

# Evidence of scawtite and tilleyite formation at ambient conditions in hydrated Portland cement blended with freshly-precipitated nano-size calcium carbonate to reduce greenhouse gas emissions

Lewis J. McDonald<sup>1</sup>, Waheed Afzal<sup>1\*</sup> and Fredrik P. Glasser<sup>1</sup>

<sup>1</sup> University of Aberdeen, School of Engineering, Aberdeen, Scotland

\* Corresponding author: Waheed Afzal; waheed@abdn.ac.uk

## Abstract

Activated calcium carbonate (a-CaCO<sub>3</sub>) is used partially to replace Portland cement. a-CaCO<sub>3</sub> is comprised of nanoscale calcium carbonate, in amorphous and calcite forms, and its enhanced carbonate activity converts calcium carbonate from being an inert filler to a reactive component. Its reaction with the C-S-H phase alters the conventional hydrate mineralogy with spontaneous formation at ~20°C of scawtite, Ca<sub>7</sub>(Si<sub>6</sub>O<sub>18</sub>)CO<sub>3</sub>·2H<sub>2</sub>O and tilleyite, Ca<sub>5</sub>Si<sub>2</sub>O<sub>7</sub>(CO<sub>3</sub>)<sub>2</sub>. Compressive strength measurements show that up to 20 mass% cement replacement by calcium carbonate does not decrease 7- and 28-day compressive strengths compared to a Portland cement benchmark. a-CaCO<sub>3</sub> also accelerates the hydration of silicate clinker minerals. Using activated calcium carbonate as a supplementary cementing material enables substantial reduction of CO<sub>2</sub> emissions, firstly by capturing part of the CO<sub>2</sub> from cement kilns to make nanoscale calcium carbonate and secondly, by using the a-CaCO<sub>3</sub> capture product to replace part of the cement.

**Keywords:** carbon capture and use (CCU), cement mineralogy, circular economy, Calcium Carbonate, Portland cement

## 1. Introduction

Portland cement is arguably the most successful building material ever invented. But it suffers from the high specific carbon dioxide emissions associated with its production [1]. These emissions, comprising perhaps 6 to 8% of total man-made CO<sub>2</sub> emissions, are increasingly a problem which may have negative consequences for the industry [2, 3, 4].

Concern over carbon dioxide emissions has been partially addressed by using formulations with lowered "clinker factors": clinker is partially substituted by reactive supplementary cementing materials such as fly ash, and slag [5]. These supplementary materials react with Portland cement, becoming part of the cementitious hydrate matrix. But suitable pozzolanic products are declining in abundance and, moreover, as their status changes from that of being "wastes" to bring "valuable supplementary materials", they increasingly attract a carbon penalty [6, 7].

Adding limestone to cement is not new. Limestone is a naturally abundant rock containing greater than 70% CaCO<sub>3</sub> and it is usually inter-ground with cement clinker [8]. Most modern specifications for Portland cement permit adding up to 5% CaCO<sub>3</sub> while allowing the product to be marketed as "Portland cement" [9]. This change in specification, allowing up to 5% limestone, has led to significant energy saving and reduction in CO<sub>2</sub> emissions. Adding more than 5% CaCO<sub>3</sub> is of course possible and indeed, such formulations are in regular use and are covered by standards (e.g. EN 197-01 [10]). Calcium carbonate reacts with calcium aluminate but behaves as a filler when added in excess (i.e. more than is able to react with calcium aluminate) and product strength gradually declines as the CaCO<sub>3</sub> content increases above 5%, hence the limit of replacement imposed on the definition of Portland cement [11, 12, 13]

This pattern of strength change – a slight increase in strength at low, ca. 1-4% replacement, followed by a progressive decline – was explained by Matschei et al. [9] as resulting from combination of two factors: Firstly, a "filler effect" operates. Limestone is softer than clinker and as a result, produces a higher proportion of fines when inter-ground with cement clinker [14, 15, 16]. The fines, enriched in calcium carbonate, improve the particle packing and, during subsequent hydration, enable better space filling by mixtures of solid hydration product and filler grains [17]. Secondly, chemical reactions occur between calcium carbonate and cement hydration products. These reactions are marked by formation of hemi- and mono-carboaluminate hydrates.

Both are AFm-type phases (general formula  $\text{Ca}_2(\text{Al,Fe})(\text{OH})_6 \cdot \text{X} \cdot \text{yH}_2\text{O}$  where X is a singly charged anion or half of a doubly charged anion) so the reaction involves essentially ion exchange, of carbonate for hydroxide and sulfate [18]. The hemi-carboaluminate AFm phase characteristically develops during early hydration as primarily an amorphous solid with some weakly crystalline material forming. As carbonate AFm forms, the amount of AFt (ettringite,  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ) increases to accommodate sulfate expelled from AFm: the low density of AFt and its high bound water content also improves space filling by cement solids, thereby contributing to strength [19].

Limited scope exists to enhance reaction between calcium carbonate and cement, as for example by increasing the clinker aluminate content to form more  $\text{CO}_3$ -AFm during subsequent hydration. This is not done because increased aluminate may have other and undesirable consequences, such as lowering resistance to sulfate attack in service conditions [20].

The title paper builds on the concept that successful supplementary cementing materials need to react chemically with Portland cement and shows that (i) scope for further reaction between cement hydration product and calcium carbonate by increasing its chemical potential and (ii), that a new Portland cement hydrate mineralogical assemblage is attained, offering scope for binding calcium carbonate into the cement matrix in the course of normal curing regimes, reaction leading to the formation of calcium carbonate-silicate minerals.

The extent of reaction between calcium carbonate and cement hydrates depends very critically on achieving high carbonate activity in the aqueous phase of hydrating cement. The activity is controlled by the calcium carbonate source. Calcium carbonate exists at low pressures as calcite, vaterite and aragonite, all crystalline [21], and as an amorphous form [22]. It is this latter form which is of special interest.

## **2. Materials and Methods**

### **2.1. Portland cement**

A commercial Portland cement supplied by Hanson Cement was used. The manufacturer arranged to grind clinker with normal gypsum but not to add limestone. The cement is therefore free of added calcium carbonate. Table 1 shows the batch composition and the calculated mineralogy, determined by x-ray fluorescence (XRF) and Bogue calculation.

### **2.2. Amorphous Calcium Carbonate**

The precipitation of amorphous calcium carbonate is done by combining a sodium carbonate - containing solution with a calcium- rich brine at 20°C. In the laboratory, the carbonate solution is conveniently prepared by dissolution of sodium carbonate in distilled water but could equally be obtained commercially by scrubbing  $\text{CO}_2$  in cement kiln exit gas into a dilute solution of NaOH, using a commercial absorption column. The title study used a 1.25 mol/L sodium carbonate solution with a measured pH of 11.3. The calcium brine was made by dissolving calcium chloride in distilled water to achieve a solution 1.25 mol/L  $\text{Ca}^{2+}$ .

