

Carbonation and durability of construction materials

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Abstract.

Lime has been used for a very extended time in history as a binder in lime mortar which helped passed civilisations to realize still existing, useful and splendid constructions in many places in the world. The hardening of lime mortar is depending on the carbonation process. Extensive studies have been done on carbonation of lime and the influence of it on the properties of lime mortar and on masonry made with it. Models have been made that explain the speed of the progress of carbonation depending on the physical nature of the mortar which has an influence on the diffusion of carbon dioxide through the porous mortar medium and the interaction with water has been taken into account. The reaction speed of the carbonation reaction has been studied and variables that influence the chemical reaction has been identified amongst others using X-Ray diffraction analysis in an ongoing carbonation experiment. It contributed to understanding the relation between carbonation conditions and the nature of the reaction products that can be amorphous or have different phases of calcium carbonate. Next the hindering factor in the acceleration of carbonation has been studied and different additives are being studied to investigate their possible impact on this hindering factor. Carbonation is also studied in other building materials that contain $\text{Ca}(\text{OH})_2$ in its composition or as a reaction product. This is the case for cement mortar or concrete. Recent research however has also “used” the carbonation process to instigate a binding process, for example using alkaline slags from stainless steel production. This and similar research seems to indicate that carbonation is not just a chemical reaction but considering the necessary conditions for carbonation (dissolution in water, accessibility of carbon dioxide, ...) can be seen as a binding process. The outcome of such carbonation processes in historical materials and construction as well as in nature (geology) helps to estimate the durability of materials generated through a carbonation process. This throws an insight on the relation between carbonation and durability which is very different from the perspective the world of concrete has on the phenomenon and it also may lead research towards materials that are durable and help reduce the carbon dioxide content in the air, which also contributes to sustainability.

The effect of lime carbonation on the properties of mortar and masonry

Lime mortar gives masonry a remarkable deformability which is beneficial in case of differential settlements and even earthquakes. The study of the tri-axial behaviour of mortar in masonry and the potential of lime mortar to deform under tri-axial compression before bricks or units break due to tensile stresses they are subjected to, explains this deformability /1/. Carbonation does slightly increase stiffness and strength of lime mortar compared to the fresh lime mortar, at the same time un-carbonated lime more than carbonated lime contributes to the self-healing capacity of mortar which helps to recover strength of masonry due to early settlements or shrinkage. In that respect lime mortar or mortar with lime contributes to longevity and durability of masonry.

Modelling the carbonation process of lime mortar

A first study aiming at modelling the carbonation of lime mortar based on understanding the diffusion of CO_2 through the porous system of the mortar and taking into account the effect of the presence of water in this porous system was published in 1994 /2/.

The carbonation process in lime mortar is influenced by the diffusion of carbon dioxide into the mortar pore system, by the kinetics of the lime carbonation reaction, and by the drying and wetting process in the mortar. All these phenomena depend on the presence of water in the mortar. Water is present in liquid form as well as vapour. Physical models and their mathematical basis are given for the factors influencing carbonation. The mathematical description of the carbonation process in lime mortar completes the information necessary to model the simulation of carbonation in conjunction with the drying process. Simulations at different carbon dioxide concentrations showed a good correlation between experiment and mathematical prediction. Reliable data were given for the model but improvements had to be made on the relation between water content and diffusivity as well as on the reaction term that express the carbonation rate related to the environmental conditions and the lime properties. The reaction term used in the equation was based on literature data from water treatment applications, which means a large quantity of water compared to the carbon dioxide content which has an influence on the absorption rate of CO_2 into the water and on the limiting factors defining the dissolution of H_2CO_3 . This dissolution is a preliminary condition for the carbonation to occur as the reaction and crystallisation happens in a liquid phase.

Measuring the parameters defining carbonation rate and progress

A later article in 2005 /3/ updated the model including a more reliable model on the impact of the presence of water on the diffusivity of CO_2 . It also reported on experiments that measured lime reactivity depending on the carbonation circumstances (CO_2 partial pressure) and properties of the lime (mass, specific surface, particle diameter size, purity). The designed and validated closed loop set-up allowed to measure the uptake of carbon dioxide due to the carbonation reaction of $\text{Ca}(\text{OH})_2$ in ambient temperature of approximately $20\text{ }^\circ\text{C}$. Different types of lime were used and the CO_2 concentration varied to identify the influence of different variables on the kinetics of the reaction. Thermal analysis (TA) was used to verify the degree of carbonation. Factor analysis on the data set demonstrated that reaction speed is not dependent upon the CO_2 concentration within the limits tested. Carbonation speed was demonstrated to depend on the specific surface of the lime. The results of this study contribute to improving the lime mortar carbonation models and to a better understanding of the carbonation process in general.

Mineral changes going along the carbonation process

Next in an article in 2012 /4/ by Ö. Cizer et al, the carbonation reaction of lime pastes was studied with a similar test set-up, however this time an X-Ray diffractometer was placed into the loop. The closed loop carbonation set-up combined the measurement of the amount of CO_2 consumed by $\text{Ca}(\text{OH})_2$ with XRD data allowing to monitor the real-time modification of portlandite and calcite phases. The reaction rates obtained from the net CO_2 uptake by $\text{Ca}(\text{OH})_2$ and that obtained from the calcite precipitation were compared for lime putty and lime hydrate pastes carbonated in environments with various CO_2 concentrations.

