

IMPROVING STRENGTH & SUSTAINABILITY

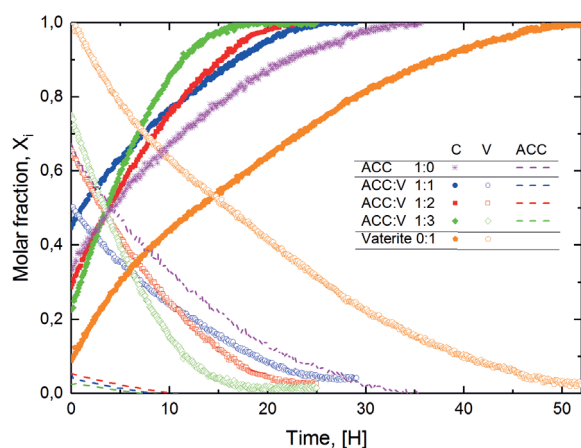
Dr Jesus Rodriguez Sanchez, Lucideon, considers how to create mechanical strength in sustainable calcium carbonate cement.

Due to the high carbon footprint of portland cement, there has been an increased interest in alternative hydraulic binders. Inspired by the mechanical properties of limestone, which is mainly composed of calcium carbonate (CaCO_3), several production pathways to form synthetic CaCO_3 binders have been investigated, the most famous being the Calera carbonation process. Another path to preparing pure CaCO_3 cements is of special interest as a model system to further investigate the properties of this kind of cement. Combes et al.¹ mixed water with two metastable CaCO_3 phases. One must be the highly reactive amorphous calcium carbonate (ACC) phase, while the other must be one of the metastable crystalline phases, either vaterite (V) or aragonite (Ar). The polymorphs ACC and V (or Ar) (re)crystallise into the most stable calcite phase during the setting process of the cement paste, to form a solid crystalline network.

Even though the (re)crystallisation of CaCO_3 polymorphs has received much attention in recent years due to its importance in several industries, the climate, and geology,²⁻⁷ this large body of knowledge has yet to be put into the context of CaCO_3 cement setting. CaCO_3 polymorphic transformation follows an energetically downhill sequence:

$\text{ACC} \rightarrow \text{V} \rightarrow \text{Ar} \rightarrow \text{Calcite}$.⁸ However, indirect transformations, or more complex mechanisms out of the classical nucleation theory, may also occur, resulting in unknown activation energies and growth/dissolution rates. Multiple studies have been carried out to unravel the mechanisms and the energetics among the CaCO_3 polymorphic transformations in solutions at both computational and experimental levels. For example, Rodriguez-Blanco et al.⁹ and Bots et al.¹⁰ found that hydrated ACC transforms into an intermediate anhydrous ACC before forming V; then, V transforms to calcite (at temperatures below 40°C) via a dissolution and reprecipitation mechanism, with the reaction rate controlled by the surface area of calcite.

Nevertheless, a cement paste represents a more complex challenge, since the amount of available water plays a key role as an external mediator/inducer of the transformation.⁹ The liquid phase remains saturated with respect to a different polymorph, depending on both their solubility and relative existence within the paste, causing the driving force of the transformation to vary with time. Moreover, the paste may experience evaporation at the paste/air interface, depending on the environmental conditions during setting. Hence, a better understanding of the



Calcite, V, and ACC mole fractions (X_i) evolution with time for three different CaCO_3 cement compositions (1:1, 1:2, and 1:3 wt.% ACC:V). Pure ACC (1:0 wt.%) and V (0:1 wt.%) pastes have also been included as references. Solid symbols represent calcite while empty symbols and dashed lines stand for V and ACC, respectively.

simultaneous transformations that CaCO_3 pastes undergo during the setting reaction is still necessary.

Considering that the properties of hardened CaCO_3 cements are a result of the (re)crystallisation that the paste undergoes when the solid reagents are mixed with water, it is of crucial importance to correlate these phase transformations with the evolution of the viscoelastic properties of the pastes during maturation. This correlation would unravel the strengthening mechanisms of this kind of cement and their kinetics.

In the present study, sustainable, 100% pure CaCO_3 cements have been synthesised following Combes' method,¹ to investigate the transformation kinetics of each phase (ACC, V, and calcite) within a paste system, as well as their structural, built-up mechanisms during setting. To address these effects, in-situ X-ray diffraction (XRD) scans and rheological measurements have been carried out respectively, over cement pastes with dissimilar mixture designs. The combination of these results aims to build up a better understanding of the relationship between CaCO_3 phase transformations and strengthening kinetics, not only for pure CaCO_3 cements but for other carbonated materials with important implications in many industrial fields.