To make amorphous calcium carbonate, the two solutions are introduced rapidly into a third and initially empty stirred vessel at a constant rate: for 2 L total solution volume, at 1 L/minute, preferably completing the mixing within 60 seconds of first contact with water. Peristaltic pumps were used to ensure constant delivery rates: this pumping arrangement also facilitates continuous rather than batch production. The indicated pH measured after mixing is typically 11.4. The resulting suspension is mixed for a further few minutes for a maximum contact time of five minutes for amorphous product but allowed to stand for a few minutes to hours at 20°C to obtain mixtures of amorphous and nanocrystalline calcite. The precipitate is conveniently separated from the solution by vacuum filtration and the wet solid is washed with distilled water to reduce the chloride content of the precipitate to <0.05%. The precipitate is spread thin and air dried at 40°C typically for up to 24 hours. The resulting dry white powder is stable for at least 7 days at 20°C.

Figure 1 shows the amorphous product: it consists of nano-scale rounded grains, some isolated but often clustered in nearly spherical superclusters comprised of amorphous calcium carbonate. At higher magnification, Figure 2, the nearly spherical clusters present a complex open structure built from linking subunits of nanospheres and ovoids. Some rhombic forms appearing in Figure 1 probably indicate partial crystallisation to calcite. These rhombs may, however, been formed as artefacts during sample preparation for microscopy as the corresponding x-ray diffraction (XRD) pattern of the solid did not disclose the presence of crystalline calcite.

Crystallinity is defined from the appearance of the X ray diffraction pattern using filtered copper K $\alpha$  radiation. Figure 3 compares diffractograms obtained from nano and - micro calcite with the amorphous solid. Further analysis is provided in Section 3.1.

### **2.3. Nano- and Micro-calcite Preparation**

Using the preparation route described above gives rise to either amorphous calcium carbonate or nanoscale calcite, depending on annealing time allowed. At 20°C, the initially formed solid is amorphous and readily recovered, filtered and washed. But if it is left to stand in contact with mother liquor, nucleation and crystallisation of nanoscale calcite occurs spontaneously within a matter of minutes. Figure 4 shows a scanning electron microscope image after an annealing time of 10 minutes at ambient temperature. The clusters of amorphous material are either absent or greatly reduced and more grains have the rhombic morphology characteristic of calcite, although individual crystallites are still nanosized.

Micro-scale calcite (Figure 5) is produced in the same manner, however the contact time with the mother liquor is increased to allow crystallisation and growth. During ageing the crystals retain their characteristic morphology, but growth steps become more prominent, probably indicative of a slowing growth rate. The crystallite size has, however, increased by an order of magnitude or more relative to nanoscale calcite shown in Figure 4. Additional size characterisation data on the particle sizing are presented in section 3.1.

### **2.4. Calcium Carbonate-Portland Cement Formulations**

The Portland cement described in section 2.1 was blended with calcium carbonate, made as described in sections 2.2 and 2.3 by mixing in an electrical mixer. The supplied Portland cement as supplied was used as a benchmark.

Mixing with low shear is sufficient to disperse the amorphous calcium carbonate through mixes with Portland cement. A correction for water content is made when using a-CaCO<sub>3</sub> slurries; but dry powders do not require a correction. Handling and mixing may be done in the temperature range 1°C to 40°C. If the rheology of fresh cement needs to be adjusted, conventional commercial plasticisers or super-plasticisers may be used. The fresh mixes may be emplaced by any standard methods such as pouring,

pumping or spraying. Set times were normal, and after emplacement, the mixes were cured according to best practise models at 20°C. The extent of substitution of Portland cement by reactive a-CaCO<sub>3</sub> may range up to 50% but we report data on substitutions in the range 0 to 20%.

Each of three types of calcium carbonate precipitate, (i) amorphous (but containing minor crystalline material), (ii) nano-sized calcite (with some amorphous material) and (iii) micron-sized calcite were used individually to produce three distinct blend formulations: nine well-spaced compositions were produced with 1-20% by mass of the respective calcium carbonate form. Furthermore, three different water/solid ratios were used, 0.5, 0.4 and 0.3. Mixing was done with a “MasterMix” benchtop electrical mixer and fresh mixes were transferred to 50x50x50 mm steel moulds where they were allowed to harden for 20 hours before being demoulded and transferred to a water bath at 20°C for 7 and 28 days. Care was taken to ensure that cements were cured in a bath containing only cubes with the same calcium carbonate type. The pH of the cement pastes was measured using a Hanna Instruments HI 9812-5 pH meter, calibrated to pH 10. The pH of the hydrating OPC, recorded at 10-minute intervals for a period of one hour remained constant at 13.1. Substitution of both 10 and 20% cement clinker with calcium carbonate gave nearly identical pH = 13.0 over the same period.

After the designated curing period, the calcium carbonate-cement blends were removed from their water bath, their surface dried, and then weighed. Within 30 minutes of being removed from the water bath, the cube samples were subjected to a compressive load that increased at a rate of 2.4 kNs<sup>-1</sup> until fracture. The machine used to apply the load was an ELE International ADR Touch Control PRO 2000 Auto with an added platform to accommodate the samples size. Each composition was tested until at least three replicate results were obtained within 5% of each other. Thus, 201 cubes were used to construct Figure 8, 198 cubes for Figure 9 and 99 for Figure 10. The error bars present represent the standard deviation from the average of at least three replicate samples.

After mechanical testing of the cement pastes, fragments were taken and ground by hand with a pestle and mortar. Also, smaller samples were cast for the purpose of mineralogical analysis and after 1 to 28 days of curing, were also ground by hand. Each sample was analysed using a Malvern Panalytical X'pert Powder Diffractometer with a PIXcel1D detector and a nickel filtered and monochromated copper radiation source. The phases present were identified using the HighScore Plus software package. Once all the Bragg reflections observed in the diffractograms were assigned, Rietveld refinement was carried out to quantify the crystalline phases.

### **3. Results**

#### **3.1. Characterisation of Calcium Carbonate**

The particle size distribution of the micro and nano-scale calcium carbonate precipitates was determined using three independent methods (i) scanning electron microscopy (ii) laser particle size analysis and (iii) X ray diffraction, The Scherrer equation was used to relate Bragg reflection broadening to particle size (Figure 3). The SEM images obtained from micro-calcite and nano-calcite are shown in Figure 4 and Figure 5 respectively. The morphological development of calcite is apparent even at nanoscale but as the crystals grow, amorphous material disappears.

Figure 6 shows a laser diffraction scan obtained from a nano-calcium carbonate preparation. The measurements were made using a Malvern Zetasizer ZS DLS. The measurements were made at room temperature using water as the dispersant. The majority, >95%, of particles are under 1000nm and ca 95% of particles lay within the size range 100 to 1000nm. Figure 7 shows a laser diffraction scan for a micro-calcium carbonate under the same conditions. Comparing Figure 6 and Figure 7, the curves have similar shapes but with order-of-magnitude shift in size. The laser particle size determinations are in accord with the visual images determined from SEM and where appropriate, crystallite size calculated from the line broadening profiles from X ray diffraction (Figure 3).

Figure 3 shows the characteristic x-ray powder patterns from different calcium carbonate preparations. They are important because XRD (copper K $\alpha$  radiation) was used as the sole determinant of crystallinity. The distinction between "crystalline" and "amorphous" was thus an operational distinction, based on the analysis of Bragg reflections. Where perceptible line broadening occurred, the preparation was deemed to be crystalline but the almost total absence of Bragg reflections, apart from broad scattering, as in Figure 3 (bottom pattern), was deemed to be amorphous. However, application of this criterion is also dependent on the wavelength of the probe radiation (1.541 Å). In general, the method is satisfactory to distinguish a crystalline from an amorphous phase but not completely satisfactory quantitatively to resolve mixtures of phases on account of the low sensitivity of X rays for detection of what we deem to be "amorphous".

