

## ***In-situ* Analysis of the Lime Cycle ( $\text{CaCO}_3 - \text{CaO} - \text{Ca(OH)}_2 - \text{CaCO}_3$ ) by Environmental TEM**

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Hitherto the 18th century, worldwide structures were built using the chemical compounds of the lime cycle – limestone ( $\text{CaCO}_3$ ), lime ( $\text{CaO}$ ) and hydrated lime ( $\text{Ca(OH)}_2$ ) – which were further converted to materials like lime plasters and lime mortars. The advancement of cement technology brought about the ordinary Portland cement (OPC) which outweighed the lime-based cementitious materials by certain properties such as shorter hardening and setting times, combined with higher mechanical properties [1]. Nevertheless, in an attempt of heritage conservation it has been observed that OPC's properties are not compatible with the limebased materials' properties, thus leading to an unfruitful restoration. Ergo, it is crucial to refurbish the lime cycle in order to optimise the properties of the chemical compounds involved and execute a proper restoration.

The starting point of the lime cycle is calcium carbonate as raw material. The latter is calcined at temperatures between  $900^\circ\text{C}$  and  $1200^\circ\text{C}$  into calcium oxide and carbon dioxide, followed by a hydration process which transforms calcium oxide into calcium hydroxide exothermically. Finally, the calcium hydroxide reacts with carbon dioxide during the carbonation process to form calcium carbonate and complete the cycle. Several studies have been carried out independently on the three different processes and mechanisms have been established on the kinetics following temperature and/or pressure. However, a complete study of the cycle for providing continuous insights on the dynamics and phase transitions was not yet performed. Herein, we present the study of the whole lime cycle using environmental TEM (E-TEM) which is the unique tool allowing to probe the morphological and structural transitions in situ and operando at a nanometric level.

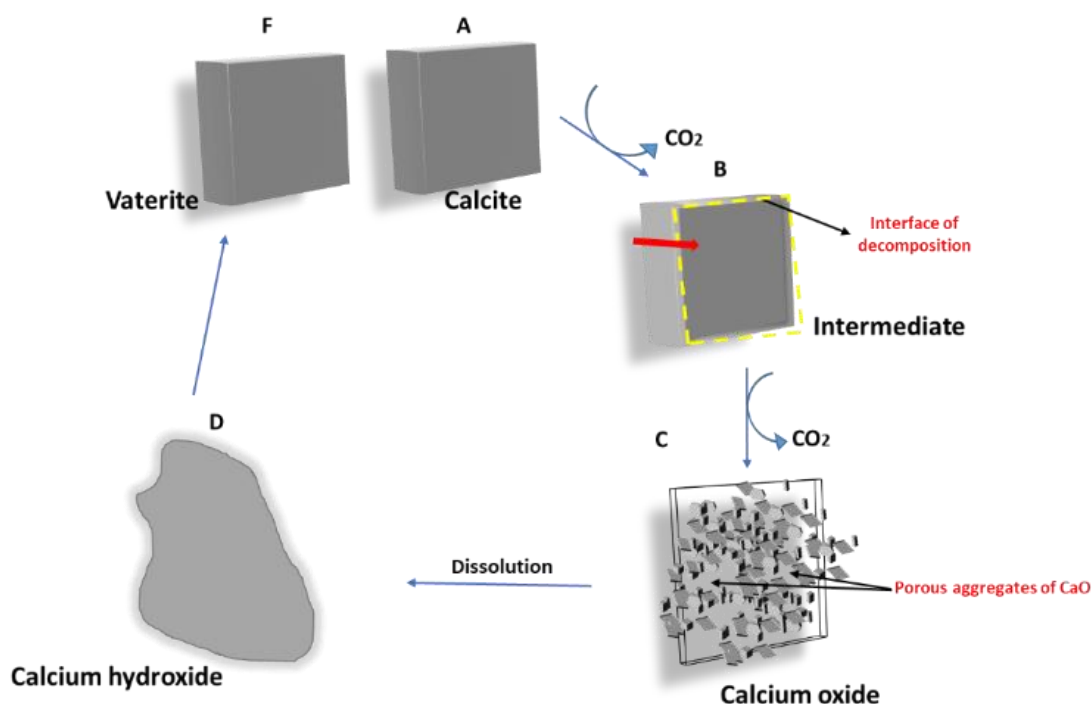
We synthesized the calcium carbonate solution using calcium chloride and sodium carbonate solutions and we deposited a drop on the silicon carbide observation window of the E-chip. The decomposition of calcium carbonate was carried out until  $850^\circ\text{C}$  at a rate of  $0,05^\circ\text{C/s}$  in a gaseous atmosphere filled with air. In a second time, water vapour was introduced in the atmosphere to hydrate the calcium oxide formed by decomposition. To complete the cycle, carbon dioxide was added to the reaction mixture to form calcium carbonate from calcium hydroxide. All these experiments were monitored and captured by videos with a JEOL 2100F TEM.

The first observation is that the thermal decomposition of calcium carbonate is a pseudomorphic reaction, given that the external shape of the (10 $\bar{1}$ 4) rhombohedron is preserved (Figure 1C and 2C). This leads to the hypothesis of a crystallographic control during the reaction. A closer study of the decomposition by in situ diffraction allowed us to confirm our assumption and also to evidence that calcium carbonate decomposes in a topotactic manner (with an angular relationship between crystallographic planes) to form calcium oxide. Furthermore, the study of the dynamics of the decomposition step demonstrated that the

reaction starts at the external surface, forming a reactant-product interface through which  $\text{CO}_2$  diffuses outside, while the interface moves towards the core of the grain, as shown in Figure 1B and 2B. The CaO particles form thus highly porous aggregates. During the hydration process of the latter, a compact liquid hydrated spherical area (Figure 1D and 2D) can be observed, suggesting a loss of porosity during this process, in agreement with the study of Ramachandran et al. [2]. The fact that the hydration was carried out at room temperature elucidates the confusion that temperature influences only the kinetics of the reaction and not the mechanism. Finally, during the introduction of carbon dioxide in order to complete the cycle, the hydrated disk dissolves to form vaterite, one of the polymorphs of calcium carbonate (Figure 1F and 2F). We hypothesize that the phase transition from calcium hydroxide to calcium carbonate is governed by epitaxial growth. The complete monitoring of the lime cycle by E-TEM has allowed us to assess the main bulk morphological and topological changes *in situ* and *operando*. Further studies will be carried out to decipher the changes in the local microstructure of the different phases as well. The aforementioned points can be considered as a first promising step towards the optimisation of the lime cycle.

#### References:

- [1] M Galván-Ruiz, J Hernández and L Baños, *Journal of Materials in Civil Engineering* **21**(11) (2009), p. 694.  
 [2] VS Ramachandran, PJ Sereda and RF Feldman, *Nature* **201**(4916) (1964), p. 288.



**Figure 1.** Illustration of the *in-situ* analysis of the lime cycle by E-TEM. A-C illustrate the decomposition of calcite to CaO with the release of  $\text{CO}_2$  followed by a hydration with water vapour to form spherical grains of calcium hydroxide (D). Vaterite is formed by the process of carbonation. Scale bar:  $2\mu\text{m}$ .