The results indicate that the carbonation reaction is initially rapid and chemically controlled at the exposed surface with a strong limitation of CO_2 diffusion into the sample by the pore water. The reaction proceeds with a chemical-reaction controlled regime at a much higher rate followed by a transition to a CO_2 -diffusion controlled regime by the carbonating depth. Drying and formation of amorphous CaCO_3 on the portlandite faces has been found to create a dormant effect for the calcite precipitation at the first stage. Lime putty indicates faster carbonation than lime hydrate due to its small particle size and morphology properties, both at a rate which is independent of the CO_2 gas concentration. These results added complementary insights in the carbonation process.

In a complementary article by Ö. Cizer et al /5/ more insights were gained on the crucial effects of relative humidity and CO_2 pressure on the (trans)formations of phase, morphology, habit, and size of calcium carbonate crystals during lime carbonation. Both the carbonation

process and the scalenohedral-to-rhombohedral transformation are kinetically favoured under high relative humidity and $p\text{CO}_2$. Carbonation can also take place via coupled dissolution/precipitation replacement of $\text{Ca}(\text{OH})_2$ crystals by calcite pseudomorphs. Calcite morphology has been found to vary with the carbonation depth and, therefore, with the exposure time to CO_2 . These results indicate that phase and morphological evolution of CaCO_3 can have strong implications in the ultimate performance of lime mortars and also in the other binding processes via carbonation.

Increasing carbonation speed and extension playing on limiting factor

From the previous research it became clear that the limiting factor in the carbonation process is the rate of dissolution of CO_2 in the alkaline water generating HCO_3^- ions which are consumed in the conversion of the dissolved $\text{Ca}(\text{OH})_2$ to CaCO_3 , the latter being deposited as solid. Recently we have been investigating analogies in nature and living organisms where hydration and dissolution of CO_2 is involved [6]. Carbonic anhydrase enzyme (CA) is a biocatalyst and belongs to a large group of zinc-based metalloenzymes that are known to catalyse the reversible hydration of carbon dioxide ($\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$) in many processes in nature such as respiration, CO_2 transport and photosynthesis. The fastest human CA enzyme (HCA II) can hydrate at least 1.4×10^6 molecules of CO_2 per second. At neutral pH and at slightly alkaline pH (ca. 8-9), this enzyme yields enzyme-bound Zn-OH^- that is readily available to react with CO_2 . As a result, HCO_3^- ions formation is enhanced and the overall hydration rate of CO_2 is increased. We have investigated the biocatalytic effect of CA enzyme on the reaction kinetics and calcium carbonate phase transformations during carbonation of lime where the pH of the system continuously decreases from ≈ 12.5 to ≈ 8.2 [6]. Results obtained from pH measurements, in-situ XRD analysis and micro Raman spectroscopy, and electron microscope clearly indicated enhancement of calcium carbonate precipitation and preferential modification of crystal habit and morphology of calcite due to the catalytic effect of CA enzyme. This biocatalyst successfully accelerated phase transformations from amorphous calcium carbonate (ACC) into calcite via an intermediate phase formations of anhydrous ACC and vaterite. This resulted in denser pore structure, and faster and higher strength development (up to 40%) of the lime mortar. Inspired from nature, the kinetic effect that CA enzyme has on lime carbonation might offer a potentially novel approach with significant benefits to lime mortar applications in construction.

Carbonation in novel binders based on AOD slags

The study of the contribution of carbonation to the binding of non-stabilized Argon Oxygen Decarburisation (AODNS) slag in powdered form helped to improve the understanding of the carbonation process as a binding process in a different environment [7]. The purpose of the research was to examine the carbon dioxide sequestration capacity of the material and its potential utilisation in the fabrication of high value building materials, like construction units comparable to bricks. The curing of the sample was carried out in two accelerated carbonation environments: (i) in a carbonation chamber, maintained at atmospheric pressure, 22 °C, 5 vol.% CO₂ and 80% RH; and (ii) in a carbonation reactor, where the CO₂ partial pressure (p_{CO_2} 8 bar) and temperature (80°C) could be further increased. In the carbonation chamber, an average compressive strength of over 20 MPa, on a 64 cm³ cubic specimen, was obtained after one week of curing, which is sufficient for many construction applications. Further carbonation resulted in a linear increase of strength up to ~30 MPa after three weeks. The CO₂ uptake followed a similar trend, reaching a maximum of 4.3 wt.%. In the reactor, the compressive strength improved significantly to 60 MPa with maximum CO₂ uptake of 8.1 wt.%. Phase analysis by X-ray powder diffraction and inspection by scanning electron microscopy showed the precipitation of calcite and formation of significant amounts of amorphous phase after carbonation. Infrared spectroscopy also pointed to the presence of aragonite and vaterite. Carbonation of the slag resulted in the reduction of basicity by up to one pH unit, and contributed to controlling the leaching of several heavy metals and metalloids. Those findings were further detailed in [7] demonstrated the binding potential of carbonation creating the conditions of dissolution and precipitation influenced also by the alkalinity of the environment.

Conclusions

This contribution aimed at referring to various studies which shed light on the carbonation process in lime mortar. From those studies it becomes clear that different circumstances of dissolution and precipitation of lime and calcite which is integrated in the carbonation process play an important role in binding materials in the construction sector. The application of carbonation on AOD slags shows that the binding effect of carbonation is not limited to lime based materials. Analogy from living organisms has helped identifying paths to overcome the factor that limits the rate of acceleration of carbonation when the amount of water in which dissolution and acceleration is taking place, is limited.

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