### 3.2. Mechanical Properties

Figure 8, Figure 9 and Figure 10 show the results of unconfined compressive strengths from Portland cements containing micro-calcite, nano-calcite and amorphous calcium carbonate, respectively. Data for the control, with no added calcium carbonate, projects along the left-hand edge.

The blend of commercial ground limestone with cement shows the expected strength-composition relations, with strength decreasing as a result of limestone addition, but with the best strength development achieved from longer cure and lower w/s ratio. The trends with other types of calcium carbonate show both similarities and differences to those made with limestone. The similarity is that other factors being comparable, strength is favoured by longer curing times and lower w/s ratios. However, and most notably, adding "reactive" calcite improves strength, notably when using mixtures of nano-scale crystalline and/or amorphous. The improved strengths extend to additions of up to 10%. For the micro-calcite, while an increase in strength is observed, it is well within the determined error. The gain in strength arising from a-CaCO<sub>3</sub> is particularly evident following 28 cure duration.

### 3.3. Mineralogical Interaction Between a-CaCO<sub>3</sub> and Portland Cement

The results of an identified pattern are shown in Figure 11 for a sample containing 5% a-CaCO<sub>3</sub> after 1, 3, 7 and 28 days of hydration. These show the formation of tilleyite and scawtite within the first few days of reaction.

Figure 11 and Figure 13 show the change in the crystalline phases calculated by Rietveld refinement of mixes made with the Portland cement described in Table 1 both without calcium carbonate and with 10% a-CaCO<sub>3</sub> respectively and a w/s of 0.5. The cement pastes were wet cured at 20°C. The X ray measurements do not include amorphous materials and do not therefore add to 100%. Moreover, they were obtained without an internal standard. So, comparison should be restricted to trends and not used to determine the amorphous content by difference. The more rapid reaction of alite and tricalcium aluminate in the presence of reactive calcium carbonate is noteworthy: nanoscale calcium carbonate significantly accelerates the cement hydration reactions. Complimentary diffraction measurements show that scawtite and tilleyite develop, together with C-S-H (calcium silicate hydrate), portlandite, with minor carbonate AFm and ettringite (AFt).

## 4. Discussion

The challenge, of reducing the carbon footprint of Portland cement is being addressed worldwide but progress has been slow. This is partly because Portland cement is a commodity, and its composition and method of production are essentially fixed. Process engineering continues to improve the thermal efficiency but with limited scope for major reduction [23]. This has led us, and others, to believe that CO<sub>2</sub> savings can best be achieved through application of supplementary cementing materials (SCM's). However, relatively few materials are available for this purpose and the search for novel SCMs has not thus far produced many viable candidate materials.

A SCM, is defined here includes inorganic solids which, while not necessarily self-cementitious, are activated by Portland cement to become cementitious. SCMs are typically used at >5% replacement of Portland cement to reduce "clinker factors" that is, the amount by which the cement content required to produce a unit mass of concrete without detriment to its engineering properties [24]. The limit of replacement is conveniently benchmarked by the development of compressive strengths achieved relative to a reference mix made with Portland cement.

SCMs are activated by cement and become part of the engineered hydrate phase assemblage [5]. This reactivity, the nature of internal bonding, and the space filling achieved by the reaction products must be able to maintain strength. In general, the performance of an SCM cannot be predicted but needs to be determined by characterisation of the SCM and empirical measurements of strength development and, in demonstrating that the many other criteria required of a satisfactory SCM blended cement can be achieved.

Many common SCMs such as iron blast furnace slag and coal combustion fly ash, are in limited and dwindling supply [25] and, moreover, are not free from carbon penalties associated with their method of production. These considerations give fresh urgency to the search for other low - carbon ways of reducing clinker factors while maintaining or enhancing the properties associated with Portland cement.

The title study shows that calcium carbonate, normally considered to be an inert diluent when added in surplus, can be made such that it becomes reactive with Portland cement. This enables hitherto unexploited pozzolanic reactions to be achieved. But reactive calcium carbonate is not presently an article of commerce and must be made. The active forms of calcium carbonate used in the title study has been made at laboratory scale. However, we have also produced up to 400 kg reactive  $\text{CaCO}_3$ /day in a pilot plant: we extracted the carbon dioxide from simulate off-gas and were able to vary the  $\text{CO}_2$  content of the gas streams between 4 and 100%  $\text{CO}_2$  at 1 bar total and are confident that the capture and conversion process will readily translate to commercial scale using cement kiln exit gas, with perhaps 20-40%  $\text{CO}_2$  content, as the source of  $\text{CO}_2$ .

The arithmetic of  $\text{CO}_2$  emission reduction arising from capture and use may be calculated approximately as follows. The goal is not to increase the strength of cement but to achieve reduction in the  $\text{CO}_2$  footprint. So, the degree of replacement is fixed at 20% to conserve the 28-day strength, therefore requires 200 kg calcium carbonate/tonne of cement. The Chatham house report [2] gives the equivalent  $\text{CO}_2$  release associated with cement production, as 951kg  $\text{CO}_2$ /tonne of cement. So, the supplemented cement will contain per tonne, 200 kg of  $\text{CaCO}_3$  formation of which requires 88 kg of captured  $\text{CO}_2$ . This capture appears as a credit in  $\text{CO}_2$  balances because it represents  $\text{CO}_2$  which is not discharged to the atmosphere. If we additionally form a composite cement with 20% calcium carbonate, the cement fraction is reduced and has an embedded theoretical carbon dioxide content  $951 - (951 * 20) - 88$  or 742 kg. i.e., an additional 199 kg reduction in  $\text{CO}_2$  emissions and a total reduction of  $(88 + 199)$  or 287 kg. Expressed as a percentage of total  $\text{CO}_2$  this is a 30% reduction.

We are aware that this calculation is simplistic, but it is meant to be indicative, not definitive. Other numerical values may be used, but at 20% replacement, trial calculations of  $\text{CO}_2$  savings remain close to 30%. These figures make no allowance for  $\text{CO}_2$  emitted in running the capture process. However, (i) capture need not be restricted to that required for making the activated calcium carbonate: other application areas will support a capture in excess of 88 kg/tonne, thereby offsetting the additional  $\text{CO}_2$  and (ii) the energy required to operate the capture process, or its  $\text{CO}_2$  equivalent, is low and can be supplied by renewables. Definitive savings can best be determined from full scale trials [26].

The new generation of active calcium carbonates greatly extend the range of blended cement compositions giving 3-, 7- and 28-day strengths equal to or greater than the benchmark. As with other pozzolans, it is desirable to differentiate strength-giving reactions from those due to filler effects but this differentiation is still very much in progress. We suggest that as hydration of active calcium carbonate–Portland cement occurs, two types of reaction occur simultaneously (i) the nanoscale calcium carbonate particulates grow in size while the amorphous phase crystallises and (ii) the nanoscale calcium carbonate reacts chemically with C-S-H forming scawtite and tilleyite. The two reactions are competitive, with the result that amorphous and nanoscale calcium carbonate are consumed within a few weeks at 20°C nano-particles do not long persist.

