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Appendix B

Derivation of the mass-transfer limited shrinking particle rate equation

The approach taken here follows that of Levenspiel [40] for fluid-solid models. For the reverse-Boudouard, there is no developing ash layer, since the product is gaseous. The carbon dioxide reaches the carbon surface by diffusion though the stationary boundary layer surrounding the sample. For this Fick I is used:

$$\frac{dm_{CO_2}}{dt} = - A \cdot D_{CO_2}\frac{dC_{CO_2}}{dx} \tag{B.1}$$

Here *m* is the mass of the diffusing species, i.e., CO_2, *A* is the area of the sample, D_{CO_2} is the self-diffusion constant and $C_{CO_2}$the concentration of carbon dioxide diffusing species in the gas phase, expressed in mass per unit volume, with d*x* the thickness of the stagnant boundary layer. The thickness of the boundary layer is almost impossible to determine in practice, and the equation is transformed to:

$$\frac{dm_{CO_2}}{dt} = - A \cdot h \cdot C_{CO_2} \tag{B.2}$$

Here *h* is the so-called convective mass transfer coefficient, and is determined experimentally via the Sherwood number *Sh*, defined by:

$$Sh = \frac{h}{D/L_c} \tag{B.3}$$

Here *D* again is the diffusion constant of the reacting gas, i.e., CO_2 in this case, and L_c is a characteristic length – which is taken as the sample diameter. The correlation for *Sh* in terms of the Reynolds number (*Re)* and the Schmidt number (*Sc*) is given in Table 5 in the main text.

Substituting B.3 into the right- hand side of B.2, and equating the rate loss of a solid carbon sphere to the rate of CO_2 consumption, we have

$$- 4\pi r^2 \rho_C \frac{dr}{dt} = 4\pi r^2 \frac{ShD_{CO_2}C_{CO_2}}{2r} \tag{B.4}$$

Cancellation of coefficients and separation of variables yield

$$- 2rdr = \frac{ShD_{CO_2}C_{CO_2}}{\rho_C}dt \tag{B.5}$$

Integration between the time-dependent radius r and the starting radius R_0, i.e.

$$-2\int_{R_0}^{r} r dr = \frac{ShD_{CO_2}C_{CO_2}}{\rho_C}\int_0^t dt \tag{B.6}$$

yields

$$R_0^2 - r^2 = \frac{ShD_{CO_2}C_{CO_2}}{\rho_C}t \tag{B.7}$$

Division of B.7 by R^2 gives

$$1 - \frac{r^2}{R_0^2} = \frac{ShD_{CO_2}C_{CO_2}}{\rho_C R^2}t \tag{B.8}$$

Finally, the definition for the extent of reaction, i.e.

$$\alpha = 1 - \frac{4/3\pi r^3}{4/3\pi R_0^3} = 1 - \frac{r^3}{R^3} \tag{B.9}$$

is substituted in B.8 to yield

$$1 - (1 - \alpha)^{2/3} = \frac{ShD_{CO_2}C_{CO_2}}{\rho_C R_0^2}t = \frac{t}{\tau} \tag{B.10}$$