



Using an experimentally-determined model of the evolution of pore structure for the calcination of cycled limestones



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HIGHLIGHTS

- A pseudo time-stepping model with spatial variation for calcination of cycled limestones.
- An experimentally determined function to describe the evolution of pore structure.
- Good fit between the model and the experimental measurements.

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ABSTRACT

A pseudo-steady state model of reaction and diffusion has been constructed to model the non-isothermal calcination of limestone particles which have been subjected to a history of cycling between the calcined and carbonated states. This typically occurs when using Ca-based materials for removing CO₂ from the flue gas of plants such as a power station, cement plant and steel factory in certain schemes for carbon capture and storage. The model uses a Cylindrical Pore Interpolation Model to describe the intraparticle mass transfer of CO₂ through the pores of the material coupled with an experimentally-determined function, $f(X)$, describing the pore evolution as a function of the conversion of the CaCO₃ present to CaO. The intrinsic rate of calcination was taken to be first order in concentration driving force. External to the limestone particle, the Stefan-Maxwell equations were used to describe the diffusion of CO₂ away from the particle and into the particulate phase of the fluidised bed. The equation of energy was used to allow for the enthalpy of the reaction. In order to validate the use of the $f(X)$ function, the theoretical predictions were compared with experiments conducted to measure the rates and extent of conversion, at various temperature and different particle sizes, of Purbeck and Compostilla limestones that had been previously cycled between the carbonated and fully-calcined state. Excellent agreement between experiment and theory was obtained, and the model using the $f(X)$ approach predicted the conversion of particles of various sizes well at temperatures different to that at which the function was derived, thus indicating that the $f(X)$ solely dependent on the evolution of the morphology of the particle.

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1. Introduction

Broadly-speaking, two classes of model exist to describe the non-catalytic reaction between a gas and a solid, namely the Shrinking Core Model (SCM) and the Continuous Reaction Model (CRM). The SCM has been commonly used to describe, for example, the calcination of non-porous, virgin particles of limestone (generally close to pure CaCO₃), where the reaction occurs at a sharp front which recedes towards the centre of the particle [1]. Generally, the rate of reaction might be limited variously by (i) chemical kinetics, (ii) diffusion through the porous product layer, (iii) transport of

heat to or from a reaction interface, or (iv) diffusion through the external gas film. On the other hand, the CRM is a better description where there is slow reaction of a gas, and, or, transfer of heat, within a porous solid across a broad front or the entire particle [1]. Fig. 1 shows the difference in local conversion profiles between two models at fixed average conversion of particle. The calcination of cycled, as opposed to virgin, limestone, possesses the characteristics of the CRM, where the initially-porous particles, containing a mixture of CaCO₃ and unreacted CaO, become more porous as the CaCO₃ is calcined to CaO during thermal decomposition. Such particles are created when raw limestone particles have been subjected to a history of cycling between the calcined and carbonated states. This typically would occur when using such Ca-based materials for removing CO₂ from the flue gas of plants

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Nomenclature

Symbols

A_A, A_K, A_C	Coefficients in pressure gradient equation ($\text{Pa s m g}^{-0.5} \text{ mol}^{-0.5}$)
$A_{s,0}$	Initial pore area per unit mass ($\text{m}^2 \text{ g}^{-1}$)
$C_{p,n}$	Molar heat capacity of species n (J/mol K^{-1})
$D_{A,nm}$	Diffusivity at arbitrary Knudsen number, for species n and m ($\text{m}^2 \text{ s}^{-1}$)
$D_{B,nm}$	Molecular diffusivity, involving species n in m ($\text{m}^2 \text{ s}^{-1}$)
$D_{K,n}$	Knudsen diffusivity of species n ($\text{m}^2 \text{ s}^{-1}$)
D_{ref}	Molecular diffusivity $D_{B,12}$ at bulk condition ($\text{m}^2 \text{ s}^{-1}$)
\bar{d}_b	Mean bubble diameter (m)
E_a	Activation energy (kJ/mol)
H_n	Partial molar enthalpy of species n (J/mol)
H_f	Partial molar enthalpy of formation (J/mol)
h	Bed height (m)
h_{mf}	Bed height at minimum fluidisation (m)
J_n	Total molar flux of species n ($\text{mol m}^{-2} \text{ s}^{-1}$)
k_c	Rate constants of calcination reaction ($\text{mol m}^{-2} \text{ s}^{-1}$)
k'_c	Modified rate constants of calcination reaction (s^{-1})
k_0	Arrhenius coefficient of rate constant k'_c (s^{-1})
\bar{k}	Rate constant of carbonation reaction (m s^{-1})
M_n	Molecular mass of species n (g mol^{-1})
P	Total pressure (bar)
P_{bulk}	Bulk pressure (bar)
$p_{\text{CO}_2 r}$	Local partial pressure of CO_2 (bar)
$p_{\text{CO}_2}^{\text{bulk}}, p_{\text{CO}_2}^{\text{eq}}$	Bulk and equilibrium partial pressure of CO_2 (bar)
q_c	Intrinsic rate of calcination per unit of surface area ($\text{mol m}^{-2} \text{ s}^{-1}$)
Q_n	Net rate of change of species n inside the particle ($\text{mol m}^{-3} \text{ s}^{-1}$)
r	Radial distance from the particle centre (m)
r_p	Radius of a limestone particle (m)
r_{pore}	Mean radius of the pore (nm)
R	Universal gas constant (kJ/mol K^{-1})
t	Time (s)
T	Absolute temperature (K)
T_{bulk}	Bulk temperature (K)

