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Kinetics in limestone decomposition

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Limestone calcination is a reaction requiring considerable input of energy. To optimize the calcination process in order to save energy and ensure product quality, the decomposition behaviour of individual pieces of carbonate under given process conditions must be known. A shrinking core model is established to simulate limestone decomposition process, which consists of five sub-processes: heat transfer from ambient to particle surface, heat conduction from surface to reaction front, chemical kinetics at front, diffusion of the CO₂ through the porous oxide layer to surface, and then transfer into ambient. Heat transfer and mass transfer between fluids and solids have already been adequately investigated, but it is difficult to measure reaction rate coefficient, thermal conductivity and the pore diffusion coefficient of CO₂ in lime layer during calcination. In this research, these three values are determined, depending on temperature and the origin and genesis of various limestones. For this purpose a method is described with which the desired values of a particular carbonate under constant ambient temperature can be estimated from linearized decomposition curve.

The calcination process is explained with a partly decomposed piece of carbonate, as shown in Fig. 1. The specimen comprises a dense carbonate core surrounded by porous oxide layer. In the calcination reactor at temperature T_A heat is transferred by radiation and convection (symbolized by α) to the solid surface with temperature T_S. By thermal conduction (λ_{Ox}) heat penetrates through the porous oxide layer with average temperature T_{Ox} to reach the reaction front, where the reaction temperature T_F exists. As the reaction enthalpy is many times bigger than the internal energy, the heat flowing further into the core is negligible during reaction. So the core temperature is only slightly lower than the front temperature. Supplied with heat, the chemical reaction (k) then takes place, for which the necessary driving force is deviation of CO₂ partial pressure from equilibrium (P_F* - P_F). The released CO₂ diffuses (D_{P,eff}) through the porous oxide layer to the surface and finally passes by convection (β) to the ambient in which the CO₂ partial pressure P_A exists.

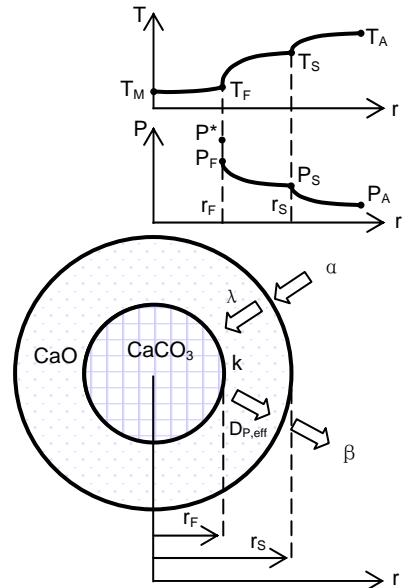


Fig. 1: Model of the decomposition of limestone

The reaction rate coefficient determined from the linearized decomposition behaviour curves is approximately independent of the temperature. The marked dependence of the decomposition time on the temperature is therefore due chiefly to the exponential temperature dependence of the equilibrium pressure. Nor is there any ascertainable influence of the CO_2 partial pressure on the reaction coefficient. In literature different some authors adopted other definition for reaction coefficient. Their values and comparison with our converted values are shown in Fig. 2.