The reactions driven by active calcium carbonate also leave a distinctive and permanent impact on the hydrate mineralogy. If we assume the composition of early-formed C-S-H is  $3\text{CaO}\cdot 2\text{SiO}_2\cdot 8\text{H}_2\text{O}$  ( $\text{C}_3\text{S}_2\text{H}_8$ ). Calcium carbonate reacts with C-S-H as follows:



Scawtite and tilleyite are novel constituents of a cementitious matrix and modify the hydrate phase assemblage, with favourable consequences to strength development and hydration kinetics. But much remains to be learnt about optimisation of the mineralogical balances. To set this work in context, we offer a general physiochemical explanation of the formation of scawtite and tilleyite.

Normal calcium carbonate, including ground limestone, has a low carbonate activity and projects at the lower end of the scale but the free higher free energy of low dimensional materials. This enables stabilisation of amorphous and nano-crystalline  $\text{CaCO}_3$  raises carbonate activities such that a new mineralogical regime is stabilised. This regime embraces scawtite and tilleyite. Although we do not have numerical values of the relevant free energies and species activities, the qualitative order and the mineralogical consequences can, we believe, be inferred from the experimental results. Note that this regime of elevated carbonate activity cannot be attained by adding well-crystallised calcite: regardless of how much is added, the carbonate activity is unchanged and, in our hypothesis, is insufficient to form either or both scawtite and tilleyite.

We believe that, once formed, tilleyite and scawtite are stable. This hypothesis is supported by the persistence of this assemblage in natural occurrences of scawtite and tilleyite with C-S-H, jennite and tobermorite.

The formation of scawtite and tilleyite has other consequences for cement hydration. Both reactions (Equations 1 and 2) release water and we postulate that the extra water is released in zones of most rapid hydration where accelerates hydration. Calcium carbonate thus acts as both a reactant and an accelerator for hydration reactions, the acceleration being most effective in the first few days or weeks of reaction.

In the equation examples, the Ca/Si ratio of early-formed C-S-H is assumed to be 1.5, resulting in an increase in portlandite content as a result of reaction by reaction 2. Changing the ratio of the C-S-H product to higher Ca/Si ratios will not much alter the nature and quantities of products and copious liquid water will still be released. The continuing presence of portlandite is sufficient to condition formation of Ca-rich C-S-H. If, however, the Ca/Si ratio of C-S-H is higher than 1.5, both reactions 1 and 2 will form, amongst other products, portlandite.

This potential, to condition formation of portlandite, is quite unique amongst SCMs. Traditional SCMs such as fly ash, silica fume and calcined clay, react with consumption of portlandite. Consequently, using reactive calcium carbonate as a SCM leaves scope for making ternary blends with another SCM which requires portlandite. We have, however, yet to verify this prediction experimentally.

An additional - and unforeseen - consequence of adding active calcium carbonate to Portland cement is the acceleration of the reaction of anhydrous clinker phases with water. The impact on alite hydration rate is especially strong. The potential of reactions 1 and 2 for making water available locally at hydrating surfaces has been noted. Suppose that the active calcium carbonate alters the reaction mechanism of alite with water as follows: alite, tricalcium silicate, dissolves incongruently with its CaO component dissolving much faster than its silica component. The incongruency of dissolution results in the development of a layer enriched in silica at the alite- water interface. This siliceous layer impedes further reaction. However, formation of scawtite and tilleyite requires silica and we hypothesise that active calcium carbonate reacts with and removes this silica., nucleating scawtite and tilleyite and leaving "clean" surfaces on alite grains which enable hydration reactions to continue. Microstructural studies are however needed to confirm this mechanism.

The question may be asked: why do both tilleyite and scawtite form? Why two carbonate -silicate hydrates? We suggest that tilleyite forms because its structure, based on  $\text{Si}_2\text{O}_7$  dimeric units, resembling those found in C-S-H [27]. Moreover, the tilleyite structure contains columns of calcium-oxygens linked into corrugated sheets; these resemble those found in both jennite and tobermorite [28]. Since jennite and tobermorite are often used as well-crystallised proxies for C-S-H, structural similarities between C-S-H and tilleyite may explain why tilleyite is formed, scawtite tends to form after tilleyite and this retardation in its formation may be because sufficient C-S-H precursor has first to form. Thus, C-S-H is seen as a precursor to tilleyite.

Comparing the chemistry of tilleyite and scawtite, the former has the highest carbonate content (mole fraction of  $\text{CaCO}_3$ , 0.28) [29], relative to scawtite (mole fraction, 0.07) [30].

On purely chemical grounds the delayed formation of scawtite into the period when the remaining supply of highly active calcium carbonate is depleted is surprising, so other factors must control the sequence of phase development. Apparently, the time required for silica to repolymerise into 6-membered, corner-sharing silicate rings, ( $\text{Si}_6\text{O}_{18}$ ), which comprise the basic silicate unit of the scawtite structure is not a limiting chemical factor.

Finally, we comment on the increased strength arising from combinations of Portland cement with active calcium carbonate. Reasons for this are not known but we offer relevant observations on two-time scales; short, up to 28 days and long, at >28 days. Firstly, and in the short term, the acceleration of hydration of the main clinker phases is likely to dominate the rate of strength gain. This, it is believed, accounts for much of the early strength gain up to 28 days, the preservation of benchmark strength at 28 days even at relatively high replacement levels of cement requires a different explanation and is viewed as arising from the incorporation of carbonate into hydration products and the favourable mineralogical evolution. The origin of the higher strengths is probably complex, due to space filling, bonding and the amount and distribution of porosity; At present we are unable to deconvolute the individual contributions.

## 5. Conclusions

In conclusion, an environmental case exists for using reactive calcium carbonate because carbon dioxide emissions from the kiln can be used to make it, thus removing carbon dioxide at the point of production and avoiding its discharge to the atmosphere. This adds a carbon negative term into the carbon dioxide balances and provides an immediate and demonstrable contribution to carbon circularity. The process for making active calcium carbonate is straightforward and is compatible with the conventional cement making process in respect of both production and use. The preferred product



of capture, active calcium carbonate, is amenable to quality control by readily available methods. Moreover, blends of Portland cement- active calcium carbonate have scope for reaction with other conventional SCMs. The products can be used in many of the post formation carbon curing cycles now being implemented, thus compounding benefit. We expect that these developments will enable the ambitious carbon reduction targets set for the industry to be achieved without need for disruptive change.