Phase transformations

CaCO_3 cement pastes were made up of mixtures of ACC and V powders in different weight ratios (wt.%): 1:0, 1:1, 1:2, 1:3, and 0:1 wt.%, with a solid volume concentration (Φ) equal to 46%.

After mixing the solid reagents with water, XRD patterns were recorded every 5 min. for a maximum of 60 hours. Since the mass of a crystalline phase (m_i) is proportional to the area (A_i) under its diffraction peak ($m_i \propto A_i$), the net area under the main V and calcite diffraction peaks were calculated

for each scan. This data was used to calculate the relative mole fractions of each phase (X_i) that coexist within the cement pastes. This was based on two assumptions: the V mole fraction in the first scan is the same as in the initial mixture, and in the final scan the cement is pure calcite. Then, the evolution of the mole fractions for V ($X_V(t)$) and calcite ($X_C(t)$) could be determined using the following relations:

$$X_C(t) = \frac{A_C(t)}{A_C(t_f)} \quad \text{and} \quad X_V(t) = X_V(t_0) \cdot \frac{A_V(t)}{A(t_0)}$$

In these equations, t represents the time and $X_V(t_0)$ the starting V mole fraction, which is determined by the mixture design, i.e. either 0, 0.5, 0.66, 0.75, or 1, for the ACC:V 1:0, 1:1, 1:2, 1:3 and 0:1 wt.% pastes, respectively. Moreover, the mole fraction evolution of ACC, $X_{ACC}(t)$ could be easily determined, since the total mole fractions follow $X_C(t) + X_V(t) + X_{ACC}(t) = 1$.

Rheological characterisation

CaCO_3 cement pastes were prepared as for phase transformation analysis and were immediately transferred into the rheometer plate for testing. From the measurements, the storage modulus (G') and the loss modulus (G'') were extracted as the characterising parameters of the viscoelastic behaviour, since those are defined by the following equation:¹¹

$$G^* = G' + iG''$$

Here, G^* is the complex modulus, which corresponds to the ratio between the complex stress (σ^*) and the complex strain (γ^*):

$$\sigma^*(t) = G^* \cdot \gamma(t)$$

To quantify the influence of ACC and V (re)crystallisation into calcite on the macroscopic mechanical properties of pastes, a constant oscillatory deformation ($\gamma = 0.003\%$) was applied to the pastes at the imposed frequency of $f = 10$ Hz, for several hours. This allowed measurement of the time evolution of the visco-elastic moduli (G' and G'') during the setting reaction. The values of strain and frequency were chosen small enough to ensure measurements within the linear elastic regime for all the tested pastes, and thus there was no perturbation of the setting and hardening dynamics.

Results and discussion

Phase transformations

The evolution of the cement compositions during the setting reaction shows that the two starting phases – ACC and V – dissolve, while the third one – calcite – grows at the expense of the other two. Moreover, the results show a clear trend: higher initial V concentration leads to faster calcite growth rates and



CaCO₃ cement specimen (20 mm dia., 40 mm height) with initial mixture design ACC:V 1:1 wt. %.

a shorter recrystallisation process. However, pure V (ACC:V 0:1 wt. %) shows the slowest transformation kinetics, probably due to its lower free-energy difference (ΔG) (6.2 KJ/mol¹²), with respect to calcite in comparison with ACC (15.0 KJ/mol⁶). Hence, to rationalise this trend, the different phase transition kinetics must be considered and compared, and those can be described by the crystal growth rate (r), which also represents dissolution if it is negative. This is shown in the following equation:

$$\frac{dm}{dt} = \pm \varphi \cdot m^{2/3}$$

Here, K is the growth rate constant (kg s⁻¹ m²); A is the reactive surface area of the growing phase; E_a is the apparent activation energy of the overall reaction; R is the gas constant; T is the absolute temperature; and $f(\Delta G)$ introduces the dependence of the overall growth rate on the supersaturation state of the system, expressed as a function (f) of the Gibbs free-energy change for the growth reaction (ΔG).

