement, (b) Reference cement 1, (c) Reference cement 2, (d) Cement mixed with 1 % CO_2 , (e) Cement mixed with 2.5 % CO_2 , (f) Cement mixed with 5 % CO_2 , (g) Cement mixed with 10 % CO_2 , (h) Cement mixed with “very much” % CO_2 . The dashed green and blue lines show the integrated areas.

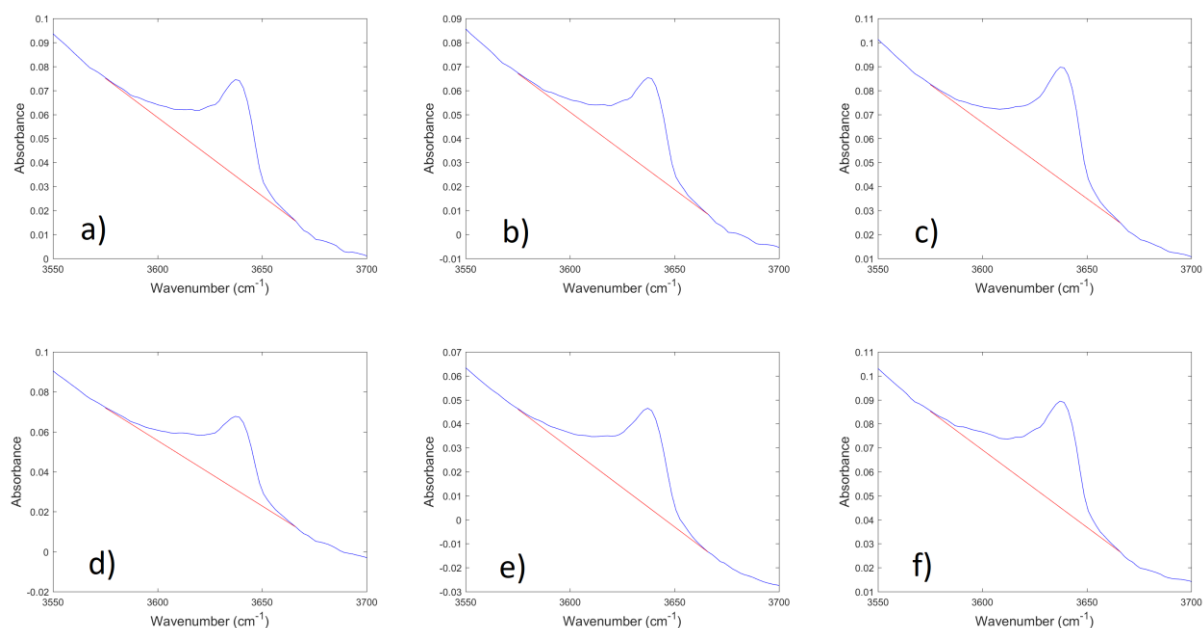


Figure 18. Integration of FTIR-spectra over a baseline between 3575 and 3666 cm^{-1} after 8 hours of a. Reference 1 b. Reference 3 c. 2.5 % CO_2 d. 5 % CO_2 e. 10 % CO_2 f. “very much” CO_2 .

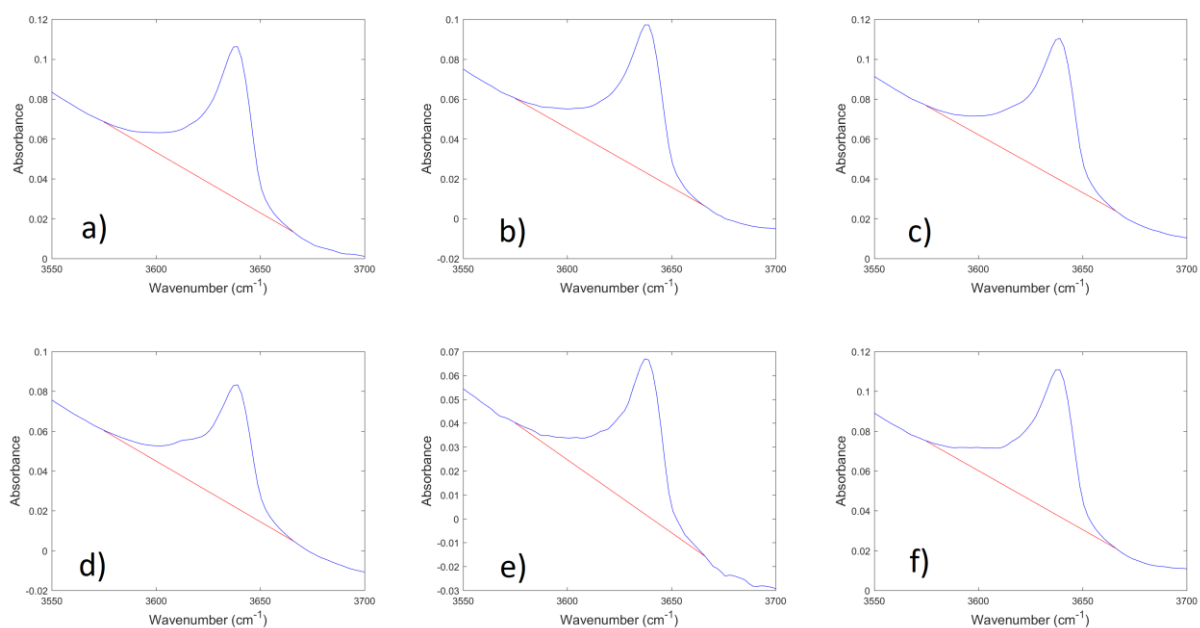


Figure 19. Integration of FTIR-spectra over a baseline between 3575 and 3666 cm^{-1} after 24 hours of a. Reference 1 b. Reference 3 c. 2.5 % CO_2 d. 5 % CO_2 e. 10 % CO_2 f. “very much” CO_2 .