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### Author Contributions

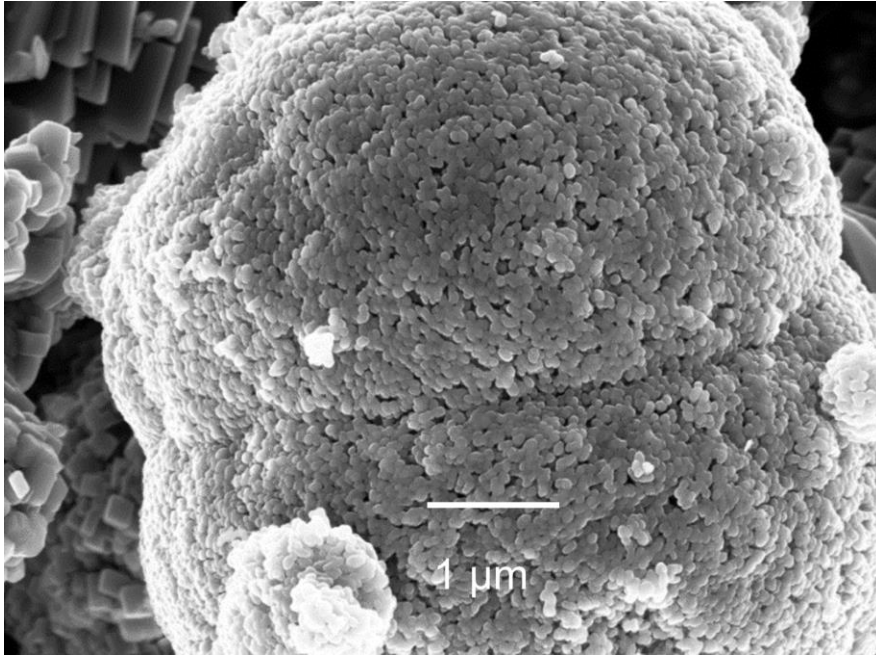
LJM was responsible for the experimental programme and drafting of the manuscript. FPG was responsible for the for concept and design of the experimental programme and providing discussion. WA was the University of Aberdeen internal academic supervisor and contributed to the discussion. The late Mohammed Imbabi was initially the internal supervisor and contributed to the early stages of this work: we dedicate this contribution to his memory.

### Tables and Figures

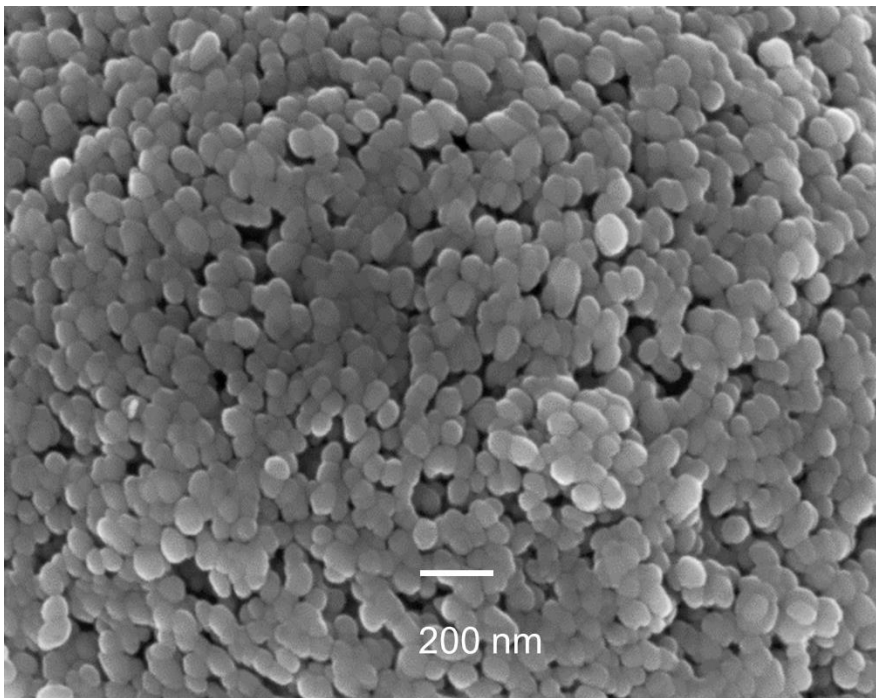
*Table 1: Mineral phases and quantities identified in the Ordinary Portland Cement used for the testing of  $\text{CaCO}_3$ -blended cements and the equivalent oxide groups.*

Mineralogical Composition*	Phase Mass (%)	Chemical Composition*	Phase Mass (%)
$\text{C}_3\text{S}$	59.65	$\text{SiO}_2$	20.28
$\text{C}_2\text{S}$	15.24	$\text{Al}_2\text{O}_3$	4.71
$\text{C}_3\text{A}$	11.81	$\text{Fe}_2\text{O}_3$	3.27
$\text{C}_4\text{AF}$	8.65	CaO	67.13
$\text{C}\$H_2$	4.65	$\text{SO}_3$	2.54
		MgO	0.67
		$\text{K}_2\text{O}$	1.40

\* Cement chemist notation: C = CaO; S =  $\text{SiO}_2$ ; A =  $\text{Al}_2\text{O}_3$ ; F =  $\text{Fe}_2\text{O}_3$ ; \$ =  $\text{SO}_3$ ; H =  $\text{H}_2\text{O}$ .



*Figure 1: SEM micrograph of amorphous calcium carbonate formed by rapid precipitation and examined shortly after precipitation, ca 5 minutes.*



*Figure 2: SEM micrograph of amorphous calcium carbonate shown in figure 1 at higher magnification.*

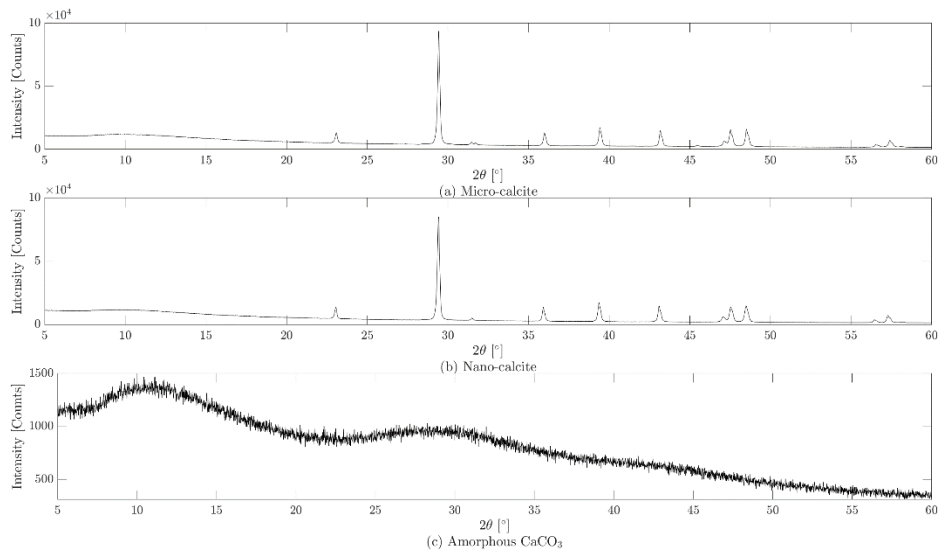


Figure 3: XRD patterns of the three calcium carbonates. The reflections observed in the nano- (Figure 4) and micro-calcite (Figure 5) patterns are noticeably absent in the amorphous (Figure 1), which lacks any distinct Bragg reflections. The nano-calcite reflections are broadened although this is not apparent in rapid scans.