To identify the rate-determining step of ACC and V transformation into calcite, the evolution of the mass (m) of each phase should be analysed and compared with the growth rate, as follows:

$$r = \frac{dm}{dt} = \pm K \cdot A \cdot \left(\frac{\Delta G}{RT}\right)^n$$

Assuming that the growth rate is constant of the transformation (K) and the supersaturation ($\Omega = \Delta G/RT$) of the system does not change with time, they can be combined into a single constant term. Moreover, the mass of a particle (m) is proportional to the cube of its length (L) ($m \propto L^3$), whereas its area (A) is proportional to the square of its length ($A \propto L^2$). Thus, the area is proportional to the power of 2/3 of the mass: $A \propto m^{2/3}$. With those considerations, the

mass obtained from the analysis of the RXD patterns can be used instead of A , and the previous equation results in the following:

$$r = \pm K \cdot A \cdot e^{\frac{-E_a}{RT}} \cdot f(\Delta G)$$

Here, the positive sign is used to describe the evolution of the mass of the growing calcite phase (m_c) and it considers that calcite precipitation is limiting the transformation of ACC and V into calcite. On the other hand, the negative sign describes the evolution of the mass of the dissolving V phase (m_v) and it considers that V dissolution controls the transformation rate of both ACC and V into calcite crystals. Both hypotheses were considered and the results showed that the transformation of V to calcite within a cement paste system is not only limited by the dissolution of V but also by the grain size change effect on the chemical potential of the system. Moreover, characteristic (re)crystallisation times (τ) could be extracted for each cement composition.

Viscoelastic properties of the pastes

The results showed that the rigidity of the pastes were different, because the solid reagents (ACC and V) were mixed with water and increased with the V:ACC ratio. This behaviour might be attributed to the larger dimension of V particles in comparison with ACC (one order of magnitude).

From the diverse starting points, the storage modulus (G') increased progressively for all pastes with time until it reached a value of ~ 0.7 MPa for all compositions – from here the evolution was less evident. Thus, two distinctive periods of building up strength could be identified; first, a fast (steep slope), and then a slow (small slope), which could be characterised by their relaxation times (τ_1). This trend suggests that the main changes of the structural built-up mechanism occur within the early stages of maturation, i.e. just after mixing the ACC and V particles with water. In comparison, a secondary mechanism continued developing the microstructure within the following hours.

In order to support a finite amount of stress without flow, CaCO₃ cement pastes must possess an internal network of particles with attractive interactions, either via direct contacts or via colloidal forces.¹³ Several mechanisms have been reported for portland cement pastes, to rationalise how a flocculated network starts to develop its structural integrity. Among those, some seem to be compatible with the captured evolutions for CaCO₃ cements.^{14,15} For example, the rise of the rigidity of the pastes within the initial short-range step can be interpreted as the geometrical redistribution of both ACC and V particles within the paste, until they start to form joints. This process took place on the order of the hour (from 0.9 hours and 2.3 hours), suggesting the existence of an electrostatic barrier between colloidal particles. On the other hand, the (re)crystallisation process seems to be the mechanism

responsible for the strengthening advance during the secondary long-term structural development. Once the solid phases (former ACC and V particles, plus the newly formed calcite crystals) are in contact, the (re)crystallisation continues, inducing growth of former calcite crystals rather than nucleating new ones (as described by the Ostwald ripening), while also increasing the area of contact within the crystals. This process had a relaxation time in the order of 12 ± 2 hours. Thus, the structural buildup of CaCO_3 pastes during this phase seemed to be due to the development of crystal joints, also known as 'bridging effect' or 'crystal entanglement'.¹⁶ How this process evolves with time not only depends on the particular (re)crystallisation kinetics and energetics of both ACC and V phases into calcite, but on their relative amount within the pastes. This is because, as shown, this parameter determines the driving force of the transformation.

Conclusion

A comparison between the characteristic (re)crystallisation times (τ_c) measured from XRD analysis and the characteristic strengthening times (τ_s) measured from rheological experiments, showed that they both follow a linear relationship and, consequently, they show that the increase on the (re)crystallisation extent is directly correlated with the progression of the structural development of the paste. These results will help to tailor the final mechanical properties of the cement samples, since those are highly determined by the total bridging area within the calcite crystals of the network. ■

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About the author

Dr Jesus Rodriguez Sanchez has a degree in Technical Architecture and a degree in Mechanical Engineering, as well as a MSc in Research on Engineering. Rodriguez Sanchez embarked on his PhD to develop and characterise new cementitious materials at the University of Oslo. At Lucideon, through the Innovate UK Knowledge and Transfer Partnerships programme, Rodriguez Sanchez is responsible for developing new foamed geopolymer pastes and products for thermal insulating applications.