**Calcium looping for thermochemical energy storage: Kinetic modeling of limestone calcination**

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**Highlights**

* Kinetic experiments of calcination in a fixed-bed reactor.
* Calcination completed in less than 15 sec under conditions tested.
* A modified RPM (GRPM) describes adequately the reaction.

**1. Introduction**

Thermochemical energy storage (TCES) is of growing interest especially for concentrated solar power plants (CSP). The current technology is based on storage of sensible thermal energy using molten salts which “suffer” from short period storage, crystallization at temperatures lower than 200°C and degradation at temperatures higher than 550°C. A promising alternative is the calcium looping (CaL) due to the highly exothermic carbonation reaction and the higher operating temperatures (~850°C). Other advantages are the non-toxicity and availability of raw materials (e.g. limestone) and their capability to be stored for long periods at ambient conditions.

Accordingly, the solar energy can drive the endothermic reaction in a calciner reactor while the reverse carbonation reaction will produce energy via a power cycle (e.g. Rankine cycle). The reaction kinetics is of great importance as it affects the overall efficiency of the process.

This work focuses on the kinetic measurements and modeling of the calcination reaction as well as on the deactivation evolution of limestone through the cycles. A fixed bed reactor flow unit was used for the experiments in order to achieve efficient gas-solid contact and eliminate the control by external transfer phenomena. A two stage mechanism was adopted for the kinetic modeling [1]. For comparison, two different models were used, namely a Prout Tompkins equation and a Generalized Random Pore Model (GRPM), which is a modified version of the RPM described by Gavalas [1, 2].The evolution of the deactivation through cycling was described with existing models [3].

**2. Methods**

The evaluation of reaction kinetics of the samples was performed in a bench scale laboratory unit operating near atmospheric pressure. The unit consists of the gas feed inlet section, a fixed bed quartz reactor (10mm ID) and a mass spectrometer (Omnistar TM GSD 320, PFEIFFER)). The material used was a limestone (Granicarb 0.1/0.8 provided by OMYA) with a particle size of 45-75μm. The tests were conducted using superficial velocity >12 cm/s to avoid the influence of mass transfer to the observed rates. For the calcination kinetic experiment the sample was calcined under 20% CO2/N2 (GHSV=22500h-1, P=1.5atm, T=950°C). The multicycle experiment (10 cycles, cycle time duration: 6min) for the deactivation assessment comprised carbonation under pure CO2 flow (27000h-1, P=1.7atm, T=890°C) and calcination under 20% CO2 in N2 (GHSV=22500h-1, P=1.5atm, T=890°C).

**3. Results and discussion**

Figure 1 (A) presents the evolution of calcination expressed as a function of time. The calcination of limestone is very fast at 950°C and is completed in 15sec. Almost 80% of the conversion is achieved in less than 7sec. The two models provide good fitting to the experimental data obtained from a fixed bed reactor apparatus. The GRPM describes better the calcination reaction compared to the P-TM especially for low conversions. It is based on the evolution of the available surface area, so it is more realistic compared to the P-TM, which is a symmetrical sigmoidal curve. For both models the pre-exponential factor *k0* was the fitted parameter (GRPM: *k0*=0.41m/s, P-TM: *k0*=4.69 10­9s-1). Due to intense sintering, the multicycle performance deteriorates as the material loses 65% of initial capacity after 10 cycles (B). The deactivation was adequately described with a semi-empirical equation with a deactivation constant of *kd*=0.48.



**Figure 1.** Calcination of limestone at 950°C along with P-TM and GRPM curves (A); Deactivation evolution of limestone through 10 cycles and modeling (B).

**4. Conclusions**

Calcination reaction as well as deactivation of limestone were studied experimentally in a fixed bed reactor unit and kinetically modeled. Two models were used for describing the experimental data. The GRPM better fits to the results compared to the P-TM. Calcination under the studied conditions is completed in a few seconds, rendering limestone appropriate as a solid heat carrier for CSP-TCES applications.

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