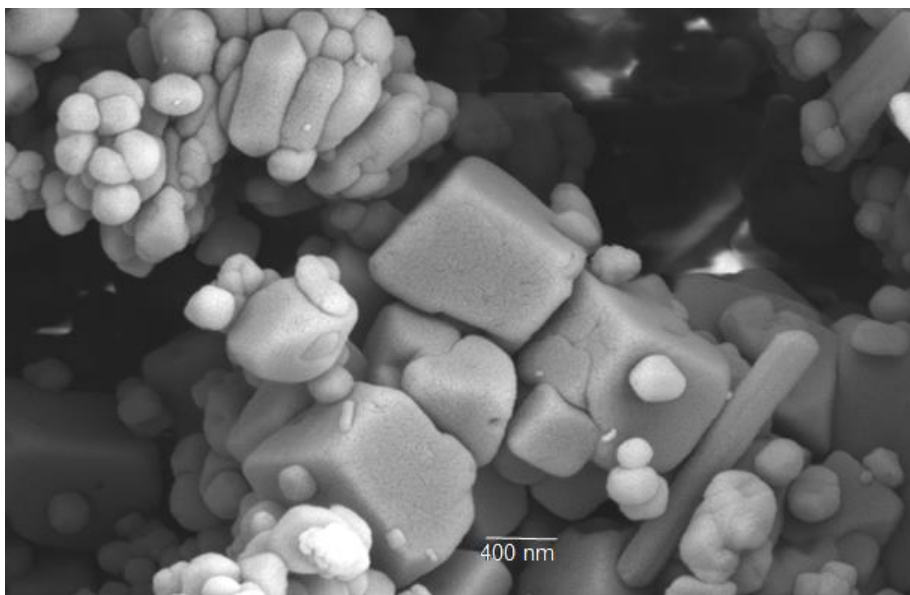


Figure 4: Nano- sized calcite produced by ageing the amorphous phase for a few more minutes at 20°C. The larger crystallites have distinct rhomboid morphology of calcite while the smaller round and often clustered elongated grains are probably amorphous calcium carbonate.

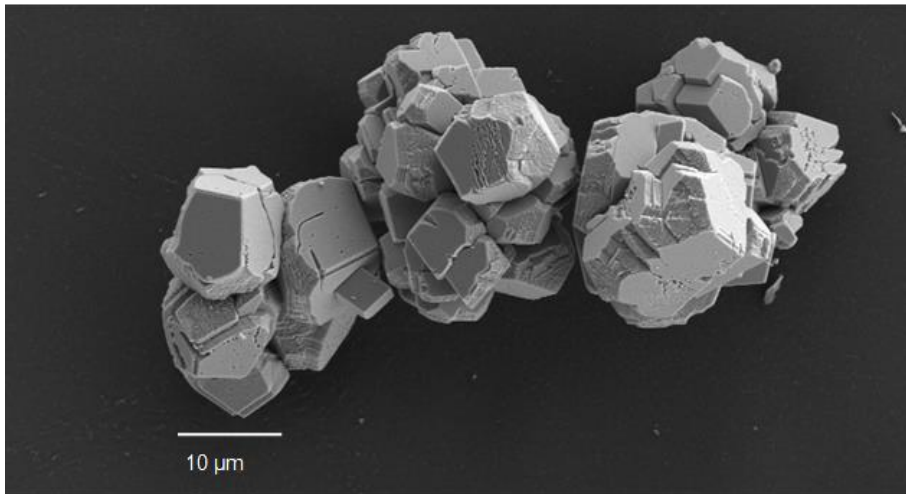


Figure 5: Micro-calcite produced with a ripening time of 2 hours showing growth steps on the faces of clustered rhomboids.

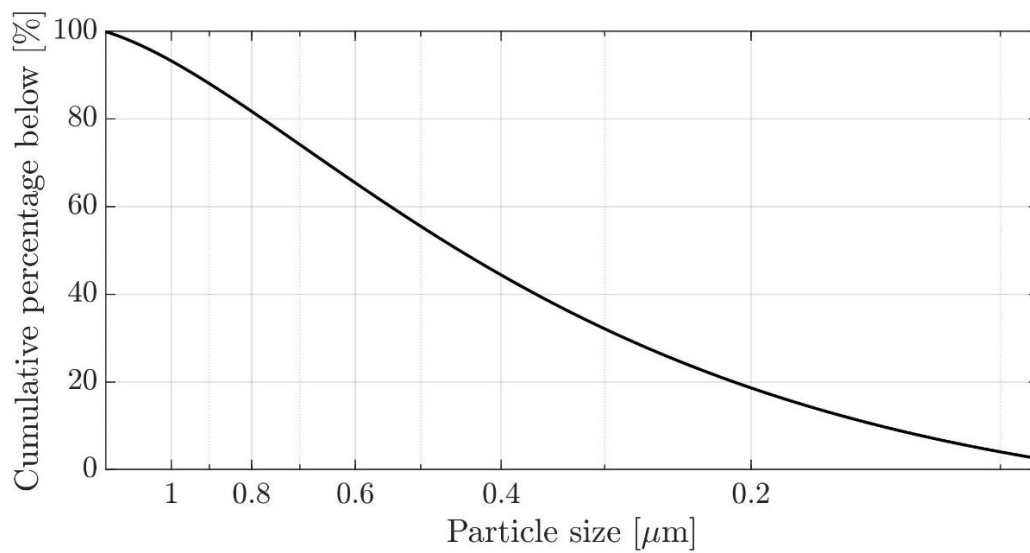


Figure 6: Particle size distribution of nano-calcite made according to section 2.3 and corresponding to the micrograph shown in Figure 4.

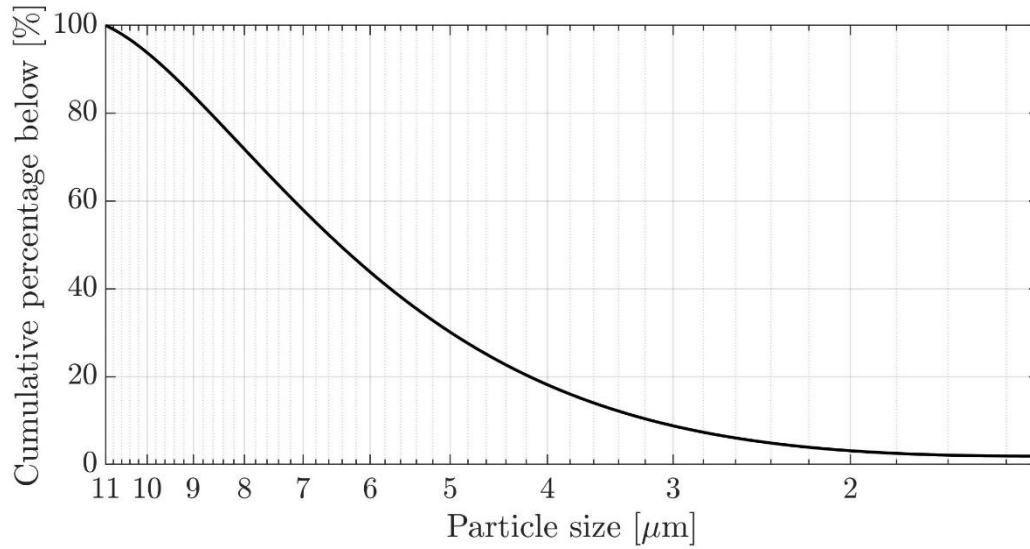


Figure 7: Particle size distribution of the micro-calcite shown in Figure 5, made according to section 2.3.

