LIMESTONE AND DOLOMITE AS THERMOCHEMICAL ENERGY STORAGE MATERIALS: REACTION KINETICS AND DEACTIVATION MODELING

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ABSTRACT

Energy storage systems are of great importance for the on-demand use of seasonal renewable sources, such as solar energy. Calcium looping (CaL) has been proposed to be used as thermochemical energy storage (TCES) system for concentrated solar power (CSP) plants [1]. 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).

$$CaO + CO_2 \leftrightarrow CaCO_3 \qquad \Delta H = -178\ kJ/mol$$

This is a promising alternative to the molten salts technology which is characterized by short time storage as well as low operating temperatures. On the other hand, carbonation reaction is highly exothermic and can take place at temperatures >850°C, increasing the power cycle efficiency. Other advantages are the non-toxicity and availability of raw materials, as well as their capability to be stored for long time periods at ambient conditions. Two candidate materials are limestone and dolomite, which both are abundant and low cost minerals. Especially limestone has been thoroughly studied for CO_2 capture applications which involve low carbonation temperatures (~650°C) and CO_2 partial pressures. On the contrary, TCES overall efficiency is favored by high reaction rates and temperatures. Thus, high temperatures and CO_2 partial pressures, especially for carbonation reaction are preferable.

This work focuses on the reaction kinetic measurements as well as on the deactivation evolution of limestone and dolomite through successive 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. The experiments were conducted under high CO_2 concentrations slightly above atmospheric pressure. For the kinetic modelling of carbonation and calcination reactions, a two stage mechanism was adopted [2], which relates the intrinsic rate with CO_2 partial pressure and reaction temperature. This was combined with a Random Pore Model (RPM) [3], a mechanistic model for the dependence of the rate on the available surface area. The evolution of the deactivation through cycling was described using a semi-empirical model [4].

The kinetic measurements showed that limestone and dolomite exhibit high reaction rates (in the order of a few seconds) both during carbonation and calcination stages. Dolomite exhibits higher reaction rates than limestone under all studied conditions, a behavior attributed to its increased surface area. The MgO content renders dolomite more sintering resistant than limestone, compensating the lower CaO concentration. The evolution of conversion as a function of time was modeled using the RPM expressions and the deactivation trend through the cycles was fitted adequately for both materials. Concluding, both limestone and dolomite are appropriate as heat carriers for TCES applications while dolomite exhibits better performance as regards on the rate of reactions and thermal stability.

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