## Title: Precipitated Calcium Carbonate: an Industrial Example of Sustainable Modification of Crystal Structure

Presenting author's name: Jesús García-Carmona<sup>1</sup>, Martín Sarobe Ugarriza<sup>1</sup> <sup>1</sup>Cales de Llierca S.A., Argelaguer 17853, (Girona), Spain E-mail: jgarciac@calcinor.com, msarobe@calcinor.com

CaCO3 is a natural mineral and amongst the most widely occurring natural minerals, approximately 4% of the Earth's crust consists of CaCO3 in the form of limestone, chalk or marble [1]. The polymorphs of CaCO3 include three anhydrous (calcite, aragonite and vaterite), two hydrated (monohydro calcite, CaCO3.H2O and ikaite, CaCO3.6H2O) crystalline phases, and amorphous calcium carbonate (ACC) [2]. Generally, the hydrated and amorphous forms are metastable and rapidly are transformed into calcite, aragonite, or vaterite. The thermodynamic stability of the crystalline anhydrous polymorphs at ambient conditions decreases in the order of calcite, aragonite, and vaterite [3]. The typical morphologies of these three polymorphs are classified as rhombohedral calcite, needle-like aragonite and spherical shape for vaterite.

The natural CaCO3 is often used without any kind of purification, but for more demanding applications CaCO3 is purified by precipitation. In this case the CaCO3 is known as Precipitated Calcium Carbonate (PCC). Among the huge industrial applications in which the PCC can be used, the most common are the following: filler for rubber, paper, ink, sealants, cosmetics, toothpastes, additives for plastics, component of pharmaceuticals, foodstuffs, etc. Nowadays the use of PCC gradually increases worldwide in various fields because PCC can be tailored or designed for each application. Morphology, particle size, crystal size distribution, surface area as well as surface chemistry (coating) are the main features which can be modified to fit the customer's needs. The possibility of obtaining CaCO3 by precipitation gives us the option of increasing the common morphologies previously mentioned.

The synthesis of PCC by carbonation is the most economically efficient process existing today. The complete process of PCC production is the following: (1)The raw material used is crushed limestone, which is burnt in a lime kiln at about 900°-1000°C, where it decomposes (calcination) into calcium oxide (CaO) (quick lime) and CO2. (2)Then the CaO is treated with water. (3) The resulting slaked lime is purified and carbonated with the CO2 obtained previously from the calcination process.

Calcination	$CaCO_3 \longrightarrow CaO (quick lime) + CO_2$	(1)
Slaking	$CaO + H_2O \longrightarrow Ca(OH)_2$ (slaked lime)	(2)
Precipitation	$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$	(3)

The industrial PCC production aims at controlling the phase, morphology, particle size and specific surface area by using additives, controlling the CO2 flow-rate, reaction temperature, etc.

The strict control of these variables leads to different crystalline habits, such as are shown in figure 1.



**Figure 1**. PCC Micrographs obtained by changing of process variables. Crystal habits shown are from the left: spheroidal, rhombohedral, prismatic, needle and scalenohedral.

The crystal habit as well as the crystal size distribution and surface coating are the main responsible of the different benefits of these PCC in many applications.

- Spheroidal and rhombohedral particles surface coated and displaying nanometer sizes used as rheology modifiers in sealants.
- Rhombohedral and prismatic forms in the micrometric size range are useful in paper coating applications.
- Needle-shaped and scalenohedral forms are used as TiO2 extender in papers and paints. They are also used in paper filling because scatters light efficiently, which significantly enhances paper opacity.

In summary, precipitated calcium carbonate is a paradigmatic example of industrially viable polymorph.

## **Bibliography**

V.K. Banth, K.P Singh, G.S. Patnaik, P. Abhishak, and V. Manoj *Quarterly Journal of Indian Pulp and Paper Technical Association*, **20**(3), 89-92. (2008).
S. Gopi, V.K. Subramanian. *Indian Journal of Chemistry*, **52**(A), 342-349, (2013).

[3] L. Brecevic, A. E. Nielsen, Jour. of Crystal Growth, 98, 504 (1989).