

Combined *operando* X-ray absorption and infrared spectroscopy of multiphase multicomponent calcium carbonate crystallization processes

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Calcium carbonate (CaCO_3) is an extensively studied material due to its abundance in nature and its varied application in industries such as fuel, pharmaceuticals and construction. Despite widespread scientific interest, there is still limited understanding of what governs CaCO_3 polymorphic transformations, crystallinity and stability. The increasing need to determine these factors, as a function of time and environment, has led to the development of time-resolved process analytical technology (PAT) techniques. Here, we present a novel PAT system for *operando* XAS studies of multiphase industrially-relevant processes. The PAT setup is a combination of a conventional lab-scale reaction vessel with a continuous flow liquid-jet XAS cell. It permits real-time probing of bulk solutions/dispersions by XAS (on-line) to determine the changes in local structure as a function of process conditions. The PAT configuration also accommodates an attenuated total reflection probe in the reaction vessel, which allows for complementary in-line infrared spectroscopy. The synthesis of CaCO_3 via the carbonation of calcium hydroxide, $\text{Ca}(\text{OH})_2$, in aqueous and non-aqueous environments has been successfully monitored *operando* at the Ca K-edge in fluorescence and total electron yield detection modes. Real-time changes in structure from $\text{Ca}(\text{OH})_2$ to different CaCO_3 forms were monitored through quick XAFS in the XANES region. Our results show formation of different polymorphic CaCO_3 forms depending on changes in the composition of the aqueous and non-aqueous phases and the $\text{Ca}(\text{OH})_2$ concentration.

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