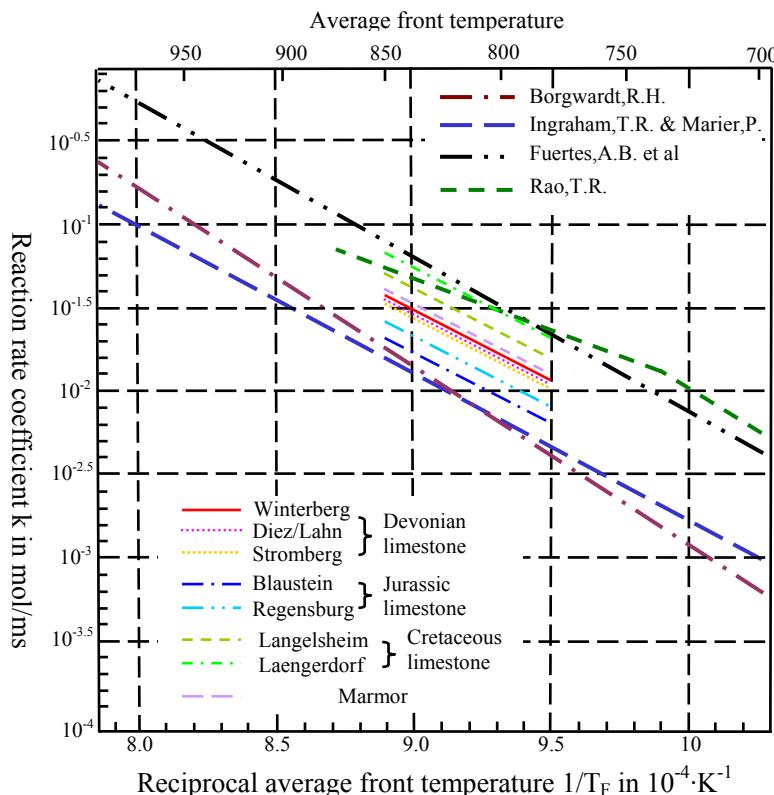


Fig. 2: Reaction rate coefficients comparison

To illustrate the contribution of each sub-process in lumpy limestone calcinations in shaft kiln, the ratio of the time portion is calculated in a case, where gas velocity W_G is assumed as 0.3m/s at 25°C and ambient CO₂ 20%. Fig. 3 shows the integral time portions of the individual sub-processes for spherical samples as a function of particle size, with different gas temperature. When particles are very fine, chemical kinetic provides biggest resistance. As size increases, this resistance decreases sharply. So for limestone powder under lower gas temperature, the decomposition can be considered as a pure chemical kinetic process. For particle bigger than 20mm, which is typical size in industrial kilns, chemical kinetic is no more important. At gas temperature 800°C, the main control step is pore diffusion through lime layer. Considering the fact that the reaction begins theoretically at 785°C to overcome the ambient 20% CO₂, the pressure difference $P^*_F - P_A$ in this case must be very small, which makes diffusion the largest resistance in decomposition. But with rising gas temperature, heat transfer and conduction become the control steps. When gas temperature is higher than 950°C, which is normally true for reaction zone in shaft kiln, heat transfer and conduction play dominant role. It is also clear that the time portion ratio of heat transfer decreases while conduction increases with particle size. By higher temperature (>1100°C), the sum up of the ratios for kinetics, diffusion and mass transfer is less than 10%. So it is a rational assumption to consider heat transfer and heat conduction as control steps in simulation of limestone decomposition under real operation conditions in shaft kiln. Under these conditions they could be neglected without leading to significant error.

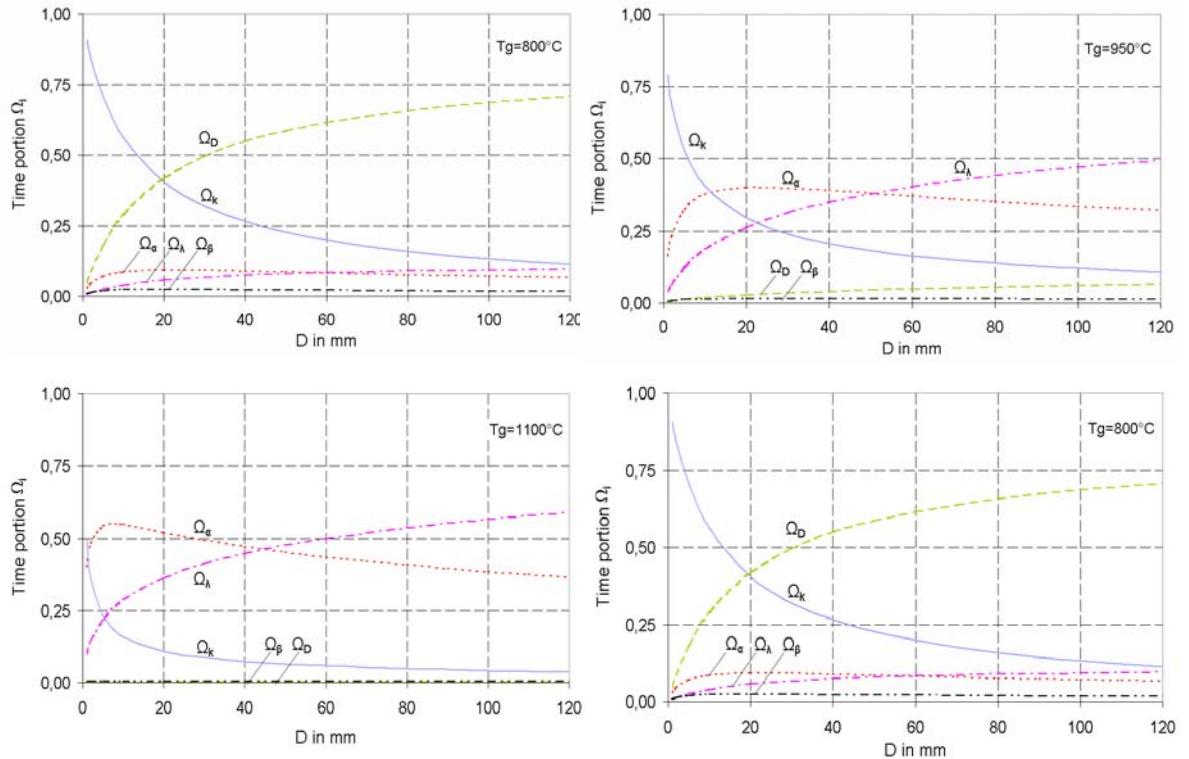


Fig. 3: Time portion of 5 sub-processes in calcination

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