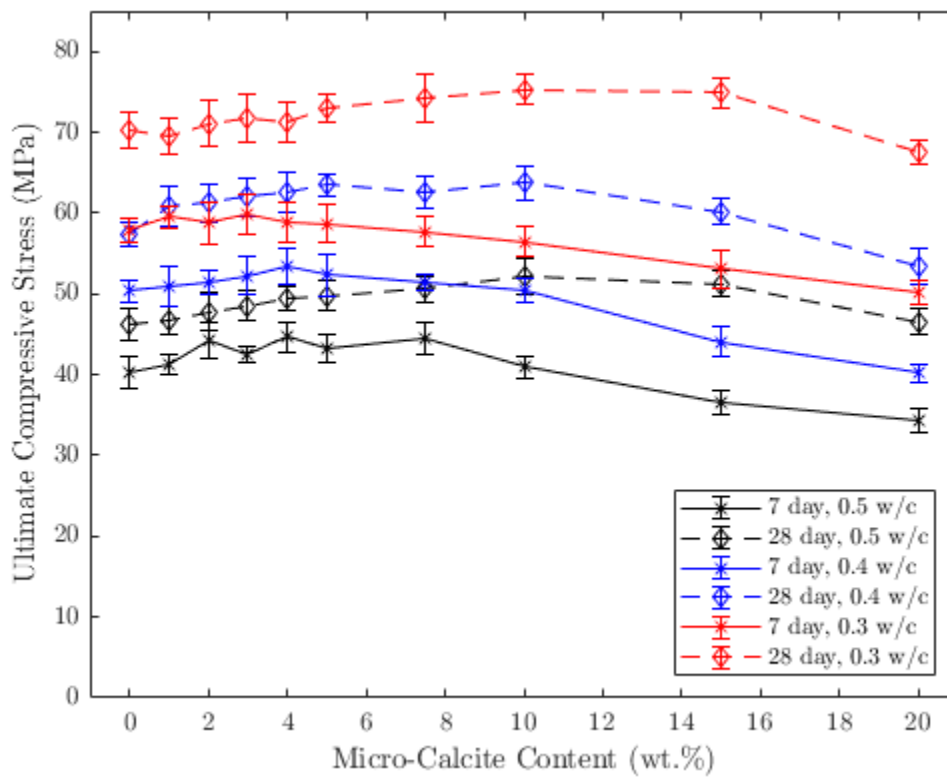


Figure 8: Compressive strength of Portland cement containing micro-calcite hydrated with varied amounts of water from 0.3 to 0.5 w/s. Each trial was hydrated for both 7 and 28 days prior to testing.

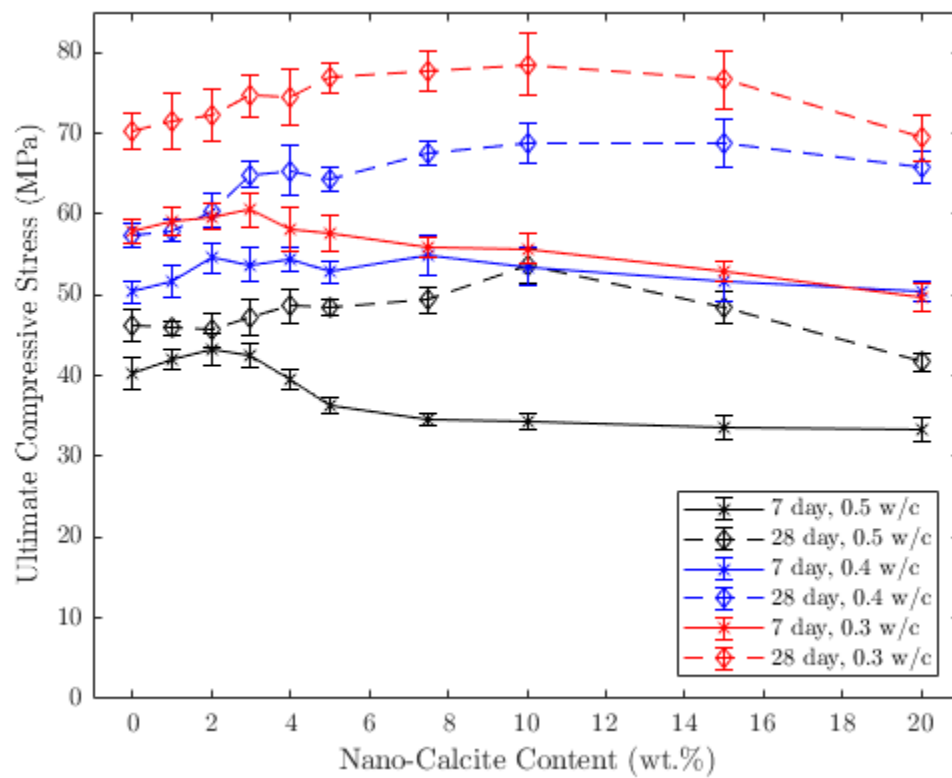


Figure 9: Compressive strength of Portland cement containing nano-calcite. For each w/s ratio, the cement pastes were hydrated for both 7 and 28 days.



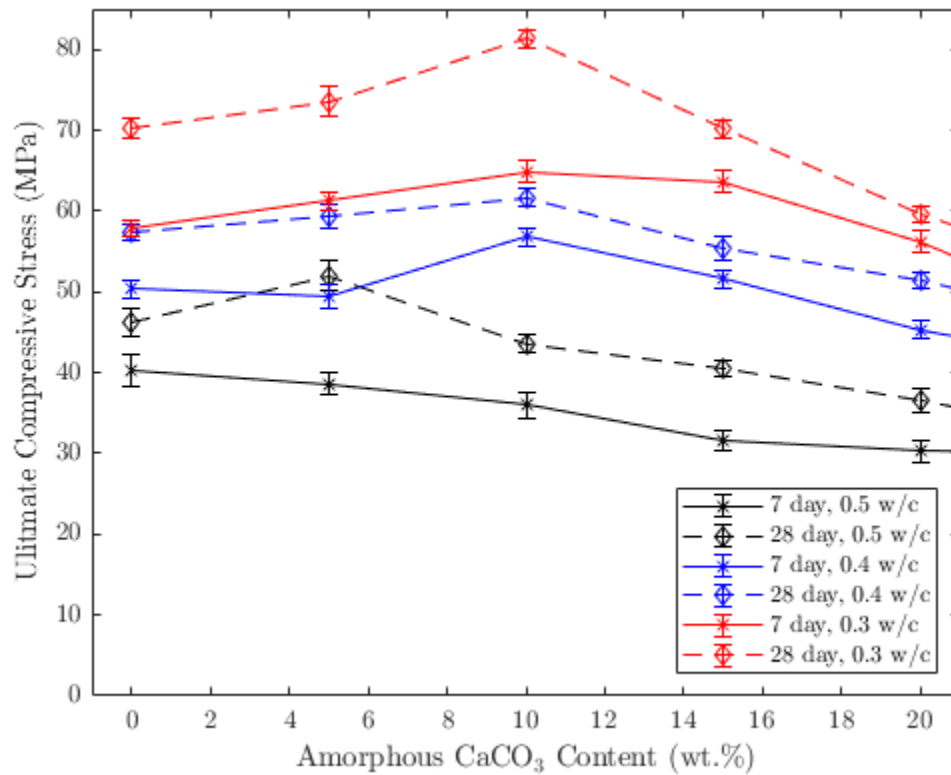


Figure 10: Compressive strength of amorphous calcium carbonate cement blends produced by the method described in section 2.2.