U_b	Bubble velocity (m s^{-1})
U_{mf}	Flow velocity at minimum fluidisation (m s^{-1})
u_M	Mass-averaged velocity (m s^{-1})
$V_{M,\text{CaO}}$	Molar volume of CaO ($\text{m}^3 \text{ mol}^{-1}$)
V_{M,CaCO_3}	Molar volume of CaCO_3 ($\text{m}^3 \text{ mol}^{-1}$)
X	Solid conversion (-)
y_n	Mole fraction of species n (-)

Greek letters

Λ_{k_c}	Pre-exponential coefficient of the rate constant k_c ($\text{mol m}^{-2} \text{ s}^{-1}$)
λ_{eff}	Effective thermal conductivity of the particle ($\text{W m}^{-1} \text{ K}^{-1}$)
ε_0	Initial porosity of the particle (-)
ε_b	Bubble fraction (-)
ε_{bed}	Porosity of the fluidised bed around the particle (-)
$\varepsilon(X)$	Porosity of the particle as a function of conversion (-)
ρ_e	Bulk density of a particle ($\text{kg m}^{-3\text{P}}$)
ρ_m	Skeletal density of the particle (kg m^{-3})
τ^2	Tortuosity factor of the particle (-)
τ_{bed}^2	Tortuosity factor of the fluidised bed (-)
δ	External diffusion boundary layer thickness (m)
η_r	Dimensionless radius (-)
ν_{mix}	Kinematic viscosity of gas mixture ($\text{m}^2 \text{ s}^{-1}$)
ν_n	Stoichiometric coefficient of species n (-)

Subscripts

$n = 1, 2$ CO_2 and N_2

Abbreviation

BET	Brunauer-Emmett-Teller
CPIM	cylindrical pore interpolation model
DGM	dusty gas model
MPTM	mean pore transport model
OCFE	orthogonal collocation on finite element
RPM	random pore model

such as a power station, cement plant and steel factory in certain schemes for carbon capture and storage. The present work is concerned with these cycled particles.

A feature of most models of non-catalytic reactions between gases and solids generally is that the intrinsic rate of reaction, r ,

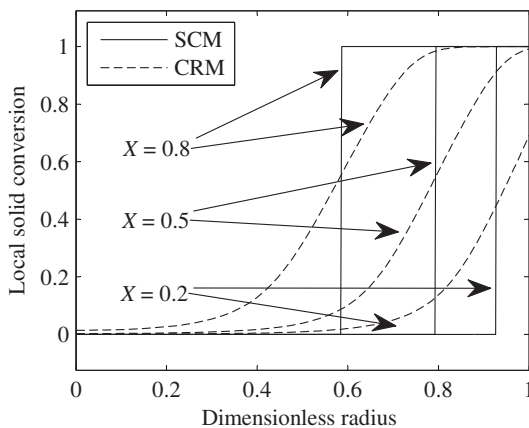


Fig. 1. Local conversion profiles of shrinking core model (SCM) and continuous reaction model (CRM) for fixed average conversion of particle.

at a local point within a solid particle is of the form $r = g(C_i, T, P) \times f(X)$ [2,3]. Here, g describes the intrinsic reaction kinetics as a function of the temperature, T , the total pressure, P , and the concentration, C_i , of the reaction gases. The term $f(X)$ is a direct function of the conversion of the particle and is correlated with the internal morphology of the particle, e.g. surface area, pore size, pore size distribution etc. at a particular conversion. In addition, $f(X)$ is not a function of C_i , T , or P .

Many researchers have sought to model the development of internal pore structure with conversion during non-catalytic gas-solid reaction. For example, Szekely & Evans [4] assumed that solid particles consisted of an array of spherical grains with the space between them making up the voids. They made the first attempt to incorporate the structural parameters such as grain size, porosity and pore size into the reaction scheme in their grain model. Their original model assumed that the pore structure was unaffected by the progress of reaction, although later variants [5] were able to account for change in grain size with reaction. More recently, Liu et al. [6] developed an overlapping grain model using a fitted size distribution of grains to account for the evolution of pore structures during reaction. On the other hand, random pore models have been developed, e.g. Bhatia & Perlmutter [3] and Gavalas [7], using different approaches based on cylindrical pore assumptions, to model the total surface area at any conversion as a function of the initial morphological parameters, e.g. the initial

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