

## **Thermal analysis, powder characterization and kinetic modeling to explain loss of activity of CaO during carbonation**

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Anthropogenic carbon dioxide (CO<sub>2</sub>) emissions are considered as the main cause of global warming. So, decrease of CO<sub>2</sub> emitted by large industrial combustion sources or power plants, is an important goal. One of the approaches is based on CO<sub>2</sub> separation and capture from flue gas, followed by sequestration in a wide range of geological formations. In this aim, CO<sub>2</sub> can be captured by sorbents like calcium oxide (CaO) in multi-cycle process of carbonation/decarbonation. However, it was shown that an important limitation of such process are related to the reversibility of reaction. CaO rapidly loses activity towards CO<sub>2</sub>, so the maximum extent of carbonation decreases as long as the number of cycles increases [1,2].

In this study, thermogravimetric (TG) analysis was done in isothermal and isobaric conditions in order to obtain kinetic data for CaO carbonation. A strong slowing down of the reaction speed is put in evidence on the TG curves and its corresponding fractional conversion is observed to depend on temperature and CO<sub>2</sub> partial pressure. Moreover the curves exhibit a sigmoid shape and an induction period which can be as long as 20 minutes [3].

A particular attention has been paid to the characterization of the solid at various fractional conversions. The key point to explain the slowing down is the evolution of texture and microstructure of the solid during carbonation. Indeed, even with a 10 mg sample, a change in the porosity characteristics due to a volume increase from CaO to CaCO<sub>3</sub> limits the access of CO<sub>2</sub> to the core of CaO aggregates.

Carbonation reaction can thus be described by a two scales model: at a nonporous grain scale for the chemical reaction and at the aggregate scale for the CO<sub>2</sub> intergranular diffusion. The kinetic modeling is able to couple both modeling scales to explain the kinetic slowing down and the influence of temperature and CO<sub>2</sub> partial pressure on the reaction rate.

The coupling is realized by the combination of the heat and mass transfers at the aggregate scale [4] with the kinetics of heterogeneous grains population [5]. Induction period being linked to the nuclei formation mechanism, the presence of large induction periods indicates that the nucleation process can be sluggish. So at the grains scale, the kinetic model was based on the assumption of one nucleus by dense grain with isotropic growth [6]. At aggregate scale, we considered spherical particles with pores of the same size which depends on the fractional conversion. Exchanges of heat and mass are governed by diffusion equations of heat and gaseous species. By finite difference it was possible to calculate the reaction rate for given T and P(CO<sub>2</sub>). This rate allows to evaluate heat and mass sources produced by the reaction. Chemical reaction thus influences the spatial and temporal evolution of the thermodynamic processes at the aggregate scale. Inversely since it modifies the kinetic constants, thermodynamic influences fractional conversion and reaction rate of the chemical reaction at grain scale. Using this approach, it was thus possible to reproduce the experimental data from the induction period up to the kinetic slowing down.

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