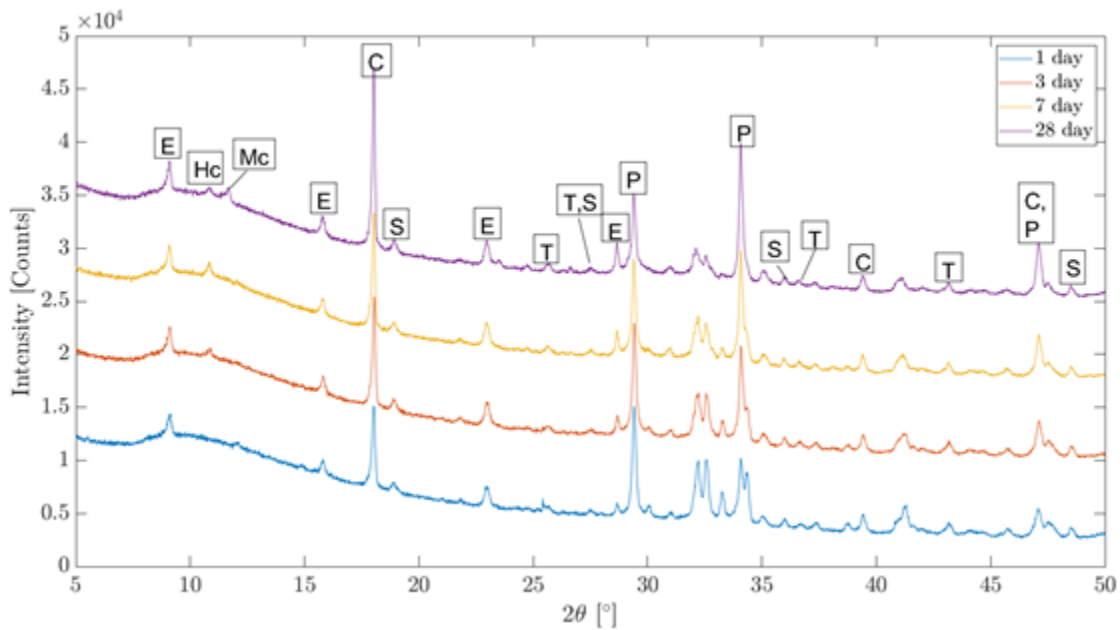


Figure 11: XRD patterns of a hardened cement paste containing 5 wt.% nano-calcite after 1, 3, 7 & 28 days with a w/s ratio of 0.5. The hydration products related to the addition of the calcite have been identified: Hc – hemihydrate; Mc – monohydrate; T – tillite; S – scawtite; E – ettringite; P –  $\text{Ca}(\text{OH})_2$ ; C - Calcite.

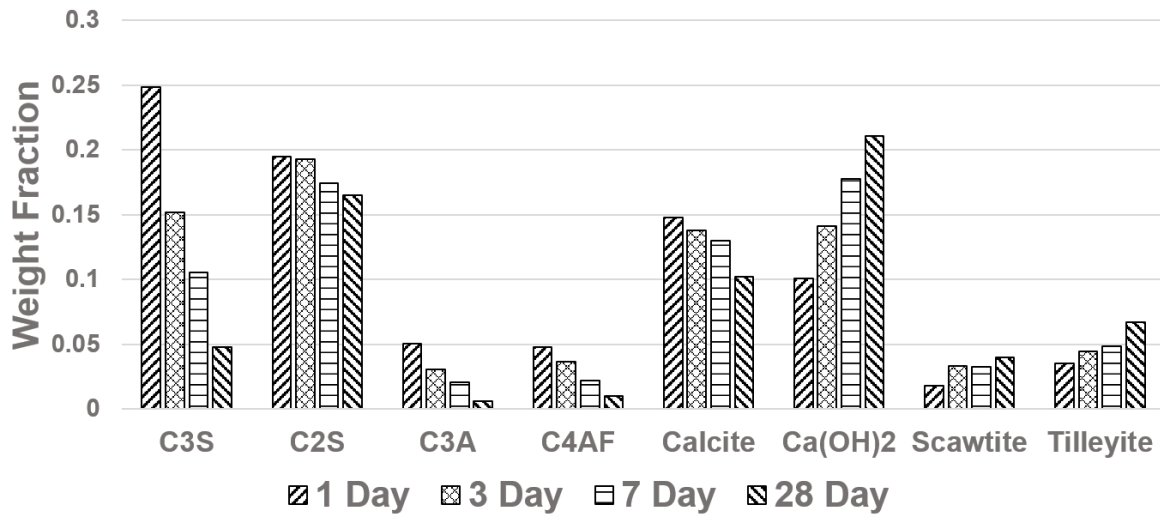


Figure 12: Depletion of the clinker phases and nano-calcite of a Portland cement containing 10% nano-calcite (Figure 4) by and w/s of 0.5. The initial value of calcite is >10% as the amorphous components of the cement paste have not been considered. The estimated standard deviation output by the Rietveld analysis is several orders of magnitude smaller than the data and has been omitted.

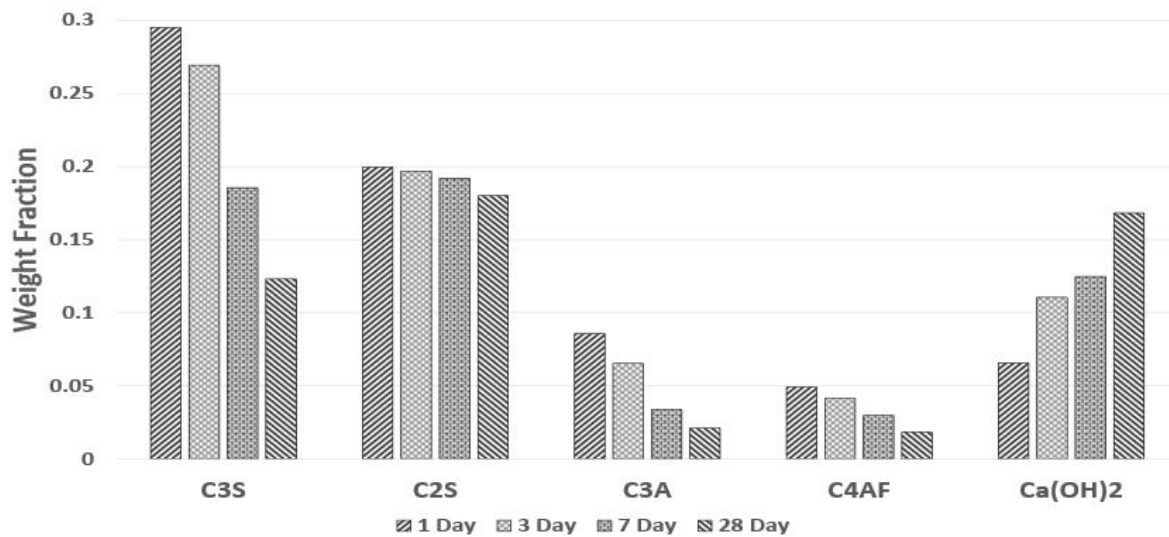


Figure 13: Depletion of the clinker phases of the same Portland cement shown in Figure 12 without added calcite.